

**Polarized Luminescence and
Chiroptical Switching Functionalities
of Liquid Crystalline and
Chiral Conjugated Polymers**

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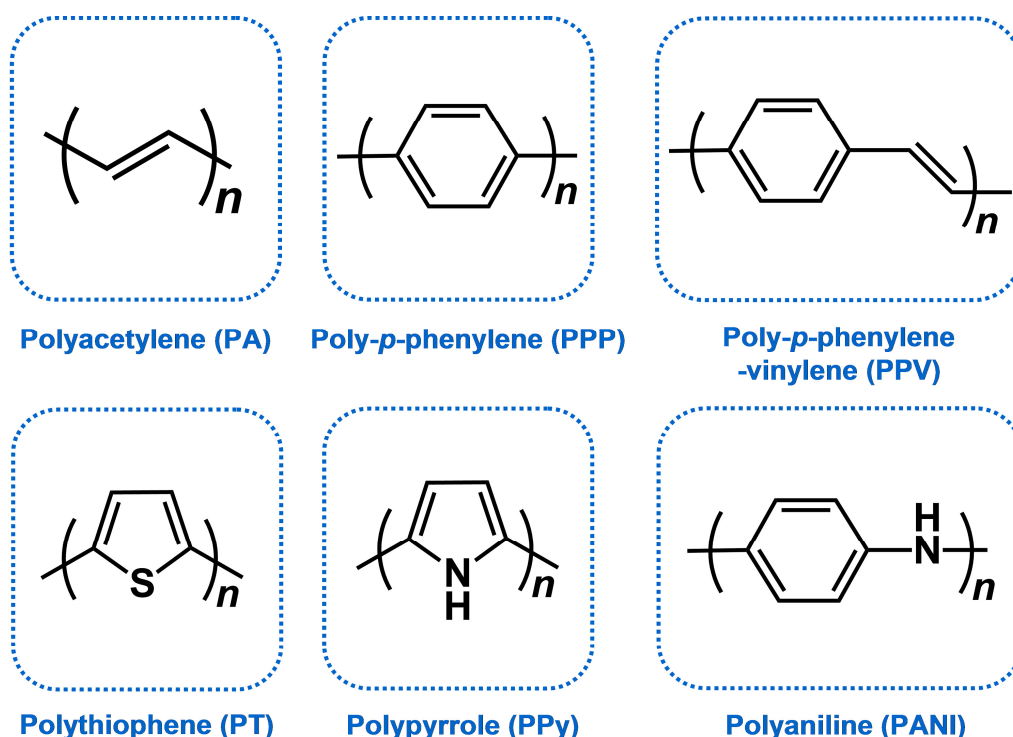
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General Introduction

1. Conjugated Polymers

Conjugated polymers are attractive materials for research due to their unique structure. The structure of conjugated polymers consists of covalently bonded atoms with alternating single and multiple bonds. This conjugated system of atomic bonds results in a delocalization of the electrons across all of the adjacent parallel aligned π -orbitals of the atoms, which increases its molecular stability and thereby lowers the energy gap of the molecule. This distinct feature of conjugated polymers and the phenomena of electron delocalization in conjugated polymer systems make them attractive materials for research.



Scheme 1. Representative conjugated polymers.

The discovery of metallic conductivity of doped polyacetylene (PA) film by MacDiarmid, Heeger and Shirakawa in 1977¹ has generated a considerable interest for the synthesis, electronic properties and applications of conjugated polymers such as poly(*para*-phenylene) (PPP), poly(*para*-phenylenevinylene) (PPV), polythiophene (PT), polypyrrole (PPy), and polyaniline (PANI).²⁻⁴ Representatives of conjugated polymers are shown in Scheme 1.

The discovery of the electroluminescent properties of PPV by Friend and coworkers in 1990⁵ represents a turning point where research on conjugated polymers started to focus on the semiconducting properties of polymers which led to the field of organic optoelectronics. The main chains of polymers in solid state are usually randomly oriented. Given that conjugated polymers were able to exhibit functionalities such as conductivity and fluorescence, arranging the polymers macroscopically in a linear or helical manner will greatly increase the potential of conjugated polymers. To realize macroscopically arranged polymers, liquid crystals (LCs) are commonly used in various procedures and polymerization methods.

2. Liquid Crystals and Liquid Crystalline Polymers

Georges Friedel in France in 1922, began the systematic classification of various LC phases. He observed that there were three main types of LC phase: the nematic liquid crystal (N-LC) phase, the smectic liquid crystal (Sm-LC) phase, and the cholesteric (Ch) or chiral nematic liquid crystal (N*-LC) phase.⁶ Models of these three phases are shown in Figure 1.

In the N-LC phase, the individual LC molecules, which can be envisioned as inflexible rod-like structures, all align in the same direction with their positions being

random. The molecules can flow freely in the direction of alignment, but not perpendicular to the direction of alignment. However, the different nematic domains often point in different directions so the overall viscosity of N-LC is high. In the Sm-LC phase, the molecules align in the same direction and are further arranged in layers, giving them an additional level of order over the N-LC phase. As molecules in a Sm-LC phase can move neither in the alignment direction nor the perpendicular direction, Sm-LCs are typically more viscous than N-LCs. Sm-LC phases are further subdivided based on the arrangement of the LC molecules within the planes. For example, in the Sm-B phase the molecules are arranged in a hexagonal pattern within smectic layers.

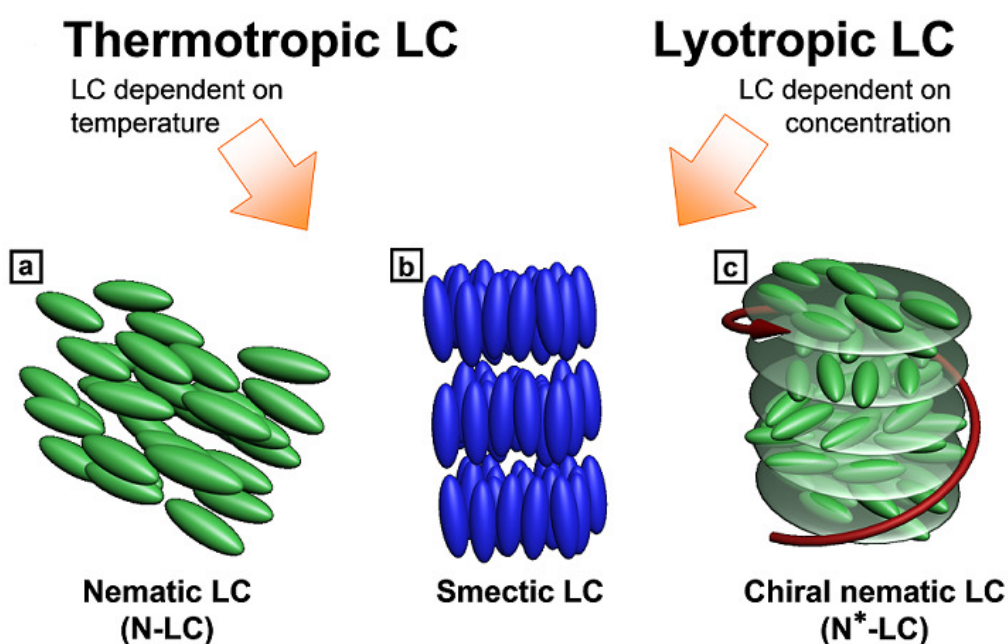


Figure 1. Some liquid crystal phases: (a) Nematic liquid crystal (N-LC) phase, (b) Smectic liquid crystal (Sm-LC) phase, (c) Chiral nematic liquid crystal (N*-LC) phase.

In the Ch phase, the alignment of the molecules within each plane is similar to the nematic phase, but every plane is slightly twisted with respect to the plane below it. This twist gives either left- or right-handed macroscopic chiral structures. Since the two

structures are not superimposable the Ch phase is optically active. The addition of a small amount of chiral dopant to N-LC results to this structure, thus this phase is commonly known as the chiral nematic phase (N^* -LC).⁷

Furthermore, LC molecules and LC polymers can be classified as either thermotropic or lyotropic. The LC phase of thermotropic LCs are dependent on temperature, while the LC phase of lyotropic LCs are dependent on concentration.

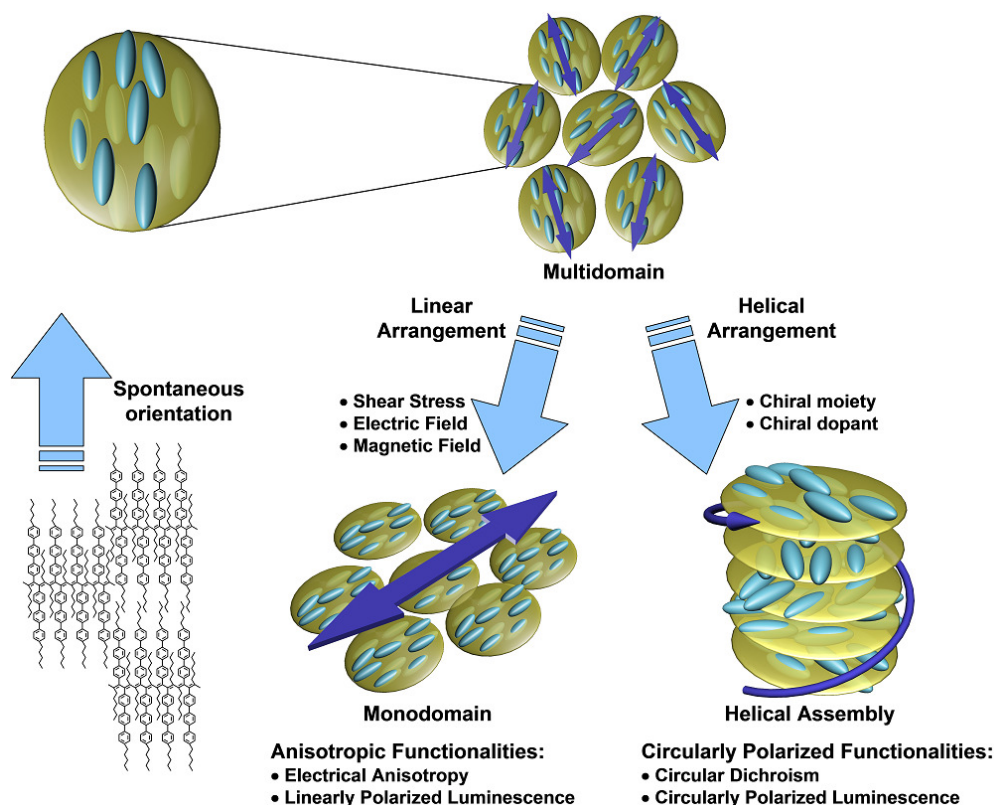


Figure 2. Schematic representation of the spontaneous orientation, linear, and helical arrangement of LC-conjugated polymers.

It is well known that polymers with LC moieties spontaneously align to form multidomains by virtue of the orientation of the LC moieties. Further linear arrangement of these polymers can be achieved by applying an external force, such as shear stress and electric or magnetic fields,^{8–10} to construct a monodomain structure on a macroscopic level. The LC polymers in a monodomain structure exhibit excellent

anisotropic properties including electrical conductivity and linearly polarized luminescence (LPL). Moreover, when LC polymers are helically arranged into higher ordered structures using chiral moieties or chiral dopants, the LC polymers can exhibit circularly polarised functionalities, such as circular dichroism (CD) and circularly polarized luminescence (CPL). Figure 2 shows the formation of multidomains, monodomains, and helical assemblies through spontaneous orientation as well as linear and helical arrangement of LC conjugated polymers.

3. Linearly Aligned Conjugated Polymers

By utilizing LCs and the LC behavior of liquid crystalline polymers, several kinds of procedures and polymerization methods for the macroscopic alignment of conjugated polymers have been developed. The introduction of LC moieties into the side chain of the polymer is one approach to align the polymer under an external force such as shear stress, rubbing or a magnetic field (Figure 3a).⁸⁻¹⁰ The use of nematic LC as a solvent, on the other hand, gave us directly aligned PA film with the aid of gravity flow or a magnetic field (Figure 3b).¹¹⁻¹²

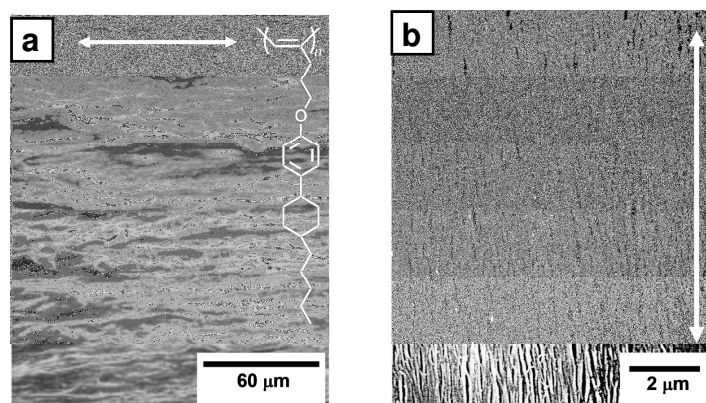


Figure 3. Examples of aligned conjugated polymers: (a) liquid crystalline polyacetylene derivative and, (b) polyacetylene film synthesized under macroscopically oriented nematic liquid crystal field. The arrows indicate the alignment direction.

4. Helical Conjugated Polymers

If it were possible to modify the structure of conjugated polymers to a helical one, one might expect novel magnetic and optical properties. It should also be interesting to investigate chirality in conjugated polymers since chiroptical functionality is one of the attractive properties of conjugated polymers with chirality. There are various methods that are employed to induce chirality to conjugated polymers. It has been shown that polymerization of acetylene in an asymmetric reaction field constructed with N^{*}-LCs showed polyacetylene films having helical chains and fibrils (Figure 4a).¹³ Another method, which uses axially chiral binaphthyl derivatives as dopants to conjugated LC polymers for chiral induction has been reported (Figure 4b).¹⁴

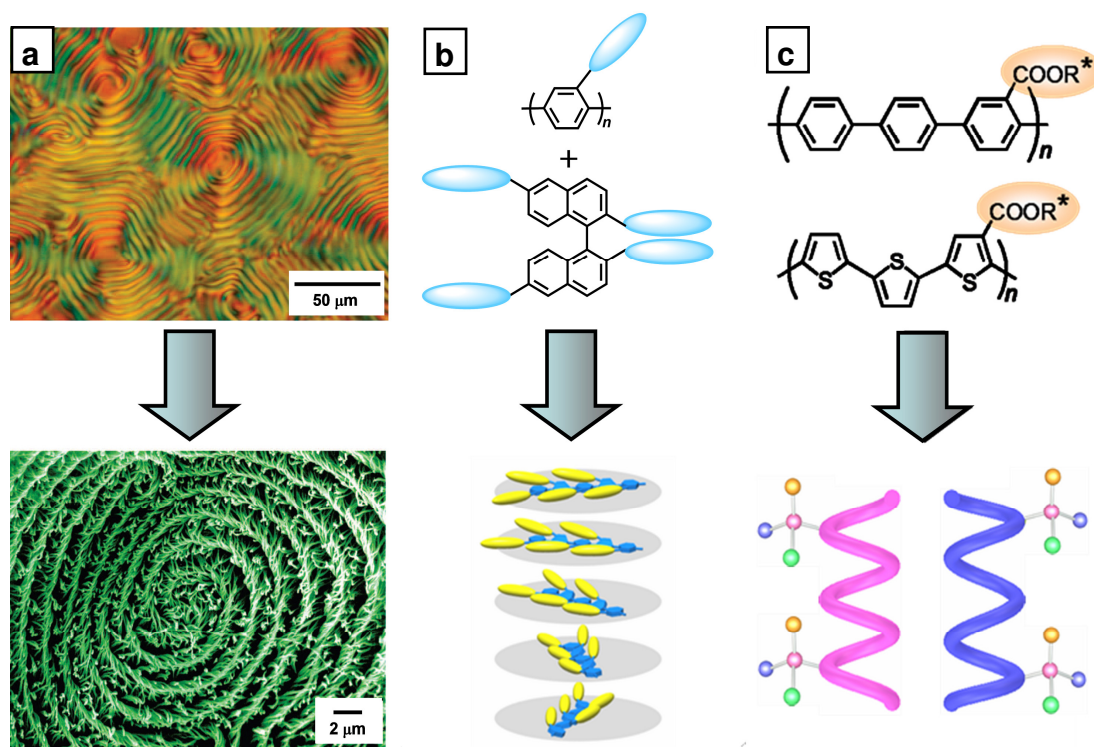


Figure 4. Methods of chiral induction to conjugated polymers: (a) polymerization under an asymmetric reaction field,¹³ (b) chiral induction by adding a chiral compound as a chiral dopant to conjugated polymers,¹⁴ and (c) chiral induction through the introduction of chiral moieties to conjugated polymers.¹⁵

The introduction of chiral moieties is another approach that is widely used to induce helicity to the main chain of conjugated polymers (Figure 4c).^{14b,15} Among the aforementioned methods, the use of chiral moieties is the most facile way of synthesizing helical conjugated polymers. In this method, there are no specific conditions that need to be considered, such as the selection of a proper LC phase and polymerization system, or consideration of the miscibility between the polymer and the chiral dopant. By employing chiral moieties, we can have flexibility in varying the chemical structure of the helical polymer.

5. Linearly and Circularly Polarized Luminescence

Recently, fluorescent LC conjugated polymers are attracting lots of interest since they could be aligned macroscopically. Upon alignment, these fluorescent conjugated polymers are able to exhibit linearly polarized luminescence (LPL) which can be used for electroluminescent (EL) applications¹⁶ and for use as a polarizing emissive filter in liquid crystal displays (LCDs).¹⁷ Fluorescent conjugated polymers are expected to show circularly polarized luminescence (CPL) when they form helical structures. In recent years, there has been a growing interest in developing organic molecules that are capable of emitting circularly polarized light because of their potential applications in display devices,¹⁸ optical storage devices,¹⁹ and in asymmetric photochemical synthesis.²⁰ Although all luminescent organic molecules that are chiral will display some CPL, the extent of circular polarization is almost always less than 0.1%.²¹ Recent strategies that have been explored to increase the circular polarization include attaching chiral side chains to conjugated polymers,²² embedding organic chromophores in a

chiral matrix,¹⁹ and the aggregation of chromophores.²³ Figure 5 describes the emergence of LPL and CPL in fluorescent conjugated polymers such as PPP.

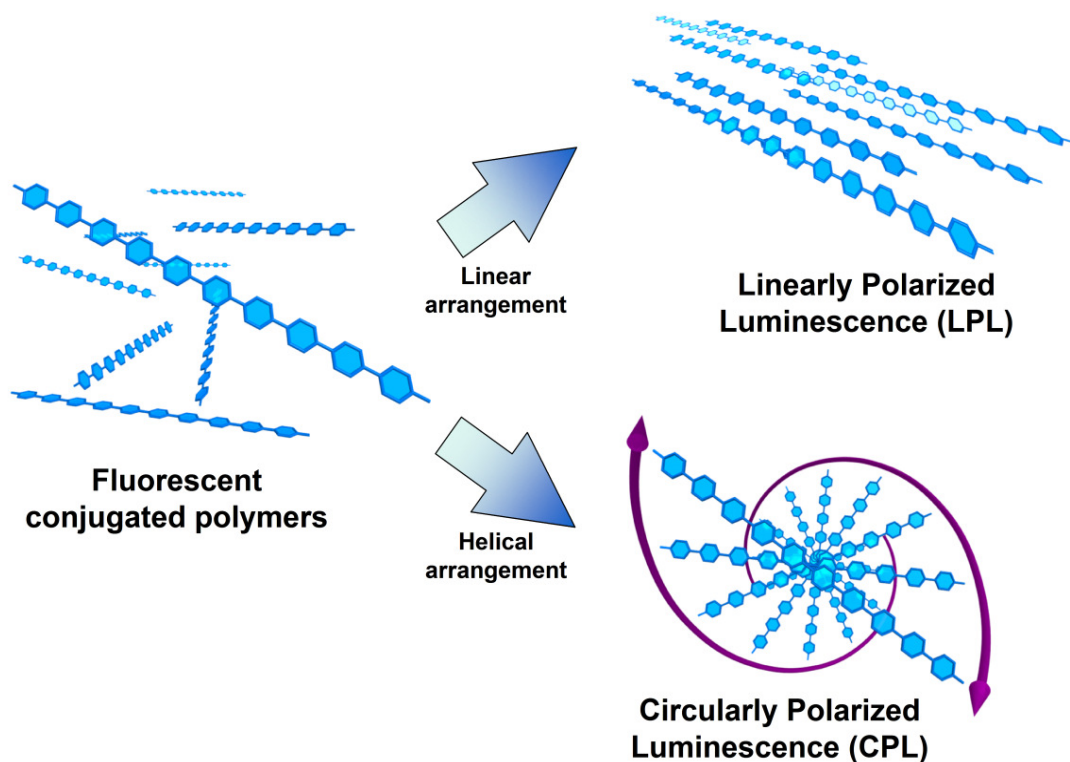


Figure 5. The emergence of linearly polarized luminescence (upper-right) and circularly polarized luminescence (bottom-right) in fluorescent conjugated polymers.

6. Selective Transmission of Circularly Polarized Light in Chiral Nematic Liquid Crystals

One outstanding feature of the N*-LCs is the selective reflection of circularly polarized light. When circularly polarized light propagates into a planar-aligned N*-LC cell²⁴ along the helical axis, the N*-LC molecules can reflect CPL with same N*-LC helical handedness at λ_{max} . On the other hand, CPL with opposite N*-LC helical handedness transmits through the planar N*-LC cell without light reflection (Figure 6). The light-reflecting behavior of N*-LCs depends on the handedness of the CPL, the so-

called “selective reflection”. The maximum wavelength of light reflection ($\lambda_{\max}$) is numerically expressed as: $\lambda_{\max} = n_{\text{av}} p$, where n_{av} is the average refractive index and p is the helical pitch length. In the case of a chirally induced N*-LC phase, the helical pitch length p is dependent on the mole ratio of the added chiral dopant. Previously, we synthesized a LC-chiral dopant with a high helical twisting power²⁵ capable of preparing a N*-LC phase with the helical pitch on the order of several hundred nanometers with the selective reflection range within visible light range. In this context, such N*-LC can be used as tunable photonic materials for applications in displays devices, optical recording, even mirrorless low-threshold lasing.²⁶

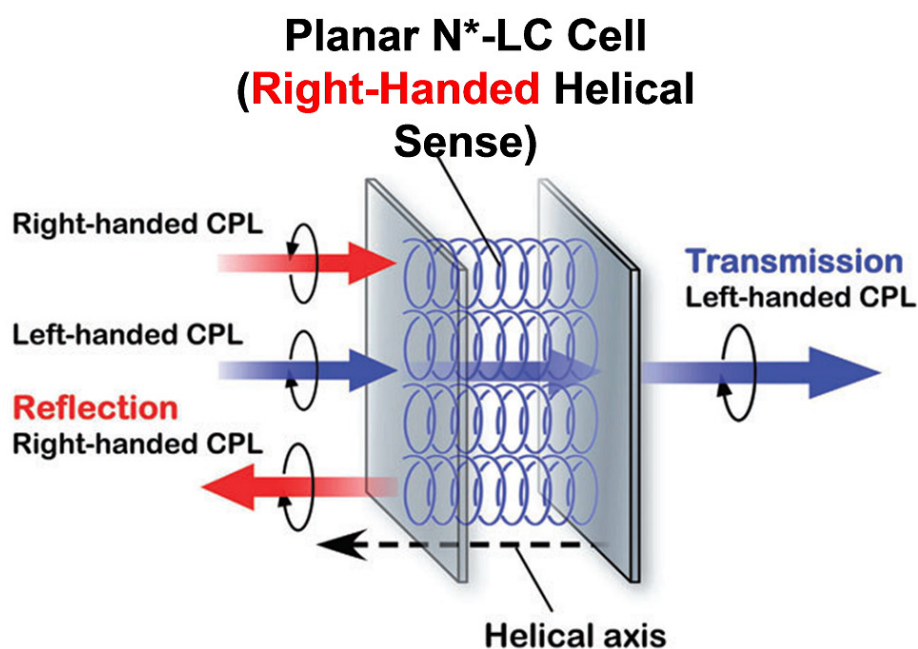


Figure 6. Selective reflection phenomena of circularly polarized light (CPL) by a planar-aligned N*-LC cell with a right-handed helical sense.

7. Helical Inversion of Optically Active Polymers

Inversion of main chain chirality in optically active polymers without changing the configuration of stereocenters is a phenomenon seldom observed. Although most polymers adopt helical conformations in solution and/or in the solid state,²⁷ optical

activity can only be observed when the polymers are prepared in an enantioselective way.

Chiral inversion in π -conjugated systems and polymers by changing the nature of the polymer environment without affecting a single stereocenter have been extensively reported.²⁸ Some reported examples are changes in chirality with changes in temperature,²⁹ pH,³⁰ salt concentrations,³¹ and changes in the handedness of the chiral complex,³² and chiral solvent used.³³ One facile way to change the handedness of conjugated polymers is through changing the polarity of its solvent environment during solvent induced aggregation. This method has been reported in conjugated polymers such as regioregular PT,³⁴ PPV,³⁵ and poly(*para*-phenylenethynylene) PPE copolymers having peptiptycene groups.³⁶

One interesting application of chiral inversion of conjugated polymers is the ability to exhibit CPL and control its handedness. Control of the handedness of CPL of PPV films organized in aggregate state has been reported (Figure 7).^{35b} Furthermore, another method of helical inversion is with the use of photoisomerizable chiral moieties such as chiral dithienylethene (DE*) on conjugated polymer helical assemblies.

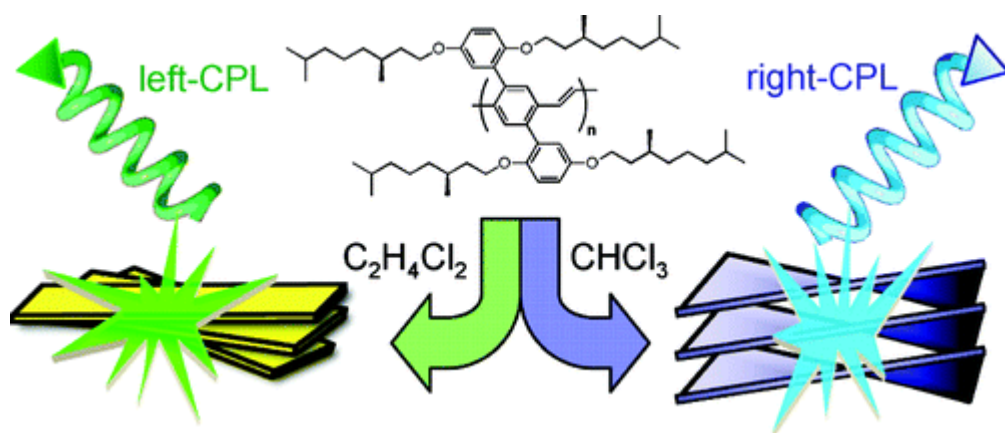


Figure 7. The inversion of circularly polarized luminescence of PPV cast films through a change in solvent environment during film casting.^{32b}

8. Photoresponsive Dithienylethene

The dithienylethene (DE) derivatives are one of the most feasible photochromic materials among various photoresponsive compounds because of their outstanding fatigue resistance, thermal stability, reactivity in solid state and reversible properties for use in optoelectronic devices such as ultrahigh-density optical data storage, molecular switches, logic gates, molecular wire, and sensors.³⁷ Photochromic dithienylethene derivatives undergo reversible photoisomerization between colorless open form and colored closed form upon irradiation with ultraviolet (UV) and visible (vis) light, as shown in Figure 8. Substitution of a photoresponsive DE molecule to a conjugated polymer can impart photodynamic behavior in their helical arrangement.

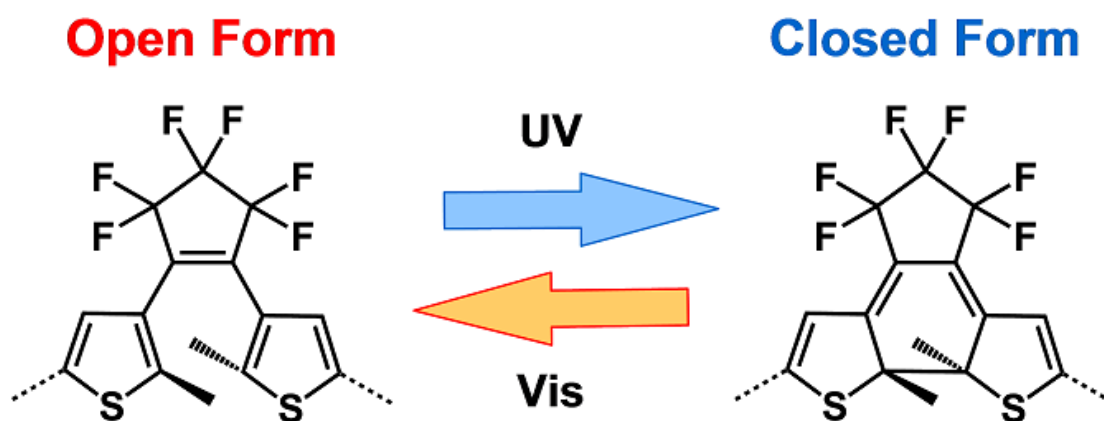


Figure 8. Photoisomerization of the dithienylethene (DE) molecule from open to closed, and vice-versa upon exposure to UV and visible light.

9. Development of Polyacetylene

PA has attracted much attention since the discovery of its metallic conductivity in doped form.¹ However pristine PA film is infusible and insoluble, limiting its possible applications (Figure 9a). By introducing alkyl substituents into the PA main chain, PA is made soluble in organic solvents to create *mono*-substituted PA (*mono*-PA).³⁸ Then

again, it is observed that the electrical conductivity of substituted PA is significantly lower compared to pristine PA film. This is due to less coplanarity on the main chain, caused by the steric repulsions between substituents. The linear chains of the substituted PA are also randomly oriented further suppressing its electrical conductivity.

The introduction of LC moieties on PA produced *mono*-substituted LCPA (*mono*-LCPA) that is stable in air, soluble in organic solvents and having liquid crystalline properties (Figure 9b).^{8a} Upon macroscopic alignment of *mono*-LCPA, it was shown that its electrical conductivity was enhanced up to two orders of magnitude compared to its unaligned iodine-doped cast film state.³⁹

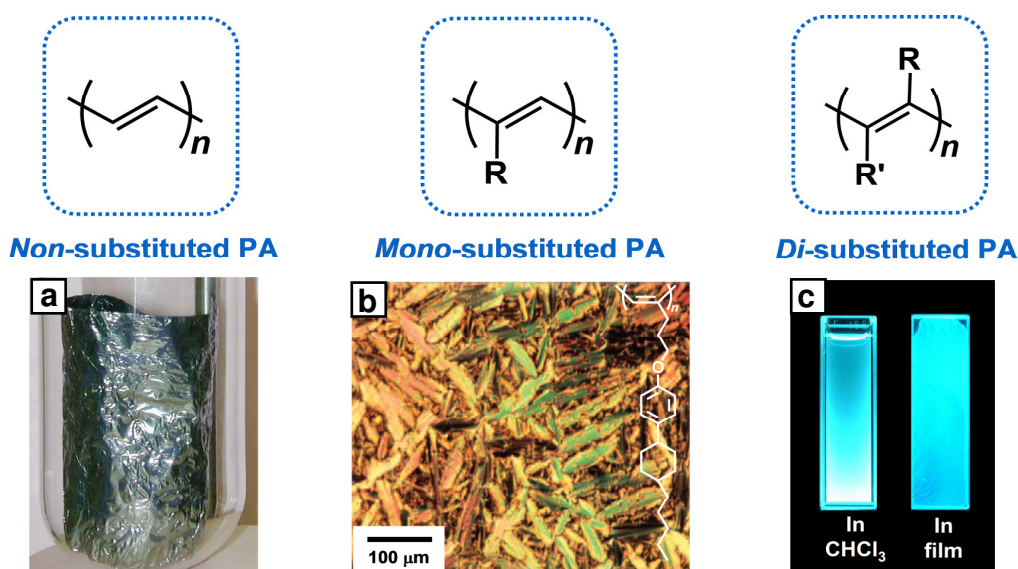


Figure 9. The development of polyacetylene: (a) pristine *non*-substituted polyacetylene film, (b) POM of *mono*-substituted liquid crystalline polyacetylene, (c) photoluminescence of *di*-substituted polyacetylene in chloroform solution (left) and in cast film (right).

Mono-PA on the other hand, has no fluorescence. By adding a second substituent to *mono*-PA, PA can be made to exhibit fluorescence producing *di*-substituted PA (*di*-PA) (Figure 9c). The steric effect of the two side chains on the polyene main chain changes

the energy levels of the exciton excited states of the polymer, thus leading to fluorescence in *di*-PA.⁴⁰ *Di*-PA bearing LC moieties shows good solubility in organic solvents, thermal stability, liquid crystallinity and fluorescence.⁴¹

10. Outline of this Thesis

In *Part I*, the functional properties of *mono*-PA such as liquid crystallinity and chirality were tuned by controlling the feeding ratio of the *mono*-PA copolymers.

In *Chapter 1* describes the synthesis of *mono*-PA copolymers consisting of a liquid crystalline acetylene monomer unit and an asymmetric center containing chiral acetylene monomer unit. It is found from polarizing optical microscopy, X-ray diffraction, and CD spectra that the copolymers exhibited a smectic A (SmA) phase and chirality, depending on the feeding ratio of the two monomers.

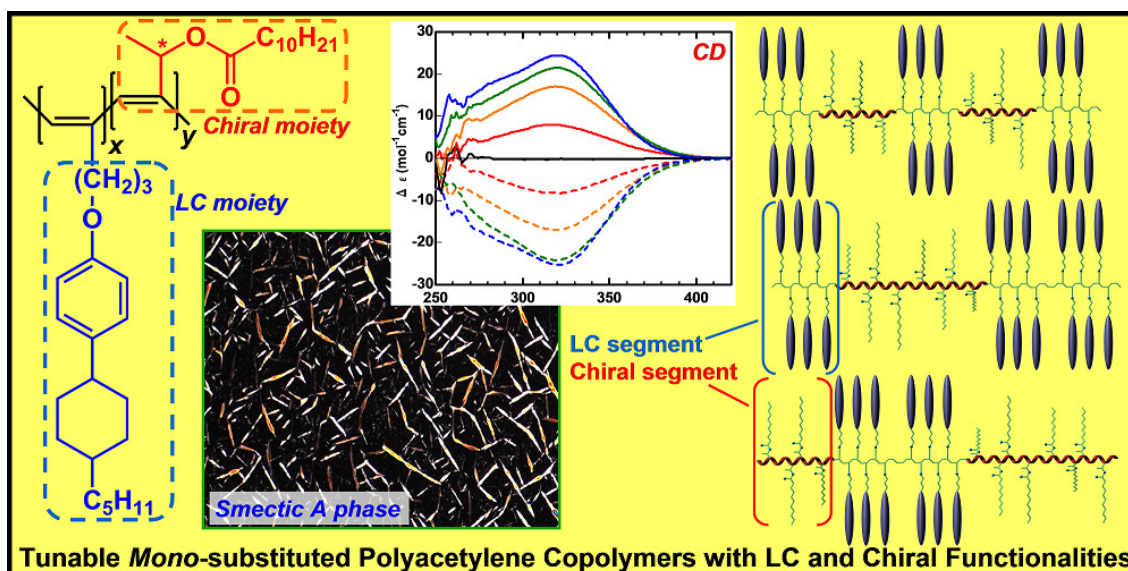


Figure 10. Synthesis of tunable chiral *mono*-substituted liquid crystalline polyacetylene through the copolymerization of liquid crystalline and chiral moiety bearing monomers.

By varying the feeding ratio of the monomers, it is enabled to tune the LC and chiral functionalities of *mono*-PA copolymers and even to impart chirality to the smectic LC phase which could potentially exhibit a chiral smectic A (SmA*) phase (Figure 10).

In **Part II**, various *di*-substituted liquid crystalline PA (*di*-LCPA) derivatives having fluorescence and liquid crystallinity were synthesized. The synthesized *di*-LCPAs were arranged linearly or helically to exhibit polarized functionalities such as LPL and CPL.

In **Chapter 2**, with the aim to synthesize *di*-LCPA with LPL, various *di*-LCPA derivatives were synthesized with LC moieties either directly attached or indirectly attached using flexible alkyl spacers to the main chain. The origin of emission of substituted PAs, with respect to their substituents and structure, was elucidated. The thermotropic and lyotropic LC properties of the *di*-LCPAs were investigated and the *di*-LCPAs were macroscopically aligned using rubbing technique. The aligned structures of the polymers are characterized through XRD measurements.

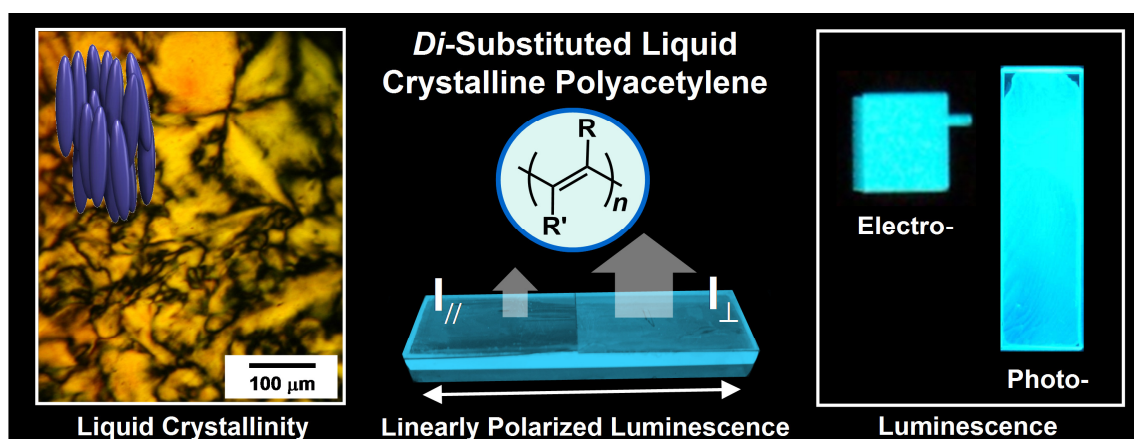


Figure 11. Synthesis of *di*-substituted liquid crystalline polyacetylene derivatives exhibiting LPL.

The macroscopically aligned films of the polymers exhibit LPL with notable dichroic ratios. The electroluminescent (EL) devices using the polymers as the emissive polymer layer emit blue light with promising EL properties (Figure 11).⁴²

In **Chapter 3**, various *di*-LCPA derivatives with thermotropic and lyotropic LC behavior were synthesized. The poly(diphenylacetylene) main chain structure of the *di*-LCPAs and the chirality induced with either chiral moieties or chiral dopants allow the formation of a highly ordered lyotropic N*-LC phase. The N*-LC state facilitates the formation of helically π -stacked structures with a high degree of helical ordering of the *di*-LCPA and is indispensable for the generation of CPL with high emission dissymmetry factors (g_{em}) on the order of 10^{-1} , the highest reported values of g_{em} for aliphatic conjugated polymers (Figure 12).^{42b,43}

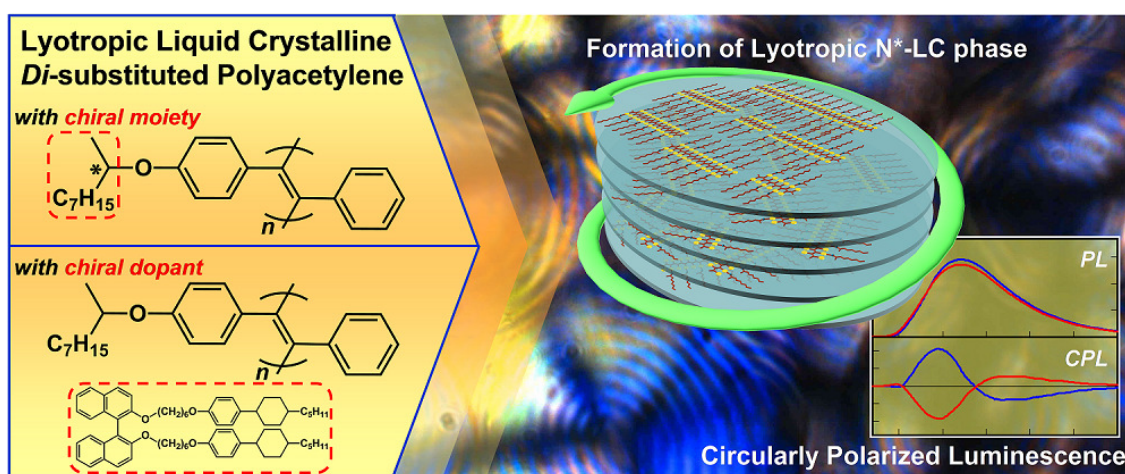


Figure 12. Synthesis of chiral *di*-substituted liquid crystalline polyacetylene showing CPL through the formation of a highly ordered lyotropic N*-LC phase.

In **Part III**, chiral conjugated polymers having helical structures in the aggregate state were synthesized. The synthesized chiral conjugated polymers exhibited novel chiral

inversion functionalities in CD and CPL. Furthermore the dynamic switching of CPL by selective transmission through a N*-LC cell was also investigated.

Chapter 4 describes the synthesis of poly(*para*-phenyleneethynylene) (PPE) derivatives having two chiral moieties in both side chains and characterized their solvent induced chiroptical properties. In varying ratios of chloroform and methanol solvents, the PPE aggregate exhibited a remarkable inversion of Cotton effects of CD and CPL. A facile way of chiral inversion of CPL in PPE through solvent induced aggregation was revealed and the nature of the helical structures present in the aggregate state was investigated (Figure 13).

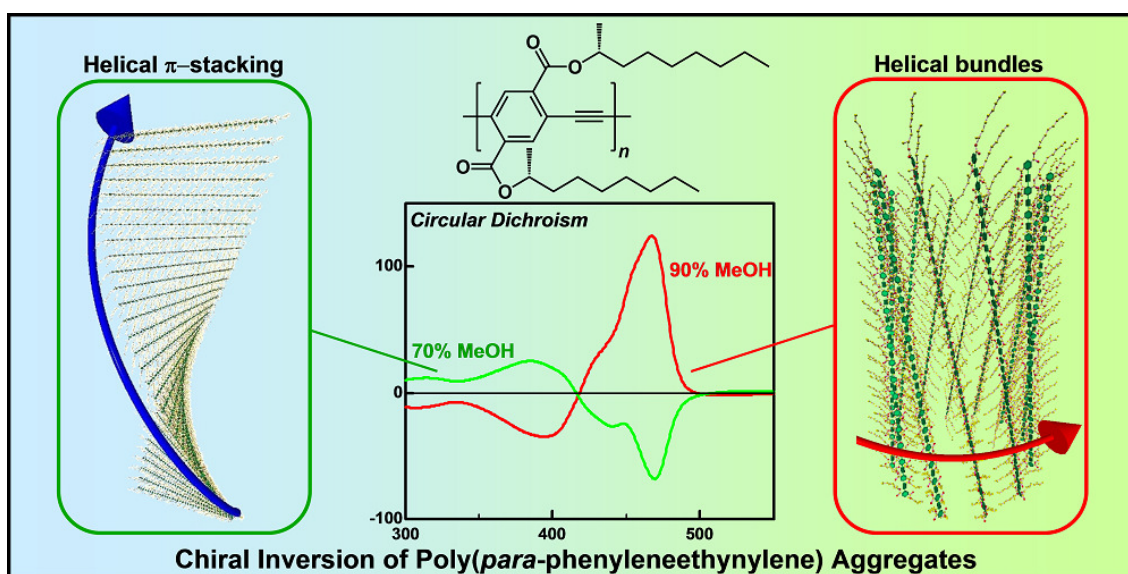


Figure 13. Synthesis of poly(*para*-phenyleneethynylene) derivatives having two chiral moieties in both side chains and characterized their solvent induced chiroptical properties. In varying solvent environments, the PPE aggregates show inversion of chirality.

In **Chapter 5**, PPP derivatives having photoresponsive chiral DE* end-groups were synthesized. In the assembled state, photoisomerization of the chiral DE* end-groups

from open to closed form leads to a change in the handedness of the helical π -stacking structures (Figure 14). Furthermore, the chiral transcription of achiral poly(bithiophenethiophene) (PBTT) by chiral PPP in assembled state was demonstrated. In addition, the chirally transcribed PBTT showed helical inversion with the photoisomerization of the PPP chiral DE* end-groups.

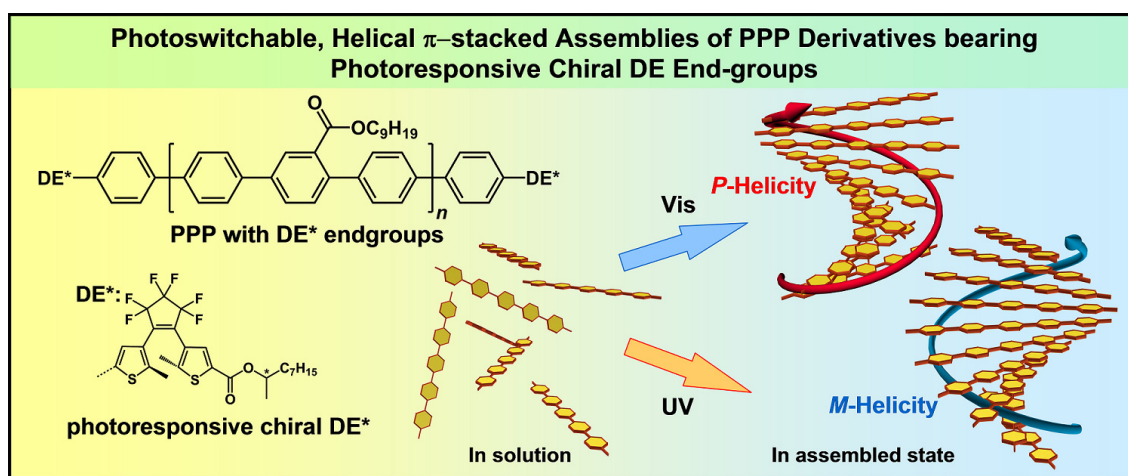


Figure 14. Synthesis of poly(*para*-phenylene) derivatives having photoresponsive chiral DE* endgroups. In the assembled state, photoisomerization of the chiral DE* endgroups leads to a change in the handedness of the helical π -stacking structures.

Chapter 6 describes the demonstration of the dynamic switching of CPL of chiral *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) from left-to right-handed CPL and vice-versa through the selective transmission of CPL across a thermotropic N*-LC phase. By combining a chiral *di*-LCPA CPL emitting film with a N*-LC cell and tuning the selective reflection band of the N*-LC phase to coincide with the CPL emission band, a CPL switchable cell was constructed. The phase change associated with the thermotropic N*-LC cell at varying temperatures leads to a change in selective transmission of CPL which enables dynamic switching of CPL (Figure 15).

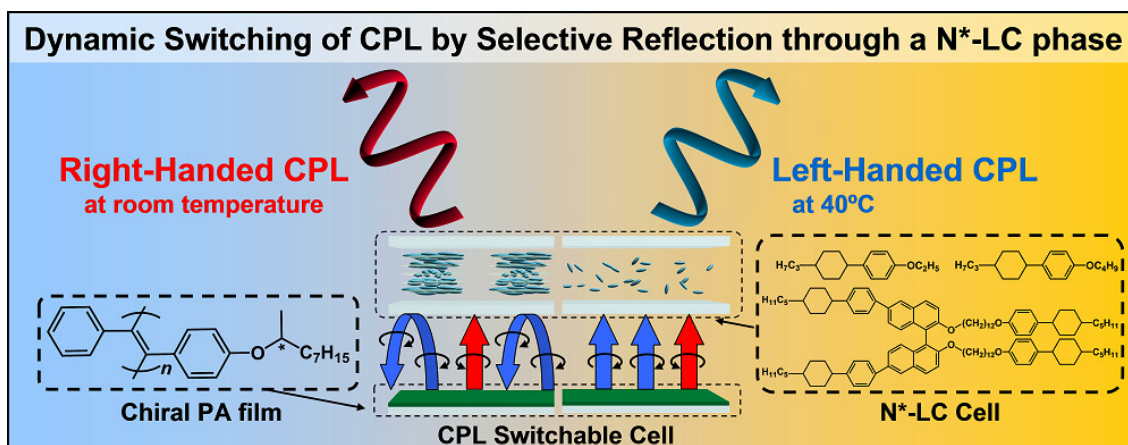


Figure 15. Dynamic switching of CPL of *di*-LCPA by selective reflection through a thermotropic N*-LC phase.

REFERENCES

- (1) Shirakawa, H.; Louis, E. J.; MacDiarmid A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Comm.* **1977**, 578.
- (2) Dekker, M. *In Handbook of Conducting Polymers, Conjugated Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R. Eds. CRC press: New York, **1998**.
- (3) Kiebooms, R.; Menon, R.; Lee, K. *In Handbook of Advanced Electronic and Photonic Materials and Devices*, Vol 8.; Nalwa, H. S. Ed. Academic press: San Diego, **2001**; p. 1.
- (4) Pron, A.; Rannou, P. *Prog. Polym. Sci.* **2002**, 27, 135.
- (5) Burroughes, J. H.; Bradley D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, 347, 539
- (6) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W.; Vill, V. *In Handbook of Liquid Crystals*; Wiley-VCH: Berlin, **1998**; Vol. 1–2.
- (7) (a) Gottarelli, G.; Hibert, M.; Samori, B.; Solladie, G.; Spada, G. P.; Zimmermann, R. J. *J. Am. Chem. Soc.* **1983**, 105, 7318. (b) Solladie, G.; Zimmermann, R. *Angew. Chem. Int. Ed.* **1984**, 23, 348. (c) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladie, G.; Zimmermann, R. *J. Org. Chem.* **1986**, 51, 589. (d) Textures of Liquid Crystals; Dierking, I., Ed.; Wiley-VCH: Weinheim, 2003.
- (8) (a) Oh, S.Y.; Akagi, K.; Shirakawa, H.; Araya, K. *Macromolecules* **1993**, 26, 6203. (b) Oh, S.Y.; Ezaki, R.; Akagi, K.; Shirakawa, H. *J. Polym. Sci. A: Polym. Chem.* **1993**, 31, 2977. (c) Akagi, K.; Shirakawa, H. *Macromol. Symp.* **1996**, 104, 137. (d) Kuroda, H.; Goto, H.; Akagi, K.; Kawaguchi, A. *Macromolecules* **2002**, 35, 1307. (e) Goto, H.; Dai, X.; Ueoka, T.; Akagi, K. *Macromolecules* **2004**, 37, 4783.
- (9) (a) Jin, S. H.; Choi, S. J.; Ahn, W.; Cho, H. N.; Choi, S. K. *Macromolecules* **1993**,

- 26, 1487. (b) Choi, S. K.; Gal, Y. S.; Jin, S. H.; Kim, H. K. *Chem. Rev.* **2000**, *100*, 1645.
- (c) Tang, B.Z.; Kong, X.; Wan, X.; Peng, H.; Lam, W. Y.; Feng, X. D. *Macromolecules* **1998**, *31*, 2419. (d) Kong, X.; Lam, J. W. Y.; Tang, B. Z. *Macromolecules* **1999**, *32*, 1722. (e) Geng, J.; Zhao, X.; Zhou, E.; Li, G.; Lam, J. W. Y.; Tang, B. Z. *Polymer* **2003**, *44*, 8095.
- (10) (a) Koltzenburg, S.; Wolff, D.; Stelzer, F.; Springer, J.; Nuyken, O. *Macromolecules* **1998**, *31*, 9166. (b) Ting, C. H.; Chen, J. T.; Hsu, C. S. *Macromolecules* **2002**, *35*, 1180. (c) Schenning, A. P. H. J.; Fransen, M.; Meijer, E.W. *Macromol. Rapid. Commun.* **2002**, *23*, 265. (d) Stagnaro, P.; Conzatti, L.; Costa, G.; Gallot, B.; Valenti, B. *Polymer* **2003**, *44*, 4443.
- (11) (a) Araya, K.; Mukoh, A.; Narahara, T.; Shirakawa, H. *Chem. Lett.* **1984**, 1141. (b) Akagi, K.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. *Polym. J.* **1987**, *19*, 185. (c) Akagi, K.; Katayama, S.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. *Synth. Met.* **1987**, *17*, 241. (d) Akagi, K.; Katayama, S.; Ito, M.; Shirakawa, H.; Araya, K. *Synth. Met.* **1989**, *28*, D51. (e) Sinclair, M.; Moses, D.; Akagi, K.; Heeger, A. J. *Phys. Rev. B: Condens. Matter.* **1988**, *38*, 10724.
- (12) (a) Montaner, A.; Rolland, M.; Sauvajol, J. L.; Galtier, M.; Almairac, R.; Ribet, J. L. *Polymer* **1988**, *29*, 1101. (b) Coustel, N.; Foxonet, N.; Ribet, J. L.; Bernier, P.; Fischer, J. E. *Macromolecules* **1991**, *24*, 5867.
- (13) (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683. (b) Akagi, K.; Piao, G.; Kaneko, S.; Higuchi, I.; Shirakawa, H.; Kyotani, M. *Synth. Met.* **1999**, *102*, 1406. (c) Akagi, K.; Higuchi, I.; Piao, G.; Shirakawa, H.; Kyotani, M. *Mol. Cryst. Liq. Cryst.* **1999**, *332*, 463. (d) Akagi, K.; Guo, S.; Mori, T.; Goh, M.; Piao, G.; Kyotani, M. *J. Am. Chem. Soc.* **2005**, *127*, 14647.

- (14) Iida, H.; Nakamura, A.; Inoue, Y.; Akagi, K. *Synth. Met.* **2003**, *135*, 91. (b) San Jose, B. A.; Matsushita, S.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 19795-19807.
- (15) Langeveld-Voss, B.; Janssen, R.; Christiaans, M.; Meskers, S.; Dekkers, H.; Meijer, E. *J. Am. Chem. Soc.* **1996**, *118*, 4908.
- (16) (a) Lemmer, U.; Vacar, D.; Moses, D.; Heeger, A. J.; Ohnishi, T.; Noguchi, T. *Appl. Phys. Lett.* **1996**, *68*, 3007. (b) Hamaguchi, M.; Yoshino, K. *Appl. Phys. Lett.* **1995**, *67*, 3381. (c) Lussem, G.; Geffrath, F.; Greiner, A.; Heitz, W.; Hopmeier, M.; Oberski, M.; Unterlechner, C.; Wendorff, J. H. *Liq. Cryst.* **1996**, *21*, 903.
- (d) Dyreklev, P.; Berggren, M.; Inganaes, O.; Andersson, M. R. ; Wennerstroem, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43.
- (17) (a) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, C.; Smith, P. *Science* **1998**, *279*, 835. (b) Montali, A.; Bastiaansen, C.; Smith, P., Weder, C. *Nature* **1998**, *392*, 261.
- (18) (a) Dyreklev, P.; Berggren, M.; Inganäs, O.; Andersson, M. R.; Wennerström, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43. (b) Grell, M.; Bradley, D. C. *Adv. Mater.* **1999**, *11*, 895. (c) Grell, M.; Oda, M.; Whitehead, K. S.; Asimakis, A.; Neher, D.; Bradley, D. D. C. *Adv. Mater.* **2001**, *13*, 577.
- (19) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506.
- (20) (a) Feringa, B. L.; van Delden, R. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 3418. (b) Sato, I.; Yamashita, R.; Kadowaki, K.; Yamamoto, J.; Shibata, T.; Soai, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1096.
- (21) Riehl, J. P.; Richardson, F. S. *Chem. Rev.* **1986**, *86*, 1.
- (22) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119*, 9909.

- (23) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. *J. Am. Chem. Soc.* **2001**, *123*, 11899.
- (24) De Vries, H. *Acta. Cryst.* **1951**, *4*, 219.
- (25) Goh, M.; Kyotani, M.; Akagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 8819.
- (26) Coles, H.; Morris, S. *Nat. Photonics* **2010**, *4*, 676.
- (27) Wulff, G. *Angew. Chem.* **1989**, *101*, 22.
- (28) Janssen, H. M.; Meijer, E. W. *Macromolecules* **1997**, *30*, 8129.
- (29) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385.
- (30) Okamoto, Y.; Nakano, T.; Ono, E.; Hatada, K. *Chem. Lett.* **1991**, *20*, 525.
- (31) (a) Pohl, F. M.; Jovin, T. M. *J. Mol. Biol.* **1972**, *67*, 375. (b) Cosstick, R.; Eckstein, F. *Biochemistry* **1985**, *24*, 3630.
- (32) Li, C.; Numata, M.; Takeuchi, M.; Shinkai, S. *Chem Asian J.* **2006**, *1*, 95.
- (33) (a) Kawagoe, Y.; Fujiki, M.; Nakano, Y. *New J. Chem.*, **2010**, *34*, 637. (b) Nakano, Y.; Lui, Y.; Fujiki, M. *Polym. Chem.*, **2010**, *1*, 460. (c) Nakano, Y.; Ichiyanagi, F.; Naito, M.; Yang, Y.; Fujiki, M. *Chem. Commun.*, **2012**, *48*, 6636.
- (34) (a) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157. (b) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702. (c) Goto, H.; Okamoto, Y.; Yashima, E. *Macromolecules* **2002**, *35*, 4590. (d) Koeckelberghs, G.; Cornelis, D.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1132.
- (35) (a) Satrijo, A.; Swager, T. M. *Macromolecules* **2005**, *38*, 4054. (b) Satrijo, A.; Meskers, S. C. J.; Swager, T. M. *J. Am. Chem. Soc.*, **2006**, *128*, 9030.
- (36) Zahn, S.; Swager, T. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4225.
- (37) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) *Molecular Switches*; Feringa, B. L.,

- Ed.; Wiley-VHC: Weinheim, 2001. (c) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85.
- (38) (a) Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Symp.* **1980**, *67*, 43. (b) Simionescu, C. I.; Percec, V. J.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497.
- (39) Akagi, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 649.
- (40) (a) Shukla, A.; Mazumdar, S. *Phys. Rev. Lett.* **1999**, *19*, 3944. (b) Hidayat, R.; Fujii, A.; Ozaki, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 597. (c) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87. (d) Vardeny, Z. V., Korovyanko, O. In *Handbook of Conducting Polymers, Conjugated Polymers*, 3rd ed.; Skotheim, T. A.; Reynolds, J. R.; Eds. CRC press: New York, **2007**; pp. 22-1–22-74.
- (41) (a) Lam, J.; Tang, B. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2607. (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799.
- (42) (a) San Jose, B. A.; Matsushita, S.; Moroishi, Y.; Akagi, K. *Macromolecules* **2011**, *44*, 6288. (b) San Jose, B. A.; Akagi, K. *Polym. Chem.* **2013**, 5144.
- (43) San Jose, B. A.; Matsushita, S.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 19795.

Part I: Tuning of the Functional Properties of
***Mono*-substituted Polyacetylene derivative**

Chapter 1

Competitive and Constructive Structural Effects of Liquid Crystalline and Chiral Units on the Functional Properties of *Mono*-Substituted Polyacetylene Copolymers

ABSTRACT:

We synthesized *mono*-substituted polyacetylene (*mono*-PA) copolymers, which consisted of a liquid crystalline acetylene monomer unit and an asymmetric center containing a chiral acetylene monomer unit. The former has a phenylcyclohexyl (PCH) mesogen linked with a trimethylene spacer, and the latter has an (*R*)-/(*S*)-1-methylpropargyl-undecanoate structure. Polarizing optical microscopy, X-ray diffraction, and circular dichroism data indicate that the copolymers exhibited a smectic A (SmA) phase and chirality, which was dependent upon the feeding ratio of the two monomers. Varying this ratio tunes the LC and chiral functionalities in *mono*-PA copolymers and imparts chirality to the smectic LC phase, which could potentially result in a chiral smectic A (SmA*) phase.

1. Introduction

The development of chiral liquid crystal (LC) phases, which exhibit handedness in their mesophase, has gained significant attention in the field of functional soft materials. Among these chiral phases, current research has focused on the chiral nematic liquid crystal (N*-LC) phase. The N*-LC phase facilitates the helical self-assembly of

LC-conjugated polymers, such as *di*-substituted polyacetylenes that show high dissymmetry factors in circularly polarized luminescence (CPL)^{1a} and thiophene-based copolymers that exhibit white CPL.^{1b} The N*-LC phase has also been employed in photonic bandgap materials² and LC lasers.^{2a,3} Additionally, the N*-LC phase was utilized as an asymmetric reaction medium for the synthesis of polyacetylene⁴ and graphitic⁵ films with hierarchical helical structures.

The chiral smectic A (SmA*) phase has also attracted increased attention. Smectic LC phases show an orientational order, which aligns the molecules along a certain direction (LC director), and exhibit a degree of positional order with the LC molecules arranged in layers. In the smectic A (SmA) phase, the LC director is perpendicular to the smectic layer plane. If at least one of the molecular components of a SmA mesophase is chiral, the mesophase becomes a chiral smectic phase (SmA*), which may exhibit an electroclinic effect.⁶⁻⁸ In the presence of an electric field (E), the LC director tilts (θ) relative to the layer normal in a direction orthogonal to the electric field. The linear relationship between θ and E at low field strengths makes it possible to generate a grayscale display between crossed polarizers. The unique photorefractive properties of SmA* LC, which are due to the electroclinic effect, can be utilized for a wide range of applications in electro-optical devices, such as tunable and micro-color filters.⁹

LC molecules with chiral moieties⁶ can be utilized to generate a chiral LC phase. Simply mixing a LC host with chiral molecules also produces a chiral LC phase in a facile manner. If a chiral binaphthyl dopant is added to a nematic LC (N-LC) host, then the LC phase changes to a N*-LC phase.^{4,6,10} However, if the mole ratio of the chiral dopant increases too much, then the N*-LC phase becomes less stable and is

eventually lost. A chiral LC phase derived from a LC conjugated polymer would be more stable, and its chiroptical properties could be utilized for the development of next-generation organic optoelectronic devices. The copolymerization of two types of monomer units bearing LC and chiral moieties is an alternative method for the generation chiral LC phases with LC conjugated polymers.

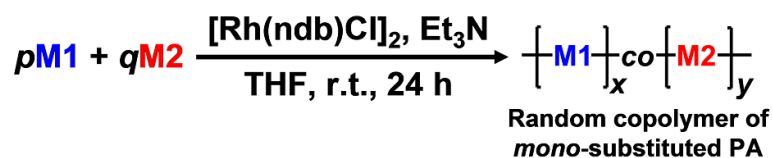
Various *mono*-substituted polyacetylene (*mono*-PA) copolymers, which had both LC and chiral moieties, were synthesized. We utilized the competitive and collaborative effects between the LC and chiral monomer units to affect the functional properties of the *mono*-PA copolymer. By varying the feeding ratio of the monomers, we developed a facile method for tuning the LC and chiral functionalities in *mono*-PA.

2. Results and Discussion

2.1. Synthesis and Characterization of Polymers

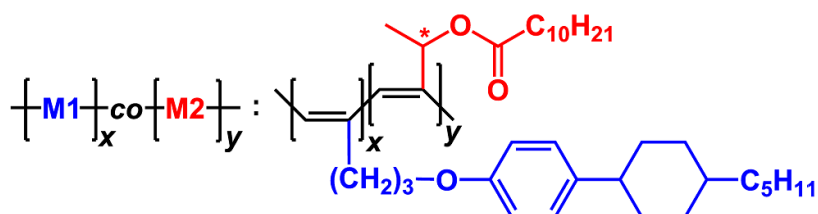
The acetylene monomers substituted with LC and chiral groups were copolymerized to form *mono*-PA derivatives (Scheme 1). The monomers were randomly copolymerized at various monomer feeding ratios, which resulted in copolymers with varying LC and chiral properties. The LC monomer is composed of a phenylcyclohexyl (PCH) mesogen core, a trimethylene chain linked, an ether-type spacer ($-(\text{CH}_2)_3\text{O}$), and a terminal pentyl chain. The LC monomer is abbreviated as **M1**. The chiral monomers, (*R*)- and (*S*)-1-methylpropargyl-undecanoate, are named (*R*)- and (*S*)-**M2**, respectively. The copolymers are named based on the mole ratio within the monomer feeding and the chiral configuration of their monomers. The homopolymer made using the LC monomer is named **PA1**, while its chiral counterparts are named as (*R*)-/(*S*)-**PA2**. A copolymer written as (*S*)-**PA**_{75.25*} describes a *mono*-PA

copolymer with a monomer feeding ratio of 75% LC side chain (**M1**) and 25% chiral side chain ((**S**)-**M2**). The gel permeation chromatography (GPC) results showed that the polymers have M_n values ranging from 30,000 to 102,300 and M_w/M_n values ranging from 1.5 to 3.4 (Table 1).



p : feeding mole ratio of LC acetylene monomer, **M1**

q : feeding mole ratio of chiral acetylene monomer, **M2**



PA1 (PA_{100-0^*})^a : $p = 100, q = 0$

(**R**)-/**(S)**-**PA**_{75-25*} : $p = 75, q = 25$

(**R**)-/**(S)**-**PA**_{50-50*} : $p = 50, q = 50$

(**R**)-/**(S)**-**PA**_{25-75*} : $p = 25, q = 75$

(**R**)-/**(S)**-**PA2** (PA_{0-100^*}) : $p = 0, q = 100$

^a The asterisk “*” symbol indicates chiral segment.

Scheme 1. Syntheses of the *mono*-substituted polyacetylene copolymers.

Table 1. Results of polymerization of the *mono*-substituted polyacetylene

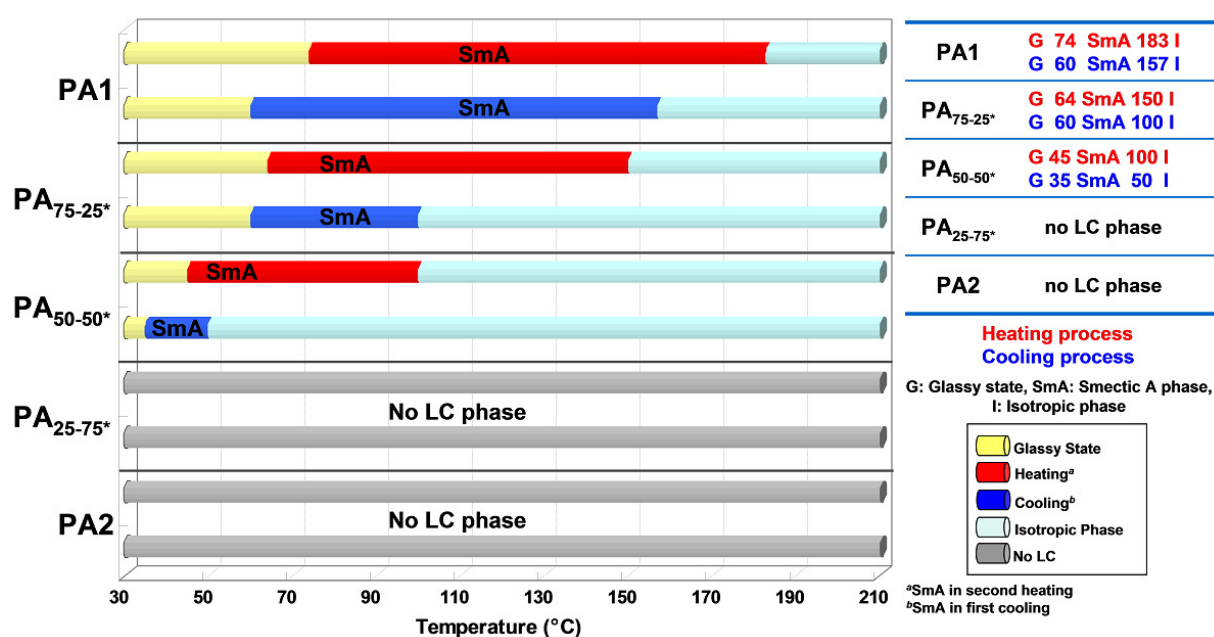
	M_w	M_n	M_w / M_n	D.P. ^a
PA1	21,000	30,000	1.5	67
(R)- PA _{75-25*}	28,000	45,000	1.6	97
(S)- PA _{75-25*}	16,000	42,000	2.7	54
(R)- PA _{50-50*}	28,000	44,000	1.6	103
(S)- PA _{50-50*}	24,000	70,000	2.9	88
(R)- PA _{25-75*}	29,000	81,000	2.8	113
(S)- PA _{25-75*}	46,000	102,000	2.2	180
(R)- PA2	27,000	93,000	3.4	116
(S)- PA2	34,000	100,000	3.0	142

^aDegree of polymerization

2.2. Liquid Crystallinity

The *mono*-PA polymer (**PA1**) and copolymers (**PA_{75-25*}**, **PA_{50-50*}**) exhibited enantiotropic liquid crystallinity (Table 2). POM analysis revealed that **PA1** has a fan-shaped texture, which is characteristic of a SmA LC phase (Figure 1a). The smectic LC temperature ranges were 74–183 °C and 60–157 °C in the heating and cooling processes, respectively. The LC phase of **PA1** was further investigated using X-ray diffraction (XRD) measurements. The XRD pattern revealed a sharp peak in the small angle region ($2\theta = 2.3^\circ$) and a broad diffraction peak in the wide angle region ($2\theta = 18.6^\circ$) (Figure 1d). This type of XRD profile is usually observed for a SmA phase.¹² The diffraction angle (18.6°) in 2θ corresponds to a value of 4.8 Å, which is assigned to be the distance between the mesogenic groups. The reflection angle (2.3°) in 2θ corresponds to a value of 38.4 Å, which is assigned to be the smectic interlayer distance between polymer chains (see Figure 3).¹³ Additionally, a secondary reflection of the smectic interlayer distance at 4.7° in 2θ (37.6 Å , $n = 2$) was also observed.

Table 2. Liquid crystal transition temperatures of the *mono*-substituted polyacetylene copolymers.



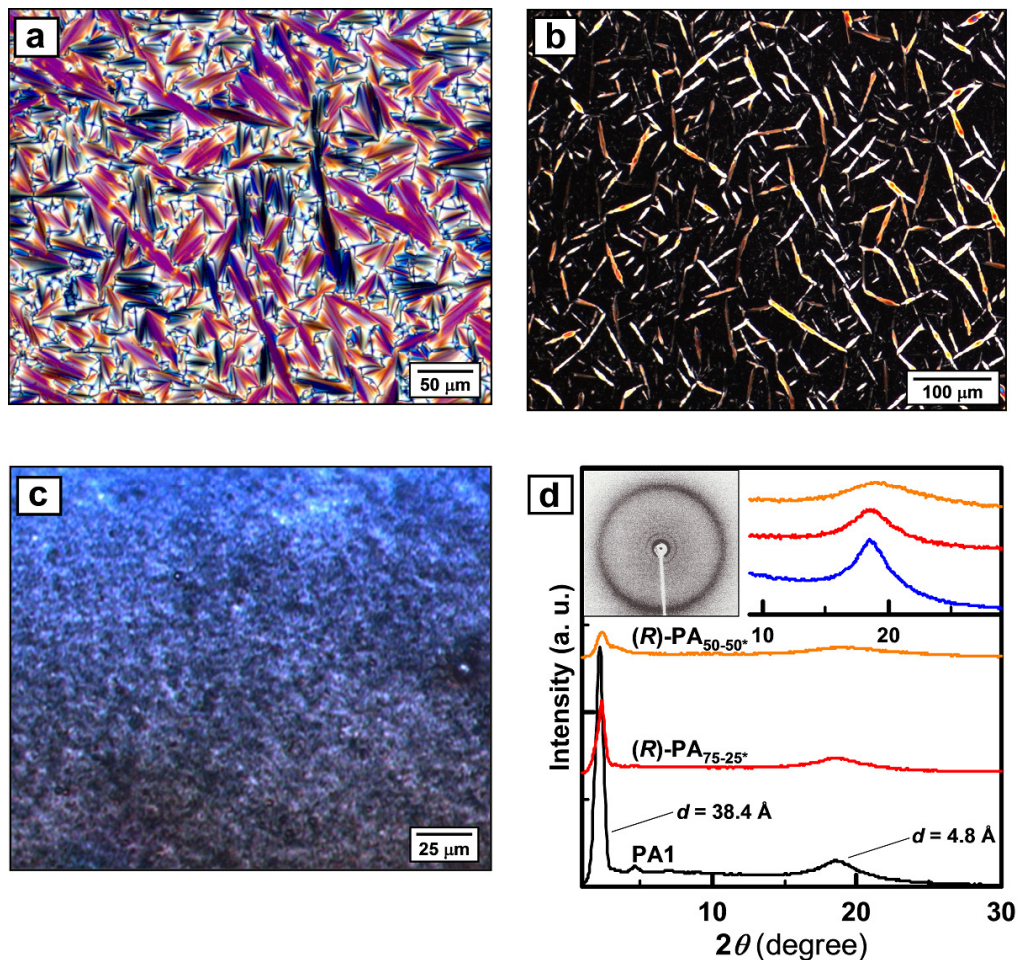


Figure 1. POM images of (a) **PA1** at 100 °C in cooling process, (b) **(R)-PA₇₅₋₂₅*** at 97 °C in cooling process, and (c) **(R)-PA₅₀₋₅₀*** at 40 °C in cooling process. (d) The XRD pattern of **PA1**, **(R)-PA₇₅₋₂₅***, and **(R)-PA₅₀₋₅₀*** showing a broad reflection at 4.8 Å (18.6° in 2θ) and a sharp peak at 38.4 Å (2.3° in 2θ), inset shows the Laue pattern of **PA1**.

Interesting trends in the LC properties can be observed when changes in the monomer feeding ratio for the *mono*-PA copolymers are made. It is observed that the transition temperatures between the glassy and LC phase, as well as between the LC and isotropic phase, decrease from **PA1** to **(R)-PA₅₀₋₅₀***. Narrowing of the LC temperature range can also be observed when the monomer feeding ratio of the LC monomer decreases from **PA1** to **(R)-PA₅₀₋₅₀***. The LC POM textures of the *mono*-PA

copolymers also changed. The POM image of **(R)-PA_{75-25*}** shows a filament texture, which is composed of smectic *batonnets*, characteristic of the SmA phase (Figure 1b).^{6,12} **(R)-PA_{50-50*}** exhibits a sandy granular texture; the smectic LC domains decreased in size compared to **PA1** and **(R)-PA_{75-25*}** (Figure 1c). Furthermore, XRD patterns show that the copolymers exhibit the same SmA phase diffraction peaks, but with decreasing intensities (Figure 1d). However, **(R)-PA_{25-75*}**, and **(R)-PA2** exhibited no LC behavior in POM and XRD. When the LC monomer ratio decreased, the smectic interlayer arrangement of the *mono*-PA copolymer became less stable. Therefore, the XRD peaks assigned to the smectic interlayer decreased in intensity and the domains of the LC textures decreased in size. Accordingly, the copolymer still maintained a stable mesophase, even for LC monomer feeding ratios up to 50%. These trends in XRD and POM observations imply that the LC and chiral monomers are in structural competition to exert their respective effects on the copolymer main chain.

POM observations and XRD measurements showed that the *mono*-PA copolymers (**(R)-PA_{75-25*}** and **(R)-PA_{50-50*}** exhibited a SmA phase. The *mono*-PA copolymers, which have both LC and chiral monomer units, could potentially exhibit a SmA* mesophase. However, it is difficult to confirm the emergence of the SmA* mesophase from POM and XRD measurements because the SmA and SmA* phases have similar XRD patterns and POM textures.^{6,7} Therefore, the chiroptical properties of the *mono*-PA copolymers were investigated to confirm their chirality.

2.3. Chiroptical Properties

The UV–vis and circular dichroism (CD) spectra of the *mono*-PA polymers and copolymers, which were prepared in chloroform (CHCl₃) solution ($c = 1.2 \times 10^{-4}$ M)

(Figure 2) and as an annealed cast film (Figure S1), were examined. The UV-vis spectrum of **PA1** in solution showed an absorption band at 320 nm, which corresponded to the π - π^* transition of the polyene main chain, and at 280 nm, which corresponded to the π - π^* transition of the PCH side chain. The UV-vis spectra of (*R*)- and (*S*)-**PA2** showed broad absorption bands, which were attributed to the π - π^* transition of the polyene main chain ($\sim$ 320 nm). Clearly, the chiral monomer ((*R*)- and (*S*)-**M2**) ratio increases with the relative intensity of the main chain absorption ($\sim$ 320 nm) and the decrease of the PCH side chain absorption ($\sim$ 280 nm).

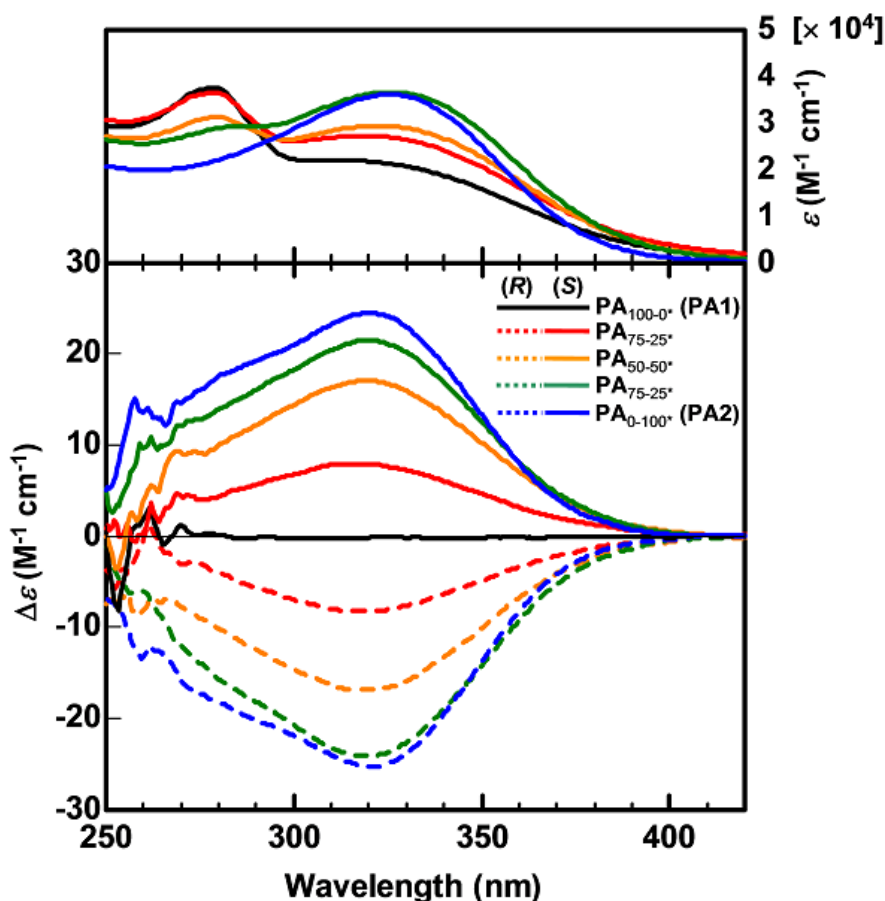


Figure 2. UV-vis (above) and CD spectra (below) of the *mono*-substituted polyacetylene copolymers in CHCl_3 solution ($c = 1.2 \times 10^{-4}$ M).

The CD spectra of the chiral *mono*-PAs, which bear (*R*)- and (*S*)- chiral moieties, showed monosignate Cotton effects at approximately 320 nm, which corresponds to the absorption of the polyene main chain. These results imply that the *mono*-PAs have a one-handed helical excess conformation and intrachain helicity.¹⁴ Annealed cast films showed similar CD spectra (Figure S1), which indicates that the *mono*-PA copolymers exhibit chirality in the LC phase.

The degree of CD was evaluated using the absorption dissymmetry factor, g_{abs} . This factor is defined by the following equation: $g_{\text{abs}} = (\epsilon_{\text{L}} - \epsilon_{\text{R}}) / [(\epsilon_{\text{L}} + \epsilon_{\text{R}}) / 2] = \Delta\epsilon / \epsilon$, where g_{abs} , $-2 < g_{\text{abs}} < 2$. The ϵ_{L} and ϵ_{R} are defined as the absorption coefficients of left and right handed polarized light, respectively. An increase in g_{abs} at 320 nm, which was from values on the order of 10^{-4} to values on the order of 10^{-3} , was observed as the feeding ratio of the chiral monomer unit increased (Table S1).

2.4. Structural Effects of the Liquid Crystalline and Chiral Units

We propose a plausible model, which is based on the LC and chiroptical properties of the *mono*-PA copolymers, where the spontaneous arrangement of the copolymer chains at their LC temperature (Figure 3). At this temperature, the main chain is supposed to consist of distinct LC and chiral segments. At LC monomer feeding ratios greater than or equal to 50% ($p \geq 50\%$), the LC segments, which have PCH moieties linked with flexible spacers, direct the copolymer main chains to a SmA arrangement.^{13,15} However, at LC monomer ratios less than 50% ($p < 50\%$), there are not enough LC segments to stabilize the SmA phase. In this situation, the copolymers are arranged in a random isotropic manner and therefore exhibit no LC behavior. The chiral segments of the *mono*-PA copolymer exhibit intrachain helicity and are

responsible for the Cotton effects observed in the CD spectra. Therefore, as the number of chiral segments increase in the copolymer main chain, the g_{abs} values also increase.

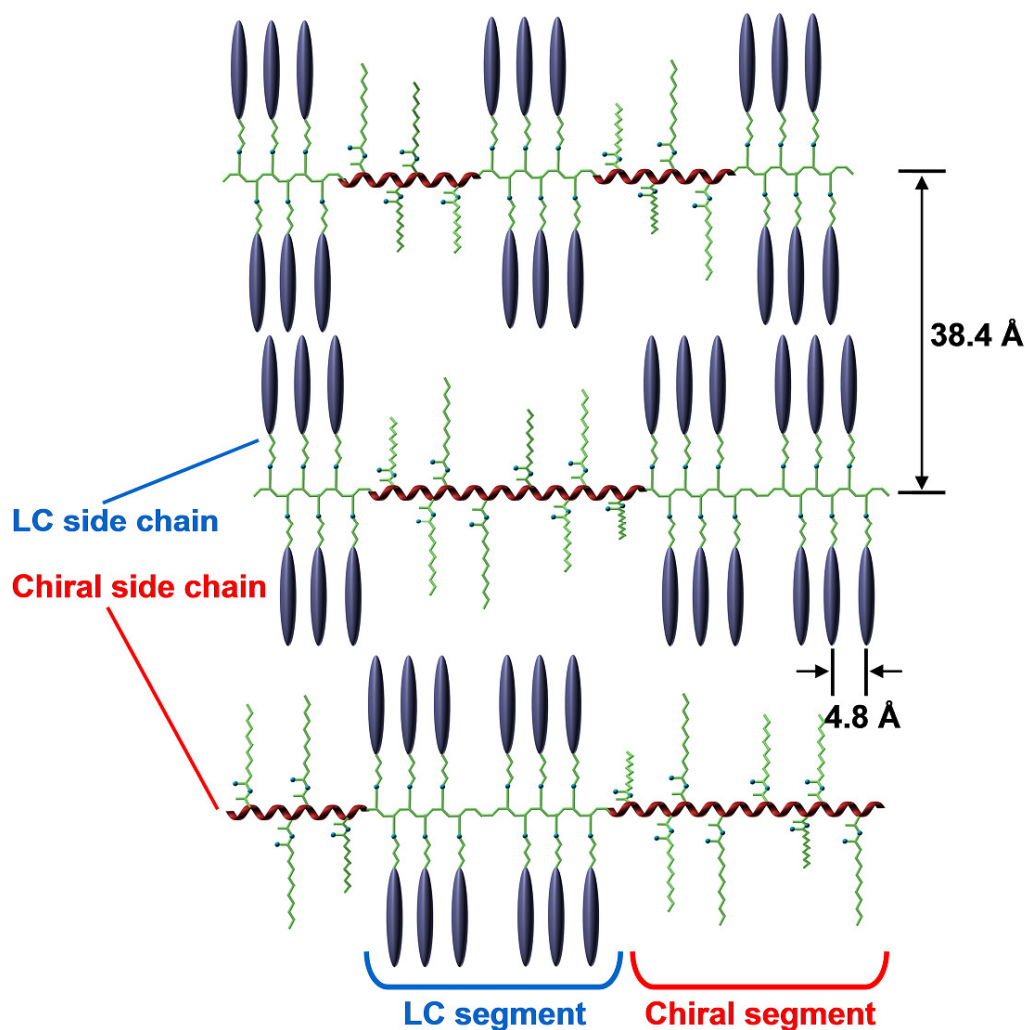


Figure 3. Model describing the arrangement of the *mono*-substituted polyacetylene copolymer in the smectic A (SmA) liquid crystal phase.

When the LC monomer feeding ratios decrease, we can also observe a decrease in the XRD peak intensity and a narrowing of the LC phase temperature range. In this situation, the increase in the amount of chiral monomer units imparts more helicity to the *mono*-PA main chain, which perturbs the interlayer arrangement of the LC segments.

This effect coincides with a decrease of the LC domain size and an increase in CD intensity. Therefore, the LC and chiral segments of the main chain behave as "competitive structural factors" when generating their effects in the *mono*-PA copolymer. When suitable feeding mole ratios between the LC and chiral molecules are employed for copolymerization, which was observed for **PA**_{75-25*} and **PA**_{50-50*}, the LC and chiral segments contribute cooperatively to afford both (LC and chiral) functionalities in the copolymer. These results contrast with the properties of the polymer mixtures, which will be discussed below. By varying the feeding ratio of the functional monomers, we developed a facile method for tuning the LC and chiral functionalities in *mono*-PA and imparting chirality to the smectic LC phase of a LC conjugated polymer.

Finally, the LC properties of polymer mixtures of **PA1** and (**R**)-**PA2** were examined and compared to the copolymers. Polymer mixtures of **PA1** and (**R**)-**PA2** at various mole ratios (75:25, 50:50 mole percent for **PA1** and (**R**)-**PA2**, respectively) were prepared. It was observed from POM measurements that the polymer mixtures of 75:25 and 50:50 showed distinct clear and colored regions in their isotropic phase. After cooling to their LC phase, dispersed domains of smectic *batonnets* were observed (Figure S2a,c). Upon further cooling, sandy granular domains surrounding the *batonnet* domains were observed (Figure S2b,d). Such POM observations suggest that the two types of polymers, **PA1** and (**R**)-**PA2**, were not miscible due to their differing structures. The *batonnet* domains are assigned to the LC phase of **PA1**, while the sandy granular domains are assigned to the LC phase of a **PA1** and (**R**)-**PA2** mixture. Copolymerization offers an alternative method for preparing a chiral LC phase. While mixing polymers leads to an inhomogeneous LC phase, which is due to the immiscibility of structurally dissimilar polymers, copolymerization can exhibit a

homogenous and stable LC phase despite using monomers with dissimilar structures.

3. Conclusion

In summary, we have synthesized *mono*-substituted PA copolymers bearing LC and chiral moieties. The copolymers show a stable SmA phase when using feeding mole ratios up to 50:50* with LC and chiral monomers. Although the SmA phase and chirality are simultaneously realized in these copolymers, electroclinic measurements are still required to unambiguously confirm the presence of the SmA* phase in these materials. We have found that the copolymerization method is a facile way to prepare a stable smectic mesophase and impart chirality to the mesophase. The synthesized *mono*-PA copolymers could be potential photorefractive materials because of the electroclinic properties associated with the SmA* phase and the evaluation of their electroclinic properties associated with the SmA* phase is ongoing.

Acknowledgement

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Chapter 1 Appendix

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1. Experimental Section

1.1. Materials

1.2. Methods

1.3. Syntheses of Monomers and Polymers

2. Supporting Information Scheme, Figures and Tables

1. Experimental Section

1.1. Materials

The chemical reagents we purchased from commercially available sources and were used as received. Bicyclo[2.2.1](hepta-2,5-diene)chlororhodium(I) dimer ($[\text{Rh}(\text{nbd})\text{Cl}]_2$) were purchased from Aldrich Co. Ltd. Diisopropylazodicarboxylate (DIAD), *n*-undecanoic acid, 4-pentyn-1-ol, (*R*)-(+)-3-butyn-2-ol, (*S*)-(-)-3-butyn-2-ol, were purchased from Tokyo Kasei Co. Ltd. *Para-trans*-4-*n*-pentyl(cyclohexyl) phenol were purchased from Kanto Chemical Co. Ltd. Triphenylphosphine (TPP) was purchased from Wako Co. Ltd. 4-Dimethylaminopyridine (DMAP), *N,N'*-dicyclohexylcarboimide (DCC), sodium sulfate (Na_2SO_4), triethyl amine (Et_3N), tetrahydrofuran (THF), methanol (MeOH), chloroform (CHCl_3), and dichloromethane (CH_2Cl_2) were purchased from Nacalai Tesque Co. Ltd. All experiments were

performed under argon (>99.9995 % purity) atmosphere. THF, Et₃N, and toluene used were distilled from sodium as a drying agent under argon gas before use.

1.2. Methods

Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either JEOL JNM EX400 400 MHz or Bruker AVANCE-600 600 MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from *tetra*-methylsilane (TMS) as an internal standard. Elemental analysis was measured using a Perkin-Elmer 2400 CHN Elemental Analyzer.

The microscope observation was carried out under crossed nicols using a Nikon ECLIPSE E400 POL POM equipped with a Nikon COOLPIX 950 digital camera and a Linkam TH600PM and L600 heating and cooling stage with temperature control. The samples for observations with POM were sandwiched between two cover glasses.

Optical absorption spectra were measured using a Hitachi U-3500 spectrometer with quartz cell (for solution) and quartz plate (for cast film). Circular dichroism spectra were measured using JASCO J-820 spectropolarimeter. CHCl₃ solutions of the *mono*-PAs were prepared at a concentration of $c = 1.2 \times 10^{-4}$ M. Annealed cast films were prepared by annealing the *mono*-PAs at their LC temperature for an hour before spectroscopic measurements were done.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μ m MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

XRD diffraction (XRD) measurements of the polymers were performed with a Rigaku ultra X18 diffractometer (Xray CuK α radiation: 40 kV/300 mA, $\lambda = 0.154$ nm; camera length: 100 cm). XRD patterns were recorded with an X-ray generator with Nickel filtered CuK α radiation and a flat plate camera (RINT2500, Rigaku). The polymers were heated up to isotropic state, and then slowly cooled to room temperature via LC states, yielding XRD samples. The diffraction pattern was recorded on an imaging plate and scanned by a R-Axis DS3A imaging plate reader at 100 μ m resolution.

1.3. Syntheses of Monomers and Polymers

The syntheses of the *mono*-PA monomers **M1** and (*R*)-/(*S*)-**M2**, and the polymers **PA1**, (*R*)-/(*S*)-**PA**_{75-25*}, (*R*)-/(*S*)-**PA**_{50-50*}, (*R*)-/(*S*)-**PA**_{25-75*}, (*R*)-/(*S*)-**PA2** are written below.

Monomer 1 (**M1**)

M1 was synthesized as follows. Into a 300 mL three-necked flask were added TPP (6.24 g 24 mmol) and *para-trans*-4-*n*-pentyl(cyclohexyl) phenol (5.32 g, 22 mmol) under argon gas and dissolved in THF (70 mL). In the addition funnel, a mixture of DIAD (12.02 g, 40 wt% in toluene, 24 mmol), 4-pentyn-1-ol (2.00 g, 44 mmol) and 30 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with

CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from MeOH and dried in vacuo to give 4.43 g (15 mmol) of **M1** as a white crystal. Yield = 66%.

Anal. Chemical Formula: $(\text{C}_{22}\text{H}_{32}\text{O})_n$ (312.49) $_n$: Calcd. C, 84.56; H, 10.32; O, 5.12; Found C, 84.66; H, 10.35. ^1H NMR (400 MHz, CDCl_3): δ = 0.89 (t, 3H, J = 7.2 Hz, $-\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 0.93–2.02 (m, 19H, $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_4\text{CH}_3$), 2.38–2.44 (m, 3H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}\equiv\text{C}-$), 2.82 (s, 1H, $-\text{C}\equiv\text{CH}$), 4.04 (t, 2H, J = 6.4 Hz, $-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_2-\text{C}\equiv\text{C}-$), 6.83 (d, 2H, J = 8.4 Hz, Ar-H *ortho* to $-\text{O}-(\text{CH}_2)_3-\text{C}\equiv\text{C}-$), 7.12 (d, 2H, J = 8.8 Hz, Ar-H *meta* to $-\text{O}-(\text{CH}_2)_3-\text{C}\equiv\text{C}-$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.0, 15.2, 22.6, 33.6, 34.6, 37.3, 43.7, 66.3, 68.6, 114.2, 127.5, 140.1, 156.7

(*R*)-Monomer 2 ((*R*)-M2)

(*R*)-M2 was synthesized as follows. *n*-undecanoic acid (3.19 g, 17 mmol), (*R*)-(+)-3-butyn-2-ol (1.00 g, 15 mmol), DCC (3.53 g, 17 mmol) and DMAP (2.10 g, 17 mmol) were added under argon gas into a 200 mL round bottom flask, dissolved in CH_2Cl_2 (70 mL) and then stirred. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give (*R*)-M2 (2.91 g 12 mmol) as a clear liquid. Yield = 86%.

Anal. Chemical Formula: $(\text{C}_{15}\text{H}_{26}\text{O}_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O,

13.42; Found C 75.83, H 11.10. ^1H NMR (400 MHz, CDCl_3): δ = 0.89 (t, 3H, J = 8.0 Hz, $-\text{OCO}-(\text{CH}_2)_9\text{CH}_3$), 1.23–1.67 (m, 19H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}\equiv\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$), 2.23–2.37 (m, 2H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 2.44 (s, 1H, $-\text{C}\equiv\text{CH}$), 5.41–5.48 (m, 1H, $-\text{C}\equiv\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 21.2, 22.7, 24.8, 29.0, 29.2, 29.4, 31.9, 34.2, 59.7, 72.6, 76.7, 77.0, 77.3, 82.2, 172.4.

(S)-Monomer 2 ((S)-M2)

(S)-M2 was synthesized as follows. Into a 200 mL round bottom flask were added *n*-undecanoic acid (3.19 g, 17 mmol), (S)-(-)-3-butyn-2-ol (1.00 g, 15 mmol), DCC (3.53 g, 17 mmol) and DMAP (2.10 g, 17 mmol) were added under argon gas, dissolved in CH_2Cl_2 (70 mL) and then stirred. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give **(S)-M2** (3.29 g 13 mmol) as a clear liquid. Yield = 97%.

Anal. Chemical Formula: $(\text{C}_{15}\text{H}_{26}\text{O}_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42; Found C 75.35, H 10.97. ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (t, 3H, J = 7.2 Hz, $-\text{OCO}-(\text{CH}_2)_9\text{CH}_3$), 1.22–1.67 (m, 19H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}\equiv\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$), 2.27–2.37 (m, 2H, $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 2.44 (s, 1H, $-\text{C}\equiv\text{CH}$), 5.38–5.49 (m, 1H, $-\text{C}\equiv\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 21.2, 22.7, 24.9, 29.0, 29.3, 29.5, 31.9, 34.2, 59.7, 72.6, 76.7, 77.0, 77.3, 82.2, 172.4.

Liquid Crystalline *mono*-PA1 (PA1)

PA1 was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (21 mg, 0.05 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min, and then **M1** (1.41 g, 4.52 mmol) was dissolved in 1 mL THF and was then added to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brownish white powder was obtained with a yield of 38% (0.54 g, 1.72 mmol). M_w . 30,000 M_w/M_n . 1.5 (GPC, PS calibration).

Anal. (C₂₂H₃₂O)_n (312.49)_n: Calcd. C, 84.56; H, 10.32; O, 5.12; Found C 82.33, H 10.09. ¹H NMR (400 MHz, CDCl₃): δ = 0.88–1.10 (br, 5H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃), 1.11–2.10 (br, 17H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₃CH₂CH₃), 2.18–2.60 (br, 3H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, and –Ar–O–(CH₂)₂CH₂–C=C–), 3.55–3.90 (br, 2H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.97 (br, 0.5H, –C=CH *cis*), 6.50–7.15 (br, 4H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 26.8, 33.7, 34.6, 37.3, 43.5, 114.1, 127.3.

(R)-PA₇₅₋₂₅*

(R)-PA₇₅₋₂₅* was synthesized as follows. Into a Schlenk flask, Et₃N (1 mL) and [Rh(nbd)Cl]₂ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.53 g, 1.69 mmol) and **(R)-M2** (0.13 g, 0.56 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum

oven to a constant weight. A light brown powder was obtained with a yield of 49% (0.32 g, 1.08 mmol). M_w . 45,000 M_w/M_n . 1.6 (GPC, PS calibration).

Anal. (C_{20.25}H_{30.50}O_{1.25})_n (294.10)_n: Calcd. C, 82.72; H, 10.48; O, 6.80; Found C 80.75, H 10.35. ¹H NMR (400 MHz, CDCl₃): δ = 0.80–1.1 (br, 4.80H, –Ar–C₆H₁₀–(CH₂)₄CH₃, and –OCO–(CH₂)₉CH₃), 1.12–1.78 (br, 19H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₄CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.79–1.98 (br, 4.3H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, –Ar–O–(CH₂)₂CH₂–C=C–, and –OCO–CH₂(CH₂)₈CH₃), 3.47–4.10 (br, 2H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.99 (br, 0.3H, –C=CH *cis*), 6.27 (br, 0.15H, –C=CH *trans*), 6.54–7.19 (br, 3H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.3, 22.7, 33.7, 34.6, 37.5, 47.1, 53.8, 59.1, 86.5, 131.6, 136.4, 136.9, 152.7, 158.4, 170.3.

(S)-PA₇₅₋₂₅*

(S)-PA₇₅₋₂₅* was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.26 g, 0.85 mmol) and (S)-**M2** (0.07 g, 0.28 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A dark light brown powder was obtained with a yield of 46% (0.15 g, 0.52 mmol). M_w . 42,000 M_w/M_n . 2.7 (GPC, PS calibration).

Anal. (C_{20.25}H_{30.50}O_{1.25})_n (294.10)_n: Calcd. C, 82.72; H, 10.48; O, 6.80; Found C 80.51, H 10.76. ¹H NMR (400 MHz, CDCl₃): δ = 0.80–1.07 (br, 5.70H,

$-\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$, and $-\text{OCO}-(\text{CH}_2)_9\text{CH}_3$, 1.12–1.64 (br, 19H,
 $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}=\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_4\text{CH}_3$,
 $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}=\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$, 1.79–2.01 (br, 4.5H,
 $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}=\text{C}-$, and $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$,
 3.48–3.97 (br, 3.3H, $-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_2-\text{C}=\text{C}-$), 5.99 (br, 0.4H, $-\text{C}=\text{CH}$ *cis*), 6.27 (br,
 0.1H, $-\text{C}=\text{CH}$ *trans*), 6.50–7.15 (br, 3H, Ar–H). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1,
 22.7, 25.0, 26.9, 29.7, 33.7, 34.6, 37.4, 37.5, 40.6, 43.7, 52.3, 60.0, 66.2, 70.7, 114.1,
 123.1, 127.3, 152.5.

(R)-PA₅₀₋₅₀*

(R)-PA₅₀₋₅₀* was synthesized as follows. Into a Schlenk flask, Et_3N (1 mL) and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.35 g, 1.13 mmol) and **(R)-M2** (0.27 g, 1.13 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A brown powder was obtained with a yield of 71% (0.44 g, 1.60 mmol). M_w . 44,000 M_w/M_n . 1.6 (GPC, PS calibration).

Anal. $(\text{C}_{18.50}\text{H}_{29}\text{O}_{1.50})_n$ (275.48) $_n$: Calcd. C, 80.66; H, 10.63; O, 8.71; Found C
 78.60, H 10.48. ^1H NMR (400 MHz, CDCl_3): δ = 0.78–1.06 (br, 5H,
 $-\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$, $-\text{OCO}-(\text{CH}_2)_9\text{CH}_3$, 1.08–1.55 (br, 19H,
 $-\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}=\text{C}-$, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$,
 $-\text{OCO}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$, and $-\text{C}=\text{C}-\text{CH}(\text{CH}_3)\text{OCO}-$, 1.69–1.91 (br, 2.8H,
 $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and $-\text{Ar}-\text{O}-(\text{CH}_2)_2\text{CH}_2-\text{C}=\text{C}-$, 2.12–2.56 (br, 2H,

–OCO–CH₂(CH₂)₈CH₃), 3.61–4.04 (br, 1H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.30–5.99 (br, 0.01H, –C=CH *cis*), 6.01–6.44 (br, 0.4H, –C=CH *trans*), 6.63–7.15 (br, 2H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 25.1, 26.8, 29.4, 29.7, 32.0, 33.7, 34.6, 37.4, 97.2, 114.1, 127.5, 140.9, 146.5, 151.5, 175.4.

(S)-PA₅₀₋₅₀*

(S)-PA₅₀₋₅₀* was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.18 g, 0.56 mmol) and (S)-**M2** (0.13 g, 0.56 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brown powder was obtained with a yield of 66% (0.21 g, 0.75 mmol). *M_w*. 70,000 *M_w*/*M_n*. 2.9 (GPC, PS calibration).

Anal. (C_{18.50}H₂₉O_{1.50})_n (275.48)_n: Calcd. C, 80.66; H, 10.63; O, 8.71; Found C 78.83, H 10.53. ¹H NMR (400 MHz, CDCl₃): δ = 0.81–1.07 (br, 5H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃, –OCO–(CH₂)₉CH₃), 1.08–1.64 (br, 21H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₃CH₂CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.43–1.70 (br, 2.8H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, and –Ar–O–(CH₂)₂CH₂–C=C–), 2.05–2.56 (br, 2.4H, –OCO–CH₂(CH₂)₈CH₃), 3.55–3.96 (br, 1H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.30–5.97 (br, 0.3H, –C=CH *cis*), 6.19–6.41 (br, 0.7H, –C=CH *trans*), 6.63–7.10 (br, 2H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 26.7, 29.4, 29.7, 31.9, 32.3, 33.7, 34.6, 37.3, 48.9, 60.6, 69.1, 72.1, 114.1, 127.4, 137.2, 144.9, 151.1.

(R)-PA₂₅₋₇₅*

(R)-PA₂₅₋₇₅* was synthesized as follows. Into a Schlenk flask, Et₃N (1 mL) and [Rh(nbd)Cl]₂ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon. **M1** (0.18 g, 0.56 mmol) and **(R)-M2** (0.40 g, 1.69 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise into the reaction flask. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A brown powder was obtained with a yield of 77% (0.44 g, 1.73 mmol). *M_w*. 81,000 *M_w/M_n*. 2.8 (GPC, PS calibration).

Anal. (C_{16.75}H_{27.50}O_{1.75})_n (256.94)_n: Calcd. C, 78.29; H, 10.81; O, 10.90; Found C 77.01, H 10.81. ¹H NMR (400 MHz, CDCl₃): δ = 0.78–0.94 (br, 6.4H, –Ar–C₆H₁₀–(CH₂)₃CH₂CH₃, –OCO–(CH₂)₉CH₃), 1.08–1.69 (br, 29H, –Ar–O–CH₂CH₂CH₂–C=C–, –O–Ar–CH(CH₂)₄CH–(CH₂)₃CH₂CH₃, –OCO–CH₂(CH₂)₈CH₃, and –C=C–CH(CH₃)OCO–), 1.82–2.11 (br, 2H, –OCO–CH₂(CH₂)₈CH₃), 2.27–2.41 (br, 3H, –O–Ar–CH(CH₂)₄CH₂–C₅H₁₁, and –Ar–O–(CH₂)₂CH₂–C=C–), 3.69–3.99 (br, 0.6H, –Ar–O–CH₂(CH₂)₂–C=C–), 5.30–5.99 (br, 0.9H, –C=CH *cis*), 6.02–6.52 (br, 1.1H, –C=CH *trans*), 6.63–7.03 (br, 1.5H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 25.0, 26.7, 29.4, 29.7, 31.9, 32.2, 33.7, 34.4, 34.6, 37.4, 43.7, 52.4, 114.1, 127.3, 140.8, 171.9.

(S)-PA₂₅₋₇₅*

(S)-PA₂₅₋₇₅* was synthesized as follows. Et₃N (1 mL) and [Rh(nbd)Cl]₂ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min. **M1** (0.09 g, 0.28 mmol) and **(S)-M2** (0.20 g,

0.85 mmol) was mixed and dissolved in 1 mL THF and was then added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A brown powder was obtained with a yield of 80% (0.23 g, 0.90 mmol). M_w . 81,000 M_w/M_n . 2.8 (GPC, PS calibration).

Anal. $(C_{16.75}H_{27.50}O_{1.75})_n$ (256.94) $_n$: Calcd. C, 78.29; H, 10.81; O, 10.90; Found C 76.07, H 10.55. 1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.94 (br, 5.3H, $-Ar-C_6H_{10}-(CH_2)_3CH_2CH_3$, $-OCO-(CH_2)_9CH_3$), 1.25–1.63 (br, 26H, $-Ar-O-CH_2CH_2CH_2-C=C-$, $-O-Ar-CH(CH_2)_4CH-(CH_2)_3CH_2CH_3$, $-OCO-CH_2(CH_2)_8CH_3$, and $-C=C-CH(CH_3)OCO-$), 1.82–1.92 (br, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 2.09–2.41 (br, 3H, $-O-Ar-CH(CH_2)_4CH_2-C_5H_{11}$, and $-Ar-O-(CH_2)_2CH_2-C=C-$), 3.66–4.03 (br, 1H, $-Ar-O-CH_2(CH_2)_2-C=C-$), 5.41–5.82 (br, 1.3H, $-C=CH$ *cis*), 5.97–6.49 (br, 1.6H, $-C=CH$ *trans*), 6.67–7.12 (br, 1.5H, Ar-H).

^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 18.9, 22.7, 29.4, 29.7, 30.9, 32.0, 37.7, 114.0, 127.6, 155.2, 164.7, 173.6.

(R)-PA2

(R)-PA2 was synthesized as follows. Into a Schlenk flask, Et_3N (1 mL) and $[Rh(nbd)Cl]_2$ (10 mg, 0.02 mmol) was stirred at room temperature for 30 min under argon, and then (R)-M2 (0.54 g, 2.26 mmol) dissolved in 1 mL THF was added to it. The reaction mixture was stirred for 24 h. The resultant solution was then added dropwise to 800 mL of MeOH under stirring. The precipitate was allowed to stand overnight, which was then filtered. The polymer was washed with MeOH and dried in a vacuum oven to a constant weight. A dark amber colored viscous liquid was

obtained with a yield of 74% (0.39 g, 1.67 mmol). M_w . 93,000 M_w/M_n . 3.4 (GPC, PS calibration).

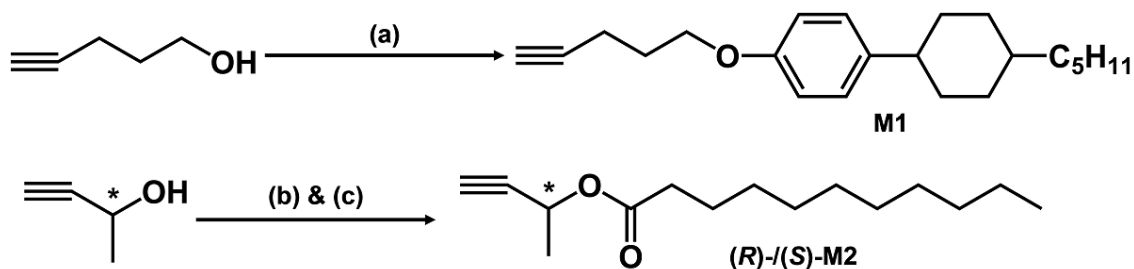
Anal. $(C_{15}H_{26}O_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42; Found C 75.43, H 10.81. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.98 (br, 3H, $-OCO-(CH_2)_9CH_3$), 1.01–1.69 (br, 19H, $-OCO-CH_2(CH_2)_8CH_3$, and $-C=C-CH(CH_3)OCO-$), 2.17–2.40 (br, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 5.50–5.70 (br, 0.75H, $-C=C-CH(CH_3)OCO-$), 6.61 (br, 0.75H, $-C=CH$ *trans*). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 22.7, 25.0, 29.3, 29.4, 29.5, 29.6, 29.7, 30.9, 31.9, 34.4, 52.4, 71.3, 122.8, 141.0, 171.9.

(S)-PA2

(S)-PA2 was synthesized as follows. Et_3N (1 mL) and $[Rh(nbd)Cl]_2$ (5 mg, 0.01 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at room temperature for 30 min, and then (S)-M2 (0.27 g, 1.13 mmol) was dissolved in 1 mL THF and was then added to the reaction mixture. The reaction mixture was stirred for 24 h. The mixture was added dropwise to 800 mL of MeOH under stirring. The polymer precipitate stirred for 24 h, which was then filtered, washed with MeOH and dried in a vacuum oven. A dark amber colored viscous liquid was obtained with a yield of 84% (0.23 g, 0.94 mmol). M_w . 100,000 M_w/M_n . 3.0 (GPC, PS calibration).

Anal. $(C_{15}H_{26}O_2)_n$ (238.37) $_n$: Calcd. C, 75.58; H, 10.99; O, 13.42; Found C 74.55, H 10.90. 1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.82 (br, 3H, $-OCO-(CH_2)_9CH_3$), 1.00–1.67 (br, 19H, $-OCO-CH_2(CH_2)_8CH_3$, and $-C=C-CH(CH_3)OCO-$), 2.17–2.40 (br, 2H, $-OCO-CH_2(CH_2)_8CH_3$), 5.50–5.70 (br, 0.8H, $-C=C-CH(CH_3)OCO-$), 6.41 (br, 0.8H, $-C=CH$ *trans*). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 20.4, 22.7, 25.0, 29.3, 29.4, 29.6, 31.9, 34.3, 71.1, 115.9, 122.7, 140.9, 171.9.

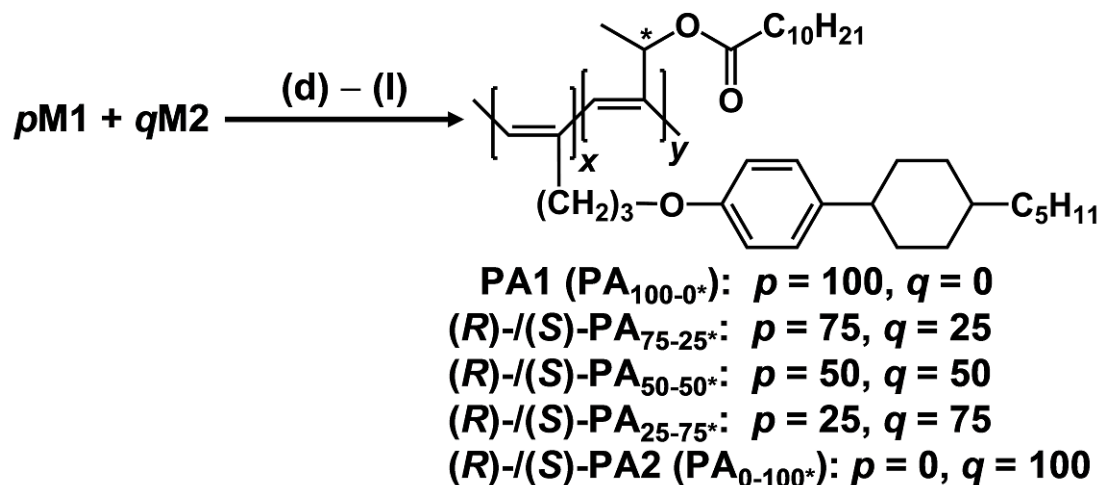
2. Supporting Information Schemes, Figures, and Tables

Scheme S1. Synthetic routes of polymers.^a

^aConditions: **Monomers:** (a) *para-trans*-4-*n*-pentyl(cyclohexyl) phenol, 4-pentyn-1-ol, TPP, DIAD, THF, r.t., 24 h; 66% for **M1**; (b) *n*-undecanoic acid, (R)-(+)-3-butyn-2-ol, DCC, DMAP, CH₂Cl₂, r.t., 24 h; 86% for **(R)-M2**; (c) *n*-undecanoic acid, (S)-(-)-3-butyn-2-ol, DCC, DMAP, CH₂Cl₂, r.t., 24 h; 97% for **(S)-M2**.

TPP = triphenylphosphine, DIAD = diisopropylazodicarboxylate,

DCC = N,N'-dicyclohexylcarboimide, DMAP = 4-dimethylaminopyridine

Scheme S2. Synthetic route of the polymers^b

^bConditions: **Polymers:** (d) **M1**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 38% for **PA1**; (e) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 49% for (**R**)-**PA_{75-25*}**; (f) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 49% for (**S**)-**PA_{75-25*}**; (g) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 71% for (**R**)-**PA_{50-50*}**; (h) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 66% for (**S**)-**PA_{50-50*}**; (i) **M1**, (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 77% for (**R**)-**PA_{25-75*}**; (j) **M1**, (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 80% for (**S**)-**PA_{25-75*}**; (k) (**R**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 74% for (**R**)-**PA2**; (l) (**S**)-**M2**, [Rh(nbd)Cl]₂, Et₃N, THF, r.t., 24 h; 84% for (**S**)-**PA2**.

[Rh(nbd)Cl]₂ = Bicyclo[2.2.1] (hepta-2,5-diene)chlororhodium (I) dimer

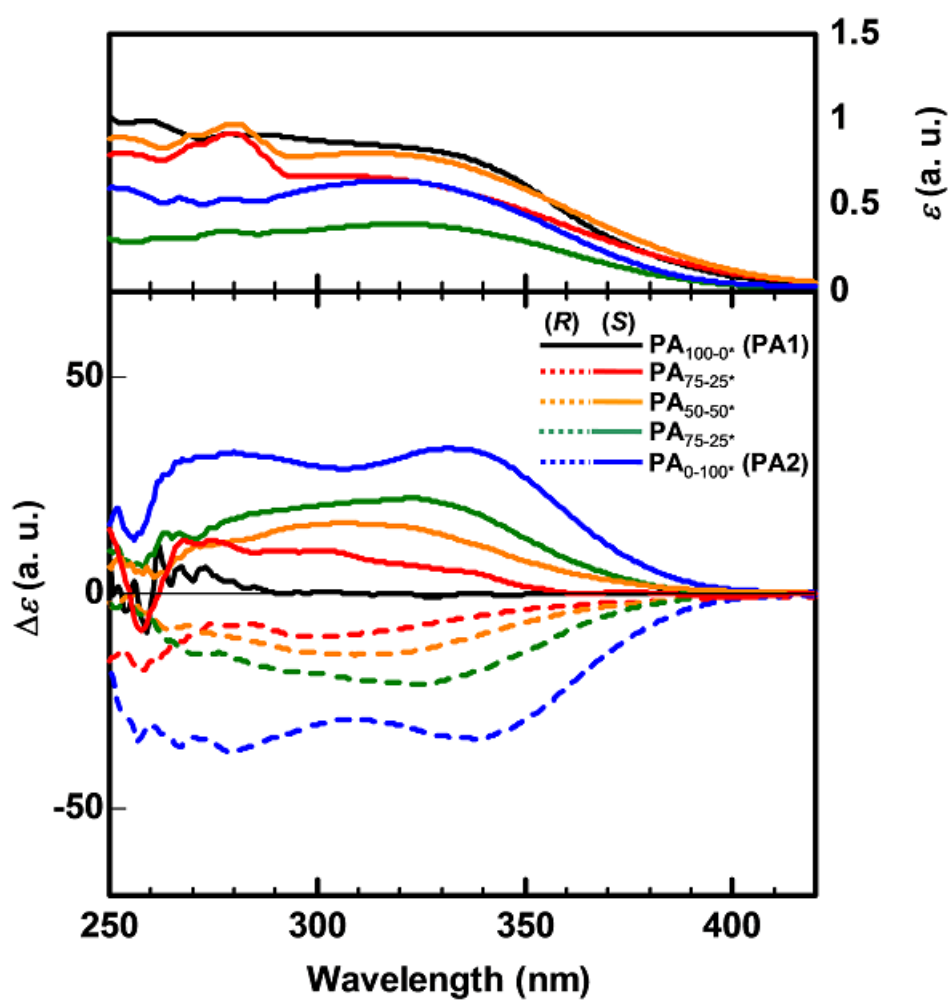


Figure S1. UV-vis (above) and CD spectra (below) of the *mono*-substituted polyacetylene copolymers in annealed cast film.

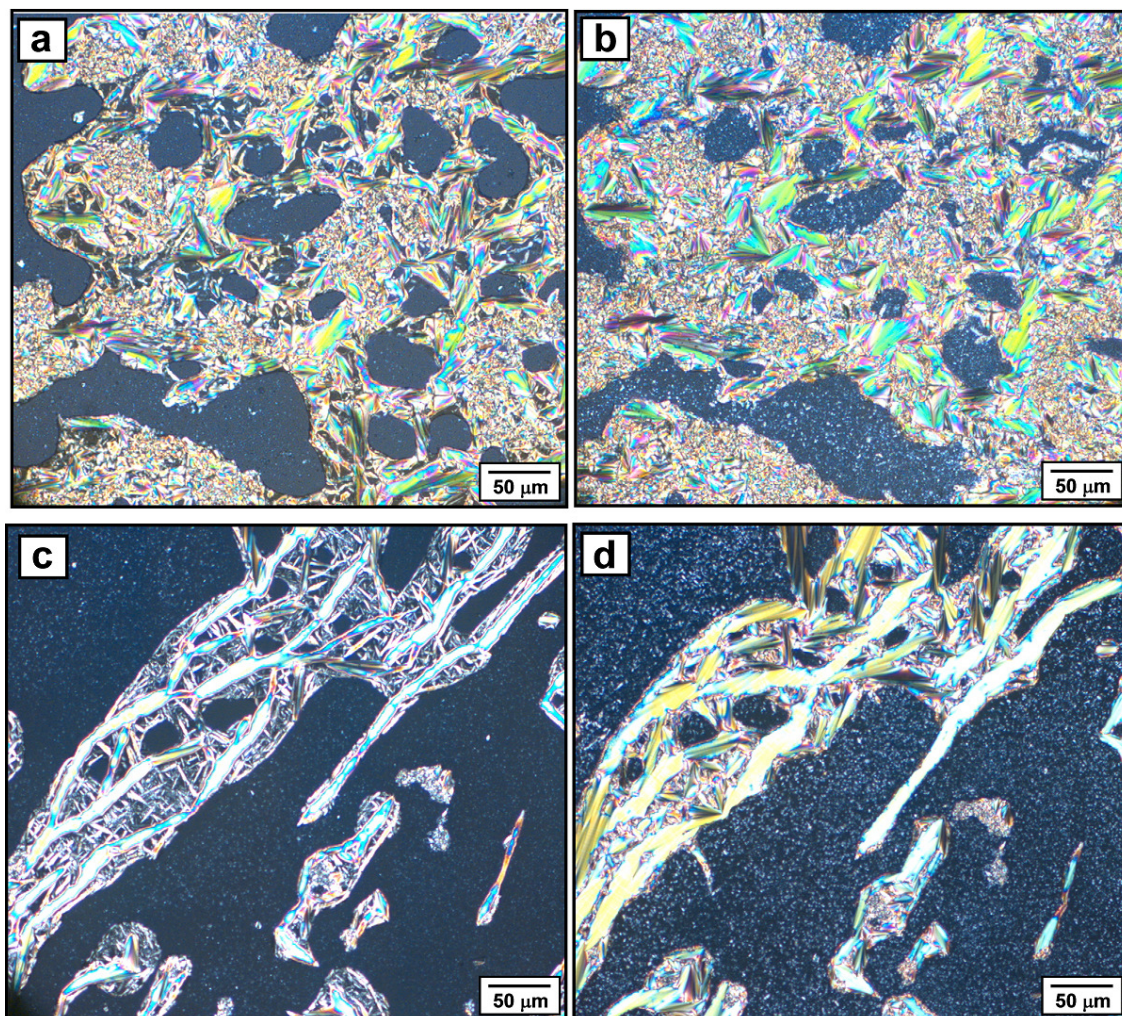


Figure S2. POM images of (a) **PA1:(R)-PA2** (75:25) mixture at 144 °C in cooling process, (b) **PA1:(R)-PA2** (75:25) mixture at 90 °C in cooling process, (c) **PA1:(R)-PA2** (50:50) mixture at 132 °C in cooling process, and (d) **PA1:(R)-PA2** (50:50) mixture at 90 °C in cooling process.

Table S1. Absorption dissymmetry factor (g_{abs}) values of the *mono*-substituted polyacetylene copolymers in CHCl_3 solution ($c = 1.2 \times 10^{-4}$ M).

g_{abs} at 320 nm	
(R)-PA_{75-25*}	-7.69×10^{-4}
(S)-PA_{75-25*}	7.85×10^{-4}
(R)-PA_{50-50*}	-1.42×10^{-3}
(S)-PA_{50-50*}	1.44×10^{-3}
(R)-PA_{25-75*}	-1.71×10^{-3}
(S)-PA_{25-75*}	1.74×10^{-3}
(R)-PA2	-1.75×10^{-3}
(S)-PA2	1.75×10^{-3}

REFERENCES

- (1) (a) San Jose, B. A.; Matsushita, S.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 19795–19807. (b) Watanabe, K.; Osaka, I.; Yorozuya, S.; Akagi, K. *Chem. Mater.* **2012**, *24*, 1011–1024.
- (2) (a) Furumi, S. *Chem. Rec.* **2010**, *10*, 394–408. (b) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506–508. (c) Grell, M.; Oda, M.; Whitehead, K. S.; Asimakis, A.; Neher, D.; Bradley, D. D. C. *Adv. Mater.* **2001**, *13*, 577–580.
- (3) (a) Coles, H.; Morris, S. *Nat. Photonics* **2010**, *4*, 676–685. (b) Humar, M.; Musevic, I. *Opt. Express* **2010**, *18*, 26995–27003.
- (4) (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683–1686. (b) Akagi, K.; Guo, S.; Mori, T.; Goh, M.; Piao, G.; Kyotani, M. *J. Am. Chem. Soc.* **2005**, *127*, 14647–14654. (c) Akagi, K. *Chem. Rev.* **2009**, *109*, 5354–5401.
- (5) Kyotani, M.; Matsushita, S.; Nagai, T.; Matsui, Y.; Shimomura, M.; Kaito, A.; Akagi, K. *J. Am. Chem. Soc.* **2008**, *130*, 10880–10881. (b) Matsushita, S.; Kyotani, M.; Akagi, K. *J. Am. Chem. Soc.* **2011**, *133*, 17977–17992.
- (6) *Textures of Liquid Crystals*; Dierking, I.; Wiley-VCH: Weinheim, **2003**.
- (7) (a) Garoff, S.; Meyer, R. B. *Phys. Rev. Lett.*, **1977**, *38*, 848–851. (b) Termine, R.; De Simone, B. C.; Golemme, A. *Appl. Phys. Lett.* **2001**, *78*, 688–690. (c) Meyer, R. B.; Pelcovits, R. A. *Phys. Rev. E* **2002**, *65*, 061704-1–061704-6. (d) Hartley, C.; Kapernaum, N.; Roberts, J.; Giesselmann, F.; Lemieux, R. P. *J. Mater. Chem.*, **2006**, *16*, 2329–2337.
- (8) (a) Bahr, C. in *Chirality in Liquid Crystals*; Kitzerow, H. S.; Bahr, C. Eds. Springer

Verlag: New York, **2001**. (b) Clark, N. A.; Lagerwall, S. T. in *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. Eds. Gordon and Breach: Philadelphia, **1991**, p. 84.

(9) Andersson, G.; Dahl, I.; Kuczynski, W.; Lagerwall, S. T.; Skarp, K.; Stebler, B. *Ferroelectrics*, **1988**, *84*, 285–315.

(10) (a) Gottarelli, G.; Hibert, M.; Samori, B.; Solladie, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318–7321. (b) Solladie, G.; Zimmermann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348–362. (c) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladie, G.; Zimmermann, R. *J. Org. Chem.* **1986**, *51*, 592–596. (d) Proni, G.; Spada, G. P.; Lustenberger, P.; Welti, R.; Diederich, F. *J. Org. Chem.* **2000**, *65*, 5522–5527. (e) Kuball, H.-G.; Turk, O.; Kiesewalter, I.; Dorr, E. *Mol. Cryst. Liq. Cryst.* **2000**, *352*, 195–204.

(11) The degree of polymerization (D.P.) was computed by dividing the measured weight-average molecular weight (M_w) of the copolymer to the calculated copolymer repeating unit molecular weight (R.U. M_w). The copolymer repeating unit molecular weight was calculated by using the formula: $\text{R.U. } M_w = [(M_1 \times M_1 \text{ feeding ratio}) + (M_2 \times M_2 \text{ feeding ratio})] / 100$.

(12) *Liquid Crystalline and Mesomorphic Polymers*; Shibaev, V. P., Lam, L., Eds.; Springer-Verlag: New York, 1994.

(13) The lengths of the *mono*-PA side chains were calculated using molecular mechanics calculations. The side chain having the PCH503 moiety, has a length (L_1) computed as 18.0 Å. The chiral side chain has a length (L_2) computed as 14.6 Å. The LC phase of the *mono*-PAs are arranged in a smectic A phase (SmA) with the interlayer distance (d)

approximate to $2L$.

(14) Berova, N.; Nakanishi, K. In *Circular Dichroism: Principles and Applications*, 2nd Edition.; Berova, N.; Nakanishi, K.; Woody, R. Eds. John Wiley and Sons, Inc : New York, **2000**; Chapter. 12, 337–382.

(15) The present analyses enabled us to draw a polymer structure where at the LC segments, the LC side chains are alternatively located at both sides of polyene chain to form a *cis*-transoid stereoregular configuration of head-tail-head-tail linkages. In the case of Rh-based catalysts, polymerization proceeds via an insertion mechanism and provides *cis*-rich *mono*-PA with a *cis*-transoidal backbone. The measured LC to LC distance of 4.8 Å at XRD is close to the calculated LC to LC distance of ~4.4 Å, which further supports the presented model.

**Part II: Synthesis and Polarized Functionalities of
Liquid Crystalline *Di*-Substituted Polyacetylene
Derivatives**

Chapter 2

Liquid Crystalline *Di*-Substituted Polyacetylene Derivatives That Exhibit Linearly Polarized Blue and Green Emissions**ABSTRACT:**

We synthesized *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) derivatives by polymerizing acetylene derivatives consisting of LC moieties either directly or indirectly attached to the main chain through flexible alkyl spacers. The *di*-LCPA derivatives show either enantiotropically thermotropic LC or lyotropic LC behavior. The origin of emission of substituted PAs, with respect to their substituents and structure, was elucidated. Depending on the substituents of the side chains, the polymers exhibit blue (470~485 nm) and green (500~540 nm) photoluminescence (PL) in chloroform and in cast film. The *di*-LCPA derivatives were macroscopically aligned using rubbing technique and the aligned structures of the polymers are characterized in terms of main chain and side chain type alignments through XRD measurements. The emission color and alignment direction towards an external force in the *di*-LCPA derivatives are crucially determined by both the linkage forms (direct or indirect attachment) between the main chain and side chains and the molecular moieties (alkyl or aromatic moiety) of the side chains. The macroscopically aligned films of the polymers exhibit linearly polarized photoluminescence (LPL) with notable dichroic ratios. We fabricate multilayer electroluminescence (EL) devices using the polymers as the emissive polymer layer that emit 480 nm light with promising EL properties.

We emphasize that although substituted PA derivatives are usually *non*-luminescent, the *di*-LCPA derivatives emit intense fluorescence with notable linear dichroism and they could be promising for optically anisotropic luminescent materials.

1. Introduction

Polymers are generally considered insulators; however, it has been demonstrated that conjugated polymers can become electrically conductive. Among these conjugated polymers, polyacetylene (PA) has attracted much attention since the discovery of its metallic conductivity in doped form. When doped with iodine, pristine PA film with a metallic luster has a black surface and a high electrical conductivity on the order of 10^4 – 10^5 S/cm.¹ This discovery accelerated research on conjugated polymers and led to developments in polymeric light emitting diodes (PLEDs),² plastic electronics,³ polymer battery cells,⁴ polymer photovoltaics,⁵ and other novel technologies.

However, pristine PA film is insoluble in organic solvents and quickly loses its electrical conductivity when exposed to atmospheric conditions. Introducing an alkyl substituent into the polymer main chain increases solubility in organic solvents depending on the length of the alkyl chain.⁶ However, the electrical conductivity of the substituted PA is significantly lower than that of the *non*-substituted PA. This phenomenon is due to less coplanarity of the main chain, which arises from steric repulsions between the substituents, a higher ionization potential and lower electron affinity. The main chain in the substituted PA is also still randomly oriented, which suppresses the electrical conductivity of the polymer.

Adding a liquid crystalline (LC) moiety to the polymer main chain makes the

polymer soluble in organic solvents and facilitates alignment by the spontaneous orientation of the LC group. For example, *mono*-substituted liquid crystalline PA (*mono*-LCPA), prepared by introducing the LC moiety into the side chain of PA, shows liquid crystallinity and stability in air.⁷ It is well known that polymers with LC moieties spontaneously align to form multi-domains by virtue of the orientation of the LC moieties. Further alignment of these polymers can be achieved by applying an external force such as shear stress or an electric or magnetic field⁸ to construct a mono-domain structure on a macroscopic level. The schematic in Figure 1 shows the formation of multi- and mono-domains through spontaneous orientation and externally forced macroscopic alignment, respectively.

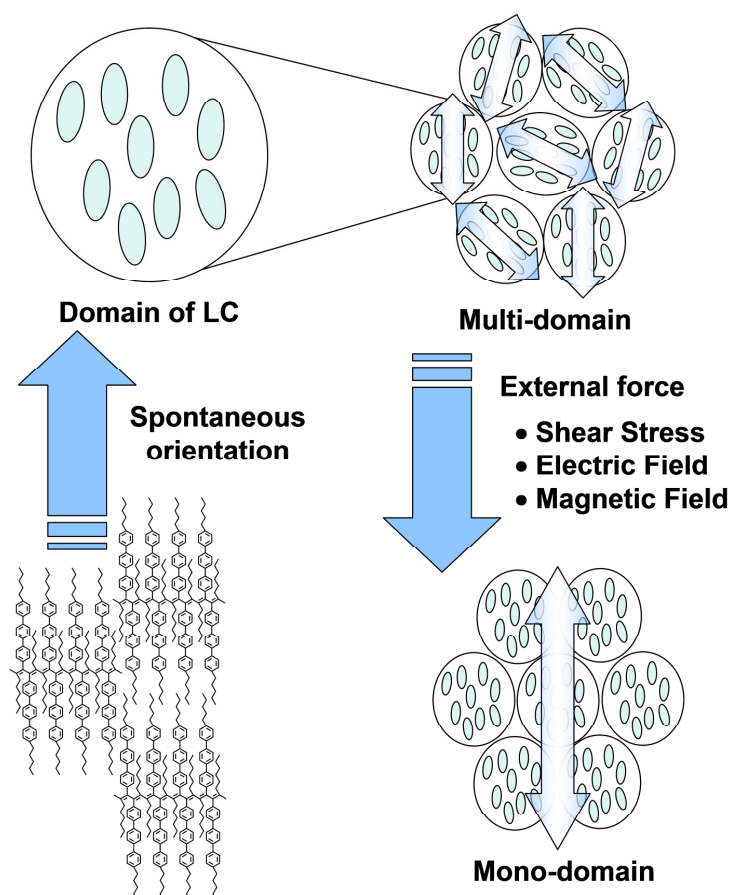


Figure 1. Schematic representation of the spontaneous and externally forced orientations of side chain type LC conjugated polymers.

Recently, we reported that *mono*-LCPA derivatives exhibit excellent macroscopic alignment under an applied magnetic field. Macroscopic alignment of the main chain led to both an electrical conductivity enhancement of two orders and an electrical anisotropy accompanied by the magnetically forced orientation of the LC side chain.⁹

Aromatic conjugated polymers have outstanding electrical properties and are fluorescent. The investigation of liquid crystallinity on aromatic conjugated polymers is worthwhile. Therefore, we synthesized and studied the electrical and fluorescent anisotropies of aromatic conjugated polymers with LC side chains,¹⁰ such as polythiophene (PT),¹¹ polythienylenevinylene (PTV),^{11d,13} poly-*para*-phenylene (PPP),⁸ poly-*para*-phenylenevinylene (PPV),⁸ polypyrrole (PPy),¹² and polyaniline (PANI) derivatives.¹⁴

Compared to aromatic conjugated polymers such as PPP and PT, the *mono*-substituted PA (*mono*-PA) is generally considered non-emissive because of the coulombic interactions between π -electrons.^{15a} Figure 2 depicts the energy levels of ground and low-lying excited states of *non*-, *mono*- and *di*-substituted polyacetylenes and the correlations between the corresponding energy states. In this figure the notations of $1A_g$, $2A_g$, and $1B_u$ are used for the intrachain excitons, and these are conserved in *mono*- and *di*-substituted polyacetylene derivatives, although their symmetries are different from *non*-substituted PA. Hence, for this series of PA derivatives, the optical transitions involving the A_g and B_u pair of states are symmetry allowed, whereas those involving two A_g states are symmetry forbidden because the transition dipole moment in the direction of the main chain is strongest and its irreducible representation is B_u .^{15e} In *trans*-PA with C_{2h} symmetry (in terms of unit cell), the transition between the ground state of $1A_g$ and the excited state of $2A_g$ is

electronically forbidden; however, the transition between $1A_g$ and the excited state of $1B_u$ is electronically allowed, according to the symmetry-based selection rule.^{15e} For *non*- and *mono*-substituted PAs, the $1B_u$ state decays into the $2A_g$ state, but the transition from $2A_g$ to $1A_g$ is electronically forbidden. Therefore, *non*- and *mono*-substituted PAs are generally non-emissive.

When another bulky group is substituted into the *mono*-PA to form *di*-substituted PA (*di*-PA), the steric effect on the polyene main chain changes the relative position of the two excited states so that the $1B_u$ excited state is lower than the $2A_g$ state. This shift enables a radiative transition from the $1B_u$ state to the $1A_g$ ground state.¹⁵ Thus, fluorescent *di*-PA can be synthesized by introducing a second side chain into the *mono*-PA main chain.

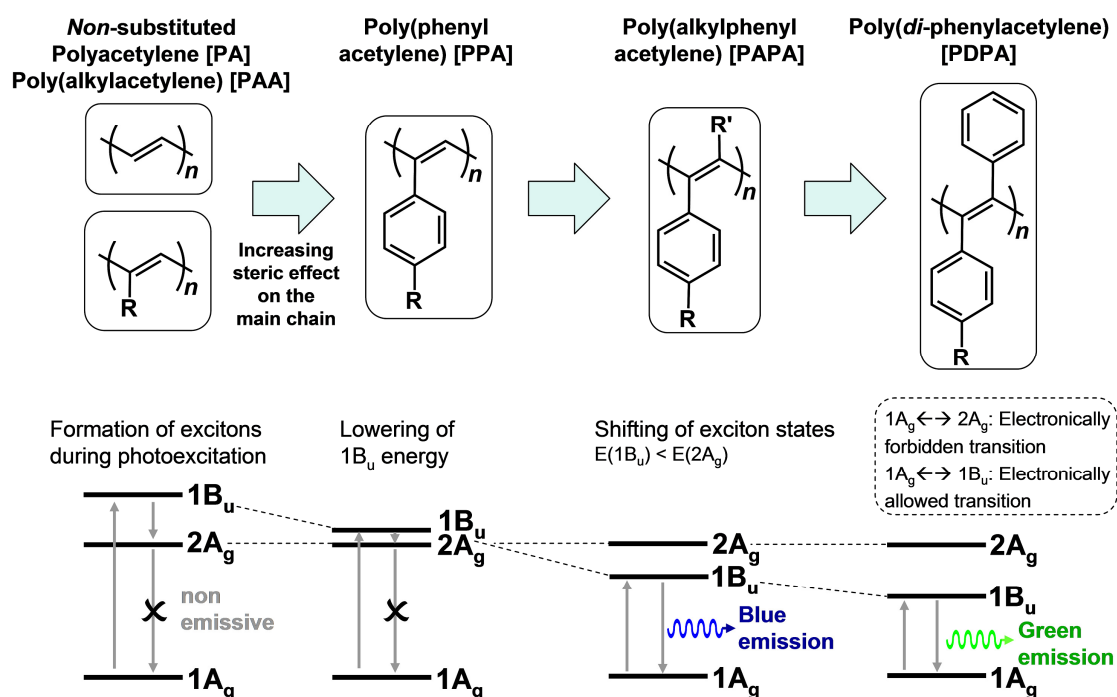


Figure 2. Energy levels of ground and low-lying excited states of *non*-, *mono*-, and *di*-substituted polyacetylenes and correlations between the corresponding energy states.

There are some reports of *di*-PA with PL;¹⁷ however, there are only a few reports of macroscopic alignment in *di*-PA to exhibit linearly polarized luminescence (LPL).¹⁸ The introduction of anisotropic functionality to aromatic conjugated polymers led to the development of advanced LC conjugated polymers with chiral induction,¹⁹ ferroelectric LC (FLC),^{20,22} and photoswitching.^{21,22} Further development of anisotropic functionality in aliphatic conjugated polymers such as *di*-PA will pave the way for novel advanced functionalities. Therefore, examining LPL in *di*-PA is worthwhile because anisotropy in the electrical conductivity or optical properties is one of the promising functions of conjugated polymers with liquid crystallinity.

In this research, various *di*-PA derivatives bearing LC moieties either directly or indirectly attached using flexible alkyl spacers to the main chain were synthesized. The effects of structural variation on the functionalities of the *di*-PA derivatives were examined. We investigated the thermotropic and lyotropic LC of the *di*-PAs, as well as their photoluminescent (PL) and electroluminescent (EL) properties. We aimed to generate dichroic fluorescence by combining the liquid crystallinity and fluorescent functionality of *di*-PA.

2. Results and Discussion

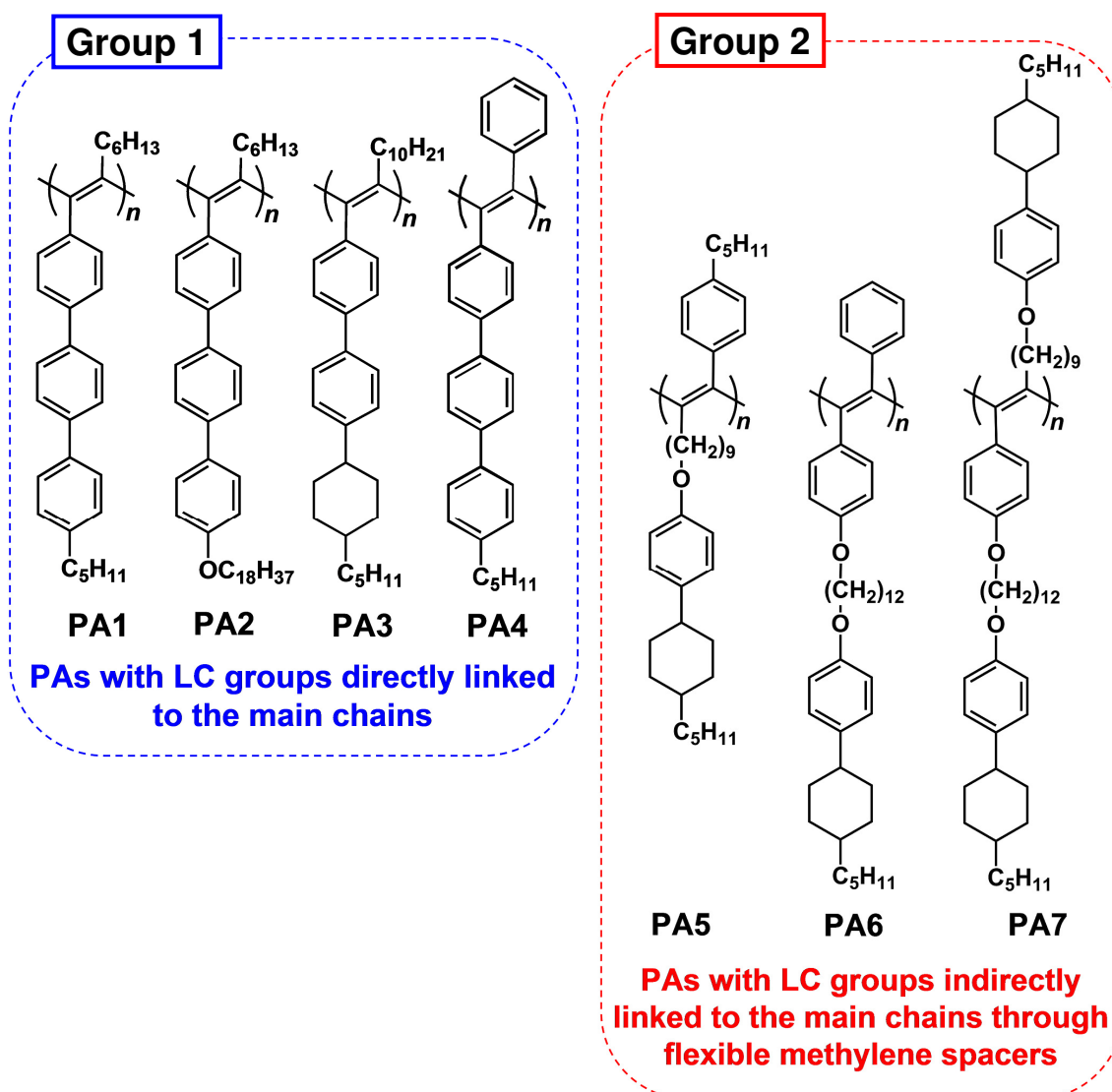
2.1. Synthesis and Characterization of Polymers

Various *di*-substituted PA derivatives with LC moieties were synthesized, including two groups with structural variations on the alkyl side chain, mesogen core, and terminal group. Group 1 *di*-PAs have the LC mesogen core directly attached to the polyene main chain, and Group 2 have the LC groups attached via flexible spacers (Scheme 1). Synthetic routes of the monomers and polymers are given in Scheme S1

at the supporting figures section.

PA1 has an *n*-hexyl group and a *para*-terphenyl mesogen core linked with an *n*-pentyl moiety. **PA2** has a similar structure, but with the *para*-terphenyl mesogen linked with an *n*-octadecyloxy moiety. **PA3** has an *n*-decyl group and a *para*-biphenylcyclohexyl mesogen core linked with an *n*-pentyl moiety. **PA4** has a phenyl group and a *para*-terphenyl mesogen core linked with an *n*-pentyl moiety.

Scheme 1. Structures of the *di*-substituted PA derivatives.



The PAs with the second group have the mesogen cores attached to the polyene main chain via flexible spacers. **PA5** has a pentyl-phenylcyclohexyl (PCH) group attached with an *n*-nonyloxy flexible spacer and an *n*-pentylphenyl group. **PA6** has two phenyl groups directly attached to the polyene main chain with the second phenyl having a PCH group attached via an *n*-dodecyloxy flexible spacer. **PA7** has a similar structure to **PA6**, with the phenyl group having a PCH moiety attached via a *n*-dodecyloxy flexible spacer. On the other side of the **PA7** main chain is a PCH group with an *n*-nonyloxy flexible spacer.

The monomers corresponding to the *di*-PA derivatives were synthesized using the Williamson reaction,²³ Sonogashira-Hagihara coupling,²⁴ Suzuki coupling,²⁵ and Mitsunobu reaction.²⁶ They were polymerized via a metathesis reaction using tantalum (V) pentachloride (TaCl₅) as a catalyst and *tetra-n*-butyltin (*n*-Bu₄Sn) as a *co*-catalyst. The polymerization reaction was conducted at 80 °C under an argon atmosphere using toluene as the solvent.

The polymerization proceeded for 24 h before washing the polymer in methanol (MeOH) under constant stirring for another 24 h. The precipitated polymers were then washed in acetone for 24 h and dried under vacuum.

The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were measured using gel permeation chromatography (GPC) and calibrated using a polystyrene (PS) standard. The GPC results showed that Group 1 polymers have M_n values ranging from 68,000 to 167,000 and M_w/M_n values ranging from 2.4 to 3.4. The Group 2 polymers had M_n values ranging from 19,000 to 210,000 and M_w/M_n values ranging from 1.7 to 4.5 (Table 1).

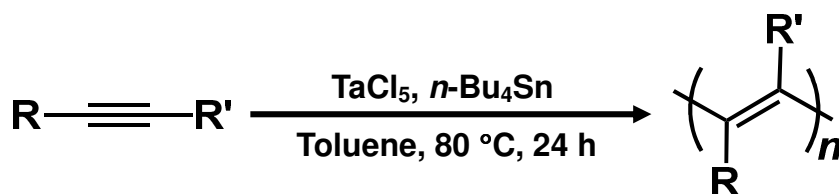


Table 1. Results of polymerizations of the di-substituted PAs.

	M_n	M_w	M_w/M_n	D.P.*	Yield (%)
PA1	68,000	190,000	2.8	166	84
PA2	167,000	409,000	2.4	227	56
PA3	81,000	267,000	3.3	172	29
PA4	89,000	302,000	3.4	222	33
PA5	64,000	168,000	2.6	117	12
PA6	210,000	367,000	1.7	345	45
PA7	19,000	89,000	4.5	22	66

*Degree of polymerization

2.2. Liquid Crystallinity

The polymers exhibited thermal stability and thermotropic liquid crystallinity with an enantiotropic nature. LC transition temperatures of the *di*-PAs are shown in Figure 3.²⁷ Polarizing optical microscopy (POM) analysis revealed that **PA2** has a nematic LC (N-LC) phase with a Schlieren texture (Figure 4a) and no isotropic phase. The temperature ranges of the N-LC phase were 125–250 and 100–250 °C in heating and cooling processes, respectively, and thermal decomposition occurred at temperatures over 250 °C.

The LC phase of **PA2** was also investigated using X-ray diffraction (XRD). The XRD patterns reveal a single broad diffraction peak in the wide angle region (Figure 4b), typical of an N-LC phase.²⁸ The broad peak at 19.6° in 2θ is 4.5 Å, and it is assigned to the distance between mesogenic groups. This assignment is supported by calculations based on *non*-substituted *trans*-PA²⁹ whose calculated distance is ~4.9 Å. Based on the present analyses, a schematic model describing the arrangement of the LC

moieties within the polyene main chain is shown in Figure 4c. In this model, the *para*-terphenyl mesogens are alternately located at both sides of the polyene main chain to form a *trans-transoid* stereoregular configuration of head-head-tail-tail linkages.^{30, 31}

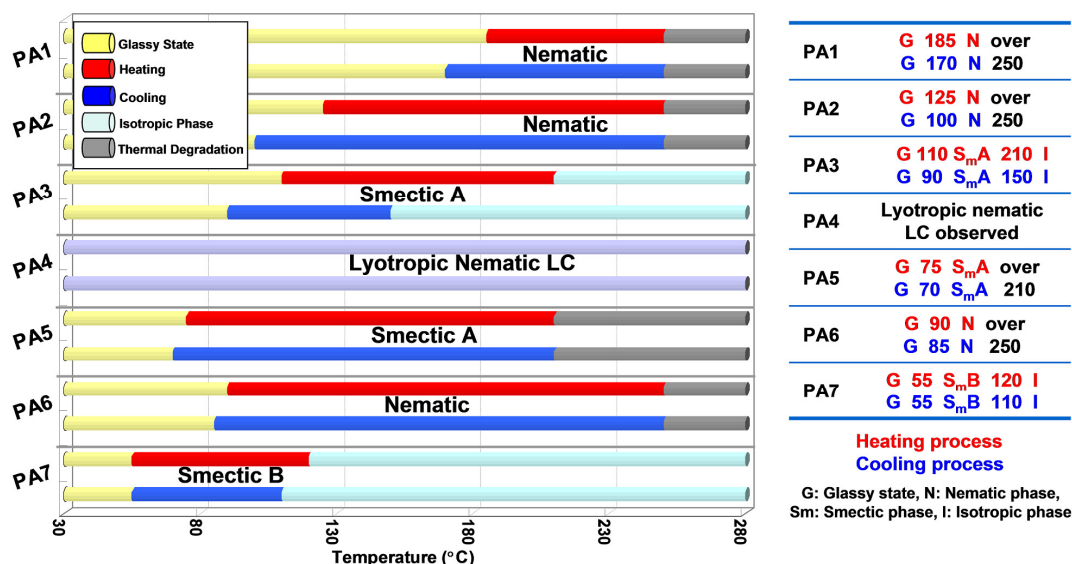


Figure 3. LC transition temperatures of the *di*-substituted PAs.

The two PCH mesogen cores attached via flexible spacers on **PA7** result in a smectic (S_m) phase (Figure 5a) with temperature ranges of 55–120 and 55–110 °C in heating and cooling processes, respectively. The XRD patterns of **PA7** have two sharp diffraction peaks at 5.2 and 19.4° in 2θ (Figure 5b), corresponding to distances of 34.4 and 4.6 Å, respectively. The former represents the smectic interlayer distance while the latter corresponds to the distance between mesogenic groups. The sharp signal in the wide angle peak of the XRD profile is typical in a hexagonal smectic B (S_mB) phase due to the regularity of the hexagonal packing arrangement. The 34.4 Å smectic interlayer distance (d) is comparable to the 36.0 Å calculated side chain length (L_1) of the side chain having the PCH50120P moiety.^{32–35} Whereas the side chain with the PCH509 moiety has a calculated side chain length (L_2) of 26.4 Å. The lengths of the **PA7** side chains were calculated using Spartan[®] modeling software.

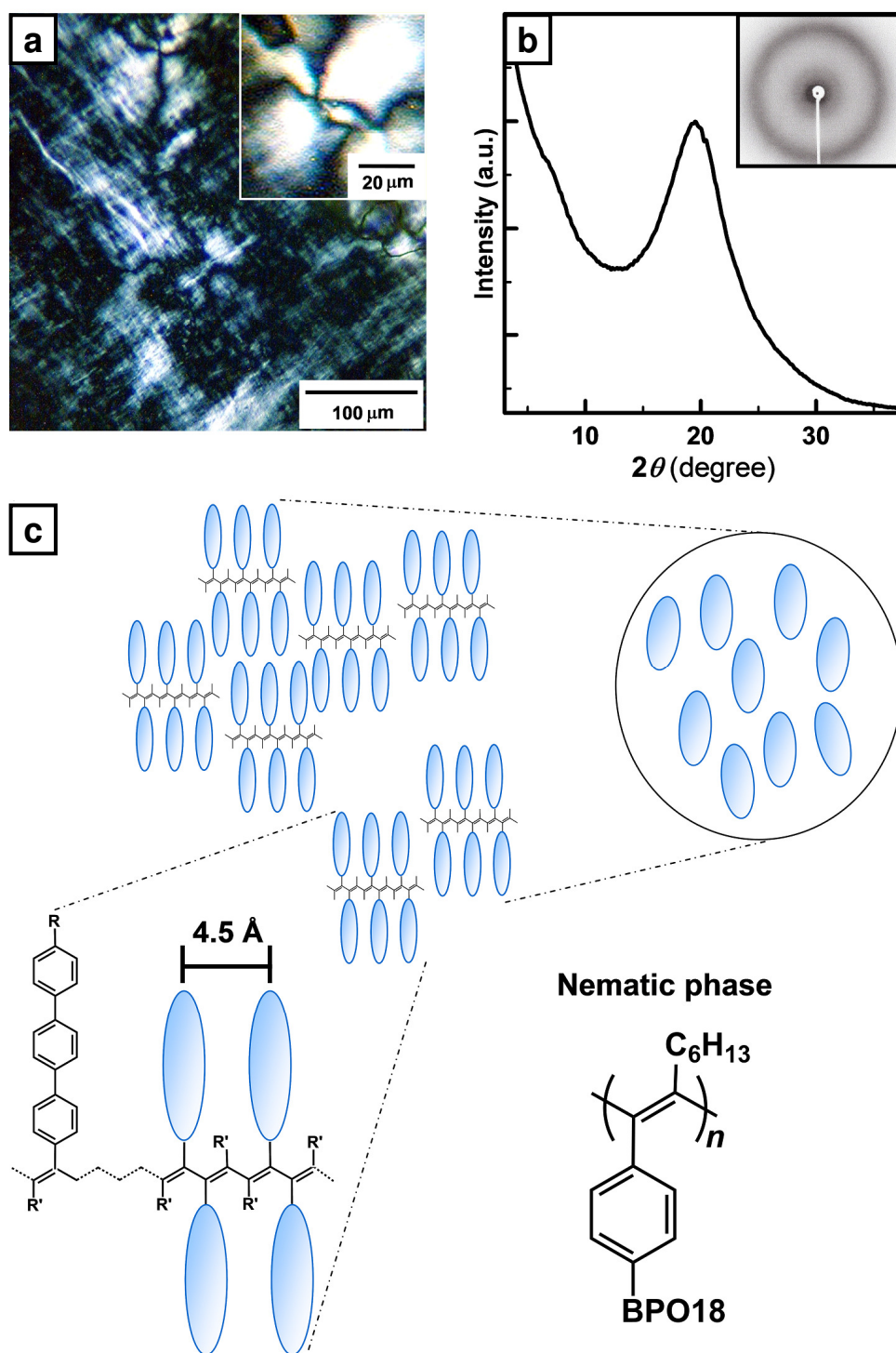


Figure 4. (a) POM image of **PA2** at 120 °C in cooling process. Inset shows a Schlieren texture of the nematic LC (N-LC) phase. (b) The XRD pattern of **PA2** shows a broad reflection at 4.5 Å (19.6° in 2θ). Inset shows the Laue pattern of **PA2**. (c) Liquid crystalline arrangement of **PA2** showing a N-LC phase.

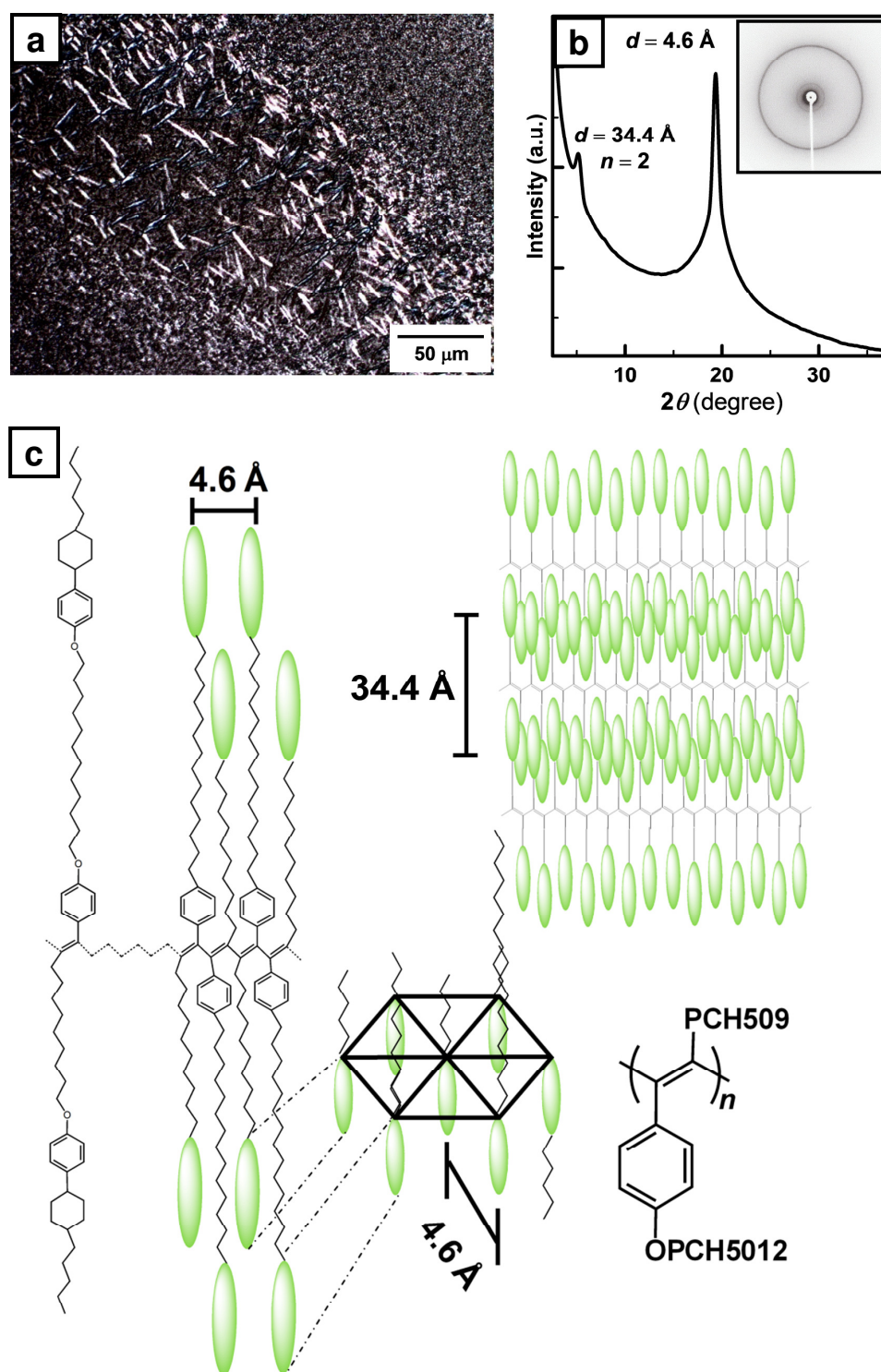


Figure 5. (a) POM image of **PA7** at 110 $^\circ\text{C}$ in cooling process. (b) The XRD pattern of **PA7** shows sharp reflections at 34.4 $\text{\AA}$ (5.2° in 2θ) and at 4.6 $\text{\AA}$ (19.4° in 2θ). Inset shows the Laue pattern of **PA7**. (c) Liquid crystalline arrangement of **PA7** showing a hexagonal packing of the smectic B (S_mB) phase.

A schematic model derived from the XRD profile shows that **PA7** has a monolayer S_mB phase^{32–35} with hexagonal packing (Figure 5c). In this model, the PCH mesogens are attached via flexible spacers and alternate on both sides of the polyene main chain to form a *trans-transoid* stereoregular configuration of head-head-tail-tail linkages. XRD profiles of **PA1**, **PA3**, **PA5** and **PA6** LC films are shown at the supporting figures section, Figure S5.

Interesting trends in the LC properties are observed with changes in the structure of the PA groups. For Group 1 PAs, **PA1** and **PA2** have comparable LC properties and have the same N-LC phase. The transition temperature from the glassy to the LC phase decreases from **PA1** (185 °C) to **PA3** (110 °C) during the heating process. Notably, **PA3** has an isotropic phase while **PA1** and **PA2** only degrade at high temperatures. It can also be noted that the LC temperature range in the cooling process increases from **PA1** (170–250 °C) to **PA2** (100–250 °C). Therefore, having a long alkyl chain or a bulky cyclohexyl group in the polymer structure stabilizes the LC phase. Meanwhile, **PA4** has no thermotropic LC phase. This may be due to stiffness of the polymer, because it has a high degree of polymerization and the phenyl and terphenyl moieties, directly attached to the main chain, form rigid side chains based on a stilbene fragment.

Among Group 2 PAs, **PA7** has a lower transition temperature (55 °C) from the glassy to LC phase than that (75 °C) of **PA5**, and has an isotropic phase. This is attributed to the two PCH LC groups in the side chains of **PA7**. Conversely, **PA6** has a higher transition temperature (90 °C) from the glassy to LC phase than that of **PA5** (75 °C), because of the main chain stiffness brought about by the directly attached phenyl and phenylene groups in the side chains.

It should be emphasized here that although **PA4** has no thermotropic liquid crystallinity, it exhibits lyotropic liquid crystallinity due to its main chain stiffness enhanced by the phenyl and terphenyl moieties in side chains and relatively high molecular weight. The lyotropic LC was prepared from a 10–15 wt% solution using toluene as a solvent. Figure 6 shows the POM image of the polymer solution, depicting an optical texture characteristic of N-LC. The XRD analysis of **PA4** shows a single broad diffraction peak at 17.6° in 2θ . The peak corresponds to $5.0 \text{ \AA}$, which is assigned to the distance between the mesogenic groups (see supporting figures section, Figure S1). The other *di*-PAs showed no lyotropic LC phases, since the conditions necessary for achieving a lyotropic LC phase were not satisfied. Namely, to achieve a lyotropic LC phase, a stiff polymer structure with high molecular weight and a good solubility toward a solvent under an appropriate concentration at room temperature are needed.²⁸

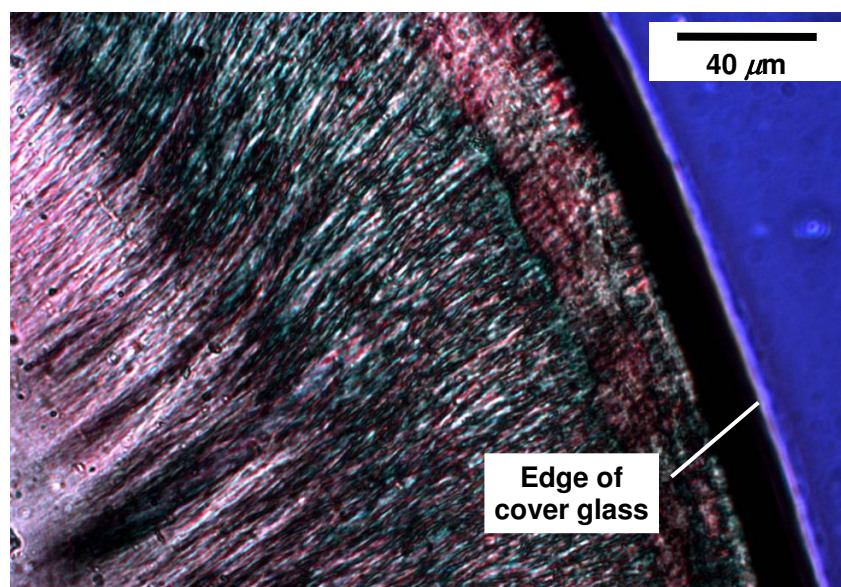


Figure 6. POM image of **PA4** showing a lyotropic nematic LC (N-LC) phase at room temperature. The lyotropic N-LC was prepared from 10–15 wt% solution using toluene as a solvent.

It is apparent that **PA4** has the most stiff polymer structure in terms of both of main chain and side chain among the present polymers, because the side chains of **PA4** are composed of aromatic rings such as phenyl and terphenyl moieties and these rigid moieties are directly attached to the main chain forming a stilbene fragment enforced by π -conjugation. Such a highly stiff polymer should be infusible upon the heating, resulting in no thermotropic LC. However, by virtue of pentyl group substituted at the terminal site of the terphenyl moiety, **PA4** is soluble in organic solvents such as a toluene and shows lyotropic LC. Note that the other polymers (**PA1~PA3**, **PA5~PA7**) are also soluble in organic solvents but they show no lyotropic LC. This is probably due to their higher solubility, which might depress the formation of spontaneously aligned self-assemblies that is prerequisite to the formation of domains of lyotropic LC. In other words, the polymers with high solubility are freely dissolved in a solvent with randomly oriented conformation, but form neither a regularly stacked nor an associated structure. This situation is far apart from the formation of the lyotropic LC. In the case of **PA4**, the stilbene fragment might be suitable for formation of an interchain π -electron overlapped association through van der Waals interactions, which enables the polymer to exhibit the lyotropic LC.

2.3. Absorption and Photoluminescence

We examined the UV-vis and PL of the *di*-PAs in chloroform (CHCl_3) solution and cast film (Table 2). Due to the *para*-terphenyl moiety, the absorption spectra of the first group of PAs in solution extend between 300 and 400 nm, corresponding to the π - π^* transitions of the polyene main chains (Figure 7a). We observe an overlap between the absorption band of the polyene main chain and the *para*-terphenyl moiety

at 300 nm, corresponding to the π - π^* transition of the *para*-terphenyl moiety. We observe this 300 nm band in the absorption spectrum of the **PA1** monomer (Figure S2). **PA5** and **PA7** have main chain absorption bands at 320 nm and a PCH mesogen absorption band at 280 nm (Figure 7b,d). Notably, **PA7** has a more defined PCH absorption peak than **PA5** due to the two PCH mesogen groups on **PA7**. Conversely, **PA6** exhibits three absorption peaks at 280, 380, and 430 nm (Figure 7c) corresponding to the absorption of the PCH moiety, the *trans*-stilbene structure, and the polyene main chain, respectively.

Table 2. Maximum absorbance (λ_{max}), emission ($E_{\text{m max}}$), excitation ($E_{\text{x max}}$), and quantum yield (Φ) of the *di*-PAs.

	λ_{max} (nm)		$E_{\text{m max}}$ (nm)		E_{x} (nm)		Φ	
	In CHCl_3	In film	In CHCl_3	In film	In CHCl_3	In film	In CHCl_3^a	In film ^b
PA1	291	294	484	478	270	289	38	31
PA2	298	301	481	472	275	310	29	24
PA3	269	274	481	470	285	310	24	22
PA4	298	300	520	542	273	366	22	19
PA5	276	277	475	433	329	335	16	36
PA6	279	272	497	513	389	371	26	5
PA7	279	278	471	429	310	310	30	12

^aUsing quinine sulfate as standard sample.

^bUsing integrating-sphere method

Figure 7 also shows the PL spectra of the PAs. The PL spectra of **PA1**, **PA2**, and **PA3** show blue colored emission, with their maximum emission ($E_{\text{m max}}$) being around 480 nm. The **PA4** fluorescence is yellow green with an $E_{\text{m max}}$ at 520 nm. This difference in emission is associated with the two bulky phenyl rings directly attached to

the polyene main chain which perturbs it. The perturbation lowers the $1B_u$ excited state, which decreases the band gap (Figure 2)¹⁵ and results in a bathochromic shift of the **PA4** emission bands. The emission spectrum of **PA4** also shifts to around 540 nm in cast film, which is related to the π - π stacking of the two phenyl groups directly attached to the polyene main chain in the cast film. This π - π stacking increases the effective conjugation of the polyene main chain leading to the yellowish-green emission color. Polymers **PA5** and **PA7** show blue emission around 475 nm, while the two phenyl groups attached to the main chain of **PA6** cause a green luminescence at around 500 nm. There is a slight red shift to 513 nm in the **PA6** cast film emission. Generally, the PAs show small emission shifts between the solution and cast film states, which is especially advantageous for applications of *di*-PAs as fluorescent materials in EL devices.

Fluorescence quantum yields (Φ) of the PAs in solution were measured using quinine sulfate in 1.0 M sulfuric acid as the standard. The quantum yields of the PAs in solution range from 16% for **PA5** to 38% for **PA1**. This result confirms that the *para*-terphenyl moiety not only contributes to good LC properties but also effective light emission. The quantum yield values of **PA5** and **PA7** double from 16 to 30% because **PA7** has two PCH moieties which act as chromophoric pendants, leading to efficient polyene main chain emission. The emission spectrum of the PCH pendants overlap with the polyene main chain absorption spectrum, enabling efficient emission from the PAs because of fluorescence resonance energy transfer (FRET).^{17,36} Absolute fluorescence quantum yields of the PAs in cast film were also measured using integrating-sphere method with quantum yields ranging from 5% for **PA6** to 36% for **PA5**.

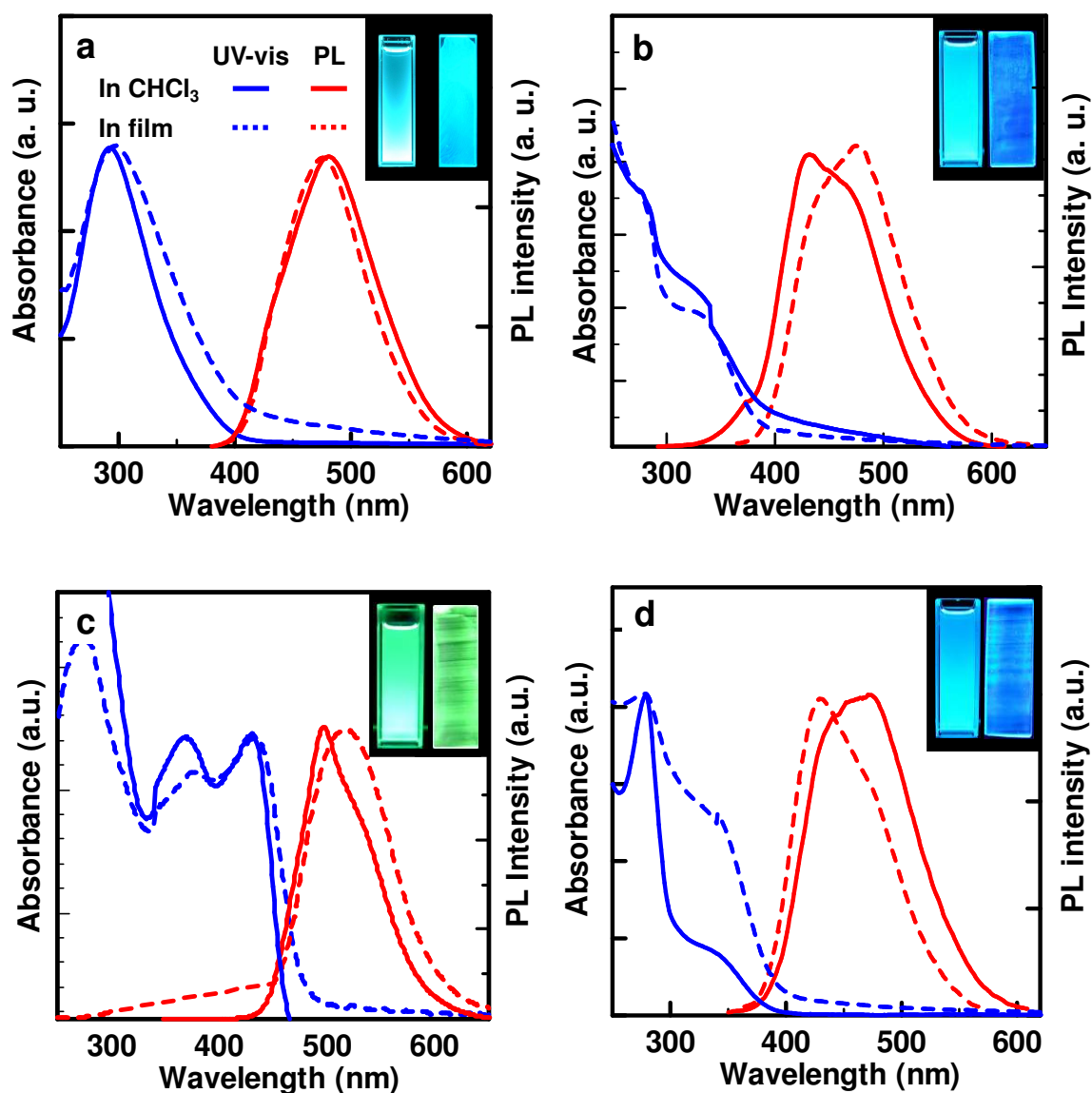


Figure 7. UV-vis and PL spectra of (a) PA1, (b) PA5, (c) PA6, and (d) PA7 in solution and in cast film, insets: PL in solution (left) and in cast film (right).

2.4. Linearly Polarized Luminescence

The macroscopic alignment of PA films was achieved using rubbing technique. Polymers on quartz substrates were heated to the LC temperature region and rubbed with a glass rod along the long axis of the quartz substrate before cooling to room temperature. In the case of PA4, lyotropic LC solution in 10–15wt% toluene was

prepared, then applied to a quartz substrate, and then rubbed with a glass rod along the long axis. The PL intensity was measured as a function of the polarizer angle with respect to rubbing direction. The dichroic ratio (DR) of the PAs are summarized in Table 3 and are defined as the ratio of parallel to perpendicularly polarized PL intensity ($DR = I_{//} / I_{\perp}$) or vice versa ($DR = I_{\perp} / I_{//}$).

Table 3. Linearly dichroic ratios of the *di*-substituted PAs.

Polymers*		Dichroic ratio
Group 1	PA1	1.8
	PA2	1.6
	PA3	1.5
	PA4	2.2
Group 2	PA5	1.2
	PA6	2.4
	PA7	1.6

*Aligned films of **PA1–PA3** and **PA5–PA7** were prepared in thermotropic LC states, and that of **PA4** was prepared in lyotropic LC state.

Three patterns of alignment and emission behavior were observed on the aligned PA films (see Figure 9). The alignment behavior of the PA films can be related to the structure of the polymer main chain and the LC moieties. In the *di*-PA derivatives, the main chain and the side chain can both act as LC mesogens. The interactions between the main chain and the LC moieties determine the alignment behavior of the PA films.

On the other hand, the emission behavior of the PA films can be related to the *di*-PAs exciton confinement (localization) – deconfinement (delocalization) mechanism.^{15a,15c,15d} Excitons are electron-hole pairs that are formed during

photoexcitation.¹⁶ For the *di*-PAs, the excitons are initially confined (localized) to the polyene main chain because of steric effects between the bulky side chains (Figure 8a). They then are deconfined (delocalized) to the phenyl moieties where they radiatively recombine (Figure 8b). The structures of the polyene main chain and the phenyl moieties of the *di*-PAs determine the polymer emission behavior.

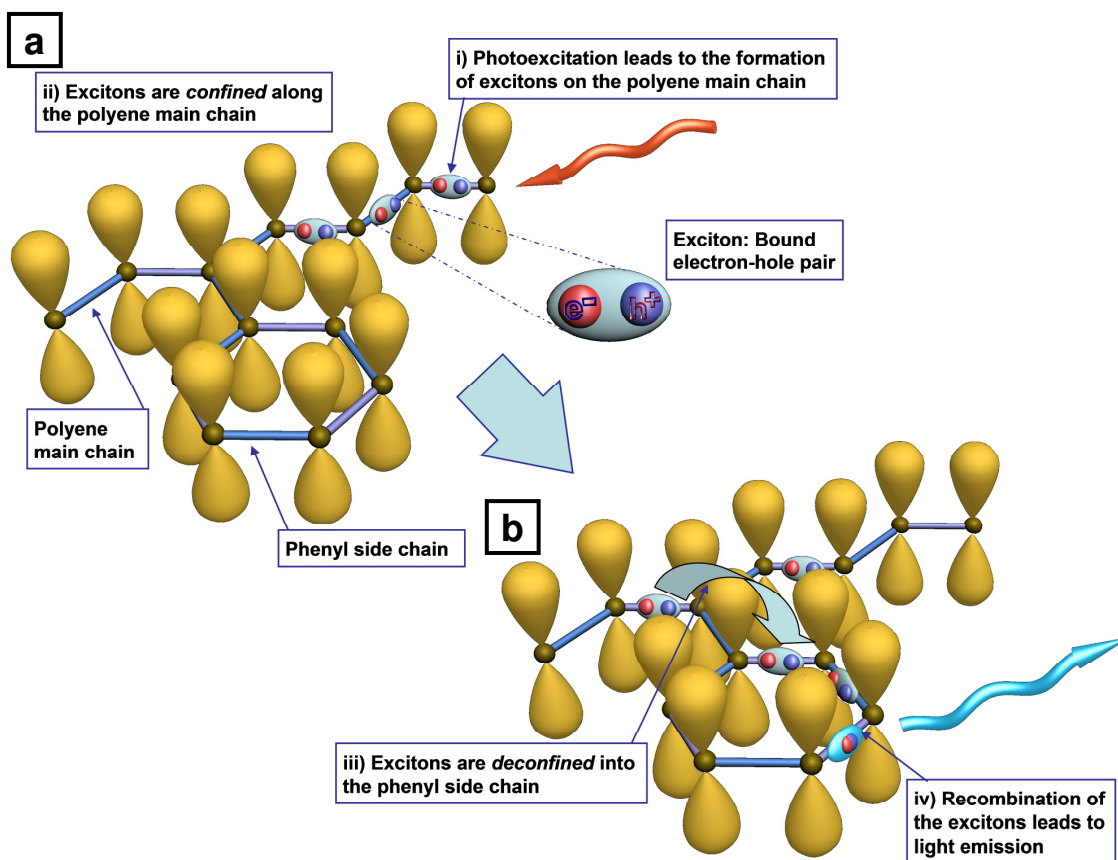


Figure 8. Exciton (a) confinement (localization) and (b) deconfinement (delocalization) behavior in *di*-substituted PA.

In Case 1, as represented by **PA2**, we observe that **PA2** has a DR of 1.6 and a higher PL intensity perpendicular to the rubbing direction (Figure 9a). The reflection of the *para*-terphenyl moiety was observed at the meridian parallel to the rubbing direction ($4.5 \text{ \AA}$, 19.6° in 2θ) in the XRD profile of the aligned **PA2** film (Figure 9b). These results imply that the *para*-terphenyl moiety and hence the polyene main chain are

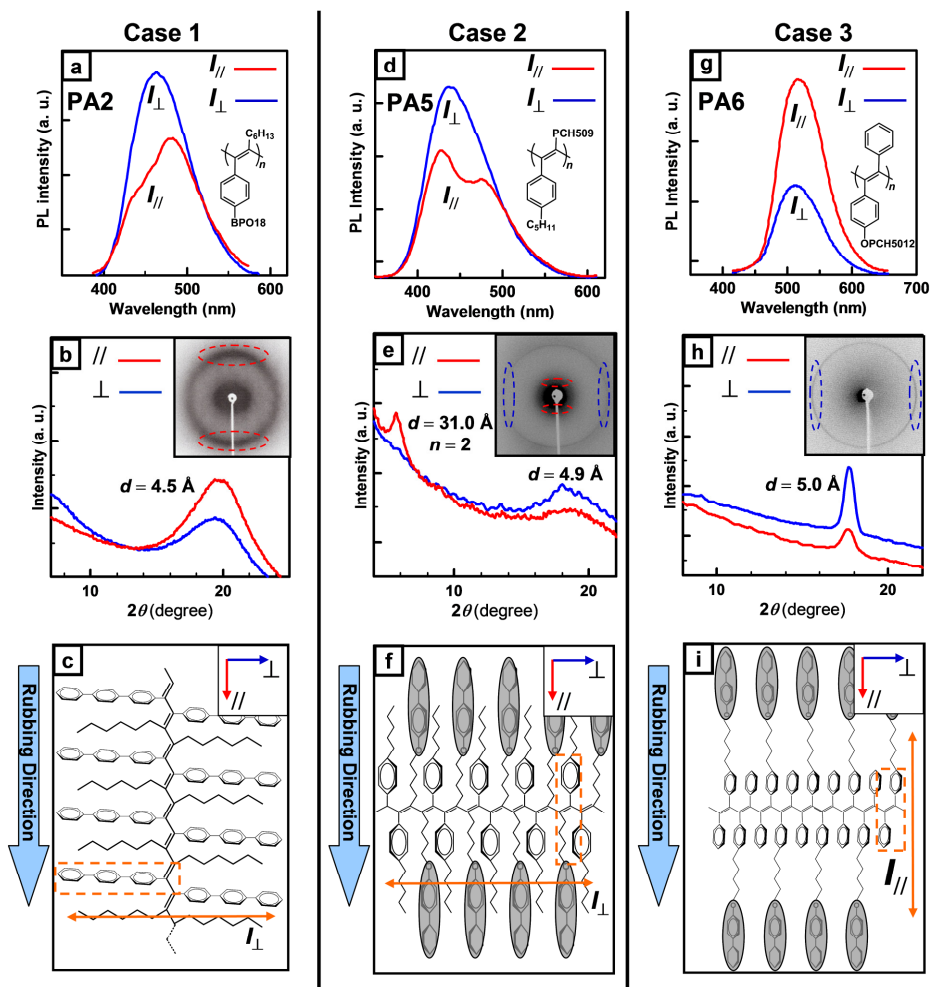


Figure 9. (a) Linearly dichroic PL of aligned **PA2**, (b) XRD pattern of aligned **PA2** shows a broad peak at 4.5 Å corresponding to the distance between the terphenyl LC moieties in the side chains, inset: XRD Laue pattern of aligned **PA2** film, and (c) orientation diagram of aligned **PA2**. (d) Linearly dichroic PL of aligned **PA5**, (e) XRD pattern of aligned **PA5** shows peaks at 31 Å and 4.9 Å corresponding to the interlayer distance of the main chains and the distance between the PCH LC moieties in the side chains, respectively, and (f) orientation diagram of aligned **PA5**. (g) Linearly dichroic PL of aligned **PA6**, (h) XRD pattern of aligned **PA6** shows a peak at 5.0 Å related to the distance between the PCH LC moieties in the side chains, and (i) orientation diagram of aligned **PA6**. Rectangles with orange broken lines in Figure 9c, 9f, and 9i indicate dominant emission moieties in the polymers.

aligned perpendicular and parallel to the rubbing direction, respectively (Figure 9c). For **PA2**, the excitons are moved to the *para*-terphenylvinyl moiety through deconfinement, thus the dominant emission of **PA2** is from the *para*-terphenylvinyl moiety with the LPL perpendicular to the rubbing direction. **PA1**, **PA2** and **PA3** exhibit the same LPL trends where the polymers show main chain type LC alignment and dominant emission brought about by the *para*-terphenylvinyl or *para*-biphenylcyclohexylvinyl moieties directly linked to the polyene main chain.

The DR of **PA5** is 1.2, with a higher PL intensity perpendicular to the rubbing direction (Figure 9d). The XRD pattern of aligned **PA5** film shows a meridional reflection at the small angle area of 5.7° in 2θ corresponding to the main chain interlayer distance of $31 \text{ \AA}$ ($n = 2$). An equatorial reflection at 18.0° in 2θ was also observed (Figure 9e). This reflection can be assigned as the distance of $4.9 \text{ \AA}$ between LC moieties aligned parallel to the rubbing direction.

Given the **PA5** LPL spectra and XRD profile, we propose an alignment structure where the polyene main chain and the LC moieties are perpendicular and parallel to the rubbing direction, respectively (Figure 9f). In **PA5**, the PCH LC moiety aligns parallel to the rubbing direction and thus it exhibits side chain type LC alignment. For **PA5**, the excitons are moved to the phenylvinyl moieties along the main chain. As a consequence, the dominant emission of **PA5** is from the phenylvinyl moieties. The Case 2 polymers, **PA5** and **PA7**, show the same side chain type LC alignment and emission behavior.

In Case 3, as represented by **PA6**, we observe that **PA6** has a DR of 2.4 and a higher PL intensity parallel to the rubbing direction (Figure 9g). The XRD pattern of aligned **PA6** film shows an equatorial reflection at the 17.8° in 2θ ($d = 5.0 \text{ \AA}$) corresponding to

the distance between LC moieties (Figure 9h). The LPL data and the XRD results imply that the PCH LC moieties and hence the polyene main chain are aligned parallel and perpendicular to the rubbing direction, respectively (Figure 9i). In **PA6**, the PCH LC moiety aligns parallel to the rubbing direction and thus it exhibits side chain type LC alignment. The stilbene moieties aligned parallel to the rubbing direction are the dominant emission sources, thus **PA6** exhibits a higher PL intensity parallel to the rubbing direction. Figure 10 shows an image of the LPL of **PA6** under polarizing plates. **PA4** and **PA6** exhibit side chain type LC alignment and dominant emission from the stilbene moiety. Table 4 shows the relationship of the macroscopic alignment and emission behavior of the *di*-LCPAs.

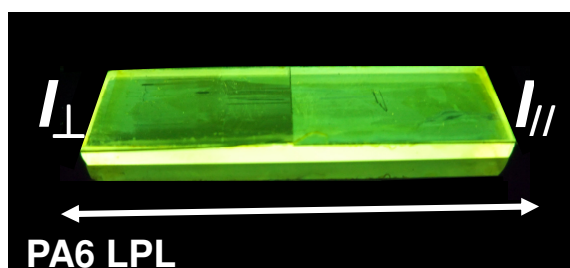


Figure 10. Photograph showing the LPL of **PA6**, where two polarizers are arranged parallel (bright) and perpendicular (dark) to the aligned direction. The white arrow indicates the alignment direction.

The PAs show LPLs with fairly low DR values that range from 1.2–2.4. These values are mainly due to the situation characteristic of the *di*-PAs where not only the LC side chain but also the conjugated polyene main chain directly linked with phenyl or phenylene moiety behave as mesogens to the external force. Since the LC side chain and the main chain are almost orthogonal in the polymer structure, the externally forced alignments of the side and main chains substantially cancel each other out, thus giving a low degree of alignment.

Table 4. Different cases of alignment and emission behavior of the *di*-substituted PAs.

	Polymers	Alignment type	Dominant Emission
Case 1	PA1, PA2, PA3	Main chain	Terphenylvinyl moiety or biphenylcyclohexylvinyl moiety ($I_{\perp}$)
Case 2	PA5, PA7	Side chain	Phenylvinyl moiety ($I_{\perp}$)
Case 3	PA4, PA6	Side chain	Stilbene moiety ($I_{//}$)

2.5. Relationships between Polymer Structure, Alignment Type and Emission Color

At this stage, it is helpful to summarize the relationships between polymer structure, alignment type and emission color, as depicted in Figure 11.

i) Among the polymers of Group 1, **PA1**, **PA2** and **PA3** are classified into Case 1, where the terphenyl or biphenylcyclohexyl group and the alkyl group are attached to both sides of the main chain. These polymers belong to poly(alkylphenylacetylenes) [PAPAs] (see Figure 11), and show blue emission at 481–484 nm. They exhibit unexpectedly main chain type alignment in which the main chain is aligned parallel to the rubbing direction (see also Figure 9c). It remains unclear why the polymers in Case 1 show the main chain type alignment upon rubbing treatment. Nevertheless, it should be emphasized that the conjugated polyene chains directly linked with the terphenyl or biphenyl moiety play a role of mesogenic core toward an external perturbation, which is similar to the terphenyl or biphenyl moiety itself in the side chain. In other words, the polymers in Case 1 have two kinds of mesogenic cores in the main chain and side chain. The existence of two kinds of mesogenic cores, that are orthogonal to each other, causes

a competitive orientation between the mesogenic cores in the main and side chains, which should weaken the alignment ability of the polymer. This may be the reason why the present polymers have unexpectedly small values in dichroic ratio such as 1.5–1.8 even after alignment (see Table 3). The direction of polymer alignment under the external perturbation should be determined by a subtle balance of the two kinds of mesogenic cores in the polymer.

ii) **PA5** and **PA7** in Group 2 are classified into Case 2, where the alkylphenyl group and the alkylphenylcyclohexyl (PCH) moiety linking with the decylmethylene chain are attached to both sides of the main chain. These polymers also belong to PAPAs and show blue emissions at 471–475 nm. Although the polymers in Case 1 and Case 2 show blue emissions, the emission bands of the polymers in Case 1 are located at longer wavelengths by about 10 nm than those in Case 2. This indicates that the former polymers (**PA1**, **PA2** and **PA3**) have longer effective conjugated lengths than the latter (**PA5** and **PA7**), because the π -conjugation between the terphenyl or biphenyl group and the vinylene moiety in Case 1 is stronger than that between the phenyl group and the vinylene moiety in Case 2. In addition, it should be noted that **PA5** and **PA7** in Case 2 show side chain type alignment in which the side chain is aligned parallel to the rubbing direction (see also Figure 9f), whereas the polymers in Case 1 show the main chain type alignment as mentioned above. The small dichroic ratios (1.2–1.6) in the polymers in Case 2 are also rationalized with the competitive orientation occurring between the mesogenic cores of the polyene main chain and the PCH side chain (see Table 3).

iii) **PA4** in Group 1 and **PA6** in Group 2 are classified into Case 3, where the terphenyl or PCH-substituted phenyl group and the phenyl group are attached to both sides of the main chain, forming the poly(*di*-phenylacetylene)s [PDPAs] (see Figure 11).

The polymers show green emissions at 497–520 nm, and they show side chain type alignment. It is worth noting that the LC moiety in **PA6**, such as PCH50120P, is not directly attached to the main chain, but indirectly linked to the main chain through the phenylene moiety. As a result, **PA6** has a stilbene type fragment consisting of a phenyl group, a vinylene moiety and the LC-substituted phenylene moiety (see Scheme 1). Thus **PA6** behaves as one of PDPA in Case 3 in the alignment under the external perturbation. The relatively large dichroic ratios (2.2–2.4) of the polymers in Case 3 are owing to the situation that the phenyl group and the phenylene moiety or terphenyl one in the both side chains are conjugated to the vinylene moiety in the main chain to form a double mesogenic core (see Table 3 and Figure 11). This allows the side chains to align more preferably parallel to the rubbing direction, although the main chain also behaves as another mesogenic core.

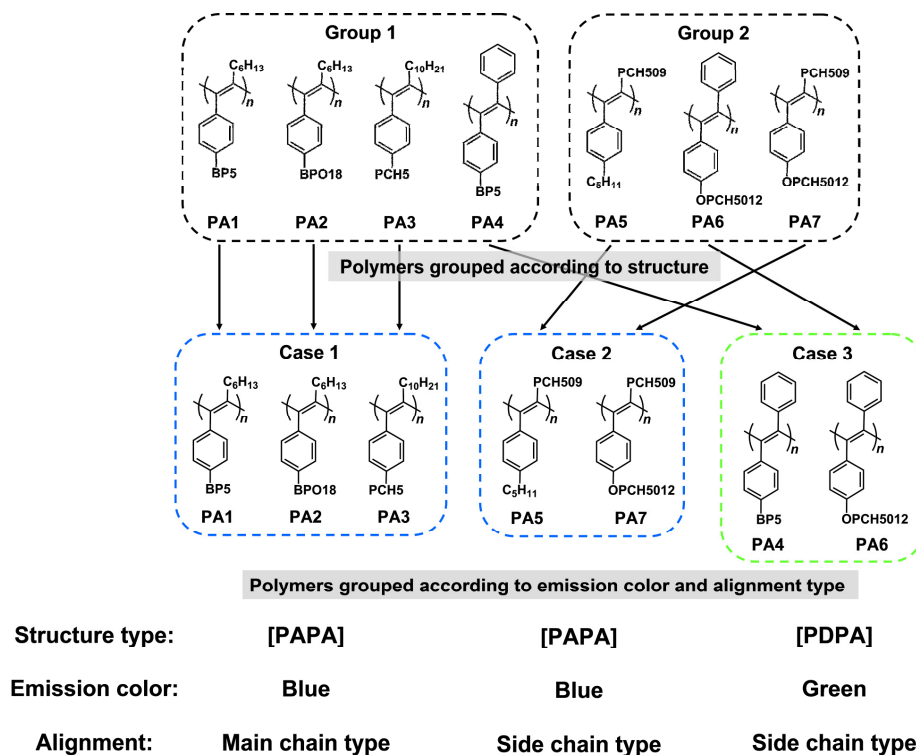


Figure 11. Correlation diagram summarizing the relationships between the polymer structure, emission color, and alignment type of the *di*-substituted PAs.

As a consequence, when one designs emissive polyacetylene derivatives with linearly dichroic nature, it is essential for the polymers to have phenylene moieties that are directly or indirectly attached to the main chain and also to introduce LC moieties in one side or both side chains. However, these polymers inevitably encounter the competitive orientation or even partial cancellation in alignment between the two mesogenic cores of the rigid polyene main chain and the LC side chain that are almost orthogonal to each other. Among *di*-substituted PAs, the polymers bearing the double mesogenic core in side chains (**PA4** and **PA6**) are the most promising for the dichroic emissive PAs, because the double mesogenic core is highly responsive to the external perturbation than the single mesogenic one, giving a alignment with substantially notable linear dichroism.

2.6. Electroluminescence

The PL results of the PAs led us to investigate their EL properties. We fabricated an EL device with a configuration of ITO / PEDOT-PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) / **PA** layer / LiF / Ca / Al (Figure 12a) using **PA1** and **PA2** as the emissive polymer layer. The EL of the PAs emit at 480 nm with CIE (*Commission Internationale de l'Eclairage*) coordinates of (0.26, 0.33) for **PA1** and (0.21, 0.30) for **PA2**. The EL spectra of **PA1** and **PA2** show no excimer sidebands and are similar to their corresponding PL spectra. The **PA1** EL spectrum is broader and exhibits a whitish-blue-colored emission (Figure 12b). Polymers **PA1** and **PA2** have a turn-on voltage at 6–8 V and show an exponential increase in luminous intensity with values up to 220 and 50 cd/m², respectively. The EL devices utilize **PA1** and **PA2** because of their high turn-on voltage and have

maximum luminous efficiencies of 0.07 and 0.08 lm/W, respectively (Table 5). Graphs showing the current efficiency, luminous efficiency, current density, and luminance of **PA1** and **PA2** are shown at supporting figures section, Figure S6. Though EL device fabrication still needs to be optimized, we show that the use of **PA1** and **PA2** as emissive layers yield promising EL properties, suggesting that the direct attachment of the *para*-terphenyl moieties to the polyene main chain has a beneficial effect on the EL of these devices.

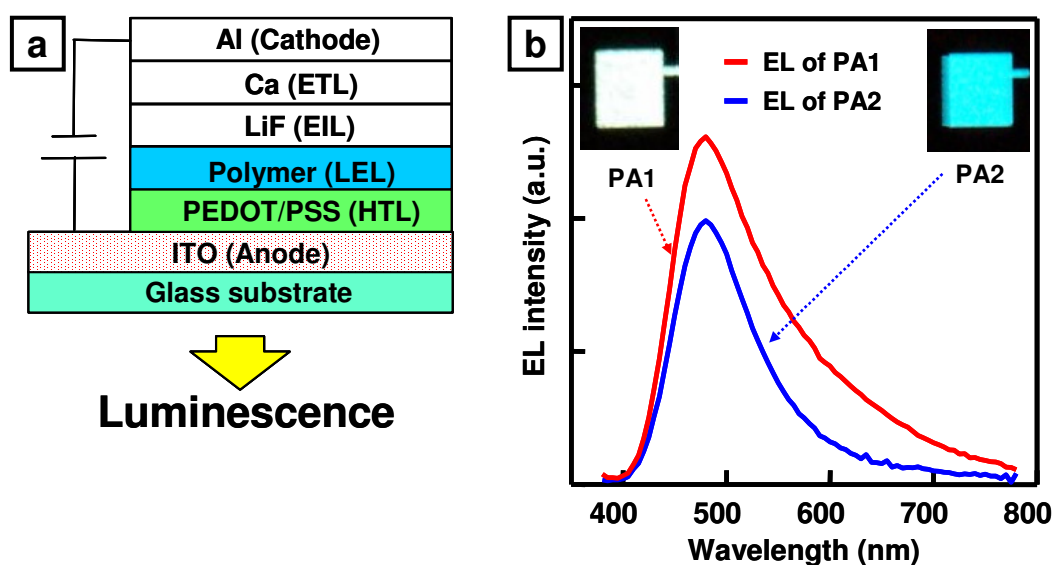


Figure 12. (a) Schematic diagram of the EL device using *di*-PA as an emissive layer. (b) EL spectra of **PA1** and **PA2**, insets: EL spectra of **PA1** (left) and **PA2** (right).

Table 5. EL characteristics of **PA1** and **PA2**.

	Thickness (nm)	Turn-on voltage (V)	E_{mmax} (nm)	Chromativity coordinates (x, y)	Maximum luminance (cd/m ²)	Maximum current efficiency (cd/A)	Maximum power efficiency (lm/W)
PA1	83	6.9	480	(0.26, 0.33)	220	0.16	0.07
PA2	91	8.4	480	(0.21, 0.30)	50	0.24	0.08

3. Conclusion

We synthesized *di*-substituted liquid crystalline PA derivatives represented by poly(alkylphenylacetylene)s [PAPAs] and poly(*di*-phenylacetylene)s [PDPAAs] and evaluated their thermal and optical properties. The polymers exhibit enantiotropically thermotropic or lyotropic liquid crystallinity. We elucidated the origin of emission of substituted PAs and also investigated fluorescent trends such as emission color and quantum yield. The polymers also show relatively low but significant PL and EL quantum yields. We found that the macroscopically aligned films of the *di*-PAs emit linearly polarized luminescence (LPL) by virtue of the functionalities associated with liquid crystallinity and fluorescence. The aligned structures of the *di*-PAs were characterized in terms of main chain and side chain type alignments through XRD measurements for the macroscopically aligned polymer films. The *di*-PAs were classified into three types, Case 1, 2 and 3 according to the emission color and alignment type. The mechanism of LPL of the *di*-LCPAs with respect to the polymer structure, alignment type and emission color were elucidated. The synthesized multifunctional *di*-substituted PA derivatives are thus very promising materials for applications such as advanced liquid crystal displays (LCDs) and other future applications that utilize linearly dichroic luminescent materials.

Acknowledgements

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Chapter 2 Appendix

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1. Experimental Section

1.1. Materials

The chemical reagents were purchased from commercially available sources and were used as received. 18-crown-6-ether, 4-iodophenylboronic acid, and *trans*-dichlorobis(triphenylphosphine)palladium (II) ($\text{PdCl}_2(\text{TPP})_2$) were purchased from Aldrich Co. Ltd. *Tetra-n*-butyltin, *tetrakis*(triphenylphosphine)palladium (0) ($(\text{TPP})_4\text{Pd}$), *tetra-n*-butylammonium hydroxide (TBA-OH), diethylazodicarboxylate (DEAD), 12-bromo-1-dodecanol, 1-octyne, 1-dodecyne, 4-bromo-4'-*n*-pentylbiphenyl, 4-bromo-4'-hydroxybiphenyl, 4-iodophenol, and stearyl alcohol were purchased from Tokyo Kasei Co. Ltd. Tantalum (V) pentachloride, *para-trans*-4-*n*-pentyl(cyclohexyl)

phenol, *para*-(*trans*-4-*n*-pentylcyclohexyl)bromobenzene, *para*-pentyl iodobenzene, and copper (I) iodide (CuI) were purchased from Kanto Chemical Co. Ltd. Triphenylphosphine (TPP), 10-undecyn-1-ol and 25% ammonia (NH₃) solution were purchased from Wako Co. Ltd. Phenyl acetylene, sodium hydrogen carbonate (NaHCO₃), potassium carbonate (K₂CO₃), sodium sulfate (Na₂SO₄), triethyl amine (Et₃N), tetrahydrofuran (THF), toluene, chloroform (CHCl₃), and acetone were purchased from Nacalai Tesque Co. Ltd. All experiments were performed under argon (>99.9995 % purity) atmosphere. THF, Et₃N, and toluene used were distilled from sodium as a drying agent under argon gas before use.

1.2. Methods

Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either JEOL JNM EX400 400 MHz or Bruker AVANCE-600 600 MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from *tetra*-methylsilane (TMS) as an internal standard. Elemental analysis was measured using a Perkin-Elmer 2400 CHN Elemental Analyzer.

The microscope observation was carried out under crossed nicols using a Nikon ECLIPSE E400 POL POM equipped with a Nikon COOLPIX 950 digital camera and a Linkam TH600PM and L600 heating and cooling stage with temperature control. The samples for observations with POM were sandwiched between two cover glasses. Thermal behavior of the polymers was investigated in a heating run at a heating rate of 10 °C/min in flowing nitrogen gas, using thermogravimetry differential thermal analysis (TG-DTA) apparatus (TG-DTA6200, Seiko). The phase transition temperatures of monomers and polymers were determined using a Perkin-Elmer differential scanning calorimeter (DSC7) and a TA instrument Q100 DSC apparatus at a constant heating and

cooling rate of 10 °C/min, where first cooling and second heating were recorded.

Optical absorption spectra were measured using a Hitachi U-3500 spectrometer, and fluorescence spectra were measured using either JASCO FP-750 spectrometer or JASCO FP-6500 spectrometer with quartz cell (for solution) and quartz plate (for cast film). Fluorescence quantum yield of the polymers was measured in solution state using quinine sulfate as standard. Absolute fluorescence quantum yield of the polymers was measured in film state using integrating-sphere method at the JASCO FP-6500 spectrometer. Dichroic fluorescence spectra were obtained using polymer films after rubbing treatment. The polymers on the quartz substrates were heated to the LC temperature region, and these were rubbed with a glass rod. Then the polymer films were cooled to room temperature, yielding samples. During the cooling process of the polymers, LC textures remained unchanged even in glassy states. In the case of **PA4**, lyotropic LC solution in 10–15wt% toluene was prepared, then applied to a quartz substrate, and then rubbed with a glass rod along the long axis.

Luminance and current-voltage curves were obtained with a Kollmorgen Instrument PR650 photospectrometer, a Kiethley model 2001 multimeter and a Takasago GP050-2 DC voltage source. The EL configuration is shown in Figure 12a. The thin film of poly(3,4-ethylenedioxythiophene) (PEDOT)/poly(styrenesulfonate) (PSS) (hole transporting layer: HTL) was prepared by spin coating on indium tin oxide (ITO: Anode) substrate at a rotational speed of 1100 rpm from commercially available PEDOT/PSS solution annealed at 200 °C for 10 min. The polymer film (light emissive layer: LEL) was spin coated at a rotational speed of 800 rpm from its toluene solution (1.5–2.5 wt%) filtered through 0.2 µm polytetrafluoroethylene (PTFE) filter and annealed at 90 °C for 1 h. The thickness of **PA1** and **PA2** were 83 and 91 nm

respectively (see Table 5). The layers of lithium fluoride (LiF) (electron injection layer: EIL), calcium (Ca) (electron transporting layer: ETL) and aluminum (Al) (cathode) were deposited in turn under vacuum ($9.2 \times 10^{-6} - 1.2 \times 10^{-4}$ Pa). The thickness of LiF, Ca, and Al layers were 4, 5, and 81 nm, respectively (see Table S1). The conditions of vapor deposition of the EL layers are summarized in supporting figures section, Table S1.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μ m MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

XRD diffraction (XRD) measurements of the polymers were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator with Nickel filtered $\text{CuK}\alpha$ radiation (40 kV/300 mA: $\lambda = 0.154$ nm) and a flat plate camera (RINT2500, Rigaku). The polymers were heated up to isotropic state, and then slowly cooled to room temperature via LC states, yielding XRD samples. Lyotropic LC samples for XRD measurements was prepared by first dissolving the polymer in toluene (10–15 wt% solution) to form a lyotropic LC phase. The lyotropic LC solution is then pulled up a XRD capillary tube (Hilgenberg Mark-tube glass #10, 0.01 mm wall thickness), yielding XRD samples. The diffraction pattern was recorded on an imaging plate and scanned by a R-Axis DS3A imaging plate reader at 100 μ m resolution.

1.3. Syntheses of Monomers and Polymers

4-(1-Octynyl)-phenylboronic acid (1)

4-(1-Octynyl)-phenylboronic acid (**1**) was synthesized as follows. Into a 300 mL three-necked flask were added 142 mg (0.20 mmol) of $\text{PdCl}_2(\text{TPP})_2$, 77 mg of CuI (0.40 mmol), 1-octyne (3.76 g, 30 mmol) and 4-iodophenylboronic acid (5.00 g, 20 mmol) and 100 mL THF under argon. After all the reagents were dissolved, 100 mL of 0.5 M aqueous NH_3 was added dropwise into the solution. The solution was stirred at room temperature overnight under argon atmosphere. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 2.72 g (12 mmol) of **1** as a yellowish white powder. Yield = 59%.

Anal. Chemical Formula: $(\text{C}_{14}\text{H}_{19}\text{BO}_2)_n$ (230.11) $_n$: Calcd. C 73.07, H 8.32, B 4.70, O 13.91; Found C 77.81, H 7.92. ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.2 Hz, $-\text{CH}_3$), 1.26–1.31 (m, 4H, $-\text{CH}_2-$), 1.43 (s, 4H, $\text{B}-(\text{OH})_2$), 1.51–1.55 (m, 2H, $-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 2.35–2.41 (m, 2H, $-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2-$), 2.75 (t, 2H, J = 1.2 Hz, $-\text{C}\equiv\text{C}-\text{CH}_2-$), 7.31 (d, 2H, J = 8 Hz, Ar-H *meta* to $-\text{B}-(\text{OH})_2$), 7.77 (d, 2H, J = 8 Hz, Ar-H *ortho* to $-\text{B}-(\text{OH})_2$). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 19.6, 22.6, 28.6, 31.4, 80.7, 93.0, 109.5, 128.3, 130.9, 135.2.

4-Bromo-4'-(*n*-octadecyloxy)biphenyl (**2**)

4-Bromo-4'-(*n*-octadecyloxy)biphenyl (**2**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (8.65g 33 mmol) and 4-bromo-4'-hydroxybiphenyl (7.48 g, 30 mmol) under argon gas and dissolved in THF (110 mL). In the addition funnel, a mixture of DEAD (14.38 g, 40 wt% in toluene, 33

mmol), stearyl alcohol (8.93 g, 30 mmol) and 10 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from *n*-hexane and dried under vacuum to give 3.37g (6.7 mmol) of **2** as a colorless crystal. Yield = 22%.

Anal. Chemical Formula: $(\text{C}_{30}\text{H}_{45}\text{BrO})_n$ (500.27) $_n$; Calcd. C 71.84, H 9.04.32, Br 15.93; Found C 71.82, H 8.94, Br 15.93. ^1H NMR (600 MHz, CDCl_3): δ = 0.88 (t, 3H, J = 14.0 Hz, $-\text{CH}_3$), 1.24–1.40 (m, 28H, $-\text{CH}_2-$), 1.46 (m, 2H, J = 31.0 Hz, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.80 (m, 2H, J = 28.4 Hz, $-\text{OCH}_2\text{CH}_2-$), 3.98 (t, 2H, J = 13.1 Hz, $-\text{OCH}_2-$), 6.95 (d, 2H, J = 8.76 Hz, Ar-H *ortho* to $-\text{OCH}_2-$), 7.40 (d, 2H, J = 8.58 Hz, Ar-H *meta* to $-\text{OCH}_2-$), 7.46 (d, 2H, J = 8.82 Hz, Ar-H *meta* to Br), 7.52 (d, 2H, J = 8.58 Hz, Ar-H *ortho* to Br). ^{13}C NMR (600 MHz, CDCl_3): δ = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 31.9, 68.1, 114.9, 120.7, 127.9, 128.3, 131.8, 132.2, 139.8, 159.0.

4-(1-Dodecynyl)-phenylboronic acid (**3**)

4-(1-Dodecynyl)-phenylboronic acid (**3**) was synthesized as follows. The reagents 1-dodecyne (1.41 g, 8.5 mmol), 4-iodophenylboronic acid (1.41 g, 5.7 mmol), $\text{PdCl}_2(\text{TPP})_2$ (40 mg, 0.07 mmol), CuI (22 mg, 0.11 mmol), and 50 mL THF was added under argon atmosphere into a 300 mL three-mouthed flask and stirred. After all the reagents were dissolved, 0.5 M aqueous NH_3 (50 mL) was added dropwise into the solution. The solution was stirred at room temperature overnight under argon

atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 0.94 g (3.3 mmol) of **3** as a yellowish white powder. Yield = 58%.

Anal. Chemical Formula: $(\text{C}_{18}\text{H}_{27}\text{BO}_2)_n$ (286.22) $_n$; Calcd. C, 75.53; H, 9.51; B, 3.78; O, 11.18; Found C 79.30, H 9.47. ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (t, 3H, J = 6.8 Hz, $-\text{C}\equiv\text{C}-(\text{CH}_2)_9\text{CH}_3$), 1.27–1.34 (m, 16H, $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 1.44 (s, 2H, $\text{Ar}-\text{B}(\text{OH})_2$), 1.60 (t, 2H, J = 6.8 Hz, $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$), 7.35 (d, 2H, J = 8.4 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{B}(\text{OH})_2$), 7.81 (d, 2H, J = 8 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{B}(\text{OH})_2$). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 22.7, 28.7, 28.9, 29.0, 29.1, 29.3, 29.6, 31.9, 80.7, 93.0, 108.5, 121.3, 130.9, 135.2.

4-(Phenylethynyl)-phenylboronic acid (**4**)

4-(Phenylethynyl)-phenylboronic acid (**4**) was synthesized as follows. Into a 300 mL three-necked flask 2.00 g of 4-iodophenylboronic acid (8.0 mmol), 1.50 g of phenyl acetylene (12.1 mmol), $\text{PdCl}_2(\text{TPP})_2$ (56 mg, 0.08 mmol), CuI (31 mg, 0.16 mmol), and 50 mL THF was added under argon atmosphere. After continuous stirring, 0.5 M aqueous NH_3 (50 mL) was added dropwise into the solution. The solution was stirred at room temperature overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried

in vacuo to give 1.04 g (4.6 mmol) of **4** as a yellowish white powder. Yield = 58%.

Anal. Chemical Formula: $(C_{14}H_{11}BO_2)_n$ (222.05) $_n$: Calcd. C, 75.73; H, 4.99; B, 4.87; O, 14.41; Found C 72.02, H 5.21. 1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 2H, $-C\equiv C-Ar-B(OH)_2$), 7.36 (m, 3H, Ar-H *meta* and *para* to $-C\equiv C-C_6H_4B(OH)_2$), 7.49 (m, 4H, Ar-H *meta* to $-B(OH)_2$ and *ortho* to $-C\equiv C-C_6H_4B(OH)_2$), 7.50 (d, 2H, J = 8.4 Hz, Ar-H *ortho* to $-B(OH)_2$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 90.5, 104.2, 123.1, 127.5, 128.2, 128.3, 131.6, 135.3.

11-(4-Pentylphenyl)undec-10-yn-1-ol (**5**)

11-(4-Pentylphenyl)undec-10-yn-1-ol (**5**) was synthesized as follows. The reagents 10-undecyn-1-ol (3.00 g, 17.8 mmol), *para*-pentyl iodobenzene (5.86 g, 21.4 mmol), $PdCl_2(TPP)_2$ (250 mg, 0.36 mmol), CuI (136 mg, 0.71 mmol), and 70 mL THF was added under argon atmosphere into a 300 mL three necked flask. After continuous stirring, 0.5 M aqueous NH_3 (50 mL) was added dropwise into the solution. The solution was stirred at room temperature and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 4.19 g (13.4 mmol) of **5** as an amber colored viscous liquid. Yield = 75%.

Anal. Chemical Formula: $(C_{22}H_{34}O)_n$ (314.50) $_n$: Calcd. C, 84.02; H, 10.90; O, 5.09; Found C 83.31, H 10.76. 1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 7.2 Hz, $-CH_3$), 1.23–1.42 (m, 14H, $-C\equiv C-CH_2(CH_2)_7CH_2OH$), 1.37 (s, 1H, $-OH$), 1.51–1.61 (m, 6H, $Ar-CH_2(CH_2)_3CH_3$), 2.37 (t, 2H, J = 7.2 Hz, $Ar-C\equiv C-CH_2-$), 2.55 (t, 2H, J =

7.6 Hz, Ar-CH₂-), 3.62 (t, H, J = 6.8 Hz, -C≡C-(CH₂)₈CH₂OH), 7.06 (d, 2H, J = 8 Hz, Ar-H *meta* to -C≡C-(CH₂)₉OH), 7.28 (d, 2H, J = 8.4 Hz, Ar-H *ortho* to -C≡C-(CH₂)₉OH). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.0, 22.5, 25.7, 28.8, 28.9, 29.1, 29.4, 30.9, 31.4, 32.8, 63.0, 80.5, 102.1, 121.0, 128.1, 131.2, 142.3.

12-(4-(4-Pentylcyclohexyl)phenoxy)dodecan-1-ol (6)

12-(4-(4-Pentylcyclohexyl)phenoxy)dodecan-1-ol (6) was synthesized as follows. Into a 500 mL three necked flask were added 4.20 g (17 mmol) of *para-trans*-4-*n*-pentyl(cyclohexyl)phenol, 3.6 g of K₂CO₃ (26 mmol) and 200 mL acetone under argon atmosphere. After all the reagents were dissolved, the solution was heated to 60 °C and refluxed under constant stirring. In the addition funnel, a solution of 12-bromo-1-dodecanol (5.0 g, 19 mmol) and 50 mL THF was prepared. The THF solution in the addition funnel was added dropwise to the solution in the flask. A catalytic amount of 18-crown-6-ether was then added, the solution was left stirring overnight and then cooled to room temperature, the layers were separated and washed with water and CHCl₃ (3×). The combined organic layers were dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The collected liquid was evaporated and dried under vacuum to give compound 6 (4.60 g, 10.6 mmol) as a white powder. Yield = 62%.

Anal. Chemical Formula: (C₂₉H₅₀O₂)_{*n*} (430.71)_{*n*}: Calcd. C, 80.87; H, 11.70; O, 7.43; Found C 80.58, H 11.81. ¹H NMR (400 MHz, CDCl₃): δ = 0.87 (t, 3H, J = 6.8 Hz, -CH₃), 1.00–1.86 (m, 37H, Ar-O-CH₂(CH₂)₁₀CH₂-OH, -O-Ar-CH(CH₂)₄CH-, and -O-Ar-C₆H₁₀-(CH₂)₄CH₃, 1.42 (s, 1H, Ar-O-(CH₂)₁₂-OH), 2.40 (m, 1H, -O-Ar-CH(CH₂)₄CH-), 3.64 (t, 2H, J = 6.4 Hz, Ar-O-(CH₂)₁₁CH₂-OH), 3.92 (t, 2H, J = 6.4 Hz, Ar-O-(CH₂)₁₁CH₂-OH), 6.81 (d, 2H, J = 8.8 Hz, Ar-H *ortho* to

–O(CH₂)₁₂OH), 7.10 (d, 2H, *J* = 8.4 Hz, Ar–H *meta* to –O(CH₂)₁₂OH). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 25.7, 26.1, 26.6, 29.5, 32.2, 32.8, 37.3, 43.7, 63.0, 67.9, 114.1, 127.4, 139.8, 157.0.

4-(Phenylethynyl)phenol (7)

4-(Phenylethynyl)phenol (7) was synthesized as follows. The reagents 4-iodophenol (4.7 g, 21 mmol), phenyl acetylene (2.8 g, 28 mmol), PdCl₂(TPP)₂ (297 mg, 0.42 mmol), CuI (162 mg, 0.85 mmol), 25 mL Et₃N and 10 mL THF was added under argon atmosphere into a 200 mL three necked flask. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 2.7 g (13.4 mmol) of 7 as a yellowish crystal. Yield = 66%. Anal. Chemical Formula: (C₁₄H₁₀O)_n (194.23)_n: Calcd. C, 86.57; H, 5.19; O, 8.24; Found C 86.81, H 5.37. ¹H NMR (400 MHz, CDCl₃): δ = 4.90 (s, 1H, –C≡C–Ar–OH), 6.81 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to –OH), 7.33 (m, 3H, Ar–H *meta* and *para* to –C≡C–C₆H₄OH), 7.43 (d, 2H, *J* = 8.8 Hz, Ar–H *meta* to –OH), 7.50 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to –C≡C–C₆H₄OH). ¹³C NMR (100 Mhz, CDCl₃): δ = 89.8, 115.3, 115.5, 127.8, 128.1, 131.3, 133.1.

1-Iodo-4-(12-(4-(4-pentylcyclohexyl)phenoxy)dodecyloxy)benzene (8)

1-Iodo-4-(12-(4-(4-pentylcyclohexyl)phenoxy)dodecyloxy)benzene (8) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (1.83g 7.66 mmol) and compound 6 (3.00 g, 6.96 mmol) under argon gas and dissolved in THF (70

mL). In the addition funnel, a mixture of DEAD (3.03 g, 40 wt% in toluene, 7.66 mmol), 4-iodophenol (1.53 g, 6.96 mmol) and 20 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from *n*-hexane and dried under vacuum to give 2.77g (4.31 mmol) of compound **8** as a white crystal. Yield = 62%.

Anal. Chemical Formula: $(\text{C}_{35}\text{H}_{53}\text{IO}_2)_n$ (632.70) $_n$: Calcd. C, 66.44; H, 8.44; I, 20.06; O, 5.06; Found C 68.13, H 9.49. ^1H NMR (400 MHz, CDCl_3): 0.88 (t, 3H, J = 6.8 Hz, $\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 0.97–1.05 (m, 2H, $\text{Ar}-\text{CH}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}-\text{C}_5\text{H}_{11}$), 1.21–1.40 (m, 27H, $\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$, $\text{Ar}-\text{CH}(\text{CH}_2)_3\text{CH}_2\text{CH}-\text{C}_5\text{H}_{11}$, and, $\text{Ar}-\text{O}-(\text{CH}_2)_2(\text{CH}_2)_8(\text{CH}_2)_2-$), 1.71–1.78 (m, 4H, $\text{Ar}-\text{CH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}-\text{C}_5\text{H}_{11}$), 1.83–1.85 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2-$), 2.38 (m, 1H, $\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-\text{C}_5\text{H}_{11}$), 3.87–3.92 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2-$), 6.65 (d, 2H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{I}$), 6.80 (d, 2H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$), 7.09 (d, 2H, J = 8.4 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$), 7.51 (d, 2H, J = 9.2 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{I}$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 2.7, 26.1, 26.7, 29.5, 30.7, 32.2, 33.7, 34.5, 37.3, 43.7, 68.1, 82.3, 114.1, 116.8, 127.4, 128.3, 128.4, 128.5, 133.5, 138.0, 158.3.

1-(4-Pentylcyclohexyl)-4-(undec-10-ynyloxy)benzene (**9**)

1-(4-Pentylcyclohexyl)-4-(undec-10-ynyloxy)benzene (**9**) was synthesized as follows. TPP (3.21 g, 12.2 mmol), and *para-trans*-4-pentyl(cyclohexyl) phenol (2.74

g, 11.12 mmol) were added under argon gas into a 300 mL three necked flask, dissolved in THF (50 mL) and then stirred. In the addition funnel, a mixture of DEAD (5.32 g, 40 wt% in toluene, 12.2 mmol), 10-undecyn-1-ol (2.06 g, 12.2 mmol) and 20 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from *n*-hexane and dried under vacuum to give 2.92 g (7.33 mmol) of compound **9** as a white crystal. Yield = 67%.

Anal. Chemical Formula: $(\text{C}_{28}\text{H}_{44}\text{O})_n$ (396.65) $_n$: Calcd. C, 84.79; H, 11.18; O, 4.03; Found C 84.71, H 11.03. ^1H NMR (400 MHz, CDCl_3): δ = 0.89 (t, 3H, J = 7.2 Hz, $\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 1.01–1.41 (m, 24H, $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_7\text{CH}_2-$), $\text{Ar}-\text{CH}(\text{CH}_2)_3\text{CH}_2\text{CH}-$, and $\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH})_4\text{CH}_3$, 1.72–1.87 (m, 3H, $\text{Ar}-\text{CH}(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{CH}-$, and $\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-$), 1.93 (m, 4H, $\text{Ar}-\text{CH}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}-$), 2.16 (m, 1H, $\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-$), 2.19 (t, 2H, J = 4.4 Hz, $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_8\text{O}-$), 2.40 (s, 1H, $\text{HC}\equiv\text{C}-(\text{CH}_2)_9\text{O}-$), 3.92 (t, 2H, J = 6.4 Hz, $-\text{C}\equiv\text{C}-(\text{CH}_2)_8\text{CH}_2\text{O}-$), 6.81 (d, 2H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{O}(\text{CH}_2)_9-\text{C}\equiv\text{C}-$), 7.10 (d, 2H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{O}(\text{CH}_2)_9-\text{C}\equiv\text{C}-$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.0, 18.6, 25.0, 26.2, 28.6, 29.3, 33.6, 34.5, 37.3, 43.8, 67.9, 114.2, 127.4, 137.0, 157.0.

LC-PA monomer 1 (M1)

M1 was synthesized as follows. Into a 100 mL round-bottom flask were added 0.5 g (2.17 mmol) of compound **1**, 0.6 g of 4-bromo-4'-*n*-pentylbiphenyl (1.98 mmol), and degassed 3 M aqueous NaHCO₃ (20 mL) and 40 mL THF. After all the reagents were dissolved, the solution was heated to 80 °C and refluxed under constant stirring. TBA-OH (10 drops) and (TPP)₄Pd (35 mg, 0.030 mmol) were then added. The solution was left stirring overnight and then cooled to room temperature, the layers were separated and washed with water and CHCl₃ (3×). The combined organic layers were dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The collected liquid was evaporated and dried under vacuum to give **M1** (0.78 mg, 1.91 mmol) as a greenish white solid. Yield = 97%.

Anal. Chemical Formula: (C₃₁H₃₆)_n (408.62)_n; Calcd. C 91.12, H 8.88; Found C 91.31, H 8.98. ¹H NMR (400 MHz, CDCl₃): δ = 0.89–0.93 (m, 6H, –CH₃), 1.33–1.37 (m, 8H, –CH₂–), 1.50–1.66 (s, 6H, –CH₂–), 2.43 (t, *J* = 7.2 Hz, 2H, –C₆H₆–CH₂–), 2.65 (t, *J* = 6.8 Hz, 2H, –C₆H₆C≡CCH₂–), 7.28 (d, 2H, *J* = 4.4 Hz, Ar–H *ortho* to –CH₂–), 7.46 (d, 2H, *J* = 8.4 Hz, Ar–H *meta* to –CH₂–), 7.54–7.68 (m, 8H, Ar–H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.5, 22.6, 28.6, 28.7, 30.7, 31.5, 35.1, 100.5, 123.0, 126.5, 126.7, 127.0, 127.2, 128.7, 131.8, 131.9, 138.0, 140.2, 179.1.

LC-PA monomer 2 (M2)

M2 was synthesized as follows. Into a 100 mL round-bottom flask were added 0.96 g (4.1 mmol) of compound **1**, 2.01 g of compound **2** (2.5 mmol) and degassed 3 M aqueous NaHCO₃ (20 mL) and 40 mL THF. After all the reagents were dissolved, the solution was heated to 70 °C and refluxed under constant stirring. TBA-OH (10 drops) and (TPP)₄Pd (75 mg, 0.067 mmol) were then added. The solution was left stirring

overnight and then cooled to room temperature, the layers were then separated and washed with water and CHCl_3 (3 $\times$). The combined organic layers were dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give **M2** (0.85 mg, 1.4 mmol) as a colorless crystal. Yield = 35%.

Anal. Chemical Formula: $(\text{C}_{44}\text{H}_{62}\text{O})_n$ (606.48) $_n$: Calcd. C 87.07, H 10.30, O 2.64; Found C 86.77, H 9.90. ^1H NMR (600 MHz, CDCl_3): δ = 0.87–0.93 (m, 6H, $-\text{CH}_3$), 1.20–1.36 (m, 34H, $-\text{CH}_2-$), 1.45–1.50 (m, 4H, $-\text{C}\equiv\text{CCH}_2\text{CH}_2-$ and $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.81 (m, 2H, J = 25.6 Hz, $-\text{OCH}_2\text{CH}_2-$), 2.43 (t, 2H, J = 10.5 Hz, $-\text{C}\equiv\text{CCH}_2$), 4.00 (t, 2H, J = 13.1 Hz, $-\text{OCH}_2-$), 6.98 (d, 2H, J = 8.8 Hz, Ar-H *ortho* to $-\text{OCH}_2-$), 7.40–7.63 (m, 10H, Ar-H). ^{13}C NMR (600 MHz, CDCl_3): δ = 14.1, 19.5, 22.6, 22.7, 26.1, 28.6, 28.8, 29.3, 29.4, 29.6, 29.7, 31.4, 31.9, 68.1, 80.4, 91.3, 114.7, 123.0, 126.4, 126.7, 127.0, 127.8, 131.5, 132.8, 138.7, 139.7, 140.0, 158.9.

LC-PA monomer 3 (M3)

M3 was synthesized as follows. Compound **3** (0.76 g, 2.70 mmol), *para*-(*trans*-4-*n*-pentylcyclohexyl)bromobenzene (0.75 g, 2.40 mmol) and degassed 3 M aqueous NaHCO_3 (20 mL) and 40 mL THF were added into a 100 mL round bottom flask. The solution was heated to 80 °C and refluxed under constant stirring. TBA-OH (10 drops) and $(\text{TPP})_4\text{Pd}$ (42 mg, 0.036 mmol) were then added. The solution was left stirring overnight and then cooled to room temperature, the layers were then separated and washed with water and CHCl_3 (3 $\times$). The combined organic layers were dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give **M3** (1.06 g, 2.2 mmol) as a greenish white solid.

Yield = 93%.

Anal. Chemical Formula: $(C_{35}H_{50})_n$ (464.72) $_n$: Calcd. C 89.29, H 10.71; Found C 86.38, H 10.53. 1H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 6H, $-CH_3$), 1.00–1.45 (m, 25H, $Ar-CH(CH_2)_4CH-(CH_2)_4-$, $Ar-C\equiv C-CH_2CH_2(CH_2)_7-$, and $Ar-CH(CH_2)_3CH_2CH-C_5H_{11}$), 1.48–1.60 (m, 6H, $Ar-CH(CH_2)_3CH_2CH-C_5H_{11}$), 1.83–1.92 (m, 3H, $Ar-C\equiv C-CH_2CH_2-$ and $Ar-CH(CH_2)_4CH-$), 2.40 (t, 2H, J = 7.2 Hz, $Ar-C\equiv C-CH_2-$), 7.06 (d, 2H, J = 8.4 Hz, $Ar-H$ *ortho* to $-C_6H_{10}-C_5H_{11}-$), 7.37 (d, 2H, J = 8.4 Hz, $Ar-H$ *meta* to $-C_6H_{10}-C_5H_{11}-$), 7.42 (d, 2H, J = 8.8 Hz, $Ar-H$ *meta* to $-C\equiv C-C_{10}H_{21}$), 7.48 (d, 2H, J = 8.8 Hz, $Ar-H$ *ortho* to $-C\equiv C-C_{10}H_{21}$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 22.7, 26.6, 28.8, 28.9, 29.2, 29.3, 29.6, 31.9, 32.2, 33.6, 34.3, 37.4, 44.3, 80.4, 104.0, 122.6, 126.7, 127.1, 128.4, 131.7, 137.9, 140.0, 145.8.

LC-PA monomer 4 (M4)

M4 was synthesized as follows. Into a 100 mL round bottom flask, 0.50 g (2.25 mmol) of compound **4**, 0.62 g (2.00 mmol) of 4-bromo-4'-*n*-pentylbiphenyl, degassed 3 M aqueous $NaHCO_3$ (20 mL) and 40 mL THF were added under argon atmosphere. The solution was stirred, heated to 80 °C and refluxed for 30 min. TBA-OH (10 drops) and $(TPP)_4Pd$ (35 mg, 0.03 mmol) were then added. The solution was left stirring overnight and then cooled to room temperature, the layers were then washed with water and were extracted using $CHCl_3$ (3 $\times$). The combined organic layers were dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The collected liquid was evaporated and dried under vacuum to give **M4** (0.58 g, 1.40 mmol) as a yellowish white solid. Yield = 70%.

Anal. Chemical Formula: $(C_{31}H_{28})_n$ (400.55) $_n$: Calcd. C, 92.95; H, 7.05; Found C 93.17,

H 7.00. ^1H NMR (400 MHz, CDCl_3): δ = 0.91 (t, 3H, J = 7.2 Hz, $-\text{CH}_3$), 1.34–1.38 (m, 4H, $\text{Ar}-(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$), 1.51–1.69 (m, 2H, $\text{Ar}-\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.66 (t, 2H, J = 8 Hz, $\text{Ar}-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 7.23–7.36 (m, 4H, $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11}$), 7.54–7.70 (m, 13H, $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-$, and $-\text{C}\equiv\text{C}-(\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11}$). ^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 22.5, 31.1, 31.5, 56.0, 89.3, 122.0, 126.7, 127.1, 128.2, 128.8, 131.5, 131.9, 137.7, 140.3.

LC-PA monomer 5 (M5)

M5 was synthesized as follows. TPP (1.86 g, 7.10 mmol), and *para-trans*-4-*n*-pentyl(cyclohexyl) phenol (1.60 g, 6.45 mmol) were added under argon gas into a 300 mL three necked flask, dissolved in THF (60 mL) and then stirred. In the addition funnel, a mixture of DEAD (3.09 g, 40 wt% in toluene, 7.10 mmol), compound **5** (2.40 g, 7.70 mmol) and 20 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was recrystallized from *n*-hexane and dried under vacuum to give 2.36 g (4.3 mmol) of **M5** as a white crystal. Yield = 67%.

Anal. Chemical Formula: $(\text{C}_{39}\text{H}_{58}\text{O})_n$ (542.88) $_n$: Calcd. C, 86.28; H, 10.77; O, 2.95; Found C 86.41, H 10.83. ^1H NMR (400 MHz, CDCl_3): δ = 0.83–0.91 (m, 6H, J = 7.2 Hz, $-\text{CH}_3$), 1.00–1.61 (m, 28H, $-\text{C}\equiv\text{C}-\text{Ar}-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$, $\text{Ar}-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{O}-$, $\text{Ar}-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 1.71–1.87 (m, 9H,

Ar-CH(CH₂)₄CH-C₅H₁₁), 2.35–2.39 (m, 3H, -C≡C-Ar-CH₂(CH₂)₃CH₃, and Ar-CH(CH₂)₄CH-C₅H₁₁), 2.55 (t, 2H, *J* = 7.6 Hz, -Ar-C≡C-CH₂-), 3.90 (t, 2H, *J* = 6.8 Hz, Ar-O-CH₂-), 6.80 (d, 2H, *J* = 8.4 Hz, Ar-H *ortho* to -(CH₂)₉-O), 7.04–7.10 (m, 2H, Ar-H *meta* to -(CH₂)₉-O, and Ar-H *meta* to -(CH₂)₉-C≡C-), 7.28 (d, 2H, *J* = 8.4 Hz, Ar-H, *ortho* to -(CH₂)₉-C≡C-). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 22.7, 26.0, 26.6, 28.8, 29.1, 29.3, 30.9, 31.4, 32.2, 35.7, 43.7, 67.9, 80.5, 108.1, 114.1, 127.4, 128.1, 131.2, 139.7, 142.2, 157.0.

LC-PA monomer 6 (M6)

M6 was synthesized as follows. Into a 100 mL three necked flask, TPP (0.87 g, 3.3 mmol), and compound **7** (0.58 g, 3.0 mmol) were added under argon gas, dissolved in THF (15 mL) and then stirred. In the addition funnel, a mixture of DEAD (1.44 g, 40 wt% in toluene, 3.3 mmol), compound **6** (1.42 g, 3.3 mmol) and 5 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The product was recrystallized from *n*-hexane and dried under vacuum to give 1.56 g (2.6 mmol) of **M6** as a white crystal. Yield = 85%.

Anal. Chemical Formula: (C₄₃H₅₈O₂)_{*n*} (606.92)_{*n*}: Calcd. C, 85.10; H, 9.63; O, 5.27; Found C 85.25, H 9.63. ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, 3H, *J* = 7.6 Hz, -C₆H₁₀-(CH₂)₄CH₃), 0.97–1.08 (m, 2H, -C₆H₁₀-(CH₂)₃CH₂CH₃), 1.11–1.45 (m, 27H,

$-\text{C}\equiv\text{C}-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2-$, and $-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}(\text{CH}_2)_3\text{CHCH}_3-$, 1.72–1.86 (m, 8H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-\text{C}_5\text{H}_{11}-$), 2.40 (m, 1H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}-\text{C}_5\text{H}_{11}-$), 3.94 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2-\text{O}-\text{Ar}$), 6.80–6.88 (m, 4H, Ar-H *meta* to $-\text{C}\equiv\text{C}-$, and Ar-H *meta* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$), 7.10 (d, 2H, $J = 8.4$ Hz, Ar-H *ortho* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$), 7.30–7.35 (m, 3H, Ar-H *meta* and *para* to $-\text{C}\equiv\text{C}-\text{Ar}-\text{O}-\text{C}_{12}\text{H}_{24}-$), 7.44–7.52 (m, 4H, Ar-H *ortho* to $-\text{C}\equiv\text{C}-$). ^{13}C NMR (100 Mhz, CDCl_3): $\delta = 14.1, 22.7, 26.0, 26.6, 29.5, 30.4, 32.2, 33.0, 37.3, 43.7, 68.0, 87.8, 114.1, 114.4, 127.4, 128.1, 131.3, 132.9, 139.8, 157.0, 159.1$.

LC-PA monomer 7 (M7)

M7 was synthesized as follows. The reagents compound **8** (1.1 g, 1.7 mmol), and compound **9** (0.6 g, 1.7 mmol), $\text{PdCl}_2(\text{TPP})_2$ (24.4 mg, 0.35 mmol), CuI (13.2 mg, 0.70 mmol), 25 mL Et_3N and 10 mL THF was added under argon atmosphere into a 200 mL three necked flask. The solution was stirred and heated to 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from ethanol and dried in vacuo to give 0.95 g (1.0 mmol) of **M7** as a white powder. Yield = 61%.

Anal. Chemical Formula: $(\text{C}_{63}\text{H}_{96}\text{O}_3)_n$ (901.43) $_n$: Calcd. C, 83.94; H, 10.73; O, 5.32; Found C 83.88, H 10.74. ^1H NMR (400 MHz, CDCl_3): $\delta = 0.87$ – 0.91 (m, 6H, $-\text{C}_6\text{H}_{10}-(\text{CH}_2)_4\text{CH}_3$), 0.97 – 1.08 (m, 4H, $-\text{C}_6\text{H}_{10}-(\text{CH}_2)_3\text{CH}_2\text{CH}_3$), 1.20 – 1.86 (m, 64H, $-\text{O}-\text{Ar}-\text{CH}(\text{CH}_2)_4\text{CH}(\text{CH}_2)_3\text{CH}_3$, $-\text{C}\equiv\text{C}-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2-\text{O}-$, and $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_7\text{CH}_2-\text{O}-$), 2.35 – 2.43 (m, 4H, Ar- $\text{CH}(\text{CH}_2)_4\text{CH}_2-\text{C}_5\text{H}_{11}$, and

$-\text{O}-(\text{CH}_2)_8\text{CH}_2-\text{C}\equiv\text{C}-\text{Ar}-$, 3.90–3.93 (m, 6H, $-\text{C}\equiv\text{C}-\text{Ar}-\text{O}-\text{CH}_2(\text{CH}_2)_{10}\text{CH}_2-\text{O}-$, and $-\text{O}-\text{CH}_2(\text{CH}_2)_8-\text{C}\equiv\text{C}-\text{Ar}-$), 6.78–6.82 (m, 6H, Ar-H *meta* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$ and *meta* to $-\text{C}\equiv\text{C}-(\text{CH}_2)_9-\text{O}-$), 7.09–7.11 (m, 4H, Ar-H *ortho* to $-\text{C}_6\text{H}_{10}\text{C}_5\text{H}_{11}$), 7.30 (d, 2H, $J = 8.8$ Hz, *ortho* to $-\text{C}\equiv\text{C}-(\text{CH}_2)_9-\text{O}-$). ^{13}C NMR (100 Mhz, CDCl_3): $\delta = 14.1, 22.7, 26.0, 26.7, 28.9, 29.5, 32.2, 33.7, 34.6, 36.4, 37.3, 37.4, 43.7, 67.9, 80.3, 101.4, 114.1, 114.2, 127.4, 132.6, 134.2, 139.8, 157.1, 160.1$.

LC-PA1 (PA1)

PA1 was synthesized as follows. Toluene (1.5 mL), TaCl_5 (36 mg, 0.1 mmol), and $n\text{-Bu}_4\text{Sn}$ (36 mg, 0.1 mmol) was added under argon into a Schlenk flask. The catalyst mixture was stirred at 80 °C for 30 min, and then **M1** (0.42 g, 1 mmol) was dissolved in 1 mL toluene and was then added to the reaction mixture. The reaction mixture was stirred at 80 °C for 24 h. The mixture was cooled to room temperature and was added dropwise to 800 mL of methanol (MeOH) under stirring. The polymer precipitate stirred for 24 h, which was then filtered and washed again in 800 mL acetone. After 24 h, the polymer was filtered, washed with acetone and dried in a vacuum oven. A greenish white powder was obtained with a yield of 84% (0.35 g, 0.84 mmol). M_w . 190,000 M_w/M_n . 2.8 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(\text{C}_{31}\text{H}_{36})_n$ (408.62) $_n$: Calcd. C 91.12, H 8.88; Found C 87.56, H 8.53. ^1H NMR (600 MHz, CDCl_3): $\delta = 0.63\text{--}2.46$ (br, 24H, $-\text{CH}_2-$ and $-\text{CH}_3$), 6.56–7.63 (br, 12H, $-\text{Ar}-\text{H}$). ^{13}C NMR (600 MHz, CDCl_3): $\delta = 14.2, 22.7, 26.7, 29.2, 29.5, 30.0, 30.2, 31.8, 32.2, 33.7, 34.1, 34.4, 37.4, 44.3, 125.5, 126.7, 127.0, 128.2, 128.7, 129.5, 129.9, 140.0, 146.5$.

LC-PA2 (PA2)

PA2 was synthesized in a similar way as **PA1**. Polymerization of **M2** (0.61 g, 1

mmol) yielded a greenish powder with a yield of 56% (0.34 g, 0.56 mmol). M_w . 409,000 M_w/M_n . 2.4 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(C_{44}H_{62}O)_n$ (606.48) $_n$: Calcd. C 87.07, H 10.30; Found C 86.06, H 9.85. 1H NMR (600 MHz, $CDCl_3$): δ = 0.77–0.91 (br, 6H, $-CH_3$), 1.26–1.48 (br, 34H, $-CH_2-$), 1.77–1.83 (br, 4H, $-C\equiv CCH_2CH_2-$ and $-OCH_2CH_2-$), 3.90–4.02 (br, 2H, $-OCH_2-$), 6.89–7.66 (br, 12H, Ar–H). ^{13}C NMR (600 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.1, 29.4, 29.7, 30.3, 31.9, 68.1, 114.8, 125.9, 126.3, 126.7, 126.8, 127.0, 127.1, 127.3, 128.0, 132.0, 138.7, 139.1.

LC-PA3 (PA3)

PA3 was synthesized in a similar way as **PA1**. Polymerization of **M3** (0.30 g, 0.6 mmol) yielded a greenish yellow solid with a yield of 51% (0.15 g, 0.31 mmol). M_w . 267,000 M_w/M_n . 3.3 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(C_{35}H_{50})_n$ (470.77) $_n$: Calcd. C 89.29, H 10.71; Found C 83.12, H 9.95. 1H NMR (400 MHz, $CDCl_3$): δ = 0.81–3.65 (br, 42H, $-CH$, $-CH_2-$, and $-CH_3$), 6.21–7.71 (br, 8H, Ar–H). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 22.7, 26.7, 29.7, 34.3, 37.3, 44.1, 110.9, 114.8, 122.1, 126.8, 148.9, 152.4.

LC-PA4 (PA4)

PA4 was synthesized in a similar way as **PA1**. Polymerization of **M4** (0.40 g, 1 mmol) yielded a yellow solid with a yield of 33% (0.13 g, 0.33 mmol). M_w . 302,000 M_w/M_n . 3.4 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(C_{31}H_{28})_n$ (400.55) $_n$: Calcd. C 92.95, H 7.05; Found C 87.43, H 7.15. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.00 (br, 3H, $-CH_3$), 1.23–3.94 (br, 8H, $-CH_2-$), 7.22–7.79 (br, 17H, Ar–H). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 16.4, 28.0, 34.2, 43.1, 50.1, 54.4, 58.8, 80.2, 88.7, 93.8, 104.5, 146.0, 152.4, 156.6, 164.7.

LC-PA5 (PA5)

PA5 was synthesized in a similar way as **PA1**. Polymerization of **M5** (0.35 g, 0.6 mmol) yielded a white powder with a yield of 12% (42 mg, 0.07 mmol). M_w . 168,000 M_w/M_n . 2.6 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(C_{39}H_{58}O)_n$ (542.88) $_n$: Calcd. C 86.28, H 10.77, O 2.95; Found C 81.82, H 11.03. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.90 (br, 6H, $-CH_3$), 1.00–1.98 (br, 37H, $-C\equiv C-Ar-CH_2(CH_2)_3CH_3$, $Ar-C\equiv C-CH_2(CH_2)_7CH_2O-$, $Ar-C_6H_{10}-(CH_2)_4CH_3$, and $Ar-CH(CH_2)_4CH-C_5H_{11}$), 2.07–2.68 (br, 5H, $-C\equiv C-Ar-CH_2(CH_2)_3CH_3$, $Ar-CH(CH_2)_4CH-C_5H_{11}$, and $-Ar-C\equiv C-CH_2-$), 3.68–3.95 (br, 2H, $Ar-O-CH_2-$), 6.64–7.51 (br, 8H, Ar-H). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 22.7, 26.7, 31.3, 32.3, 33.7, 37.3, 43.7, 67.8, 93.3, 114.1, 127.3, 139.5, 157.1.

LC-PA6 (PA6)

PA6 was synthesized in a similar way as **PA1**. Polymerization of **M6** (0.30 g, 0.5 mmol) yielded a green solid with a yield of 45% (0.14 g, 0.23 mmol). M_w . 367,000 M_w/M_n . 1.7 (GPC, polystyrene calibration).

Anal. Chemical Formula: $(C_{43}H_{58}O_2)_n$ (606.92) $_n$: Calcd. C 85.10, H 9.63, O 5.27; Found C 85.25, H 9.63. 1H NMR (400 MHz, $CDCl_3$): δ = 0.32–0.51 (br, 3H, $-CH_3$), 0.80–2.17 (br, 37H, $-O-Ar-CH(CH_2)_4CH-C_5H_{11}-$, $-Ar-CH(CH_2)_4CH(CH_2)_3CHCH_3-$, $-C_6H_{10}-(CH_2)_3CH_2CH_3$, and $-C\equiv C-Ar-O-CH_2(CH_2)_{10}CH_2-$), 2.40 (br, 1H, $-O-Ar-CH(CH_2)_4CH-C_5H_{11}-$), 3.19–3.83 (br, 4H, $Ar-O-CH_2(CH_2)_{10}CH_2-O-Ar$), 6.91–7.71 (br, 13H, Ar-H). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 13.3, 18.3, 26.6, 42.0, 52.4, 54.9, 68.4, 83.3, 89.4, 92.7, 102.4, 110.6, 117.1, 147.0, 150.6, 152.5, 162.7, 175.5.

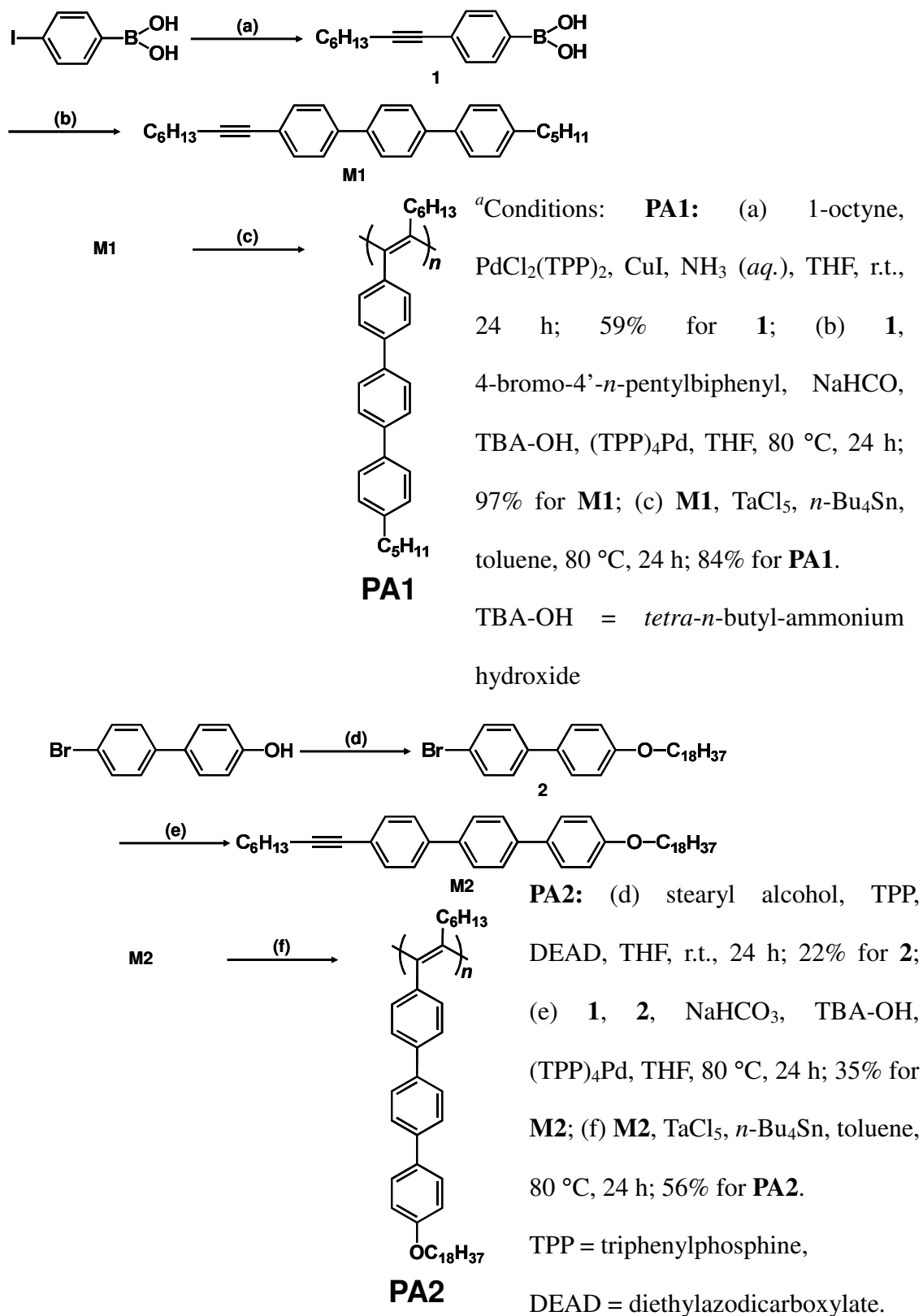
LC-PA7 (PA7)

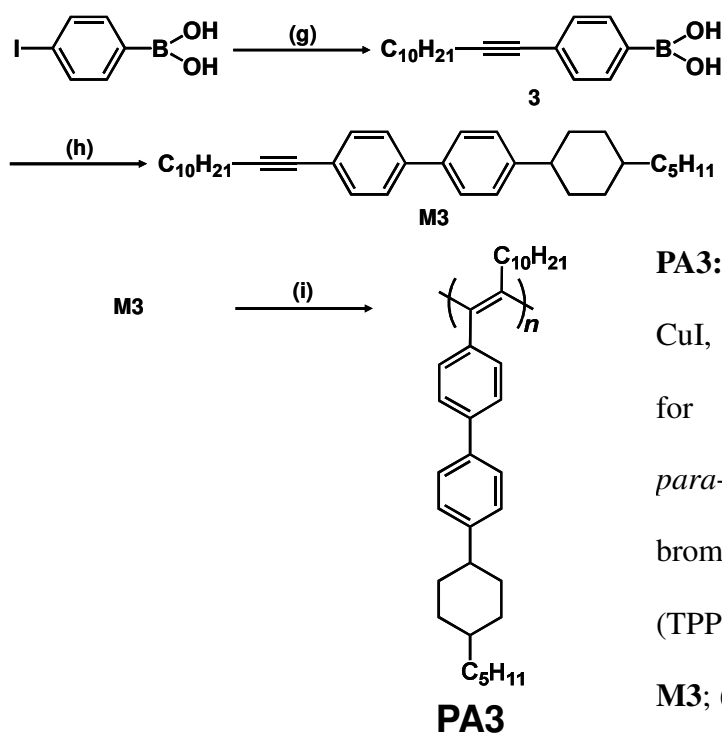
PA7 was synthesized in a similar way as **PA1**. Polymerization of **M7** (0.5 g, 0.6

mmol) yielded a yellow solid with a yield of 66% (0.33 g, 0.33 mmol). M_w . 89,000 M_w/M_n . 4.5 (GPC, polystyrene calibration).

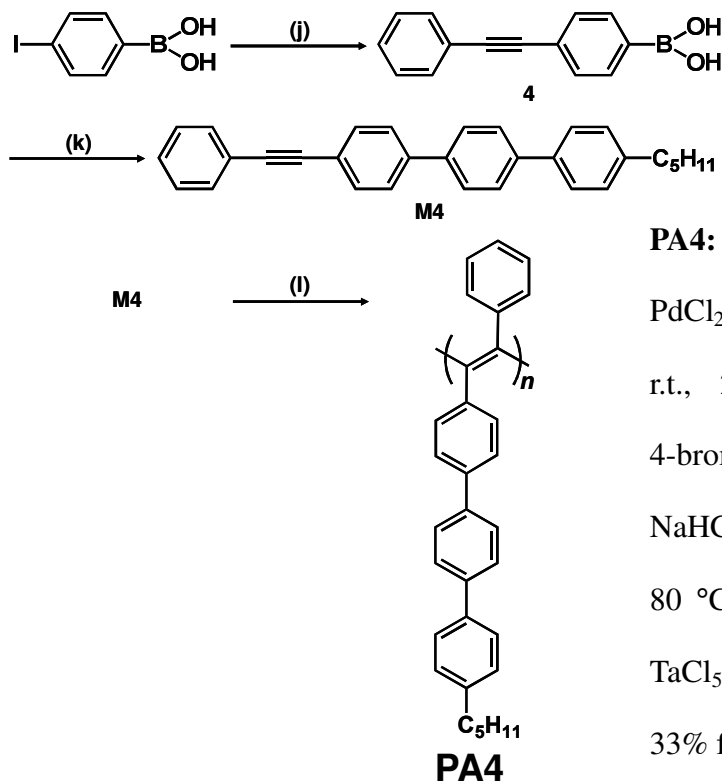
Anal. Chemical Formula: $(C_{63}H_{96}O_3)_n$ (901.43) $_n$: Calcd. C 83.94, H 10.73, O 5.32; Found C 80.94, H 10.73 1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.94 (br, 6H, $-C_6H_{10}-(CH_2)_4CH_3$), 0.96–1.09 (br, 4H, $-C_6H_{10}-(CH_2)_3CH_2CH_3$), 1.18–2.81 (br, 64H, $-O-Ar-CH(CH_2)_4CH(CH_2)_3CH_3$, $-C\equiv C-Ar-O-CH_2(CH_2)_{10}CH_2-O-$, and $-C\equiv C-CH_2(CH)_7CH_2-O-$), 2.35–2.43 (m, 4H, $Ar-CH(CH_2)_4CH_2-C_5H_{11}$, and $-O-(CH_2)_8CH_2-C\equiv C-Ar$), 3.49–3.83 (br, 6H, $-C\equiv C-Ar-O-CH_2(CH_2)_{10}CH_2-O-$, and $-O-CH_2(CH_2)_8-C\equiv C-Ar$), 6.56–6.76 (br, 6H, $Ar-H$ *meta* to $-C_6H_{10}C_5H_{11}$ and *meta* to $-C\equiv C-(CH_2)_9-O-$), 6.80–7.19 (br, 4H, $Ar-H$ *ortho* to $-C_6H_{10}C_5H_{11}$), 7.20–7.26 (br, 2H, *ortho* to $-C\equiv C-(CH_2)_9-O-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 22.7, 28.5, 30.9, 33.7, 34.6, 37.4, 43.8, 67.8, 101.5, 114.2, 127.5, 128.3, 135.8, 151.5, 157.3, 159.8.

2. Supporting Figures

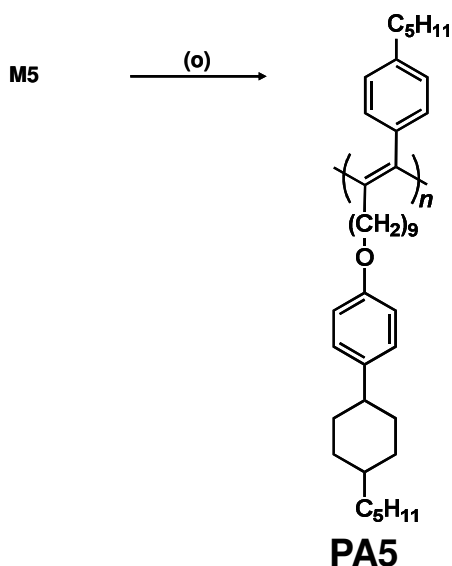
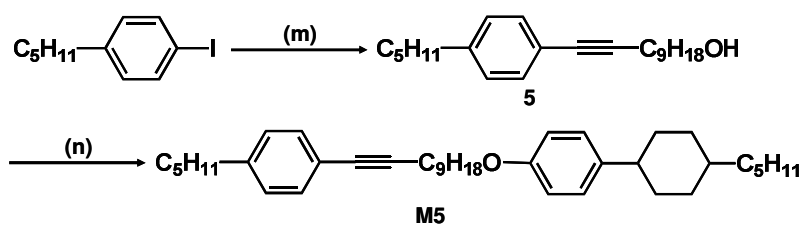
Scheme S1. Synthetic routes of polymers.^a



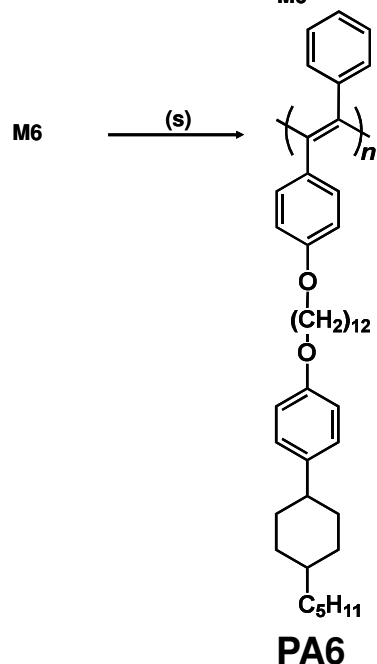
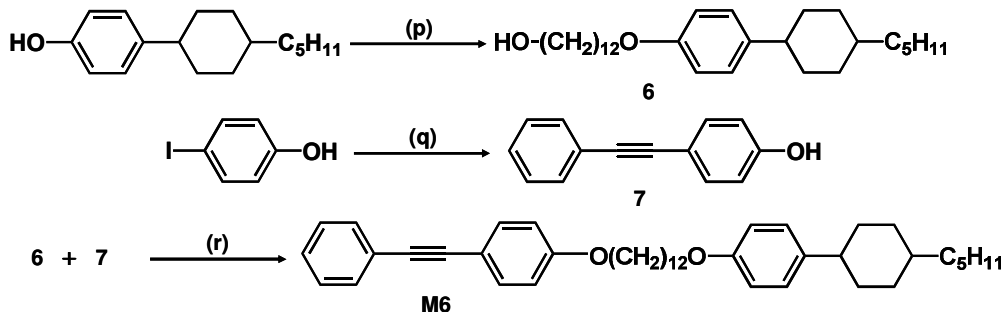
PA3: (g) 1-dodecyne, $\text{PdCl}_2(\text{TPP})_2$, CuI , NH_3 (aq.), THF, r.t., 24 h; 58% for **3**; (h) **3**, *para*-(*trans*-4-*n*-pentylcyclohexyl) bromobenzene, NaHCO_3 , TBA-OH, $(\text{TPP})_4\text{Pd}$, THF, 80 °C, 24 h; 93% for **M3**; (i) **M3**, TaCl_5 , *n*- Bu_4Sn , toluene, 80 °C, 24 h; 51% for **PA3**.



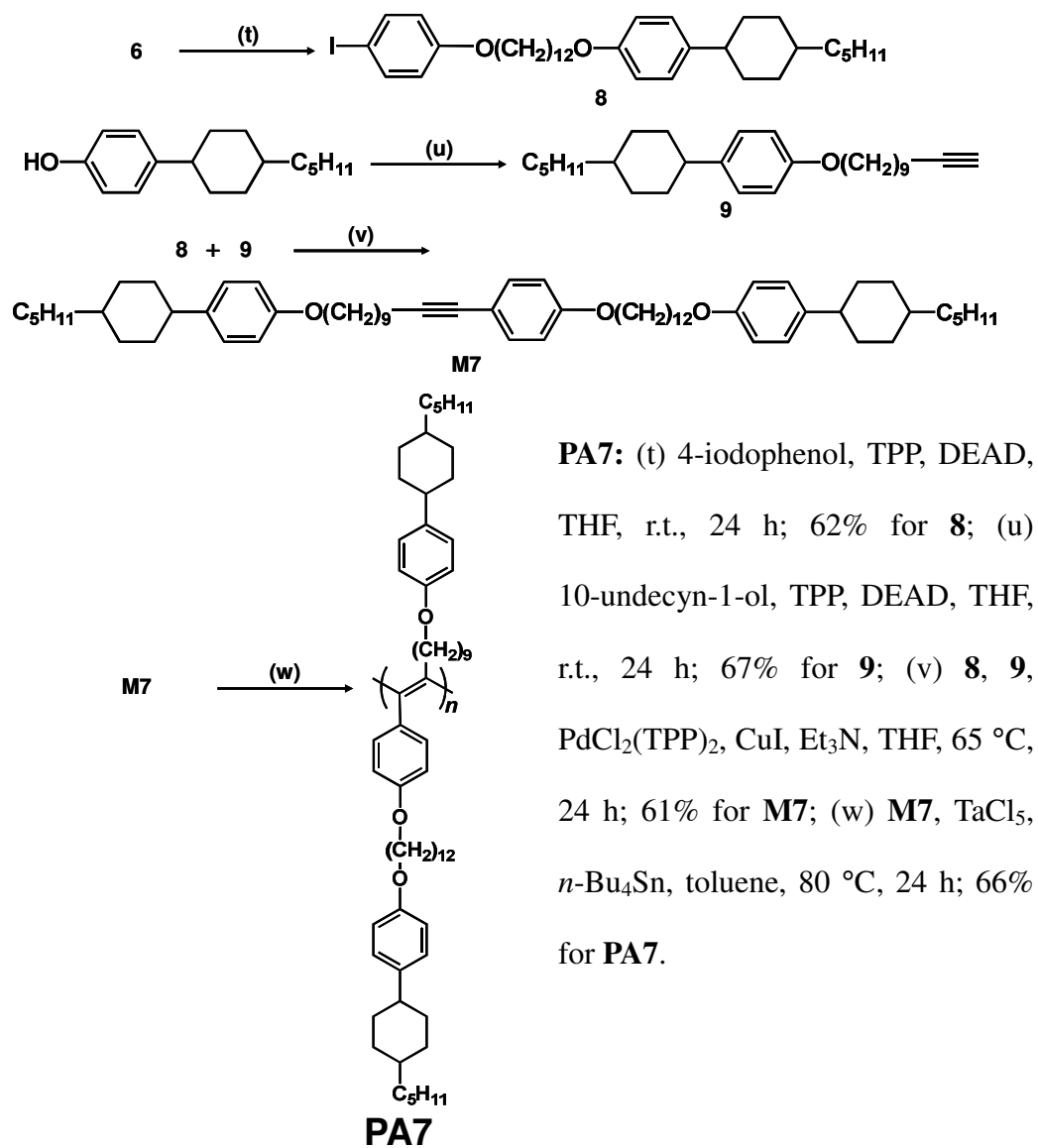
PA4: (j) phenyl acetylene, $\text{PdCl}_2(\text{TPP})_2$, CuI , NH_3 (aq.), THF, r.t., 24 h; 58% for **4**; (k) **4**, 4-bromo-4'-*n*-pentylbiphenyl, NaHCO_3 , TBA-OH, $(\text{TPP})_4\text{Pd}$, THF, 80 °C, 24 h; 70% for **M4**; (l) **M4**, TaCl_5 , *n*- Bu_4Sn , toluene, 80 °C, 24 h; 33% for **PA4**.



PA5: (m) 10-undecyn-1-ol, $\text{PdCl}_2(\text{TPP})_2$, CuI , NH_3 (aq.), THF, r.t., 24 h; 75% for **5**; (n) **5**, *para-trans*-4-*n*-pentyl(cyclohexyl) phenol, TPP, DEAD, THF, r.t., 24 h; 67% for **M5**; (o) **M5**, TaCl_5 , *n*- Bu_4Sn , toluene, 80 °C, 24 h; 12% for **PA5**.



PA6: (p) 1-bromo-1-dodecanol, K_2CO_3 , 18-crown-6-ether, THF, 60 °C, 24 h; 62% for **6**; (q) phenyl acetylene, $\text{PdCl}_2(\text{TPP})_2$, CuI , Et_3N , THF, 65 °C, 24 h; 66% for **7**; (r) **6**, **7**, TPP, DEAD, THF, r.t., 24 h; 85% for **M6**; (s) **M6**, TaCl_5 , *n*- Bu_4Sn , toluene, 80 °C, 24 h; 45% for **PA6**.



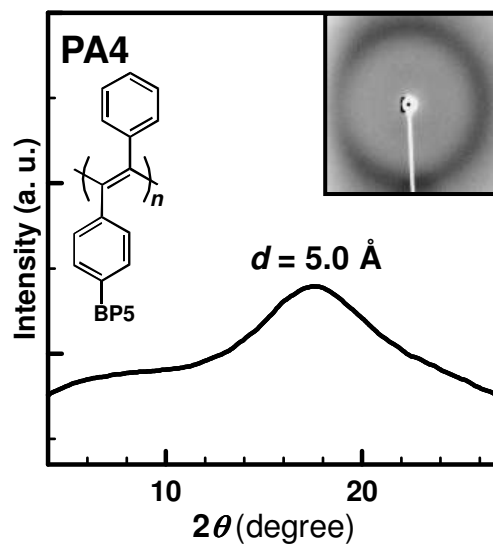


Figure S1. XRD pattern of **PA4** showing a broad reflection at $5.0 \text{ \AA}$ (17.6° in 2θ) characteristic of the Nematic LC phase, inset shows the Laue pattern of **PA4**.

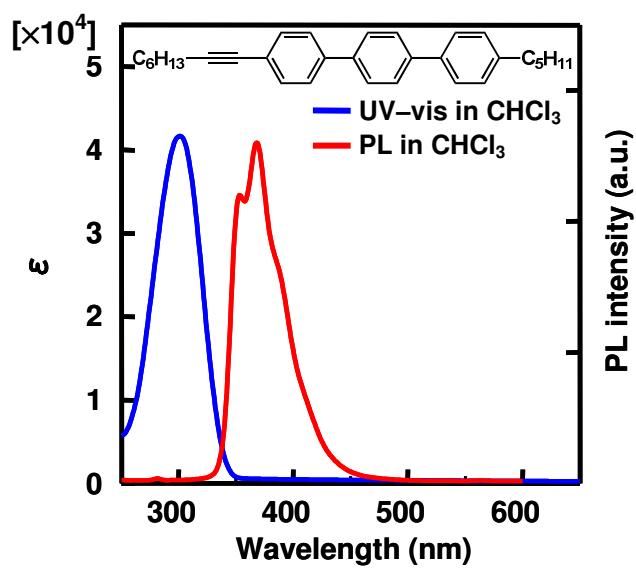


Figure S2. UV-vis (blue) and PL (red) spectra of **M1**.

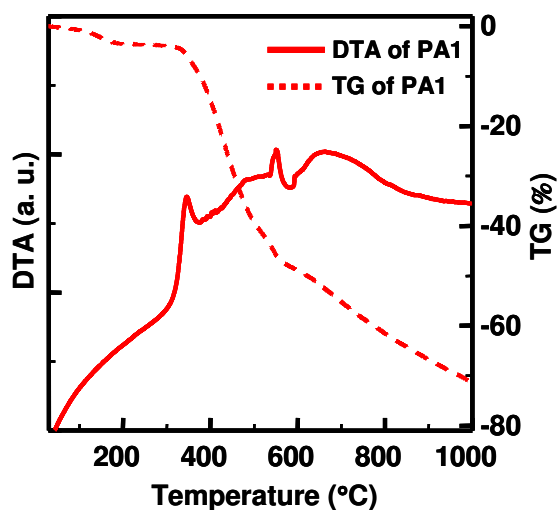


Figure S3. Thermogravimetry-differential thermal analysis (TG-DTA) curves of **PA1** measured under nitrogen gas at a heating rate of 10 °C/min. The lack of a *cis-trans* isomerization peak (DTA at 170 °C) of the polyene main chain confirms that *di*-substituted PA polymerized using TaCl₅ metathesis catalyst has a *trans-transoidal* conformation.

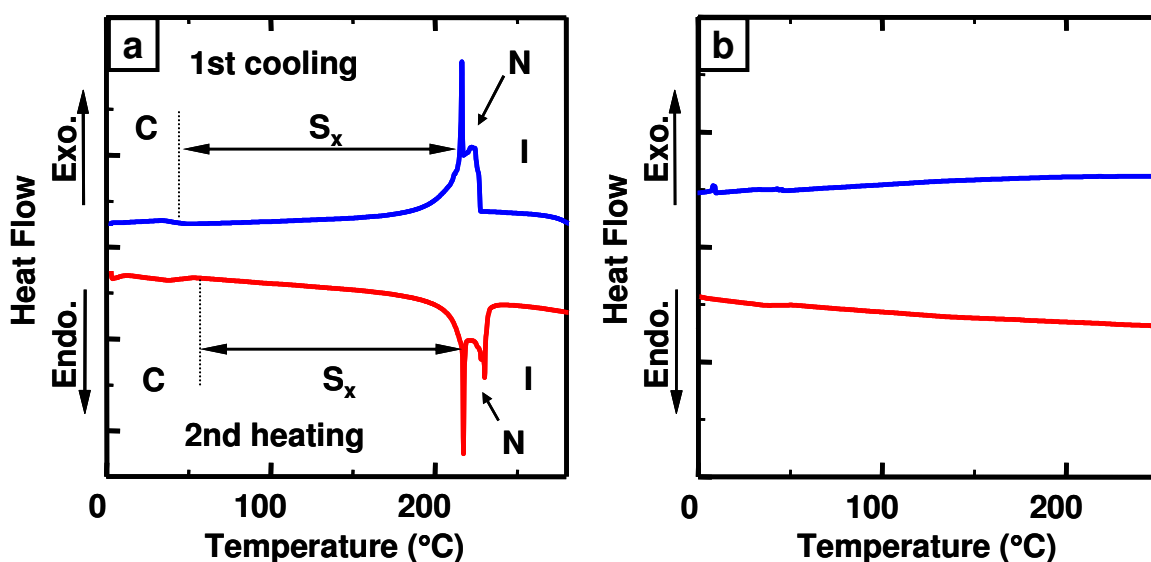


Figure S4. Differential scanning calorimetry (DSC) curves of (a) **M1**, and (b) **PA1** measured under nitrogen gas at a heating or cooling rate of 10 °C/min. C, S, N and I denote crystalline, smectic, nematic and isotropic phases, respectively.

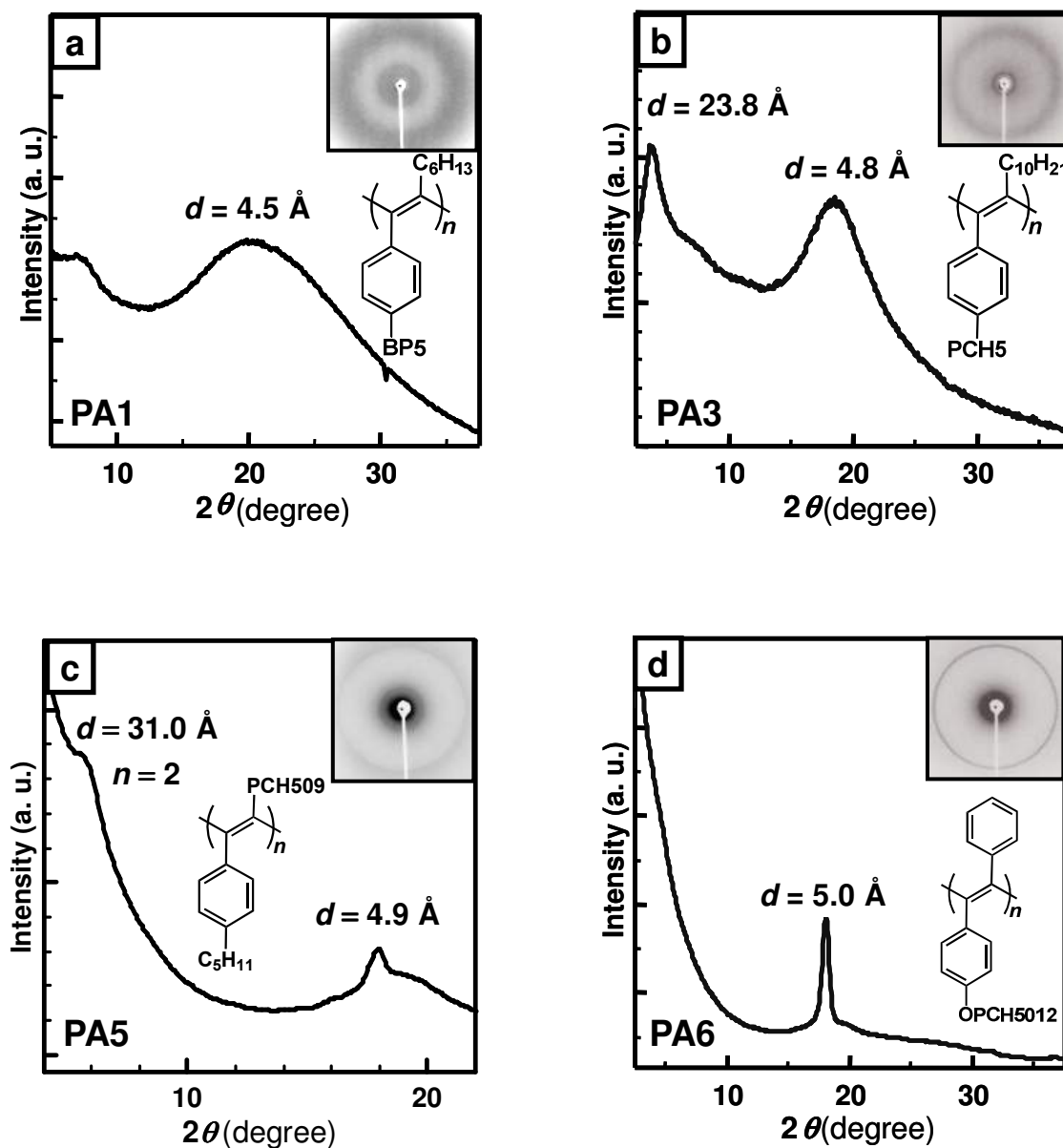


Figure S5. XRD patterns showing the (a) Nematic LC (N-LC) phase of **PA1** (19.6° in 2θ), (b) Smectic A (S_mA) LC phase of **PA3** (3.7° and 18.4° in 2θ), (c) S_mA LC phase of **PA5** (5.7° and 18.0° in 2θ), and (d) N-LC phase of **PA6** (17.8° in 2θ), insets show the Laue pattern of the polymers.

Table S1. Conditions of vapor deposition.

Metals	Degree of vacuum (Pa)	Rate (Å/s)	Thickness (nm)
LiF	1.0×10^{-5}	0.10	4
Ca	9.2×10^{-6}	0.13	5
Al	1.2×10^{-4}	1–4.5	81

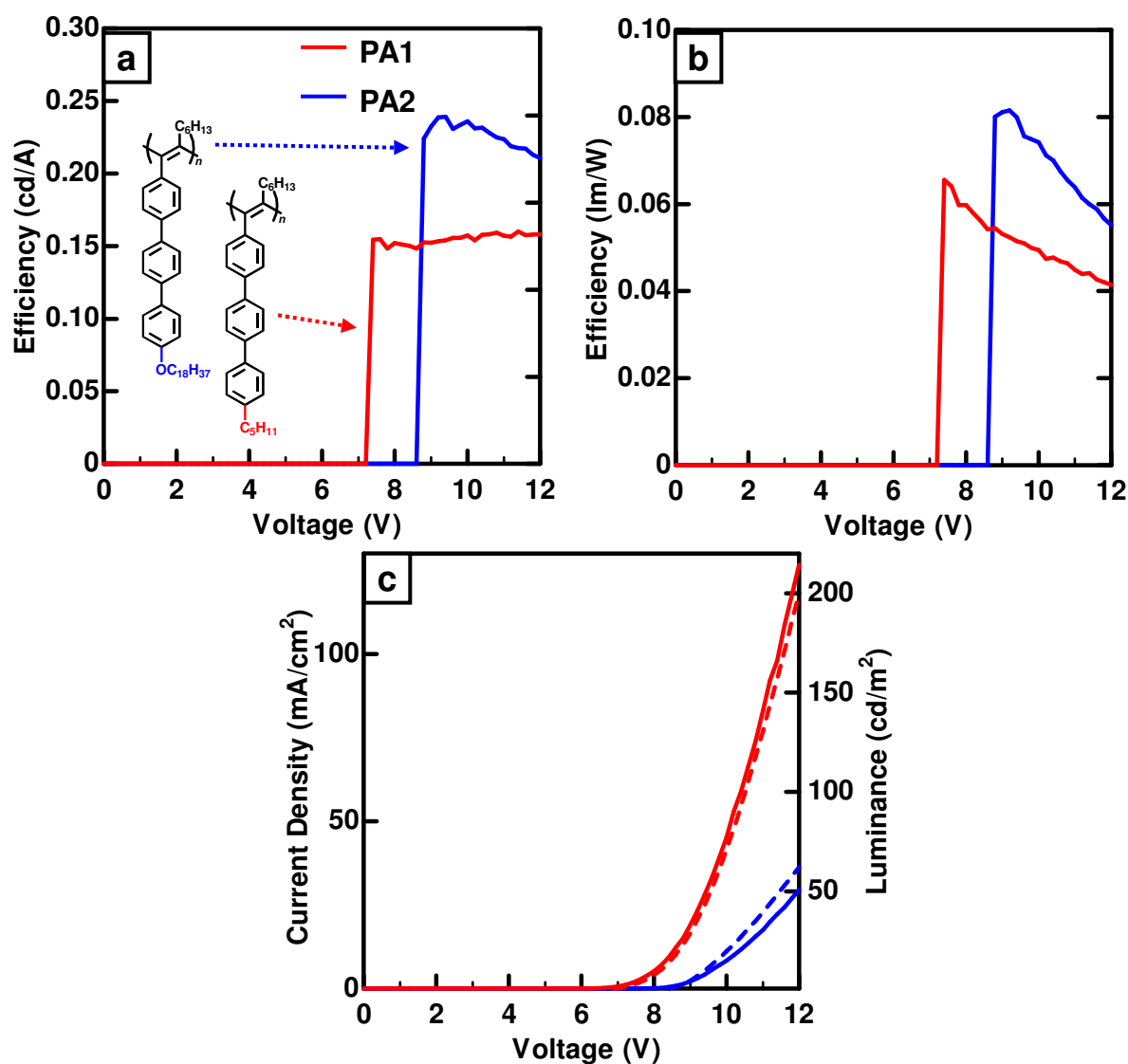


Figure S6. Device performance of the polymer EL devices: (a) Current efficiency of PA1 (red) and PA2 (blue), (b) Luminous efficiency of the polymers, and (c) Changes in the current density and luminance of the polymers with applied voltage (Current density: 20 mA/cm²).

REFERENCES

- (1) (a) Naarmann, H.; Theophilou, N. *Synth. Met.* **1987**, 22, 1–8. (b) Akagi, K.; Suezaki, M.; Shirakawa, H.; Kyotani, H.; Shimomura, M.; Tanabe, Y. *Synth. Met.* **1989**, 28, D1–D10. (c) Tsukamoto, J.; Takahashi, A.; Kawasaki, K. *Jpn. J. Appl. Phys.* **1990**, 29, 125–130.
- (2) (a) Burroughes, J. H.; Bradley, D. C. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, 347, 539–541. (b) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, 357, 477–479. (c) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. C. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, 356, 47–49. (d) Grem, G.; Lditzky, G.; Ulrich, B.; Leising, G. *Adv. Mater.* **1992**, 4, 36–37. (e) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, 365, 628–630. (f) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Edit.* **1998**, 37, 402–428. (g) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, 34, 359–369.
- (3) (a) Shacklette, L. W.; Eckhardt, H.; Chance, R. R.; Miller, G. G.; Ivory, D. M.; Baughman, R. H. *J. Chem. Phys.* **1980**, 73, 4098–4102. (b) McCullough, R. D.; Trisramnagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, 115, 4910–4911. (c) Marks, R. N.; Halls, J. J. M.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *J. Phys. Condens. Matter.* **1994**, 6, 1379–1394. (d) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C. *Nature* **1995**, 376, 498–500. (e) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, 382, 695–697. (f) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, 280, 1741–1744.
- (4) Suga, T.; Konishi, H.; Nishide H. *Chem. Commun.* **2007**, 1730–1732.
- (5) (a) Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stucky, G.

- Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585–587. (b) Yu, G.; Heeger, A. *J. Appl. Phys.* **1995**, *78*, 4510–4515. (c) Granstrom, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257–260. (d) Daubler, T. K.; Glowacki, I.; Scherf, U.; Ulanski, J.; Horhold, H. -H.; Neher, D. *J. Appl. Phys.* **1999**, *86*, 6915–6923. (e) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425–2427. (f) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533–4542.
- (6) (a) Trepka, W. J.; Sonnenfeld, R. J.; *J. Polym. Sci.* **1970**, *8*, 2721–2724. (b) Kern, R. *J. Polym. Sci.* **1969**, *7*, 621–631. (c) Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Symp.* **1980**, *67*, 43–71.
- (7) (a) Oh, S. Y.; Akagi, K.; Shirakawa, H. *Macromolecules.* **1993**, *26*, 6203–6206. (b) Ting, C.-H.; Chen, J.-T.; Hsu, C.-S. *Macromolecules.* **2002**, *35*, 1180–1189. (c) Liu, K.-P.; Yu, Z.-Q.; Liu, J.-H.; Chen, E.-Q. *Macromol. Chem. Physic.* **2009**, *210*, 707–716. (d) Koltzenburg, S.; Wolff, D.; Stelzer, F.; Springer, J.; Nuyken, O. *Macromolecules.* **1998**, *26*, 9166–9173. (e) Choi, S.K.; Gal, Y.S.; Jin, S.H.; Kim, H.K. *Chem. Rev.*, **2000**, *100*, 1645–1682. (f) Chen, Y.; Chen, L.; Zhou, W.; Zha, D.; Zhou, D.; Bai, F.; Wan, M. *Synth. Met.* **2009**, *159*, 1649–1656.
- (8) (a) Akagi, K.; Oguma, J.; Shirakawa, H. *J. Photopolym. Sci. Tech.* **1998**, *11*, 249–252. (b) Akagi, K.; Oguma, J.; Shibata, S.; Toyoshima, R.; Osaka, I.; Shirakawa, H. *Synth. Met.* **1999**, *102*, 1287–1288. (c) Oguma, J.; Kawamoto, R.; Goto, H.; Itoh, K.; Akagi, K. *Synth. Met.* **2001**, *119*, 537–538. (d) Oguma, J.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1999**, *101*, 86–87. (e) Oguma, J.; Dai, X.-M.; Akagi, K. *Mol. Cryst. Liq. Cryst.* **2001**, *365*, 331–338. (f) Suda, K.; Yoshida, J.; Nimori, S.; Akagi, K. *Synth. Met.* **2009**, *159*, 943–948.
- (9) Akagi, K. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 649–661.

- (10) Akagi, K. Liquid Crystalline Conjugated Polymers Synthesis and Properties, In *Thermotropic Liquid Crystals: Recent Advances*; Ramamoorthy, A., Ed.; Springer: Dordrecht (Netherlands), **2007**; Chapter 9, pp. 249–275.
- (11) (a) Akagi, K.; Tanaka, H.; Toyoshima, R.; Shirakawa, H. *Trans. Mater. Res. Soc. Jpn.* **1994**, *15A*, 513. (b) Toyoshima, R.; Narita, M.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1995**, *69*, 289–290. (c) Koide, N.; Iida, H. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 427–436. (d) Toyoshima, R.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1997**, *84*, 431–432. (e) Akagi, K.; Narita, M.; Toyoshima, R.; Shirakawa, H.; *Mol. Cryst. Liq. Cryst.* **1998**, *318*, 157–178. (f) Akagi, K. Liquid Crystalline and Electroresponsive Polythiophenes, In *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*; Perepichka, I. F., Perepichka, D. F., Eds.; John Wiley Sons: New York, **2009**; Chapter 12, pp. 497–515.
- (12) (a) Vicentini, F.; Barrouillet, J.; Laversanne, R.; Mauzac, M.; Bibonne, F.; Parneix, J. P. *Liq. Cryst.* **1995**, *19*, 235–240. (b) Ibison, P.; Foot, P. J. S.; Brown, W. *Synth. Met.* **1996**, *76*, 297–300.
- (13) (a) Osaka, I.; Shibata, S.; Toyoshima, R.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1999**, *102*, 1437–1438. (b) Osaka, I.; Goto, H.; Itoh, K.; Akagi, K. *Synth. Met.* **2001**, *119*, 541–542. (c) Osaka, I.; Goto, H.; Itoh, K.; Akagi, K. *Mol. Cryst. Liq. Cryst.* **2001**, *365*, 339–346.
- (14) (a) Goto, H.; Itoh, K.; Akagi, K. *Synth. Met.* **2001**, *119*, 351–352. (b) Goto, H.; Akagi, K. *Macromolecules* **2002**, *35*, 2545–2551.
- (15) (a) Shukla, A.; Mazumdar, S. *Phy. Rev. Lett.* **1999**, *19*, 3944–3947. (b) Hidayat, R.; Fujii, A.; Ozaki, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 597–598. (c) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87–90. (d)

Ghosh, H.; Shukla, A.; Mazumdar, S. *Phys. Rev. B.* **2000**, *19*, 12763–12774. (e) Vardeny, Z. V., Korovyanko, O. In *Handbook of Conducting Polymers, Conjugated Polymers*, 3rd ed.; Skotheim, T. A.; Reynolds, J. R.; Eds. CRC press: New York, **2007**; pp. 22-1–22-74.

(16) Excitons are formed during the photoexcitation of the electron to the lowest unoccupied molecular orbital (LUMO) and the vacating of a hole in the highest occupied molecular orbital (HOMO). This electron-hole pair is bound together by coulombic attraction. During the radiative recombination of excitons, the excited electron drops down to the ground state and combines with the paired hole to release a photon. Upon the formation of excitons, the radiative recombination of excitons occurs in the order of nanoseconds. During this time scale, the excitons have already been delocalized into the phenyl side chains, thus the radiative recombination occurs at the phenyl side chains.

(17) (a) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 2607. (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799–5867. (c) Yang, S.-H.; Huang, C.-H.; Chen, C.-H.; Hsu, C.-S. *Macromol. Chem. Physic.* **2009**, *210*, 37–47. (d) Peng, H.; Chen, Y.; Chen, L.; He, X.; Li, F. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5679–5692.

(18) (a) Kwak, G.; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Chem. Mater.* **2007**, *19*, 3654–3661. (b) Kwak, G.; Fukao, S.; Fujiki, M.; Sakaguchi, T.; Masuda, T. *Chem. Mater.* **2006**, *18*, 5537–5542. (c) Kwak, G.; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Macromolecules* **2008**, *41*, 2743–2746. (d) Lee, W.-E.; Kim, J.-W.; Oh, C.-J.; Sakaguchi, T.; Fujiki, M.; Kwak, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 1406–1409.

- (19) Iida, H.; Nakamura, A.; Inoue, Y.; Akagi, K. *Synth. Met.* **2003**, *135*, 91–92.
- (20) Suda, K.; Akagi, K. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3591–3610.
- (21) (a) Hayasaka, H.; Tamura, K.; Akagi, K. *Macromolecules* **2008**, *41*, 2341–2346. (b) Hayasaka, H.; Miyashita, T.; Tamura, K.; Akagi, K. *Adv. Func. Mater.* **2010**, *20*, 1243–1250.
- (22) Akagi, K. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2463–2485.
- (23) Williamson, A. W. *J. Chem. Soc.* **1852**, *4*, 229–239.
- (24) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470. (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46–49.
- (25) (a) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866–867. (b) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437–40.
- (26) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380–2382.
- (27) For LC conjugated polymers, such as *di*-LCPA, it is typical that endothermic and exothermic phase transition peaks are not clearly observed in DSC. Usually broad peaks are observed for LC conjugated polymers in DSC spectra thus POM was used to observe and determine the phase transitions of the *di*-LCPAs. Typical DSC curves of Monomer1 (**M1**) and Polymer1 (**PA1**) are shown at supporting figures section, Figure S4.
- (28) *Liquid Crystalline and Mesomorphic Polymers*; Shibaev, V. P., Lam, L., Eds.; Springer-Verlag: New York, 1994.
- (29) Chien, J. C. W. Polymerization, In *Polyacetylene: Chemistry, Physics, and Material Science*; Academic Press: London, **1984**; Chapter 2, pp. 24–83.
- (30) It is widely researched that Tantalum-catalyzed polymerizations of *di*-substituted polyacetylenes give *trans*-rich polyacetylenes having a *trans-transoid* stereoisomer.

Looking at the planar spatial structure of a double C=C bond, the strain of an individual double bond adopting *cis*-configuration is higher than that of the *trans*-double bond. This is due to the existence of a strong steric interaction between substituents located at the double bond in the *cis*-position compared to the *trans*-position. Thus the resultant *trans*- main chain structure is determined by the stronger tendency of *di*-substituted polyacetylene to minimize the strain of individual double bonds. Therefore for *di*-substituted polyacetylene the *trans-transoid* configuration is most favored to minimize the steric hindrance of the substituents located between individual double bonds. One evidence that the present polymers adopt a *trans-transoid* structure is that no peak for *cis*- to *trans*- isomerization is present in the Differential Thermal Analysis (DTA) of **PA1**, as seen in supporting figures section (Figure S3).

(31) (a) Khotimsky, V. S.; Tchirkova, M. V.; Litvinova, E. G.; Rebrov, A. I.; Bordarenko, N.G. *J. Polym. Sci. Pol. Chem.* **2003**, *41*, 2133–2155. (b) Masuda, T. *J. Polym. Sci. Pol. Chem.* **2007**, *45*, 165–180.

(32) The lengths of the **PA7** side chains were calculated using Spartan[®] modeling software. The side chain having the PCH50120P moiety, has a length (L_1) computed as 36.0 Å, while the side chain with the PCH509 moiety has a length (L_2) of 26.4 Å. The *mono*-layer type S_m phase has a relationship of $d = L$. By contrast, a *bi*-layer type S_m phase has the inter-layer distance twice that of the side chain length, $d = 2L$. Since the smectic interlayer distance (d) is comparable to the side chain (L_1), we can deduce that **PA7** exhibits a monolayer S_mB LC phase.

(33) Shibaev, V. P., Plate, N.A. In *Advances in Polymer Science.*; Gordon, M.; Plate, N. M.; Eds. Springer-Verlag: New York, **1984**; Vol. 60, 173.

(34) The smectic B phase can be further distinguished as either the hexagonal smectic B

phase (S_mB) or the crystalline smectic B phase (CrB). X-ray diffraction (XRD) can be used to distinguish between the two LC phases. Usually a sharp ring around 20° in 2θ is observed for the hexagonal S_mB phase, which is indicative of the short range interlayer distance between the smectic planes. This pattern is distinguishable from the crystalline CrB phase, in which many other peaks beyond 20° in 2θ appear due to long-range order. In the present case, the sharp ring at 19.4° was observed at the XRD pattern of **PA7** (Figure 5b) while smaller peaks at the wide angle area, characteristic of the CrB phase, are not observed. Thus with these XRD observations, **PA7** can be assigned as the hexagonal S_mB phase.

(35) *Liquid Crystals: Experimental study of physical properties and phase transitions*; Kumar, S., Ed.; Cambridge University Press: Cambridge, 2001, pp. 65–94.

(36) Cheng, Y. J.; Luh, T. Y. *Chem. Eur. J.* **2004**, *10*, 5361–5368

Chapter 3

**Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers
Based on *Di*-Substituted Polyacetylene Derivatives that Exhibit High Dissymmetry
Factors in Circularly Polarized Luminescence**

ABSTRACT:

We synthesized *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) derivatives bearing 4-nonyloxy phenyl groups with lyotropic and thermotropic LC behavior. The poly(diphenylacetylene) (PDPA) main chain structure of the *di*-LCPAs and the chirality induced with either chiral moieties or chiral dopants allow the formation of a highly ordered lyotropic N*-LC phase. Circular dichroism (CD) spectra of the *di*-LCPAs imply that one-handed intrachain helical structures are formed in solution, while interchain helical π -stacking between the polymer main chains are formed in cast film and in the N*-LC state. Absorption dissymmetry factors (g_{abs}) in the N*-LC state show values on the order of 10^{-1} . The N*-LC state facilitates the formation of helically π -stacked structures with a high degree of helical ordering of the *di*-LCPA and is indispensable for the generation of circularly polarized luminescence (CPL) with high emission dissymmetry factors (g_{em}) on the order of 10^{-1} . To the best of our knowledge, this is the highest reported value of CPL achieved for aliphatic, conjugated polymers. As an alternative to the thermotropic N*-LC phase, we have found that the lyotropic N*-LC phase of *di*-LCPA could be promising materials possessing CPL functionality

for use in next-generation π -conjugated organic optoelectronic devices, displays, and sensors.

1. Introduction

Circularly polarized luminescence (CPL) of organic and polymeric materials has attracted considerable interest in photonic devices, such as light emitting diodes, optical amplifiers, and optical information storage.^{1,2} CPL can also be used to illuminate liquid crystal displays (LCDs). As a specific example, LCDs using a CPL backlight have been shown to exhibit several advantages, including steeper transmission-voltage characteristics and higher brightness, compared with LCDs using linearly polarized luminescence (LPL) illumination.¹ Hence, considerable effort has been devoted to the generation of CPL emission using various materials and methods.

CPL from conjugated polymer systems was first reported using polythiophene (PT) having a chiral side chain with emission dissymmetry factors (g_{em}) values of up to 5.0×10^{-3} .³ Subsequently, circularly polarized electroluminescence (CPEL)² was reported using an EL cell with poly(*para*-phenylenevinylene) (PPV) bearing a chiral side chain as an emissive layer. The CPEL device has reported values of g_{em} up to -1.7×10^{-3} . In chiral substituted conjugated polymers, the chiroptical properties are assumed to evolve mainly from interchain interactions within chiral aggregates. There has been a CPEL device described that is constructed with a thermotropic liquid crystalline polyfluorene (PF) bearing chiral side chains with g_{em} values of up to -2.5×10^{-1} .⁴ The combination of well-defined chiral packing of the liquid crystalline PF as well as chiral interchain interactions is the key for the increase in g_{em} values of the PF-based CPEL device. Subsequently, CPL in other aromatic conjugated polymers has also been

reported.^{5,6}

Meanwhile, research concerning the generation of CPL from chiral nematic liquid crystal (N*-LC) materials has been pursued. Liquid crystals (LCs) are anisotropic fluids of supramolecular assemblies that exist as an intermediate phase between isotropic fluid and solid crystal phases. LCs can be classified as either thermotropic or lyotropic.⁷ N*-LC materials exhibit optical activity, circular dichroism (CD), and even selective reflection at specific wavelengths of circularly polarized light of a certain handedness.⁸

The first approach to produce CPL with high g_{em} involved using a fluorescent dye embedded in a N*-LC host.⁹ Recently, this research was expanded to include CPL generated within the selective reflection band of the N*-LC¹⁰ and wavelength-tunable CPL.⁸ Furthermore, N*-LCs are used as platforms for the generation of low-threshold lasing,^{11,12} and CPL lasers.¹² These developments demonstrate that the supramolecular helical ordering of the N*-LC phase can be utilized to generate CPL with high g_{em} values.

One-handed helical conjugated polymers can be excellent N*-LC materials for the generation of CPL, due to their fluorescence and their ability to exhibit LC functionalities. Many approaches to synthesize helical conjugated polymers have been proposed. Helical polyacetylene (H-PA) films, having helical chains and fibrils, have been synthesized through the polymerization of acetylene in an asymmetric reaction field constructed with N*-LC and Ziegler-Natta catalyst.¹³ The introduction of chiral moieties as side chains is widely used to induce helicity to the main chain of conjugated polymers.^{4,5} It was also shown that when chiral dopants are added to the N-LC phase of poly-*para*-phenylene (PPP) with LC side chains, the resulting film exhibits

chiroptical activity.¹⁴

Thermotropic N*-LC systems in conjugated polymers have been widely used for generating CPL.^{4,5a,5b,5e,5f,14} On the other hand, it would be appealing to investigate lyotropic N*-LC systems as alternative circularly polarized optical materials for use in optoelectronic devices and displays. The effects of the solvent, solution concentration, and chiral dopant employed on the lyotropic N*-LC system would be of particular interest especially in relation to the helical structure of the LC phase and its chiroptical properties.

Various helical polymers with lyotropic LC behavior such as polyisocyanate,^{15a} cellulose derivatives,^{15b} deoxyribonucleic acid (DNA),^{15c,d,e} and tobacco mosaic virus (TMV)^{15f,g} have been extensively studied. The substitution of two bulky side chains directly into the main chain of polyacetylene leads to *di*-substituted polyacetylene (*di*-PA) exhibiting fluorescence.^{16,18} It was reported that fluorescent *di*-PA adopting a poly(diphenylacetylene) (PDPA) structure with alkyl side chains exhibits lyotropic LC behavior.^{17,18} The PDPA structure, with phenyl moieties directly attached to the main chain, has a stiff main chain that acts as a LC mesogen, which will self-assemble into a lyotropic LC phase above a critical concentration.

Investigations on the lyotropic LC behavior of PDPAs have been published; however, there are only a small number of reports of PDPAs exhibiting the lyotropic N*-LC phase.^{17c} Therefore, examining the lyotropic N*-LC of *di*-PA is worthwhile because it has been shown that N*-LC materials demonstrate supramolecular helical ordering that leads to CPL with high g_{em} and that lyotropic liquid crystallinity has excellent potential for use in CPL devices. For these reasons, we aim to synthesize *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) having a lyotropic N*-LC

phase to generate CPL with high g_{em} .

In this research, various *di*-LCPA derivatives having either a poly(alkylphenylacetylene) (PAPA) structure or a PDPA main chain structure were synthesized. Chirality in *di*-LCPA was induced by means of substitution of chiral moieties to the side chains or with the use of chiral dopants. The structural effects on the functionalities of the *di*-LCPA derivatives were examined. We focused on the thermotropic and lyotropic LC of the *di*-LCPAs, as well as their photoluminescent (PL), chiroptical, and CPL properties.

In this study, we demonstrate that chiral *di*-LCPA derivatives form a lyotropic N*-LC film, and they exhibit CPL having a high g_{em} value. To the best of our knowledge, the g_{em} values on the order of 10^{-1} are the highest values of CPL achieved in the aliphatic conjugated polymers. In this work, we have found that the highly ordered lyotropic N*-LC phase is essential for the generation of CPL with high g_{em} values.

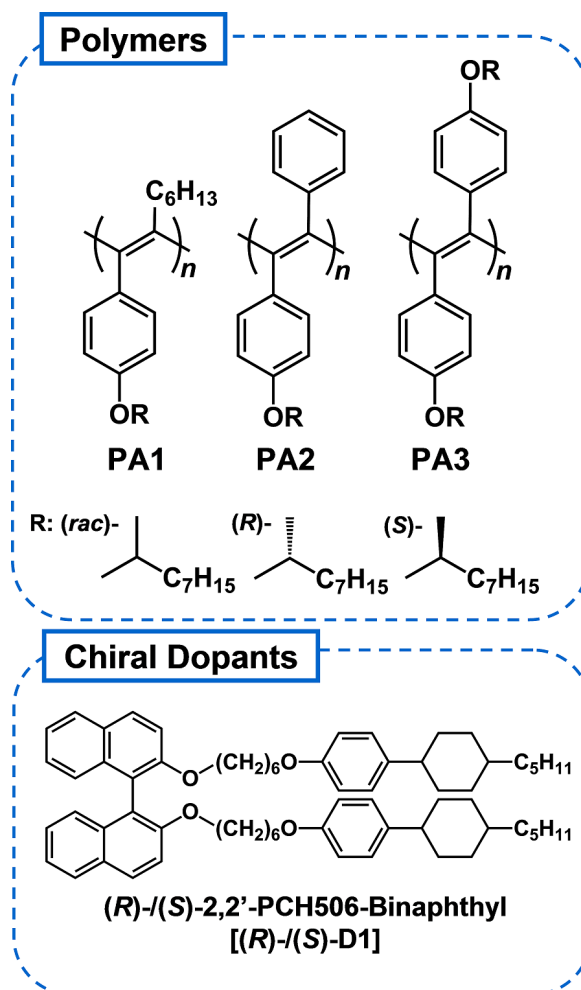
2. Results and Discussion

2.1. Synthesis and Characterization of Polymers

Various *di*-substituted LCPA derivatives and chiral dopants were synthesized (Scheme 1). The three *di*-LCPA derivatives have a 4-nonyloxy phenyl groups with either racemic (*rac*)-, (*R*)-, or (*S*)- handedness. **PA1** has a poly(alkylphenylacetylene) (PAPA) structure, while **PA2** and **PA3** have a poly(diphenylacetylene) (PDPA) structure that is responsible for both green fluorescence and lyotropic liquid crystallinity. Axially chiral dopants were synthesized as described in a previous report.¹³ (*R*)-/(*S*)-2,2'-PCH506-Binaphthyl, abbreviated as (*R*)-/(*S*)-**D1**, have phenylcyclohexyl

(PCH) LC moieties that are substituted at the 2,2' position of the binaphthyl rings. The substituted PCH LC moieties of **(R)-/(S)-D1** improve the miscibility between the polymer and the chiral dopant and also give rise to the chiral induction between them.

Scheme 1. Structures of the *di*-substituted LCPA derivatives and chiral dopants.



The synthesis routes of the monomers, and polymers are given in Scheme S1 at the supporting figures section. The monomers of the *di*-LCPA derivatives and the chiral dopants were synthesized using chemical reactions, such as Sonogashira-Hagihara coupling,^{19a,b} Mitsunobu reaction,^{19c} and Williamson etherification reaction.^{19d} The monomers were polymerized via a metathesis reaction using tungsten hexachloride (WCl_6) as a catalyst with *tetra*-phenyltin (Ph_4Sn) as a *co*-catalyst. The polymerization

reaction was conducted at 80 °C under an argon atmosphere using toluene as a solvent. The polymerization proceeded for 24 h followed by washing of the polymer in methanol (MeOH) under constant stirring for 24 h. The precipitated polymers were subsequently dried under a vacuum.

The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were measured using gel permeation chromatography (GPC) and calibrated using a polystyrene (PS) standard. The GPC results showed that the polymers have M_n values ranging from 12,700 to 48,300 and M_w/M_n values ranging from 1.7 to 2.8 (Table 1).

Table 1. Weight-average (M_w), number-average (M_n) molecular weights, dispersion degree (M_w/M_n), and degree of polymerization (D.P.) of the *di*-substituted LCPAs.

	M_w	M_n	M_w / M_n	D.P. ^a
(rac)-PA1	100,000	48,300	2.1	151
(R)-PA1	46,400	26,700	1.7	83
(S)-PA1	73,500	44,400	1.7	139
(rac)-PA2	53,000	22,000	2.4	70
(R)-PA2	53,000	23,000	2.1	72
(S)-PA2	56,000	25,000	2.3	77
(rac)-PA3	27,100	13,400	2.0	29
(R)-PA3	21,000	12,700	2.8	16
(S)-PA3	33,000	14,000	2.3	30

^a Degree of Polymerization

2.2. Liquid Crystallinity

The *di*-LCPAs exhibited lyotropic and thermotropic liquid crystallinity. **PA1** exhibited thermotropic LC behavior having a Smectic A (S_A) LC phase (see supporting figures section, Figure S1), while **PA2** and **PA3** showed main chain type lyotropic LC behavior. In the case of the **PA1**, the alternating phenyl moieties attached at the polymer main chain act as LC mesogens, and **PA1** shows side chain type liquid crystallinity arranged in a layered S_A phase. Even with the presence of chiral moieties in the side chain of (*R*)-/(*S*)-**PA1**, the side chain type liquid crystalline behavior of **PA1** aligns the main chain into a layered S_A LC phase.

Previously, we observed main chain type lyotropic LC behavior in *di*-LCPAs having a PDPA structure, which showed a lyotropic nematic LC (N-LC) phase.¹⁸ The main chains of **PA2** and **PA3** have a stiff polymer structure because their side chains are composed of phenyl moieties directly attached to the main chain forming a stilbene fragment enforced by π -conjugation. A polymer exhibiting this elevated level of stiffness should be infusible upon the heating, resulting in an LC with no thermotropic behavior. Instead, by virtue of the nonyloxy group substituted at the phenyl moiety, **PA2** and **PA3** are soluble in organic solvents, such as a toluene, and show lyotropic LC behavior. Note that **PA1** is also soluble in organic solvents, but it shows no lyotropic LC. This finding is probably due to its higher solubility, which might depress the formation of spontaneously aligned self-assemblies that is a prerequisite to the formation of domains of lyotropic LC. In other words, polymers with high solubility are freely dissolved in a solvent with randomly oriented conformation and form neither a regularly stacked nor an associated structure. This situation is far from what is necessary for the formation of the lyotropic LC. In the case of the PDPA structure of

PA2 and **PA3**, the stilbene fragment might be suitable for the formation of an interchain π -electron overlapped association through van der Waals interactions, which enables the polymers to exhibit the lyotropic LC.

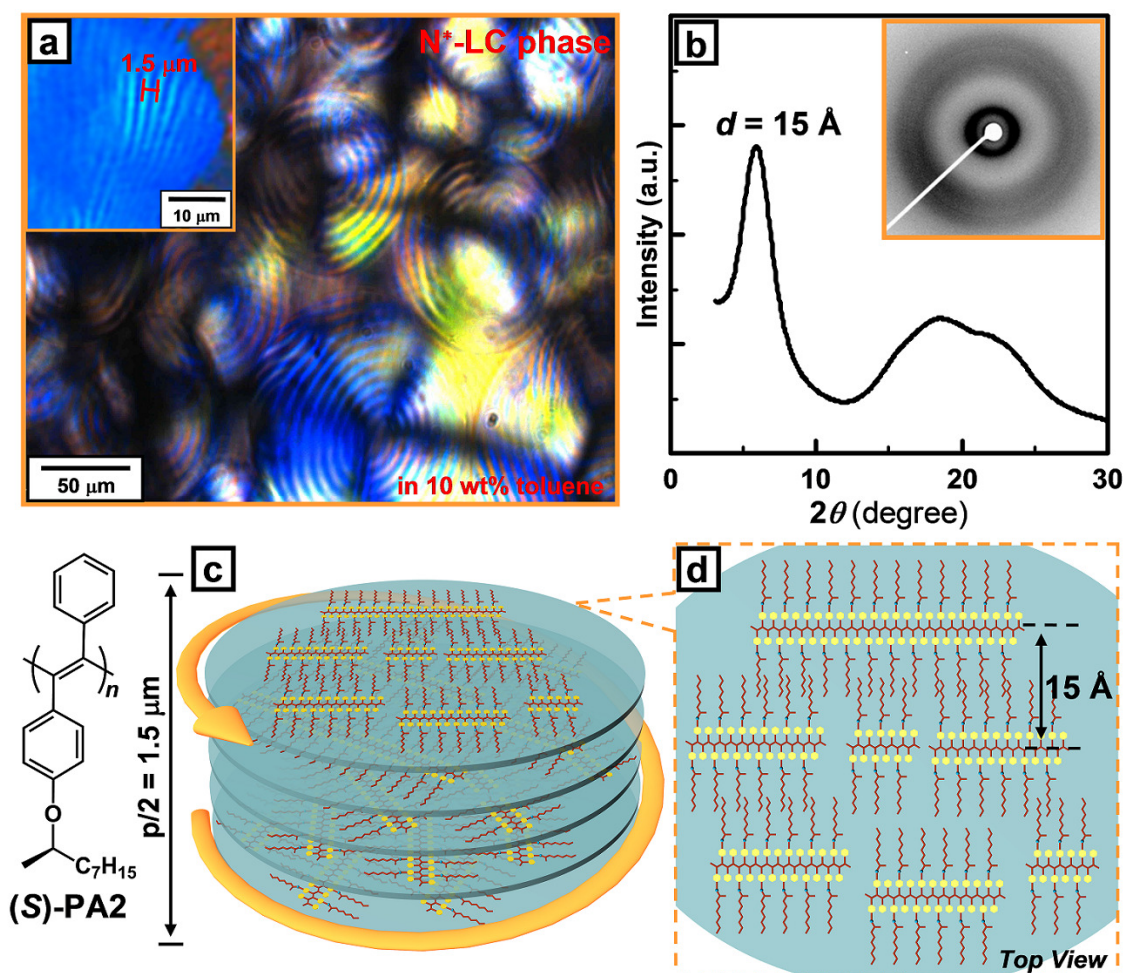


Figure 1. (a) POM image of the N*-LC phase of (S)-PA2 in 10 wt% lyotropic LC solution in toluene showing a double-spiraled texture. Inset shows a fingerprint texture with a half helical pitch of 1.5 μm. (b) The XRD pattern of (S)-PA2 shows a reflection at 15.0 Å (5.9° in 2θ) describing the polymer interchain distance within a N*-LC domain. Inset shows the Laue pattern of (S)-PA2. (c) Schematic representation of the N*-LC phase of (S)-PA2. (d) Top view of a N*-LC domain describing the polymer interchain distance.

In the lyotropic LC phase of **(S)-PA2**, the polymer main chains act as LC mesogens, which spontaneously align to form a helically twisted structure in a N*-LC phase. Polarizing optical microscopy (POM) analysis reveals a lyotropic N*-LC phase prepared from 10 wt% solution using toluene as solvent (Figure 1a). Figure 1a shows a double-spiraled texture characteristic of the N*-LC phase.²⁰ The inset of Figure 1a shows a fingerprint texture with a distance of 1.5 μm between striae, which corresponds to the half helical pitch of the N*-LC phase. We performed X-ray diffraction (XRD) on the N*-LC film of **(S)-PA2**. The XRD profile of the **(S)-PA2** N*-LC film (Figure 1b) shows a peak corresponding to a distance of 15.0 Å, which is assigned as the polymer interchain distance within a N*-LC domain (Figure 1d).²¹ The XRD pattern also shows a broad scattering signal in the wide angle range from 15 to 25° (4 to 6 Å) due to the distance between sidechains and/or π -stacking of phenyl rings in the side chain, similar to previous reports of PDPA showing lyotropic LC.^{17a,b} Figure 1c shows a schematic representation of the N*-LC phase of **(S)-PA2**.

In Figure 2, the chiral induction of **(rac)-PA2** forming a N*-LC phase is illustrated. The POM image of **(rac)-PA2** shows a Schlieren texture characteristic of lyotropic N-LC phase²⁰ prepared from 10 wt% toluene solution (Figure 2a). Upon addition of chiral dopant **(S)-D1** at 10 wt%, the N-LC phase of **(rac)-PA2** changes into a N*-LC phase (Figure 2b). The POM image of **(S)-D1/(rac)-PA2** reveals a fingerprint texture with a half helical pitch of 2.0 μm .²² XRD analysis on the N-LC film of **(rac)-PA2** and N*-LC film of **(S)-D1/(rac)-PA2** (Figure S2) showed XRD profiles similar to **(S)-PA2** (Figure 1b).²¹

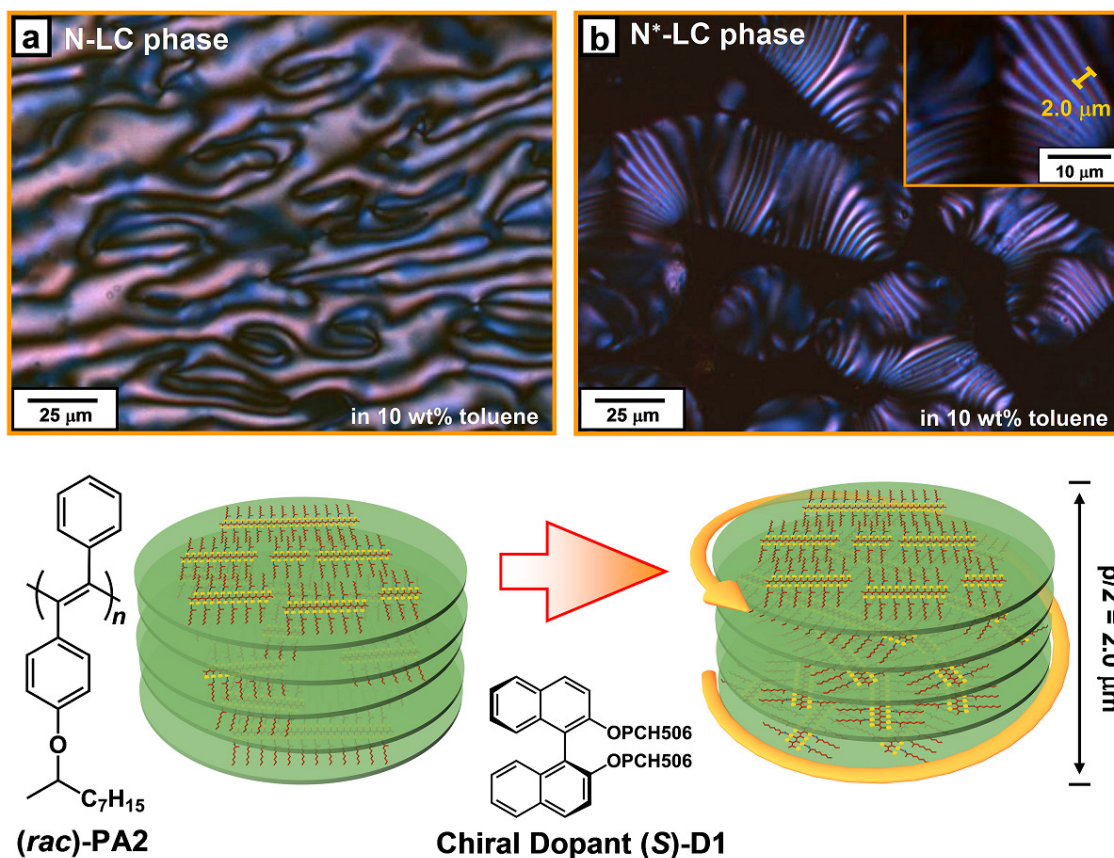


Figure 2. Schematic model of the chiral induction of **(rac)-PA2** into a N*-LC phase.

Upon the addition of the chiral dopant **(S)-D1** at 10 wt% into the N-LC phase of **(rac)-PA2** (left), a N*-LC phase is induced (right). (a) POM image of the N-LC phase of **(rac)-PA2** 10 wt% lyotropic LC solution in toluene showing a Schlieren texture. (b) POM image of the N*-LC phase of **(S)-D1/(rac)-PA2** in 10 wt% lyotropic LC solution in toluene showing a fingerprint texture. Inset shows the half helical pitch of 2.0 μm .

Table 2 summarizes the LC phases of the *di*-LCPAs. **PA1**, having a PAPA structure, exhibited a thermotropic S_A phase. **PA2** and **PA3** demonstrate lyotropic liquid crystallinity at a critical concentration range from 5–10 wt % in toluene. Analogous to thermotropic LCs which show an isotropic phase above a critical temperature, lyotropic

LCs become isotropic liquids below 5 wt % concentration in toluene, where the polymer main chains (which act as LC mesogens) are dispersed randomly without any ordering. At the lyotropic LC concentration range, there are weak π -interactions between the aromatic stilbene structure and toluene. In such a situation, the toluene enhances the attraction between polymer main chains for spontaneous self-assembly to occur and also provide enough fluidity in the system for liquid crystallinity to take place.

(*rac*)-PA2 and (*rac*)-PA3 displayed a lyotropic N-LC phase, while (*R*)-/(*S*)-PA2 (Figure 1a) and (*R*)-/(*S*)-PA3 (Figure S3a) exhibited a lyotropic N*-LC phase. D1-doped (*rac*)-PA2 (Figure 2b) and D1-doped (*rac*)-PA3 (Figure S3b) also exhibited a N*-LC phase through chiral induction. Thus, by introducing chirality to *di*-LCPA, either with a chiral moiety on the side chain or with the addition of a chiral dopant, a lyotropic N*-LC phase was formed in *di*-LCPA, as long as the PDPA structure is adopted in the polymer main chain.

Table 2. Thermotropic and lyotropic liquid crystallinity of the *di*-substituted LCPAs.

Polymers		LC phase	
(<i>rac</i>)-PA1	Thermotropic	G 95 S_A over G 65 S_A 300	
(<i>R</i>)-/(<i>S</i>)-PA1	Thermotropic		
(<i>rac</i>)-PA2	Lyotropic	N	(5–10wt % in toluene)
(<i>R</i>)-/(<i>S</i>)-PA2	Lyotropic	N*	(5–10wt % in toluene)
(<i>rac</i>)-PA3	Lyotropic	N	(5–10wt % in toluene)
(<i>R</i>)-/(<i>S</i>)-PA3	Lyotropic	N*	(5–10wt % in toluene)
(<i>R</i>)-/(<i>S</i>)-D1 (<i>rac</i>)-PA2	Lyotropic	N*	(5–10wt % in toluene)
(<i>R</i>)-/(<i>S</i>)-D1 (<i>rac</i>)-PA3	Lyotropic	N*	(5–10wt % in toluene)

Heating process
 Cooling process

G: Glassy state, N: Nematic, N*: Chiral Nematic, S_A: Smectic A

2.3. Absorption and Photoluminescence

In the case of polymer solutions in a good solvent such as chloroform (CHCl_3), the high solubility of the polymer main chains in the solvent depresses the spontaneous self-assembly required for liquid crystallinity to occur. To investigate the optical properties of the *di*-LCPAs in an isotropic state, we prepared the *di*-LCPA solutions using CHCl_3 in a concentration of 1.2×10^{-4} M. We examined the UV-vis, PL, absolute fluorescence quantum yield (Φ), and specific rotation ($[\alpha]_D$) of the *di*-LCPAs in isotropic solution (CHCl_3) and as cast films (Table 3).

Table 3. Spectroscopic data for absorption (λ_{max}), fluorescence ($E_{\text{m,max}}$), excitation ($E_{\text{x,max}}$), quantum yield (Φ), and specific rotation ($[\alpha]_D$) of the *di*-substituted LCPAs

	λ_{max} (nm)		$E_{\text{m,max}}$ (nm)		$E_{\text{x,max}}$ (nm)		Φ (%) ^a		$[\alpha]_D$ ^b
	In CHCl_3	film	In CHCl_3	film	In CHCl_3	film	In CHCl_3	film	
(rac)-PA1	340	340	454	444	337	340	26	12	–
(R)-PA1	338	338	452	444	338	338	21	10	– 241°
(S)-PA1	344	341	452	445	336	341	22	11	+ 247°
(rac)-PA2	430	428	501	502	361	374	29	11	–
(R)-PA2	430	430	502	500	376	378	24	14	+ 229°
(S)-PA2	432	428	501	501	365	374	28	13	– 226°
(rac)-PA3	438	438	501	494	372	365	34	13	–
(R)-PA3	440	444	501	493	372	365	29	12	+ 2080°
(S)-PA3	436	438	498	493	372	365	33	13	– 2158°

^aAbsolute quantum yield measured using integrating-sphere method

^bSpecific rotation measured at room temperature in chloroform

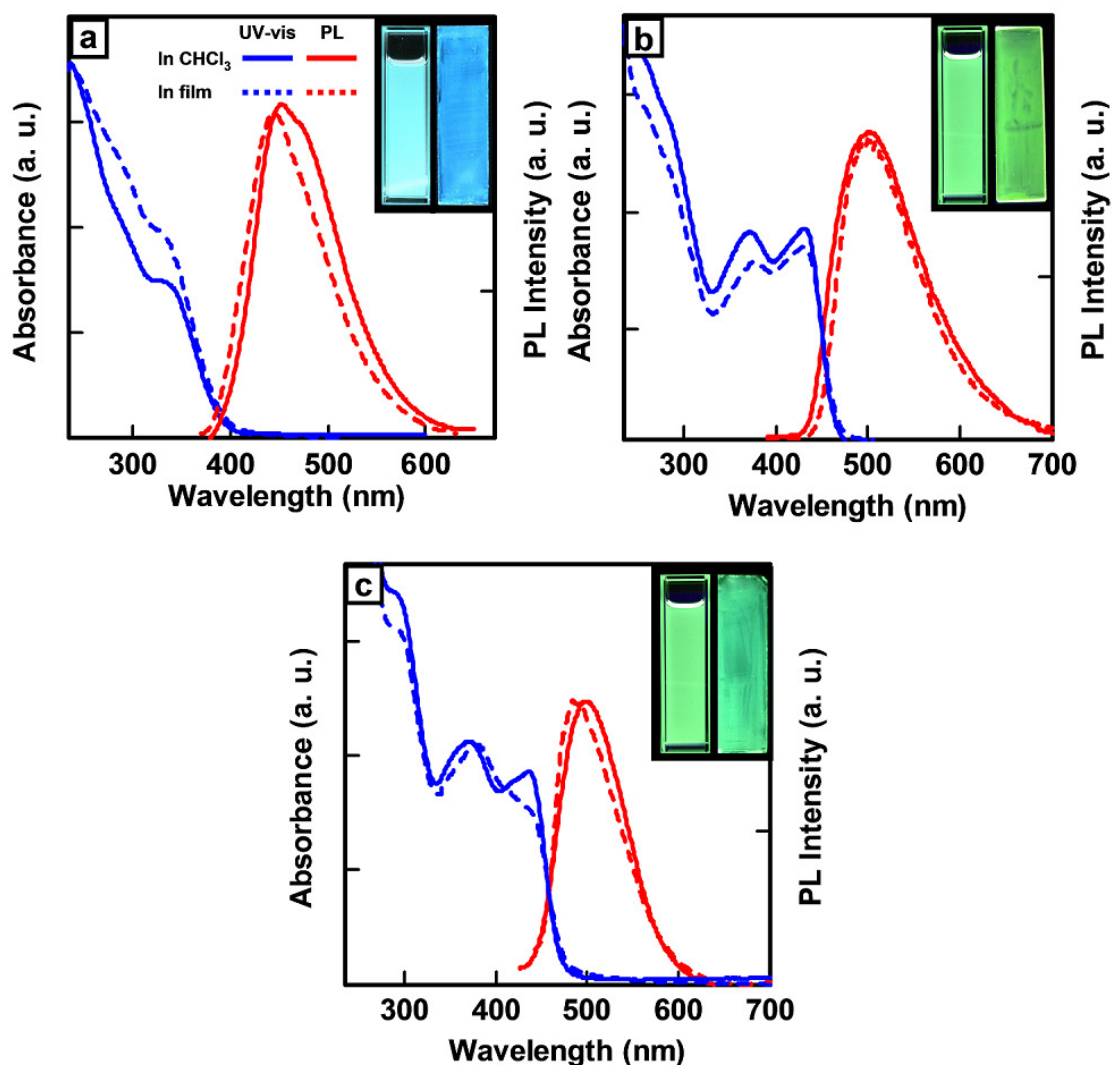


Figure 3. UV-vis and PL spectra of (a) (*R*)-PA1, (b) (*R*)-PA2, (c) (*R*)-PA3 in CHCl₃ solution ($c = 1.2 \times 10^{-4}$ M) and in cast film. Insets: PLs in CHCl₃ solution (left) and in cast film (right).

PA1 exhibits a main chain absorption band measuring approximately 340 nm and a blue-colored emission measuring approximately 450 nm in both solution and film (Figure 3a). Conversely, **PA2** and **PA3** show a main chain absorption band of approximately 440 nm and a *trans*-stilbene moiety-based absorption band measuring approximately 380 nm. **PA2** and **PA3** display a green colored emission of

approximately 500 nm in both solution and film (Figure 3b,c). Previously, we elucidated the origin of emission of substituted PAs and investigated the fluorescent trends of *di*-LCPA.¹⁸ In that earlier work, we observed that *di*-LCPAs with PAPA and PDPA structures generally exhibit blue and green emissions, respectively. The green emission color of the latter is associated with the PDPA structure in which two bulky phenyl rings are directly attached to the polyene main chain. Specifically, the two bulky side chains contribute to lower the $1B_u$ excited state and later to decrease the band gap,²³ resulting in a bathochromic shift of the **PA2** and **PA3** emission bands. Generally, the PAs show small emission shifts between the solution and cast film, which is advantageous for applications of *di*-LCPAs as fluorescent materials in EL devices. Absolute fluorescence quantum yields (Φ) of the *di*-LCPAs in solution and in cast film were measured using the integrating-sphere method. The quantum yields of the *di*-LCPAs in solution range from 21 to 34%, while those in cast film from 10 to 14%. Specific rotation ($[\alpha]_D$) measurements showed that (*R*)-/(*S*)-**PA3** ($\sim \pm 2,100^\circ$) have values an order of magnitude higher than (*R*)-/(*S*)-**PA1** ($\sim \pm 240^\circ$) and (*R*)-/(*S*)-**PA2** ($\sim \pm 220^\circ$).

2.4. Circular Dichroism

With the aim to investigate the helical conformation and arrangement of the polymer chains in an isotropic, aggregate, and liquid crystalline self-assembled state, we measured the circular dichroism (CD) spectra of the *di*-LCPA derivatives in CHCl_3 solution, cast film, and N*-LC film.

Solutions of the *di*-LCPAs were prepared using CHCl_3 ($c = 1.2 \times 10^{-4}$ M) as solvent. The cast film samples were prepared by dissolving the *di*-LCPAs in CHCl_3 , and later

casting the solution onto a quartz plate. The N*-LC film samples were prepared by dissolving the *di*-LCPAs or the *di*-LCPAs with chiral dopant²⁴ in toluene (5–10 wt%) to form a lyotropic LC state. The LC solution was subsequently cast onto a quartz plate, which was later exposed under toluene vapor for one hour and was dried slowly at room temperature. Toluene vapor exposure of the N*-LC film was performed to increase the domain size of the N*-LC phase.

The CD spectra of the *di*-LCPAs in CHCl₃ solution showed monosignate Cotton effects at the absorption region of the polymer main chains (Figure 4a,b,c).²⁵ These results imply that the *di*-LCPAs have a one-handed helical excess conformation. The monosignate Cotton effects of the CD spectra of the *di*-LCPAs suggest intrachain helicity of the polyene main chains. The degree of CD was evaluated using absorption dissymmetry factor, g_{abs} . This factor is defined by the following equation: $g_{\text{abs}} = (\varepsilon_{\text{L}} - \varepsilon_{\text{R}}) / [(\varepsilon_{\text{L}} + \varepsilon_{\text{R}}) / 2] = \Delta\varepsilon / \varepsilon$, where $|g_{\text{abs}}| < 2$. The ε_{L} and ε_{R} are defined as the absorption coefficients of left and right handed polarized light, respectively. The CD spectra of **(R)-/(S)-PA1** and **(R)-/(S)-PA2** in solution showed g_{abs} values on the order of 10^{-4} , while g_{abs} values of **(R)-/(S)-PA3** shown g_{abs} values on the order of 10^{-3} (Table 4) which suggest that **(R)-/(S)-PA3** in solution may have a more strongly twisted main chain helical conformation compared to **(R)-/(S)-PA1** and **(R)-/(S)-PA2**. The two chiral nonyloxy moieties in **(R)-/(S)-PA3** induce a stronger helical conformation to the main chain, as quantified by $\Delta\varepsilon$ and g_{abs} values observed in the CD spectra in solution. The measured specific rotation values of the *di*-LCPAs in solution (Table 3) also support the CD results, where **(R)-PA3** (+2,080°) and **(S)-PA3** (−2,158°) showed values an order higher than **(R)-PA1** (−241°), **(S)-PA1** (+247°), **(R)-PA2** (+229°), and **(S)-PA2** (−226°).

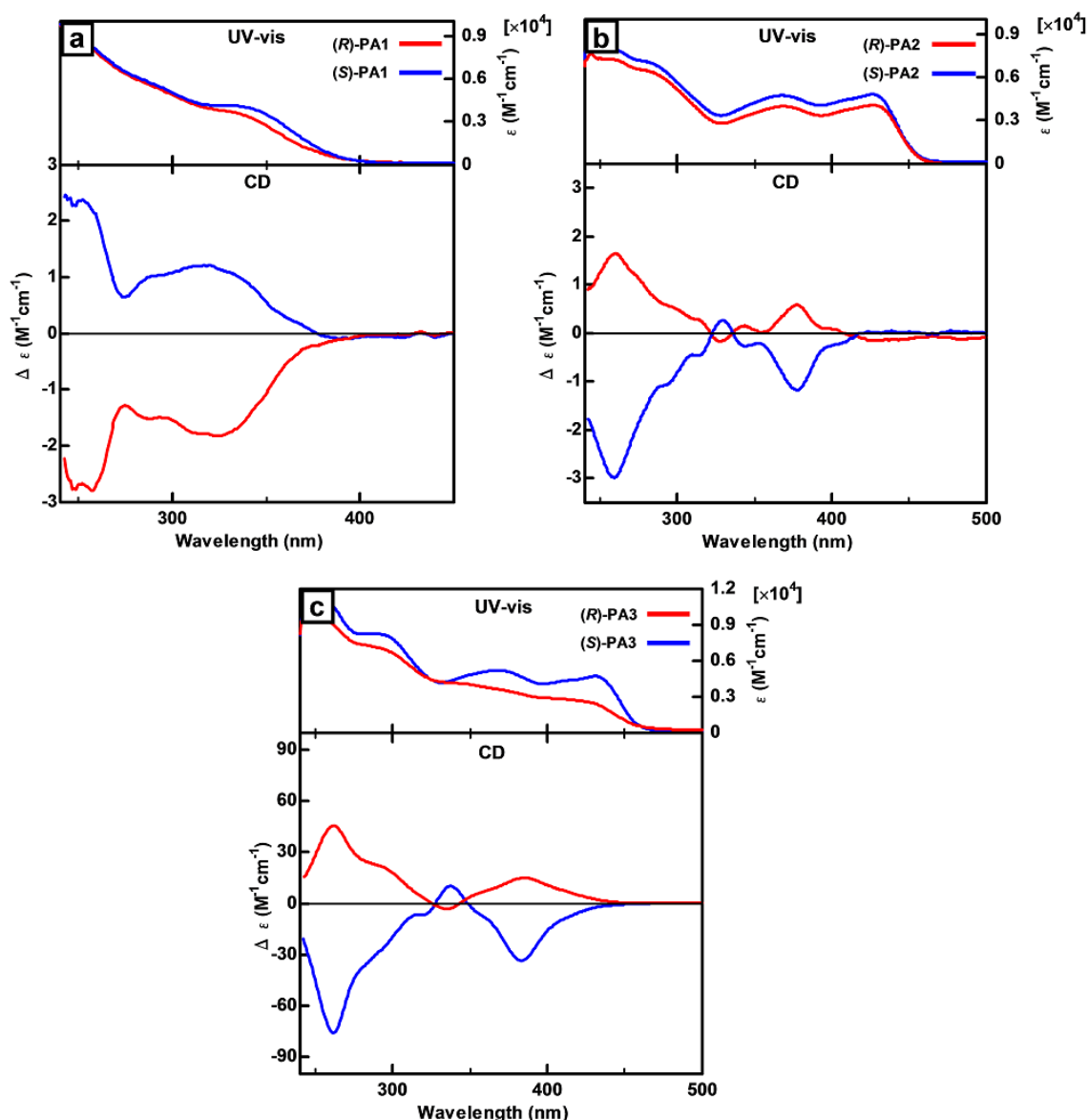


Figure 4. UV-vis (upper) and CD spectra (lower) in CHCl_3 solution ($c = 1.2 \times 10^{-4} \text{ M}$) of (a) **(R)-/(S)-PA1**, (b) **(R)-/(S)-PA2**, and (c) **(R)-/(S)-PA3**.

Cast films of **(R)-/(S)-PA1** showed monosignate Cotton effects in the absorption region of the polymer main chain (Figure 5a). For the other samples, the CD spectra of **(R)-/(S)-PA2** and **(R)-/(S)-PA3** in cast film and in N^* -LC film exhibited bisignate Cotton effects in the absorption region of the polymer main chain.²⁶ Using the exciton coupling theory,²⁷ we can deduce that **(R)-/(S)-PA2** and **(R)-/(S)-PA3** have interchain

helical π -stacking between the polymer main chains. **(R)-PA2**, which has a positive and negative Cotton effect at longer wavelengths and shorter wavelengths, respectively, can be assigned as having *P*-helicity with a right-handed (clockwise) π -stacked structure, while **(S)-PA2** can be assigned as having *M*-helicity with a left-handed (counterclockwise) π -stacked structure (Figure 5b). From the CD spectra, **(R)-PA3** and **(S)-PA3** are assigned as having *M*-helicity and *P*-helicity, respectively (Figure 5c). The cast films of **(R)-/(S)-PA2** and **(R)-/(S)-PA3** exhibited similar CD spectra and handedness to the **PA2** and **PA3** N*-LC samples (Figure S5a,b). It should be noted that the CD spectra of **(R)-/(S)-PA1** in cast film form showed no bisignate CD signal in the polymer main chain absorption region. These results suggest that the PDPA structure of **(R)-/(S)-PA2** and **(R)-/(S)-PA3** facilitates helical π -stacking in cast film and N*-LC state.

It should be noted that **(R)-PA2** and **(R)-PA3**, having the same configuration of chiral moieties, exhibit the same intrachain helical sense in solution (Figure 4b and 4c, Table 4). However, in cast films and N*-LC films, **(R)-PA2** and **(R)-PA3** exhibit opposite bisignate Cotton effects with *P*- and *M*-helicity, respectively (Figure 5b and 5c, Table 4). Such behavior may be related to the chiral organization of the polymer main chains during self-assembly from a disordered (solution) state to a helical π -stacked structure in cast film and N*-LC states. The degree of the attractive interchain π -stacking interactions during self-assembly would be quite different for **(R)-PA2** and **(R)-PA3** because the latter has a more twisted helical main chain conformation induced by its two chiral nonyloxy moieties. Such a difference in attractive π -stacking interactions would be sufficient to favor a different helical sense during the self-assembly of **(R)-PA2** and **(R)-PA3**.

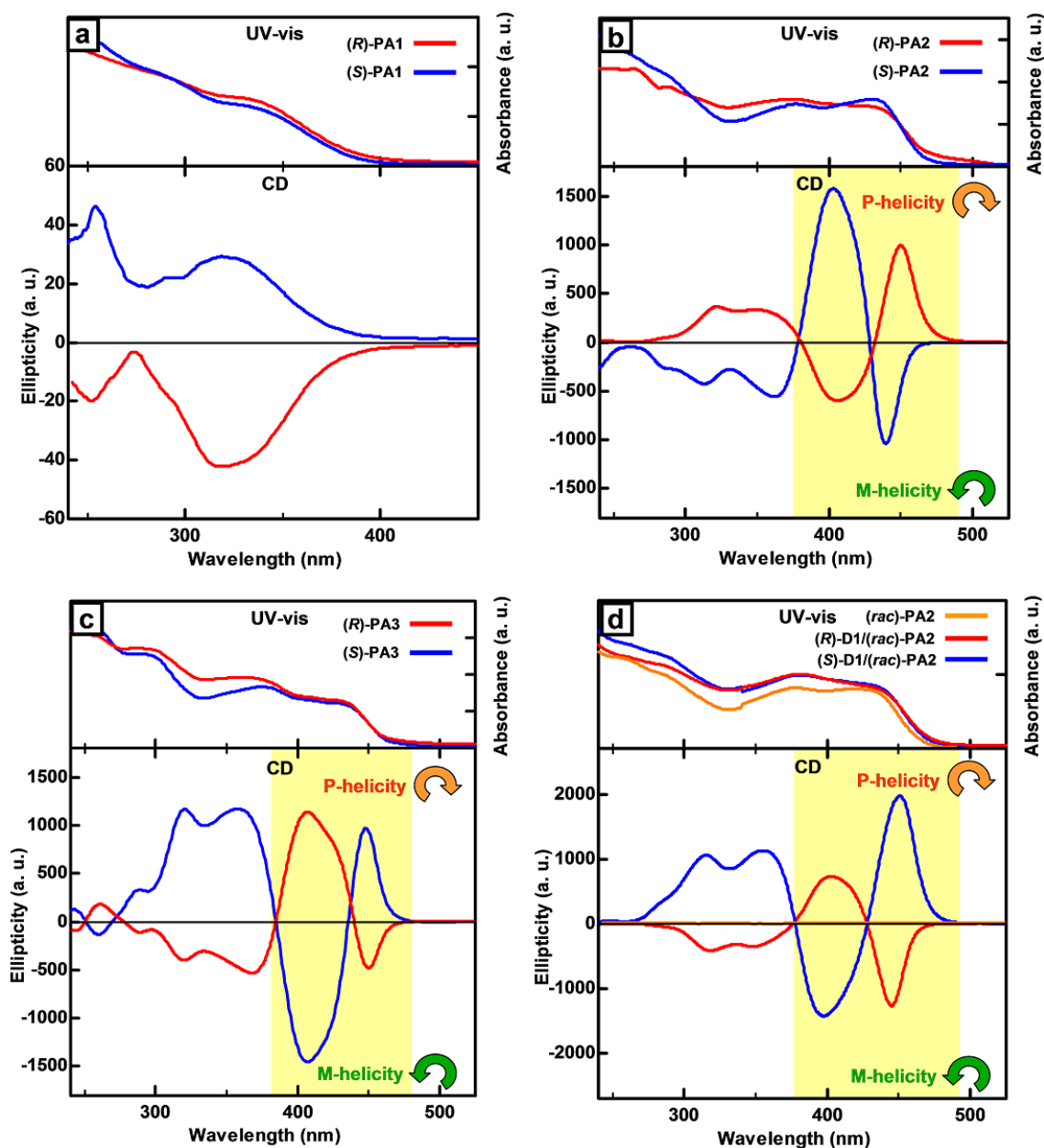


Figure 5. UV-vis (upper) and CD spectra (lower) of (a) **(R)-/(S)-PA1** cast film, and (b) **(R)-/(S)-PA2** N*-LC film, (c) **(R)-/(S)-PA3** N*-LC film, (d) **(R)-/(S)-D1** doped **(rac)-PA2** (10 wt%) N*-LC film.

D1-doped **(rac)-PA2** N*-LC films exhibited bisignate Cotton effects at the polymer main chain region. It was observed that **(R)-D1/(rac)-PA2** N*-LC film showed *M*-helicity, while **(S)-D1/(rac)-PA2** N*-LC film showed *P*-helicity (Figure 5d). The

CD spectra of **(rac)-PA2** displayed no optical handedness; therefore, the chirality of **D1**-doped **(rac)-PA2** originated from the chiral induction of the **(rac)-PA2**. Moreover, **D1**-doped **(rac)-PA3** in N*-LC film also showed a bisignate CD spectra (Figure S5c).

It is also interesting that **(R)-PA2** and **(R)-D1/(rac)-PA2** N*-LC films showed bisignate Cotton effects with *P*- and *M*- helicity, respectively (Figures 5b and 5d, Table 4). The chiral organization of these two N*-LC films during self-assembly would be quite different because the chirality of **(R)-PA2** and **(R)-D1** exhibits central chirality and axial chirality, respectively. Similarly, differences in the type of chirality would be sufficient to favor a different helical sense during the self-assembly of **(R)-PA2** and **(R)-D1/(rac)-PA2** N*-LC films. **(R)-PA3** (Figure 5c) and **(R)-D1/(rac)-PA3** (Figure S5c) films also exhibit opposite helical sense in helical π -stacking.

Table 4. Absorption dissymmetry factors (g_{abs}) of the *di*-substituted LCPAs in CHCl₃ solution, cast film, and N*-LC film.

	g_{abs} (wavelength/ nm) ^a	
	CHCl ₃	cast film / N*-LC film
(R)-PA1	-8.3×10^{-4} (325)	-6.8×10^{-4} (326)^b
(S)-PA1	4.9×10^{-4} (320)	5.9×10^{-4} (326)^b
(R)-PA2	1.5×10^{-4} (378)	1.7×10^{-1} (455)^c
(S)-PA2	-2.6×10^{-4} (378)	-1.3×10^{-1} (445)^c
(R)-PA3	4.8×10^{-3} (388)	-2.9×10^{-2} (453)^c
(S)-PA3	-7.3×10^{-3} (385)	5.4×10^{-2} (451)^c
(R)-D1/(rac)-PA2	—	-4.2×10^{-2} (449)^c
(S)-D1/(rac)-PA2	—	6.1×10^{-2} (459)^c

^aWavelength at which g_{abs} was evaluated

^bIn cast film, ^cin N*-LC film

(R)-/(S)-PA1 in cast film form showed g_{abs} values on the order of 10^{-4} , and **(R)-/(S)-PA3** and **D1-doped (rac)-PA2** N*-LC films showed g_{abs} values on the order of 10^{-2} , while **(R)-/(S)-PA2** N*-LC films showed g_{abs} values up to 10^{-1} (Table 4).²⁸ It can be observed that the g_{abs} values of the **(R)-/(S)-PA2** and **(R)-/(S)-PA3** cast films are an order smaller than those of **(R)-/(S)-PA2** and **(R)-/(S)-PA3** N*-LC films (Table S1).

The CD spectra of the *di*-LCPAs indicate that one-handed intrachain helical structure is formed in solution, while the interchain helical π -stacking between the polymer main chains is formed in cast films and in N*-LC films. The *di*-LCPAs in solution showed g_{abs} values of up to orders of 10^{-3} , while *di*-LCPAs in N*-LC film are in orders of up to 10^{-1} . These results indicate that an increase in interchain interactions from solution to cast film and a subsequently further increase in N*-LC film, leading to a higher degree of helical π -stacked ordering.

2.5. Circularly Polarized Luminescence

We investigated the potential of circularly polarized luminescence (CPL) of the *di*-LCPAs. Even though the *di*-LCPAs in solution and in cast film showed Cotton effects in their CD spectra, they exhibited no CPL.

However, **(R)-/(S)-PA2** in N*-LC film showed bisignate CPL bands centered around the PL emission band (Figure 6a). **(R)-PA2** bearing *P*-helicity in the π -stacked structure exhibited positive and negative CPL bands at wavelengths shorter and longer than 530 nm, respectively. **(S)-PA2**, which has *M*-helicity in the π -stacked structure, exhibited CPL bands with handedness opposite to **(R)-PA2**. The degree of CPL was evaluated by the emission dissymmetry factor, g_{em} . The emission dissymmetry factor is defined as $g_{\text{em}} = (I_{\text{L}} - I_{\text{R}}) / [(I_{\text{L}} + I_{\text{R}}) / 2] = \Delta I / I$, where $|g_{\text{em}}| < 2$. The I_{L} and I_{R} are defined

as the intensities of left and right handed polarized light, respectively. The CPL spectra of **(R)-/(S)-PA2** in N*-LC film showed g_{em} values up to orders of 10^{-1} (Table 5).²⁸ These high g_{em} values suggest the formation of higher ordered helical π -stacked structures in the N*-LC film of **(R)-/(S)-PA2**. The g_{em} values on the order of 10^{-1} are the highest values of CPL achieved in the aliphatic conjugated polymers to the best of our knowledge.

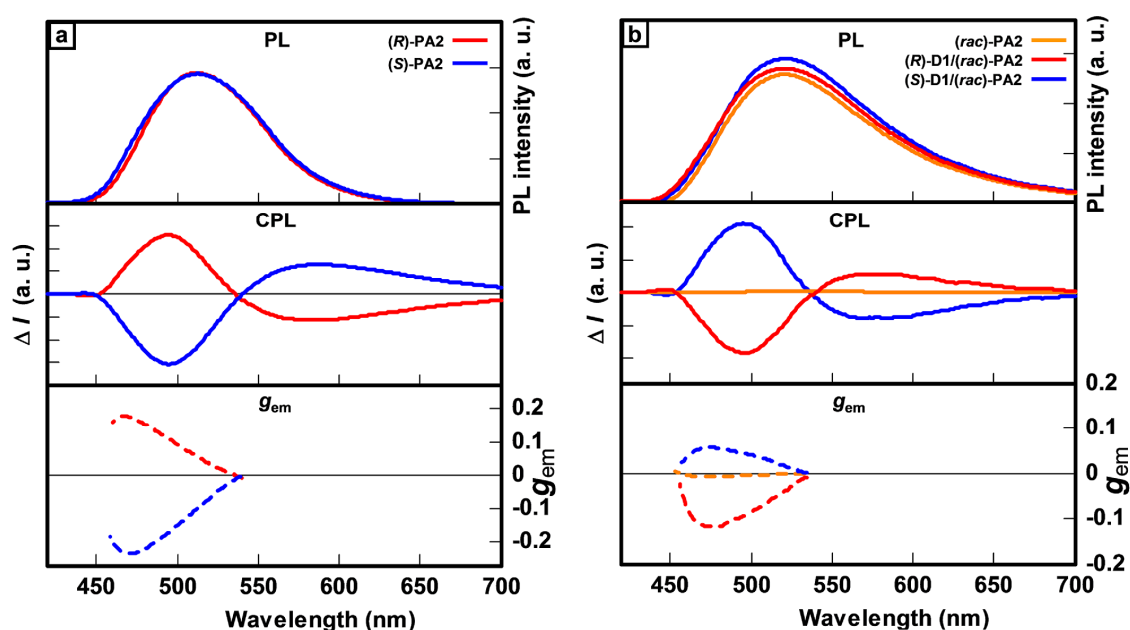


Figure 6. PL (upper), CPL spectra (middle), and g_{em} (lower) spectra of (a) **(R)-/(S)-PA2** N*-LC film, and (b) **(R)-/(S)-D1** doped **(rac)-PA2** (10 wt%) N*-LC film. The measurements were performed with excitation using unpolarized light at 367 nm.

The N*-LC film of **D1**-doped **(rac)-PA2** exhibited CPL similar to that of **(R)-/(S)-PA2** (Figure 6b). The CPL spectra of **D1**-doped **PA2** films show handedness opposite to their counterparts in **(R)-/(S)-PA2** with g_{em} values up to orders of 10^{-1} . The CPL spectrum of **(rac)-PA2** showed no CPL; therefore, the CPL of **D1**-doped **(rac)-PA2** originated from the chiral induction of the **(rac)-PA2**. **(R)-/(S)-PA3** and

D1-doped (*rac*)-PA3 N*-LC films also exhibited CPL (Figure S6, Table S2).

It should be noted that **(*R*)-PA2** and **(*R*)-D1/(*rac*)-PA2** N*-LC films, which showed *P*- and *M*- helicity, respectively, in their helical π -stacked structure, also exhibited g_{em} values with opposite signs. The same trend of opposite signs in the g_{abs} and g_{em} values was also observed in **(*R*)-PA2** and **(*R*)-PA3**. This finding suggests that the chiral organization of the helically π -stacked structures influences the CPL behavior of the *di*-LCPAs.

Table 5. Emission dissymmetry factors (g_{em}) of the *di*-substituted LCPAs in N*-LC films.

	$g_{em}(\text{wavelength/ nm})^a$
(<i>R</i>)-PA2	1.8×10^{-1} (466)
(<i>S</i>)-PA2	-2.3×10^{-1} (471)
(<i>R</i>)-D1/(<i>rac</i>)-PA2	-1.2×10^{-1} (478)
(<i>S</i>)-D1/(<i>rac</i>)-PA2	5.9×10^{-2} (473)

^aWavelength at which g_{em} was evaluated

In contrast to **PA2** and **PA3**, **(*R*)-/(*S*)-PA1**, bearing a PAPA main chain structure, exhibited no CPL in cast films. These results, along with the CD data, suggest that the PDPA main chain structure is much more suitable for the helical π -stacking necessary for CPL in *di*-LCPA. Furthermore, the lyotropic LC properties of the PDPA main chain enables the formation of a higher-ordered helical arrangement through the N*-LC phase that is essential for the emergence of CPL with high values of g_{em} .

2.6. Relationships between helical arrangement, interchain interaction and *g*-factors of *di*-LCPAs

At this stage, it is helpful to summarize the relationships between helical arrangement, interchain interaction and *g*-factors of *di*-LCPAs, as represented by **(R)-PA2**, depicted in Table 6. The relationship between the degree of helical arrangement and the magnitude of interchain interactions of the *di*-LCPAs can be elucidated by comparing the measured *g*-factors in CD and CPL at different states. In the case of **(R)-PA2** in CHCl₃ solution, we observed intrachain helicity with weak interchain interactions. The CD spectrum of **(R)-PA2** in solution revealed monosignate Cotton effects with *g*_{abs} values on the order of 10⁻⁴. On the other hand, in the cast film of **(R)-PA2**, the interchain interactions are large enough to give interchain helical π -stacking. The emergence of a bisignate Cotton effect in CD spectra with *g*_{abs} values up to orders of 10⁻² indicates that the helical π -stacking between polymer main chains is formed through polymer interchain chiral aggregation. While in the N*-LC state, very large interchain interactions are present, resulting in a highly ordered interchain helical arrangement. The CD and CPL spectra of **(R)-PA2** in the N*-LC state show high *g*_{abs} and *g*_{em} values of up to orders of 10⁻¹, respectively. This trend in the CD and CPL results of the *di*-LCPAs leads us to believe that the use of the N*-LC phase facilitates a high degree of supramolecular helical ordering and is indispensable for the emergence of CPL with high *g*-factors.

As a consequence, when one designs polyacetylene derivatives with CPL having a high *g*_{em}, it is essential to adopt a PDPA main chain structure, to introduce helicity to the main chain, and to utilize the lyotropic LC behavior of PDPA to form a higher-ordered helical structure through the N*-LC phase.

Table 6. Summary of the relationship between helical arrangement, interchain interaction, and g -factors of (*R*)-PA2 at various states.

	In solution	In cast film	In N*-LC film
Helical arrangement	Intrachain helicity	Interchain π -stacking	Higher ordered helical arrangement
Interchain interaction	weak	large	very large
g_{abs} of (<i>R</i>)-PA2 (λ , nm) ^a	1.5×10^{-4} (378)	3.7×10^{-2} (445)	1.7×10^{-1} (455)
g_{em} of (<i>R</i>)-PA2 (λ , nm) ^a	–	–	1.8×10^{-1} (466)

^aWavelength at which g_{abs} and g_{em} was evaluated

3. Conclusion

We synthesized chiral *di*-LCPA derivatives that show a highly ordered lyotropic N*-LC phase, thereby giving rise to a high degree of circular polarization. The PDPA main chain structure of the *di*-LCPAs, along with chirality induced with either chiral nonyloxy phenyl moieties or chiral dopants, allows the formation of a highly ordered lyotropic N*-LC phase. We found that the highly ordered lyotropic N*-LC phase is indispensable for the generation of CPL with high g_{em} values. In addition to having the highest values of CPL in aliphatic conjugated polymers, our approach represents an attractive alternative to thermotropic LC systems for the development of LC-based optoelectronic devices and future applications that utilize circularly polarized optical materials.

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Chapter 3 Appendix

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1. Experimental Section

1.1. Materials

The chemical reagents we purchased from commercially available sources and were used as received. *Trans*-dichlorobis(triphenylphosphine)palladium(II) ($\text{PdCl}_2(\text{TPP})_2$) was purchased from Aldrich Co. Ltd. Diethylazodicarboxylate (DEAD), *tetra*-phenyltin (Ph_4Sn), 1-octyne, 4-iodophenol, trimethylsilylacetylene, and 2-nonanol were purchased from Tokyo Kasei Co. Ltd. Tungsten(VI) hexachloride (WCl_6), and copper(I) iodide (CuI) were purchased from Kanto Chemical Co. Ltd. Triphenylphosphine (TPP), (*R*)-(-)-2-nonanol, (*S*)-(+)-2-nonanol, and 25% ammonia (NH_3) solution were purchased from Wako Co. Ltd. Phenylacetylene, potassium carbonate (K_2CO_3),

sodium sulfate (Na_2SO_4), triethyl amine (Et_3N), tetrahydrofuran (THF), toluene, methanol (MeOH), hexane ($n\text{-C}_6\text{H}_{14}$), ethyl acetate, and chloroform (CHCl_3) were purchased from Nacalai Tesque Co. Ltd. All experiments were performed under argon (>99.9995 % purity) atmosphere. THF, Et_3N , and toluene used were distilled from sodium as a drying agent under argon gas before use.

1.2. Methods

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either JEOL JNM EX400 400 MHz or JEOL AL-400 400MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from *tetra*-methylsilane (TMS) as an internal standard. Elemental analysis was measured using Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100 and Dionex ICS-1500.

The microscope observation was carried out under crossed nicols using a Carl Zeiss Axio Imager M1m polarizing microscope equipped with a Carl Zeiss AxioCam MRc5 digital camera and a Linkam TH600PM and L600 heating and cooling stage with temperature control. The samples for observations with POM were sandwiched between two cover glasses.

Optical absorption spectra were measured using a JASCO V-570 UV/VIS/NIR spectrophotometer, and fluorescence spectra were measured using JASCO FP-750 spectrometer with quartz cell (for solution) and quartz plate (for cast film). Absolute fluorescence quantum yield of the polymers was measured using integrating-sphere method at the JASCO FP-6500 spectrometer. Optical purity of the chiral compounds and polymers were evaluated with specific rotation measured by JASCO P2300

polarimeter. Circular dichroism spectra were measured using JASCO J-820 spectropolarimeter. Circularly polarized luminescence was measured using JASCO CPL-200S spectrometer.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

XRD diffraction (XRD) measurements of the polymers were performed with a Rigaku ultra X18 diffractometer (Xray $\text{CuK}\alpha$ radiation: 40 kV/300 mA, $\lambda = 0.154$ nm; camera length: 100 mm) and a Rigaku Nanoviewer Micromax-007HF diffractometer (Xray $\text{CuK}\alpha$ radiation: 40 kV/30 mA, $\lambda = 0.154$ nm; camera length: 120 mm). XRD patterns were recorded with an X-ray generator with Nickel filtered $\text{CuK}\alpha$ radiation and a flat plate camera (RINT2500, Rigaku). The polymers were heated up to isotropic state, and then slowly cooled to room temperature via LC states, yielding XRD samples. Lyotropic LC samples for XRD measurements were prepared by first dissolving the polymer in toluene (5–10 wt% solution) to form a lyotropic LC phase. The lyotropic LC solution is then pulled up a XRD capillary tube (Hilgenberg Mark-tube glass #10, 0.01 mm wall thickness) and allowed to dry, yielding XRD samples. The diffraction pattern was recorded on an imaging plate and scanned by a R-Axis DS3A imaging plate reader at 100 μm resolution.

1.3. Syntheses of Monomers and Polymers

The synthesis route of the precursor compounds **1** to **14**, the *di*-LCPA monomers

(*rac*)-/(*R*)-/(*S*)-**M1–M3**, and the *di*-LCPAs (*rac*)-/(*R*)-/(*S*)-**PA1–PA3** are written below.

Synthesis of the chiral dopants (*R*)-/(*S*)-**D1** were synthesized as described in a previous report.¹³

4-(1-Octynyl)-phenol (**1**)

4-(1-Octynyl)-phenol (**1**) was synthesized as follows. Into a 300 mL three-necked flask were added 0.16 g (0.23 mmol) of PdCl₂(TPP)₂, 93 mg of CuI (0.49 mmol), 1-octyne (3.00 g, 27 mmol) and 4-iodophenol (5.00 g, 23 mmol), and 120 mL THF under argon. After all the reagents were dissolved, 80 mL of 0.5 M aqueous NH₃ was added dropwise into the solution. The solution was stirred at room temperature overnight under argon atmosphere. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 2 : 1). The collected liquid was evaporated and dried under vacuum and dried in vacuo to give 3.24 g (16 mmol) of **1** as a viscous deep red liquid. Yield = 70%.

Anal. Chemical Formula: (C₁₄H₁₈O)_n (202.14)_n; Calcd. C 83.12, H 8.97, O 7.91; Found C 81.18, H 8.39. ¹H NMR (400 MHz, CDCl₃): δ = 0.92 (t, 3H, *J* = 6.8 Hz, –CH₃), 1.21–1.67 (m, 8H, –(CH₂)₄–), 2.39 (t, 2H, *J* = 7.2 Hz, –C≡C–CH₂(CH₂)₄CH₃), 4.75 (s, 1H, HO–Ar–C≡C–(CH₂)₅CH₃), 6.75 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to HO–), 7.30 (d, 2H, *J* = 8.4 Hz, Ar–H *meta* to HO–). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.0, 19.4, 22.5, 28.5, 28.8, 31.3, 88.8, 105.5, 115.1, 132.9, 159.6. HRMS (DART) calcd for C₁₄H₁₈O [M + H⁺]: 203.1430. Found: 203.1431.

4-(Phenylethynyl)phenol (**2**)

4-(Phenylethynyl)phenol (**2**) was synthesized as follows. The reagents 4-iodophenol (4.7 g, 21 mmol), phenyl acetylene (2.8 g, 28 mmol), PdCl₂(TPP)₂ (297 mg, 0.42 mmol), CuI (162 mg, 0.85 mmol), 25 mL Et₃N, and 10 mL THF were added under argon atmosphere into a 200 mL three necked flask. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 2.7 g (13.4 mmol) of **2** as a yellowish crystal. Yield = 66%. Anal. Chemical Formula: (C₁₄H₁₀O)_n (194.23)_n: Calcd. C, 86.57; H, 5.19; O, 8.24; Found C 86.81, H 5.37. ¹H NMR (400 MHz, CDCl₃): δ = 4.90 (s, 1H, -C≡C-Ar-OH), 6.81 (d, 2H, *J* = 8.8 Hz, Ar-H *ortho* to -OH), 7.33 (m, 3H, Ar-H *meta* and *para* to -C≡C-C₆H₄OH), 7.43 (d, 2H, *J* = 8.8 Hz, Ar-H *meta* to -OH), 7.50 (d, 2H, *J* = 8.8 Hz, Ar-H *ortho* to -C≡C-C₆H₄OH). ¹³C NMR (100 Mhz, CDCl₃): δ = 89.8, 115.3, 115.5, 127.8, 128.1, 131.3, 133.1. HRMS (DART) calcd for C₁₄H₁₀O [M + H⁺]: 195.0804. Found: 195.0806.

1-Iodo-4-(nonan-2-yloxy)benzene (**3**)

1-Iodo-4-(nonan-2-yloxy)benzene (**3**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (10.38 g, 40 mmol) and 4-iodophenol (9.50 g, 43 mmol) under argon gas and dissolved in THF (60 mL). In the addition funnel, a mixture of DEAD (20.00 g, 40 wt% in toluene, 40 mmol), 2-nonanol (5.20 g, 36 mmol), and 50 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was

added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound **3** (9.56 g, 27.6 mmol) as a light amber colored oil. Yield = 77%.

Anal. Chemical Formula: $(\text{C}_{15}\text{H}_{23}\text{IO})_n$ (346.25) $_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.17; H, 6.82. ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (t, 3H, J = 6.8 Hz, $-\text{CH}_3$), 1.15–1.50 (m, 13H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.51–1.75 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 4.22–4.36 (m, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.65 (d, 2H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{I}$), 7.53 (d, 2H, J = 8.6 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{I}$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.7, 36.3, 74.1, 82.1, 118.1, 138.0, 157.9. HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{23}\text{IO}$ [M^+]: 346.0788. Found: 346.0783.

(*R*)-1-Iodo-4-(nonan-2-yloxy)benzene (4)

(*R*)-1-Iodo-4-(nonan-2-yloxy)benzene (**4**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (10.00 g, 38 mmol) and 4-iodophenol (9.14 g, 42 mmol) under argon gas and dissolved in THF (80 mL). In the addition funnel, a mixture of DEAD (19.26 g, 40 wt% in toluene, 38 mmol), (*S*)-(+)-2-nonanol (5.00 g, 34 mmol), and 50 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of

the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound **4** (8.12 g, 23.6 mmol) as a light amber colored oil. Yield = 68%.

Anal. Chemical Formula: $(\text{C}_{15}\text{H}_{23}\text{IO})_n$ (346.25) $_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.25; H, 6.76. ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.2 Hz, $-\text{CH}_3$), 1.23–1.50 (m, 13H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.51–1.71 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 4.27–4.32 (m, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.54 (d, 2H, J = 7.2 Hz, Ar-H *meta* to $-\text{I}$), 7.53 (d, 2H, J = 6.8 Hz, Ar-H *ortho* to $-\text{I}$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 74.1, 82.1, 118.1, 138.1, 158.0. HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{23}\text{IO}$ [M^+]: 346.0788. Found: 346.0783. $[\alpha]_D^{25}$ -3.54° (c 1.0, CHCl_3).

(S)-1-Iodo-4-(nonan-2-yloxy)benzene (5)

(S)-1-Iodo-4-(nonan-2-yloxy)benzene (**5**) was synthesized as follows. TPP (10.00 g, 38.2 mmol), 4-iodophenol (9.14 g, 42 mmol) were added under argon gas into a 300 mL three necked flask, dissolved in THF (70 mL) and then stirred. In the addition funnel, a mixture of DEAD (19.28 g, 40 wt% in toluene, 38.2 mmol), (*R*)-(-)-2-nonanol (5.00 g, 34 mmol), and 50 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then

purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound **5** (9.34 g, 27.0 mmol) as a light amber colored oil. Yield = 78%.

Anal. Chemical Formula: $(\text{C}_{15}\text{H}_{23}\text{IO})_n$ (346.25) $_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.59; H, 6.85. ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.2 Hz, $-\text{CH}_3$), 1.21–1.56 (m, 13H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.64–1.72 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 4.24–4.31 (m, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.64 (d, 2H, J = 6.4 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{I}$), 7.50 (d, 2H, J = 6.4 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{I}$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 74.1, 82.1, 118.1, 138.0, 157.9. HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{23}\text{IO}$ [M^+]: 346.0788. Found: 346.0782. $[\alpha]_D^{25} +3.66^\circ$ (c 1.0, CHCl_3).

Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**6**)

Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**6**) was synthesized as follows. Into a 200 mL three-necked flask were added compound **3** (9.4 g, 27.1 mmol), trimethylsilylacetylene (4.00 g, 40.7 mmol), $\text{PdCl}_2(\text{TPP})_2$ (0.38 g, 0.54 mmol), CuI (0.21 g 1.10 mmol), 30 mL Et_3N , and 120 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography using CHCl_3 as eluent. The product was evaporated and dried under vacuum to give compound **6** (7.76 g, 24.5 mmol) as a light amber colored oil. Yield = 90%.

Anal. Chemical Formula: $(\text{C}_{20}\text{H}_{32}\text{OSi})_n$ (316.55) $_n$: Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87. Found C, 75.80; H, 10.40. ^1H NMR (400 MHz, CDCl_3): δ = 0.00 (t, 9H,

Ar-C≡C-Si(CH₃)₃), 0.64 (t, 3H, *J* = 7.3 Hz, Ar-O-CH(CH₃)(CH₂)₆CH₃), 0.91–1.31 (m, 13H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 1.33–1.59 (m, 2H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 4.09–4.14 (m, 1H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 6.55 (d, 2H, *J* = 8.8 Hz, Ar-H *meta* to -C≡C-Si(CH₃)₃), 7.14 (d, 2H, *J* = 8.6 Hz, Ar-H *ortho* to -C≡C-Si(CH₃)₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.0, 22.0, 24.8, 28.6, 28.9, 31.2, 35.7, 73.3, 91.5, 114.8, 132.7, 157.7. HRMS (APCI) calcd for C₂₀H₃₂OSi [M + H⁺]: 317.2295. Found: 317.2285.

(*R*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (7)

(*R*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**7**) was synthesized as follows. Into a 200 mL three-necked flask were added compound **4** (3.42 g, 9.87 mmol), trimethylsilylacetylene (1.45 g, 14.81 mmol), PdCl₂(TPP)₂ (139 mg, 0.20 mmol), CuI (75 mg, 0.39 mmol), 20 mL Et₃N, and 70 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography using CHCl₃ as eluent. The product was evaporated and dried under vacuum to give compound **7** (2.75 g, 8.69 mmol) as a light amber colored oil. Yield = 88%.

Anal. Chemical Formula: (C₂₀H₃₂OSi)_{*n*} (316.55)_{*n*}; Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87. Found C, 75.67; H, 9.92. ¹H NMR (400 MHz, CDCl₃): δ = 0.00 (t, 9H, Ar-C≡C-Si(CH₃)₃), 0.64 (t, 3H, *J* = 7.3 Hz, Ar-O-CH(CH₃)(CH₂)₆CH₃), 1.04–1.31 (m, 13H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 1.31–1.55 (m, 2H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 4.09–4.14 (m, 1H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 6.54 (d, 2H, *J* = 6.8 Hz, Ar-H *meta* to -C≡C-Si(CH₃)₃), 7.14 (d, 2H, *J* = 6.8 Hz, Ar-H

ortho to $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 73.9, 92.1, 115.4, 133.3, 158.0. HRMS (APCI) calcd for $\text{C}_{20}\text{H}_{32}\text{OSi} [\text{M} + \text{H}^+]$: 317.2295. Found: 317.2285. $[\alpha]^{25}_{\text{D}} -0.62^\circ$ (*c* 1.0, CHCl_3).

(S)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (8)

(S)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**8**) was synthesized as follows. The reagents compound **5** (2.2 g, 6.35 mmol), trimethylsilylacetylene (0.94 g, 9.53 mmol), $\text{PdCl}_2(\text{TPP})_2$ (89 mg, 0.13 mmol), CuI (48 mg, 0.26 mmol), 10 mL Et_3N , and 50 mL THF were added under argon atmosphere into a 300 mL three-mouthed flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3×). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography using CHCl_3 as eluent. The product was evaporated and dried under vacuum to give compound **8** (1.83 g, 5.78 mmol) as a light amber colored oil. Yield = 91%.

Anal. Chemical Formula: $(\text{C}_{20}\text{H}_{32}\text{OSi})_n$ (316.55) $_n$: Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87; Found C, 75.89; H, 10.43. ^1H NMR (400 MHz, CDCl_3): δ = 0.00 (t, 9H, $\text{Ar}-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$), 0.62 (t, 3H, J = 7.2 Hz, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 1.00–1.28 (m, 13H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.30–1.55 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 4.10–4.14 (m, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.53 (d, 2H, J = 7.0 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$), 7.20 (d, 2H, J = 6.8 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.0, 19.5, 22.5, 25.4, 29.1, 29.4, 31.7, 36.2, 73.8, 92.0, 115.3, 133.2, 158.2. HRMS (APCI) calcd for $\text{C}_{20}\text{H}_{32}\text{OSi} [\text{M} + \text{H}^+]$: 317.2295. Found: 317.2284. $[\alpha]^{25}_{\text{D}} +0.67^\circ$ (*c* 1.0, CHCl_3).

1-Ethynyl-4-(nonan-2-yloxy)benzene (9)

1-Ethynyl-4-(nonan-2-yloxy)benzene (**9**) was synthesized as follows. Into a 100 mL round-bottom flask were added compound **6** (7.39 g, 23.4 mmol), K₂CO₃ (1.61 g, 11.7 mmol), 10 mL MeOH, and 10 mL THF. After continuous stirring, solution was left overnight at room temperature. The solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography using CHCl₃ as eluent. The product was evaporated and dried under vacuum to give compound **9** (5.44 g, 22.3 mmol) as an amber colored oil. Yield = 92%.

Anal. Chemical Formula: (C₁₇H₂₄O)_n (244.37)_n: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.42; H, 10.02. ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 3H, *J* = 6.8 Hz, –CH₃), 1.19–1.47 (m, 13H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 1.50–1.78 (m, 2H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 2.98 (s, 1H, –O–Ar–C≡CH), 4.33–4.38 (m, 1H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 6.81 (d, 2H, *J* = 6.8 Hz, Ar–H *meta* to –C≡C–Si(CH₃)₃), 7.40 (d, 2H, *J* = 7.0 Hz, Ar–H *ortho* to –C≡C–Si(CH₃)₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 75.5, 83.7, 113.6, 115.5, 133.4, 158.5. HRMS (APCI) calcd for C₁₇H₂₄O [M + H⁺]: 245.1900. Found: 245.1894.

(R)-1-Ethynyl-4-(nonan-2-yloxy)benzene (10)

(*R*)-1-Ethynyl-4-(nonan-2-yloxy)benzene (**10**) was synthesized as follows. Into a 100 mL round-bottom flask were added compound **7** (2.65 g, 8.36 mmol), K₂CO₃ (2.31 g, 16.72 mmol), 50 mL MeOH, and 50 mL THF. After continuous stirring, solution was left overnight at room temperature. The solution was then filtered, evaporated and the

residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography using CHCl_3 as eluent. The product was evaporated and dried under vacuum to give compound **10** (1.88 g, 7.69 mmol) as an amber colored oil. Yield = 92%.

Anal. Chemical Formula: $(\text{C}_{17}\text{H}_{24}\text{O})_n$ (244.37) $_n$: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.28; H, 9.97. ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (t, 3H, J = 7.0 Hz, $-\text{CH}_3$), 1.25–1.39 (m, 13H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.51–1.69 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 2.96 (s, 1H, $-\text{O}-\text{Ar}-\text{C}\equiv\text{CH}$), 4.31–4.36 (m, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.78 (d, 2H, J = 6.8 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$), 7.38 (d, 2H, J = 7.0 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.7, 22.6, 25.5, 29.1, 29.5, 31.8, 36.3, 76.6, 81.0, 113.5, 115.5, 133.4, 157.0. HRMS (APCI) calcd for $\text{C}_{17}\text{H}_{24}\text{O}$ [$\text{M} + \text{H}^+$]: 245.1900. Found: 245.1892. $[\alpha]_{\text{D}}^{25}$ -6.24° (c 1.0, CHCl_3).

(S)-1-Ethynyl-4-(nonan-2-yloxy)benzene (11)

(S)-1-Ethynyl-4-(nonan-2-yloxy)benzene (**11**) was synthesized as follows. Compound **8** (1.80 g, 5.69 mmol), K_2CO_3 (0.39 g, 2.84 mmol), 50 mL MeOH, and 50 mL THF were added to a 100 mL round-bottom flask. The solution was stirred overnight at room temperature under argon atmosphere. The solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography using CHCl_3 as eluent. The product was evaporated and dried under vacuum to give compound **11** (1.21 g, 4.94 mmol) as an amber colored oil. Yield = 87%.

Anal. Chemical Formula: $(C_{17}H_{24}O)_n$ (244.37) $_n$: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.31; H, 10.11. 1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.21–1.40 (m, 13H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 1.46–1.49 (m, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 2.91 (s, 1H, $-O-Ar-C\equiv CH$), 4.26–4.31 (m, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.74 (d, 2H, J = 8.0 Hz, $Ar-H$ *meta* to $-C\equiv C-Si(CH_3)_3$), 7.33 (d, 2H, J = 6.8 Hz, $Ar-H$ *ortho* to $-C\equiv C-Si(CH_3)_3$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 36.4, 75.4, 83.7, 113.5, 115.5, 133.4, 158.5. HRMS (APCI) calcd for $C_{17}H_{24}O$ [$M + H^+$]: 245.1900. Found: 245.1892. $[\alpha]_D^{25} +6.39^\circ$ (c 1.0, $CHCl_3$).

4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**12**)

4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**12**) was synthesized as follows. The reagents compound **9** (4.00 g, 16.4 mmol), 4-iodophenol (3.28 g, 14.9 mmol), $PdCl_2(TPP)_2$ (0.21 g, 0.30 mmol), CuI (0.11 g, 0.60 mmol), 30 mL Et_3N , and 70 mL THF were added under argon atmosphere into a 100 mL three-mouthed flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **12** (3.66 g, 10.89 mmol) as a reddish solid. Yield = 73%.

Anal. Chemical Formula: $(C_{23}H_{28}O_2)_n$ (336.47) $_n$: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.22; H, 8.36. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.1 Hz, $-CH_3$), 1.22–1.35 (m, 13H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 1.51–1.78 (m, 2H,

Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.31–4.42 (m, 1H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.84 (s, 1H, HO–Ar–C≡C–Ar), 6.79 (d, 2H, *J* = 6.6 Hz, Ar–H *ortho* to –O–CH(CH₃)(CH₂)₆CH₃), 6.81 (d, 2H, *J* = 7.1 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, *J* = 5.8 Hz, Ar–H *meta* to HO–), 7.42 (d, 2H, *J* = 6.1 Hz, Ar–H *meta* to –O–CH(CH₃)(CH₂)₆CH₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.0, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.5, 88.5, 115.3, 115.6, 132.7, 132.9, 155.2. HRMS (DART) calcd for C₂₃H₂₈O₂ [M + H⁺]: 337.2162. Found: 337.2160.

(*R*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (13**)**

(*R*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**13**) was synthesized as follows. The reagents compound **10** (1.77 g, 7.3 mmol), 4-iodophenol (1.45 g, 6.6 mmol), PdCl₂(TPP)₂ (93 mg, 0.13 mmol), CuI (50 mg, 0.26 mmol), 10 mL Et₃N, and 10 mL THF were added under argon atmosphere into a Schlenk flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **13** (1.39 g, 4.13 mmol) as a reddish solid. Yield = 63%.

Anal. Chemical Formula: (C₂₃H₂₈O₂)_n (336.47)_n: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.03; H, 8.29. ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 3H, *J* = 7.6 Hz, –CH₃), 1.23–1.33 (m, 13H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 1.50–1.77 (m, 2H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.32–4.40 (m, 1H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.93 (s, 1H, HO–Ar–C≡C–Ar), 6.79 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to

–O–CH(CH₃)(CH₂)₆CH₃), 6.83 (d, 2H, *J* = 8.1 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, *J* = 6.1 Hz, Ar–H *meta* to HO–), 7.41 (d, 2H, *J* = 8.3 Hz, Ar–H *meta* to –O–CH(CH₃)(CH₂)₆CH₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.0, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 83.5, 84.1, 115.3, 115.6, 132.7, 132.9, 156.6. HRMS (DART) calcd for C₂₃H₂₈O₂ [M + H⁺]: 337.2162. Found: 337.2149. [α]_D²⁵ +3.26° (*c* 1.0, CHCl₃).

(S)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (14**)**

(S)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**14**) was synthesized as follows. The reagents compound **11** (0.90 g, 3.7 mmol), 4-iodophenol (0.74 g, 3.3 mmol), PdCl₂(TPP)₂ (47 mg, 0.07 mmol), CuI (26 mg, 0.13 mmol), 10 mL Et₃N, and 10 mL THF were added under argon atmosphere into a Schlenk flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **14** (1.39 g, 2.94 mmol) as a reddish solid. Yield = 88%.

Anal. Chemical Formula: (C₂₃H₂₈O₂)_n (336.47)_n: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.06; H, 9.71. ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (t, 3H, *J* = 6.8 Hz, –CH₃), 1.20–1.46 (m, 13H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 1.50–1.80 (m, 2H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.32–4.40 (m, 1H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.85 (s, 1H, HO–Ar–C≡C–Ar), 6.79 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to –O–CH(CH₃)(CH₂)₆CH₃), 6.83 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, *J* = 6.4 Hz, Ar–H *meta* to HO–), 7.41 (d, 2H, *J* = 6.0 Hz, Ar–H *meta* to

–O–CH(CH₃)(CH₂)₆CH₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.5, 88.0, 115.3, 115.6, 132.7, 132.9, 155.2. HRMS (DART) calcd for C₂₃H₂₈O₂ [M + H⁺]: 337.2162. Found: 337.2152. $[\alpha]_D^{25}$ –3.21° (*c* 1.0, CHCl₃).

(rac)-Monomer 1 ((rac)-M1)

(rac)-M1 was synthesized as follows. Into a 100 mL three-necked flask were added compound **1** (0.81 g, 5.69 mmol), and TPP (1.37 g, 5.22 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (2.64 g, 40 wt% in toluene, 5.22 mmol), 2-nonanol (0.68 g, 4.74 mmol), and 30 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The product was evaporated and dried under vacuum to give 0.78 g (2.37 mmol) of **(rac)-M1** as a light yellow oil. Yield = 50%.

Anal. Chemical Formula: (C₂₃H₃₆O)_{*n*} (328.53)_{*n*}: Calcd. C, 84.09; H, 11.04; O, 4.87; Found C 83.84, H 10.98. ¹H NMR (400 MHz, CDCl₃): δ = 0.79–0.98 (m, 6H, –CH₃), 1.21–1.48 (m, 18H, Ar–O–CH(CH₃)(CH₂)₆CH₃, –C≡C–(CH₂)₂(CH₂)₃CH₃), 1.49–1.78 (m, 5H, Ar–O–CH(CH₃)(CH₂)₆CH₃, –C≡C–CH₂CH₂(CH₂)₃CH₃), 2.38 (t, 2H, *J* = 7.2 Hz, –C≡C–CH₂(CH₂)₄CH₃), 4.28–4.39 (m, 1H, Ar–O–CH(CH₃)(CH₂)₆CH₃), 6.78 (d, 2H, *J* = 8.8 Hz, Ar–H *meta* to C₆H₁₃–C≡C–), 7.30 (d, 2H, *J* = 9.2 Hz, Ar–H *ortho* to C₆H₁₃–C≡C–). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.1, 21.9, 22.0, 24.9, 28.0, 28.2,

28.6, 28.9, 30.8, 31.2, 35.8, 73.3, 79.6, 87.9, 114.9, 115.2, 132.1, 156.9. HRMS (DART) calcd for $C_{23}H_{36}O$ $[M + H]^+$: 329.2839. Found: 329.2829.

(R)-Monomer 1 ((R)-M1)

(R)-M1 was synthesized in a similar way as **(rac)-M1**. Into a 100 mL three-necked flask were added compound **1** (1.05 g, 5.19 mmol), and TPP (1.25 g, 4.76 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (2.41 g, 40 wt% in toluene, 4.75 mmol), (S)-(+)-2-nonanol (0.62 g, 4.32 mmol), and 30 mL THF was prepared. The reagents were then stirred overnight at room temperature. The reaction yielded a light yellow oil with a yield of 66% (0.93 g, 2.84 mmol).

Anal. Chemical Formula: $(C_{23}H_{36}O)_n$ (328.53)_n: Calcd. C, 84.09; H, 11.04; O, 4.87; Found C 82.52, H 9.90. 1H NMR (400 MHz, $CDCl_3$): δ = 0.81–0.95 (m, 6H, $-CH_3$), 1.18–1.46 (m, 18H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$, $-C\equiv C-(CH_2)_2(CH_2)_3CH_3$), 1.48–1.80 (m, 5H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$, $-C\equiv C-CH_2CH_2(CH_2)_3CH_3$), 2.38 (t, 2H, J = 7.2 Hz, $-C\equiv C-CH_2(CH_2)_4CH_3$), 4.21–4.39 (m, 1H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$), 6.65–6.78 (m, 2H, $Ar-H$ meta to $C_6H_{13}-C\equiv C-$), 7.28–7.53 (m, 2H, $Ar-H$ ortho to $C_6H_{13}-C\equiv C-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.6, 22.5, 22.6, 25.5, 28.6, 29.2, 29.5, 29.8, 31.4, 31.8, 36.3, 74.1, 82.1, 88.5, 115.5, 118.1, 132.7, 158.0. HRMS (DART) calcd for $C_{23}H_{36}O$ $[M + H]^+$: 329.2839. Found: 329.2828. $[\alpha]_D^{25}$ -2.95° (c 1.0, $CHCl_3$).

(S)-Monomer 1 ((S)-M1)

(S)-M1 was synthesized in a similar way as **(rac)-M1**. Into a 100 mL three-necked flask were added compound **1** (1.05 g, 5.19 mmol), and TPP (1.25 g, 4.76 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (2.41 g, 40 wt% in toluene, 4.75 mmol), (R)-(-)-2-nonanol (0.62 g, 4.32 mmol), and 30 mL THF was prepared. The reagents were then stirred overnight at room temperature.

The reaction yielded a light yellow oil with a yield of 82% (1.17 g, 3.55 mmol).

Anal. Chemical Formula: $(C_{23}H_{36}O)_n$ (328.53) $_n$: Calcd. C, 84.09; H, 11.04; O, 4.87; Found C 82.91, H 9.97. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.00 (m, 6H, $-CH_3$), 1.20–1.51 (m, 18H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$, $-C\equiv C-(CH_2)_2(CH_2)_3CH_3$), 1.52–1.79 (m, 5H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$, $-C\equiv C-CH_2CH_2(CH_2)_3CH_3$), 2.38 (t, 2H, J = 6.8 Hz, $-C\equiv C-CH_2(CH_2)_4CH_3$), 4.27–4.34 (m, 1H, $Ar-O-CH(CH_3)(CH_2)_6CH_3$), 6.66–6.79 (m, 2H, $Ar-H$ *meta* to $C_6H_{13}-C\equiv C-$), 7.26–7.52 (m, 2H, $Ar-H$ *ortho* to $C_6H_{13}-C\equiv C-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.7, 22.5, 22.6, 25.5, 28.6, 29.2, 29.5, 29.5, 31.4, 31.8, 36.3, 73.9, 82.1, 88.5, 115.5, 118.1, 132.7, 157.5. HRMS (DART) calcd for $C_{23}H_{36}O$ $[M + H]^+$: 329.2839. Found: 329.2824. $[\alpha]_D^{25} +3.00^\circ$ (c 1.0, $CHCl_3$).

(rac)-Monomer 2 ((rac)-M2)

(rac)-M2 was synthesized as follows. Into a 100 mL three-necked flask were added compound **2** (330 mg, 1.70 mmol), and TPP (491 mg, 1.87 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (816 mg, 40 wt% in toluene, 1.87 mmol), 2-nonanol (246 mg, 1.70 mmol), and 20 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The product was recrystallized from ethanol and dried under vacuum to give 0.37 g (1.14 mmol) of **(rac)-M2** as a white crystal. Yield = 67%.

Anal. Chemical Formula: $(C_{23}H_{28}O)_n$ (320.47) $_n$: Calcd. C, 86.20; H, 8.81; O, 4.99; Found C 86.15, H 8.85. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.19–1.50 (m, 13H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 1.52–1.68 (m, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 4.29–4.46 (m, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.84 (d, 2H, J = 8.8 Hz, $Ar-H$ *ortho* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.40–7.47 (m, 3H, $Ar-H$ *meta* and *para* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.49–7.55 (m, 4H, $Ar-H$ *ortho* to $-C\equiv C-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.8, 89.4, 114.8, 115.6, 127.7, 128.1, 131.3, 132.9, 158.2. HRMS (APCI) calcd for $C_{23}H_{28}O$ $[M + H^+]$: 321.2213. Found: 321.2211.

(R)-Monomer 2 ((R)-M2)

(R)-M2 was synthesized in a similar way as **(rac)-M2**. Into a 200 mL three-necked flask were added compound **2** (1.61 g, 8.29 mmol), and TPP (2.39 g, 9.12 mmol) under argon gas and dissolved in THF (60 mL). In the addition funnel, a mixture of DEAD (3.97 g, 40 wt% in toluene, 9.12 mmol), (*S*)-(+)-2-nonanol (1.20 g, 8.29 mmol), and 20 mL THF was prepared. The reagents were then stirred overnight at room temperature. The reaction yielded a white crystal with a yield of 82% (2.17 g, 6.80 mmol).

Anal. Chemical Formula: $(C_{23}H_{28}O)_n$ (320.47) $_n$: Calcd. C, 86.20; H, 8.81; O, 4.99; Found C 86.26, H 8.83. 1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 3H, J = 7.0 Hz, $-CH_3$), 1.29–1.53 (m, 13H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 1.54–1.59 (m, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 4.35–4.37 (m, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.86 (d, 2H, J = 8.6 Hz, $Ar-H$ *ortho* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.24–7.34 (m, 3H, $Ar-H$ *meta* and *para* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.43–7.50 (m, 4H, $Ar-H$ *ortho* to $-C\equiv C-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.5, 29.5, 31.8, 36.4, 73.9, 87.7, 89.6, 115.0, 115.6, 123.7, 127.7, 128.1, 131.3, 132.9, 158.2. HRMS (APCI) calcd

for $C_{23}H_{28}O$ $[M + H^+]$: 321.2213. Found: 321.2213. $[\alpha]_D^{25} +4.73^\circ$ (c 1.0, $CHCl_3$).

(S)-Monomer 2 ((S)-M2)

(S)-M2 was synthesized in a similar way as **(rac)-M2**. Into a 200 mL three-necked flask were added compound **2** (0.65 g, 3.35 mmol), and TPP (0.97 g, 3.68 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (1.88 g, 40 wt% in toluene, 3.68 mmol), (*R*)-(-)-2-nonanol (0.58 g, 4.02 mmol), and 20 mL THF was prepared. The reagents were then stirred overnight at room temperature. The reaction yielded a white crystal with a yield of 72% (0.77 g, 2.41 mmol).

Anal. Chemical Formula: $(C_{23}H_{28}O)_n$ $(320.47)_n$: Calcd. C, 86.20; H, 8.81; O, 4.99; Found C 86.28, H 8.81. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.2 Hz, $-CH_3$), 1.29–1.51 (m, 13H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 1.53–1.57 (m, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 4.35–4.38 (m, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.84 (d, 2H, J = 8.8 Hz, $Ar-H$ *ortho* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.26–7.35 (m, 3H, $Ar-H$ *meta* and *para* to $-O-CH(CH_3)(CH_2)_6CH_3$), 7.43–7.52 (m, 4H, $Ar-H$ *ortho* to $-C\equiv C-$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 31.8, 36.4, 73.9, 89.4, 91.6, 114.8, 115.6, 123.5, 127.7, 128.1, 131.3, 132.9, 156.9. HRMS (APCI) calcd for $C_{23}H_{28}O$ $[M + H^+]$: 321.2213. Found: 321.2213. $[\alpha]_D^{25} -4.95^\circ$ (c 1.0, $CHCl_3$).

(rac)-Monomer 3 ((rac)-M3)

(rac)-M3 was synthesized as follows. Into a 100 mL three-necked flask were added compound **12** (1.10 g, 3.27 mmol), and TPP (0.94 g, 3.60 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (1.82 g, 40 wt% in toluene, 3.60 mmol), 2-nonanol (0.61 g, 4.25 mmol), and 30 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the

solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The product was evaporated and dried under vacuum to give compound (*rac*)-**M3** (0.95 g, 2.06 mmol) as a yellow oil. Yield = 63%. Anal. Chemical Formula: $(\text{C}_{32}\text{H}_{46}\text{O}_2)_n$ (462.71) $_n$: Calcd. C, 83.06; H, 10.02; O, 6.92; Found C 82.30, H 10.38. ^1H NMR (400 MHz, CDCl_3): δ = 0.83–0.94 (m, 6H, $-\text{CH}_3$), 1.22–1.48 (m, 26H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.51–1.79 (m, 4H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 4.32–4.41 (m, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 6.79–6.87 (d, 4H, J = 8.8 Hz, $\text{Ar}-\text{H}$ *ortho* to $-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 7.37–7.45 (d, 4H, J = 8.4 Hz, $\text{Ar}-\text{H}$ *meta* to $-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.8, 87.8, 115.3, 115.6, 132.7, 157.9. HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{46}\text{O}_2$ [$\text{M} + \text{H}^+$]: 463.3571. Found: 463.3570.

(*R*)-Monomer 3 ((*R*)-**M3**)

(*R*)-**M3** was synthesized in a similar way as (*rac*)-**M3**. Into a 100 mL three-necked flask were added compound **13** (1.30 g, 3.86 mmol), and TPP (1.11 g, 4.25 mmol) under argon gas and dissolved in THF (30 mL). In the addition funnel, a mixture of DEAD (2.15 g, 40 wt% in toluene, 4.25 mmol), (*S*)-(+)-2-nonanol (0.72 g, 5.02 mmol), and 30 mL THF was prepared. The reagents were then stirred overnight at room temperature. The product was evaporated and dried under vacuum to give compound (*R*)-**M3** (1.25 g, 2.69 mmol) as a yellow oil. Yield = 70%.

Anal. Chemical Formula: $(\text{C}_{32}\text{H}_{46}\text{O}_2)_n$ (462.71) $_n$: Calcd. C, 83.06; H, 10.02; O, 6.92; Found C 81.83, H 9.78. ^1H NMR (400 MHz, CDCl_3): δ = 0.81–0.92 (m, 6H, $-\text{CH}_3$),

1.19–1.48 (m, 26H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 1.50–1.79 (m, 4H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.31–4.41 (m, 2H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 6.79–6.87 (d, 4H, *J* = 8.8 Hz, Ar–H *ortho* to –O–CH(CH₃)(CH₂)₆CH₃), 7.38–7.46 (d, 4H, *J* = 8.0 Hz, Ar–H *meta* to –O–CH(CH₃)(CH₂)₆CH₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.8, 115.3, 115.6, 132.7, 157.9. HRMS (APCI) calcd for C₃₂H₄₆O₂ [M + H⁺]: 463.3571. Found: 463.3571. [α]_D²⁵ +7.87° (*c* 1.0, CHCl₃).

(*S*)-Monomer 3 ((*S*)-M3)

(*S*)-M3 was synthesized in a similar way as (*rac*)-M3. Into a 100 mL three-necked flask were added compound **14** (488 mg, 1.33 mmol), and TPP (384 g, 1.46 mmol) under argon gas and dissolved in THF (20 mL). In the addition funnel, a mixture of DEAD (637 mg, 40 wt% in toluene, 1.46 mmol), (*R*)-(-)-2-nonanol (192 mg, 1.33 mmol), and 20 mL THF was prepared. The reagents were then stirred overnight at room temperature. The product was evaporated and dried under vacuum to give compound (*S*)-M3 (0.38 g, 0.81 mmol) as a yellow oil. Yield = 61%.

Anal. Chemical Formula: (C₃₂H₄₆O₂)_{*n*} (462.71)_{*n*}: Calcd. C, 83.06; H, 10.02; O, 6.92; Found C 82.16, H 10.52. ¹H NMR (400 MHz, CDCl₃): δ = 0.81–0.96 (m, 6H, –CH₃), 1.19–1.50 (m, 26H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 1.52–1.79 (m, 4H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 4.25–4.45 (m, 2H, Ar–O–CH(CH₃)CH₂(CH₂)₅CH₃), 6.77–6.96 (d, 4H, *J* = 8.8 Hz, Ar–H *ortho* to –O–CH(CH₃)(CH₂)₆CH₃), 7.36–7.48 (d, 4H, *J* = 8.8 Hz, Ar–H *meta* to –O–CH(CH₃)(CH₂)₆CH₃). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 29.6, 31.8, 36.4, 73.9, 87.8, 115.3, 115.6, 132.7, 157.9. HRMS (APCI) calcd for C₃₂H₄₆O₂ [M + H⁺]: 463.3571. Found: 463.3571. [α]_D²⁵ –7.26° (*c* 1.0, CHCl₃).

(rac)-PA1

(rac)-PA1 was synthesized as follows. Toluene (1.0 mL), WCl_6 (17.1 mg, 0.04 mmol) and $n\text{-Ph}_4\text{Sn}$ (36.8 mg, 0.08 mmol) were added under argon into a Schlenk flask. The catalyst mixture was stirred at 80 °C for 30 min, and then **(rac)-M1** (0.28 g, 0.86 mmol) was dissolved in 1 mL toluene and was then added to the reaction mixture. The reaction mixture was stirred at 80 °C for 24 h. The mixture was cooled to room temperature and was added dropwise to 800 mL of methanol under stirring. The polymer precipitate was stirred for 24 h, which was then filtered and dried in vacuo. A yellowish solid was obtained with a yield of 8.6% (23.3 mg, 0.08 mmol). M_w , 48,300 M_w/M_n , 2.1 (GPC, PS calibration).

Anal. Chemical Formula: $(\text{C}_{23}\text{H}_{28}\text{O})_n$ (328.53) $_n$: Calcd. C, 84.09; H, 11.04; O, 4.87; Found C 81.23, H 10.34. ^1H NMR (400 MHz, CDCl_3): δ = 0.50–0.95 (br, 6H, $-\text{CH}_3$), 0.97–1.84 (br, 25H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$, $-\text{C}\equiv\text{C}-(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$, $-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$, $-\text{C}\equiv\text{C}-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 3.81–4.49 (br, 1H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 7.21–7.39 (br, 4H, Ar-H). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.0, 19.1, 21.5, 22.6, 23.9, 29.3, 30.7, 31.8, 73.0, 80.0, 100.5, 114.0, 133.2, 155.1.

(R)-PA1

(R)-PA1 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(R)-M1** (0.35 g, 1.06 mmol) yielded a yellowish solid with a yield of 41% (0.15 g, 0.44 mmol). M_w , 26,700 M_w/M_n , 1.7 (GPC, PS calibration).

Anal. Chemical Formula: $(\text{C}_{23}\text{H}_{28}\text{O})_n$ (328.53) $_n$: Calcd. C, 84.09; H, 11.04; O, 4.87; Found C 83.33, H 11.65. ^1H NMR (400 MHz, CDCl_3): δ = 0.55–0.98 (br, 6H, $-\text{CH}_3$), 1.00–1.81 (br, 25H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$, $-\text{C}\equiv\text{C}-(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$,

Ar-O-CH(CH₃)(CH₂)₆CH₃, -C≡C-CH₂CH₂(CH₂)₃CH₃, -C≡C-CH₂(CH₂)₄CH₃,
 3.80–4.47 (br, 1H, Ar-O-CH(CH₃)(CH₂)₆CH₃), 7.19–7.31 (br, 4H, Ar-H). ¹³C NMR
 (100 Mhz, CDCl₃): δ = 14.0, 19.6, 22.1, 22.6, 23.1, 29.3, 29.7, 32.0, 71.2, 80.7, 102.7,
 114.1, 134.5, 157.3. [α]_D²⁵ -241° (c 1.0, CHCl₃).

(S)-PA1

(S)-PA1 was synthesized in a similar way as (rac)-PA1. Polymerization of (S)-M1
 (0.35 g, 1.06 mmol) yielded a yellowish solid with a yield of 5.9% (20.8 mg, 0.06
 mmol). *M*_w. 44,400 *M*_w/*M*_n. 1.7 (GPC, PS calibration).

Anal. Chemical Formula: (C₂₃H₂₈O)_n (328.53)_n: Calcd. C, 84.09; H, 11.04; O, 4.87;
 Found C 79.09, H 11.24. ¹H NMR (400 MHz, CDCl₃): δ = 0.55–0.99 (br, 6H, -CH₃),
 1.10–1.85 (br, 25H, Ar-O-CH(CH₃)(CH₂)₆CH₃, -C≡C-(CH₂)₂(CH₂)₃CH₃,
 Ar-O-CH(CH₃)(CH₂)₆CH₃, -C≡C-CH₂CH₂(CH₂)₃CH₃, -C≡C-CH₂(CH₂)₄CH₃),
 3.79–4.51 (br, 1H, Ar-O-CH(CH₃)(CH₂)₆CH₃), 7.15–7.32 (br, 4H, Ar-H). ¹³C NMR
 (100 Mhz, CDCl₃): δ = 14.1, 18.5, 22.3, 22.5, 23.2, 29.1, 30.2, 31.8, 73.6, 82.4, 101.3,
 113.7, 130.7, 157.7. [α]_D²⁵ +247° (c 1.0, CHCl₃).

(rac)-PA2

(rac)-PA2 was synthesized in a similar way as (rac)-PA1. Polymerization of
 (rac)-M2 (0.28 g, 0.86 mmol) yielded a greenish powder with a yield of 45% (0.12 g,
 0.39 mmol). *M*_w. 22,000 *M*_w/*M*_n. 2.4 (GPC, PS calibration).

Anal. Chemical Formula: (C₂₃H₂₈O)_n (320.47)_n: Calcd. C, 86.20; H, 8.81; O, 4.99;
 Found C 83.96, H 8.65. ¹H NMR (400 MHz, CDCl₃): δ = 0.81–0.95 (br, 3H, -CH₃),
 1.20–1.61 (br, 15H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃, and
 Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃), 3.96–4.21 (br, 1H, Ar-O-CH(CH₃)CH₂(CH₂)₅CH₃),
 6.91–7.61 (br, 9H, Ar-H). ¹³C NMR (100 Mhz, CDCl₃): δ = 14.1, 19.5, 23.5, 25.4, 31.0,

33.7, 85.5, 114.9, 122.5, 124.7, 131.5, 151.6.

(R)-PA2

(R)-PA2 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(R)-M2** (0.30 g, 0.9 mmol) yielded a greenish powder with a yield of 6% (16.7 mg, 0.06 mmol). M_w . 23,000 M_w/M_n . 2.1 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{23}H_{28}O)_n$ (320.47) $_n$: Calcd. C, 86.20; H, 8.81; O, 4.99; Found C 81.56, H 9.57. 1H NMR (400 MHz, $CDCl_3$): δ = 0.80–1.00 (br, 3H, $-CH_3$), 1.05–1.80 (br, 15H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$, and $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 3.95–4.18 (br, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.92–7.52 (br, 9H, $Ar-H$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.6, 22.7, 25.4, 29.5, 32.0, 85.1, 114.9, 122.6, 124.7, 139.8, 156.6. $[\alpha]^{25}_D +229^\circ$ (c 1.0, $CHCl_3$).

(S)-PA2

(S)-PA2 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(S)-M2** (0.30 g, 0.94 mmol) yielded a greenish powder with a yield of 80% (0.24 g, 0.75 mmol). M_w . 25,000 M_w/M_n . 2.3 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{23}H_{28}O)_n$ (320.47) $_n$: Calcd. C, 86.20; H, 8.81; O, 4.99; Found C 83.00, H 8.87. 1H NMR (400 MHz, $CDCl_3$): δ = 0.82–0.98 (br, 3H, $-CH_3$), 1.03–1.78 (br, 15H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$, and $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 3.90–4.15 (br, 1H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 6.95–7.50 (br, 9H, $Ar-H$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 19.6, 22.7, 25.4, 29.5, 83.1, 114.2, 122.0, 139.8, 152.8. $[\alpha]^{25}_D -226^\circ$ (c 1.0, $CHCl_3$).

(rac)-PA3

(rac)-PA3 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(rac)-M3** (0.30 g, 0.65 mmol) yielded a greenish powder with a yield of 7% (21.7 mg,

0.05 mmol). M_w . 13,400 M_w/M_n . 2.0 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{32}H_{46}O_2)_n$ (462.71) $_n$: Calcd. C, 83.06; H, 10.02; O, 6.92; Found C 79.40, H 8.91. 1H NMR (400 MHz, $CDCl_3$): δ = 0.72–0.96 (br, 6H, $-CH_3$), 0.98–1.80 (br, 30H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 3.95–4.20 (br, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 5.90–6.20 (br, 4H, $Ar-H$ *ortho* to $-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 7.08–7.40 (br, 4H, $Ar-H$ *meta* to $-O-CH(CH_3)CH_2(CH_2)_5CH_3$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 20.4, 22.5, 27.3, 30.0, 32.2, 36.1, 74.3, 87.4, 123.4, 132.3, 157.8.

(R)-PA3

(R)-PA3 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(R)-M3** (0.30 g, 0.65 mmol) yielded a greenish powder with a yield of 11% (32.6 mg, 0.07 mmol). M_w . 12,700 M_w/M_n . 2.8 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{32}H_{46}O_2)_n$ (462.71) $_n$: Calcd. C, 83.06; H, 10.02; O, 6.92; Found C 78.17, H 9.58. 1H NMR (400 MHz, $CDCl_3$): δ = 0.79–0.98 (br, 6H, $-CH_3$), 0.99–1.71 (br, 30H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 4.00–4.20 (br, 2H, $Ar-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 5.91–6.22 (br, 4H, $Ar-H$ *ortho* to $-O-CH(CH_3)CH_2(CH_2)_5CH_3$), 7.18–7.40 (br, 4H, $Ar-H$ *meta* to $-O-CH(CH_3)CH_2(CH_2)_5CH_3$). ^{13}C NMR (100 Mhz, $CDCl_3$): δ = 14.1, 20.7, 22.7, 27.4, 29.9, 31.1, 36.2, 74.9, 85.4, 122.4, 131.4, 158.1. $[\alpha]_D^{25} +2080^\circ$ (c 1.0, $CHCl_3$).

(S)-PA3

(S)-PA3 was synthesized in a similar way as **(rac)-PA1**. Polymerization of **(S)-M3** (0.30 g, 0.65 mmol) yielded a greenish powder with a yield of 30% (90.1 mg, 0.19 mmol). M_w . 14,000 M_w/M_n . 2.3 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{32}H_{46}O_2)_n$ (462.71) $_n$: Calcd. C, 83.06; H, 10.02; O, 6.92;

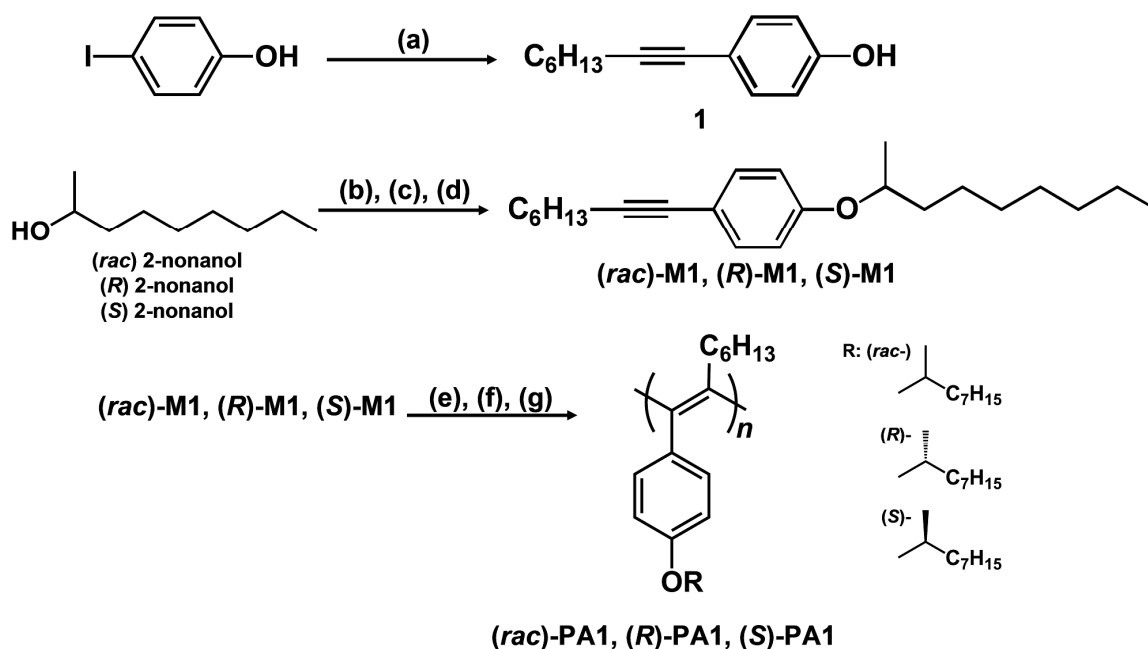
Found C 82.91, H 10.58. ^1H NMR (400 MHz, CDCl_3): δ = 0.75–0.98 (br, 6H, $-\text{CH}_3$), 1.00–1.69 (br, 30H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 3.96–4.19 (br, 2H, $\text{Ar}-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 5.94–6.22 (br, 4H, Ar-H *ortho* to $-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 7.19–7.38 (br, 4H, Ar-H *meta* to $-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2(\text{CH}_2)_5\text{CH}_3$). ^{13}C NMR (100 Mhz, CDCl_3): δ = 14.1, 21.4, 22.7, 27.7, 29.3, 32.0, 36.5, 74.1, 82.2, 119.4, 131.4, 157.9. $[\alpha]_D^{25} -2158^\circ$ (*c* 1.0, CHCl_3).

2. Liquid Crystallinity of PA1 Polymers

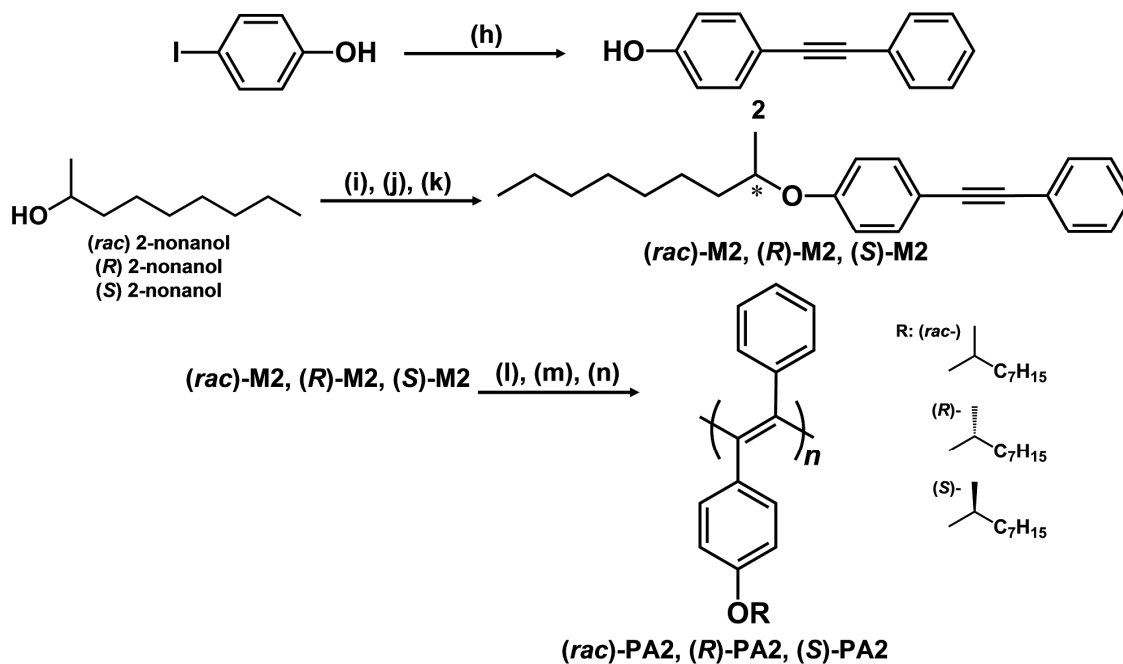
PA1, having a PAPA structure, exhibited thermotropic LC behavior having a Smectic A (S_A) LC phase. Polarizing optical microscopy (POM) analysis revealed that **PA1** has a nematic LC (N-LC) phase with a sandy LC texture (Figure S1a) and no isotropic phase. The temperature ranges of the N-LC phase were 95–300 and 65–300 $^\circ\text{C}$ in heating and cooling processes, respectively, and thermal decomposition occurred at temperatures over 300 $^\circ\text{C}$.

The LC phase of **PA1** was also investigated using X-ray diffraction (XRD). The XRD patterns of **PA1** have two sharp diffraction peaks at 5.5 and 17.9 $^\circ$ in 2θ (Figure S1b), corresponding to distances of 16.0 and 5.0 $\text{\AA}$, respectively. The former represents the smectic interlayer distance while the latter corresponds to the distance between phenyl nonyloxy groups. The 16.0 $\text{\AA}$ smectic interlayer distance is comparable to the 14.5 $\text{\AA}$ calculated side chain length (L_1) of the side chain having the 4-nonyloxy phenyl moiety. Whereas the side chain with the hexyl moiety has a calculated side chain length (L_2) of 6.9 $\text{\AA}$. The lengths of the **PA1** side chains were calculated using molecular mechanics calculations

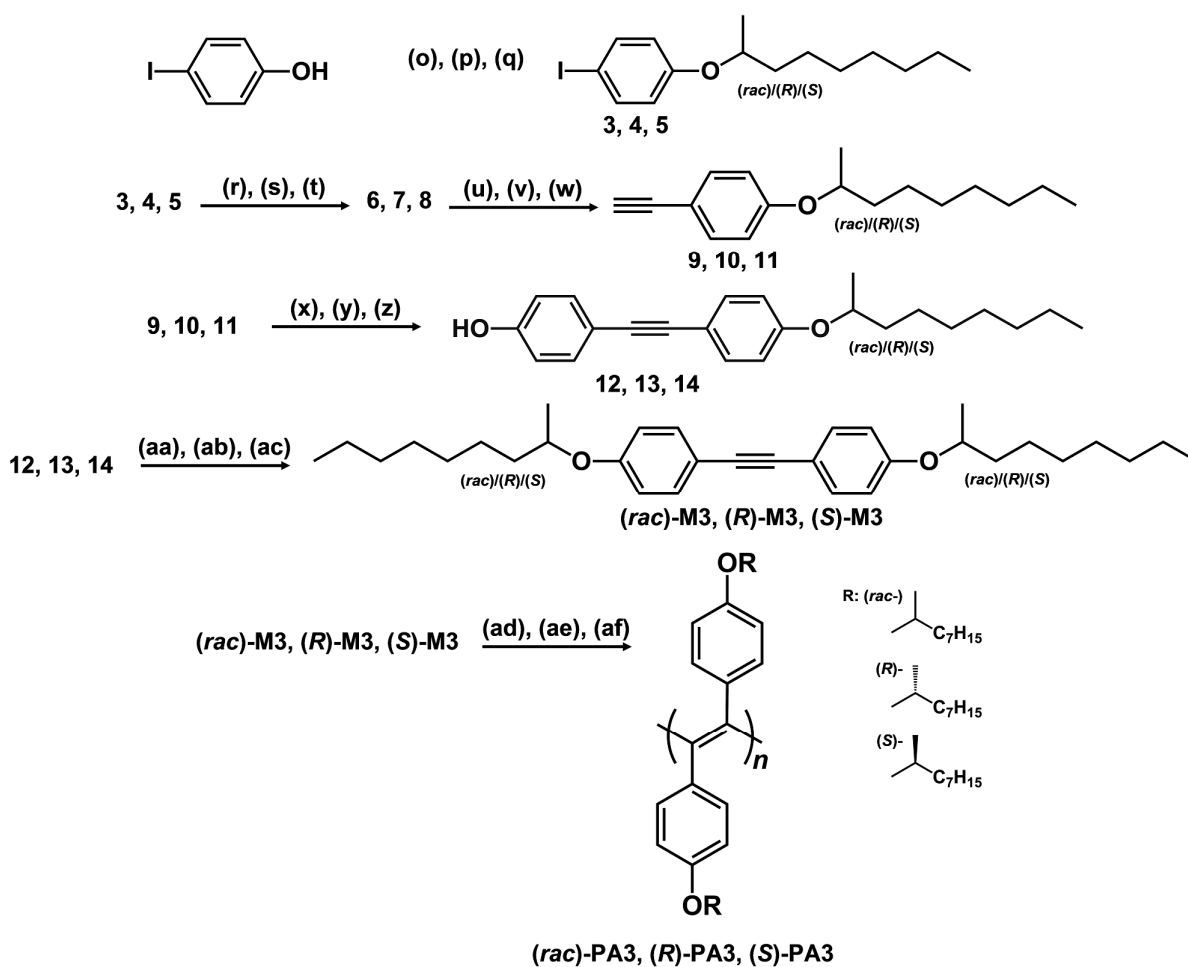
3. Supporting Figures

Scheme S1. Synthetic routes of polymers.^a

^aConditions: **PA1**: (a) 1-octyne, PdCl₂(TPP)₂, CuI, NH₃ (aq.), THF, r.t., 24 h; 70% for **1**; (b,c,d) **1**, (*rac*)/(*S*)/(*R*)-2-nonanol, DEAD, TPP, THF, r.t., 24 h; 50% for (*rac*)-**M1**, 66% for (*R*)-**M1**, 82% for (*S*)-**M1**; (e,f,g) (*rac*)-**M1**, (*R*)-**M1**, (*S*)-**M1**, WCl₆, Ph₄Sn, toluene, 80 °C, 24 h; 8% for (*rac*)-**PA1**, 41% for (*R*)-**PA1**, 6% for (*S*)-**PA1**.



PA2: (h) phenyl acetylene, $\text{PdCl}_2(\text{TPP})_2$, CuI , Et_3N , THF, 65°C , 24 h; 66% for **2**; (i,j,k) **2**, (rac)/(S)/(R)-2-nonanol, DEAD, TPP, THF, r.t., 24 h; 67% for **(rac)-M2**, 82% for **(R)-M2**, 72% for **(S)-M2**; (e,f,g) **(rac)-M2**, **(R)-M2**, **(S)-M2**, WCl_6 , Ph_4Sn , toluene, 80°C , 24 h; 45% for **(rac)-PA2**, 6% for **(R)-PA2**, 80% for **(S)-PA2**.



PA3: (o,p,q) 4-iodophenol, (rac)/(S)/(R)-2-nonanol, DEAD, TPP, THF, r.t., 24 h; 77% for **3**, 68% for **4**, 78% for **5**; (r,s,t) **3**, **4**, **5**, $\text{PdCl}_2(\text{TPP})_2$, CuI, Et_3N , THF, 65 °C, 24 h; 90% for **6**, 88% for **7**, 91% for **8**; (u,v,w) **6**, **7**, **8**, K_2CO_3 , MeOH, THF, r.t., 24 h; 92% for **9**, 92% for **10**, 87% for **11**; (x,y,z) **9**, **10**, **11**, $\text{PdCl}_2(\text{TPP})_2$, CuI, Et_3N , THF, 65 °C, 24 h; 73% for **12**, 63% for **13**, 88% for **14**; (aa,ab,ac) **12**, **13**, **14**, (rac)/(S)/(R)-2-nonanol, DEAD, TPP, THF, r.t., 24 h; 63% for (rac)-**M3**, 70% for (R)-**M3**, 61% for (S)-**M3**; (ad,ae,af) (rac)-**M3**, (R)-**M3**, (S)-**M3**, WCl_6 , Ph_4Sn , toluene, 80 °C, 24 h; 7% for (rac)-**PA3**, 11% for (R)-**PA3**, 30% for (S)-**PA3**.

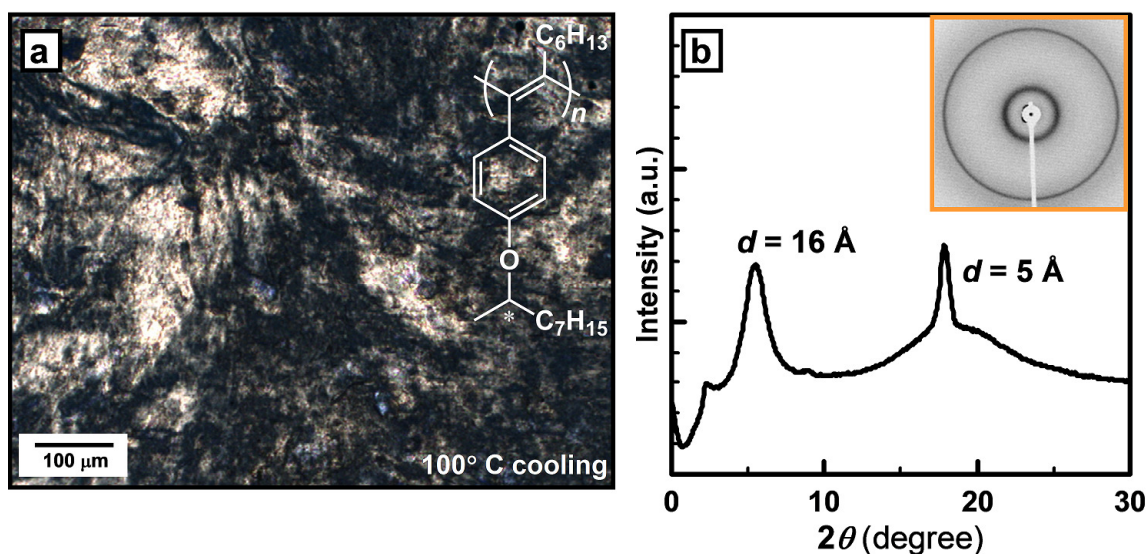


Figure S1. (a) POM image of (*R*)-PA1 at 100 °C in cooling process. (b) XRD patterns showing the Smectic A (S_A) LC phase of (*R*)-PA1 (5.5° and 17.9° in 2θ), inset shows the Laue pattern of the polymer.

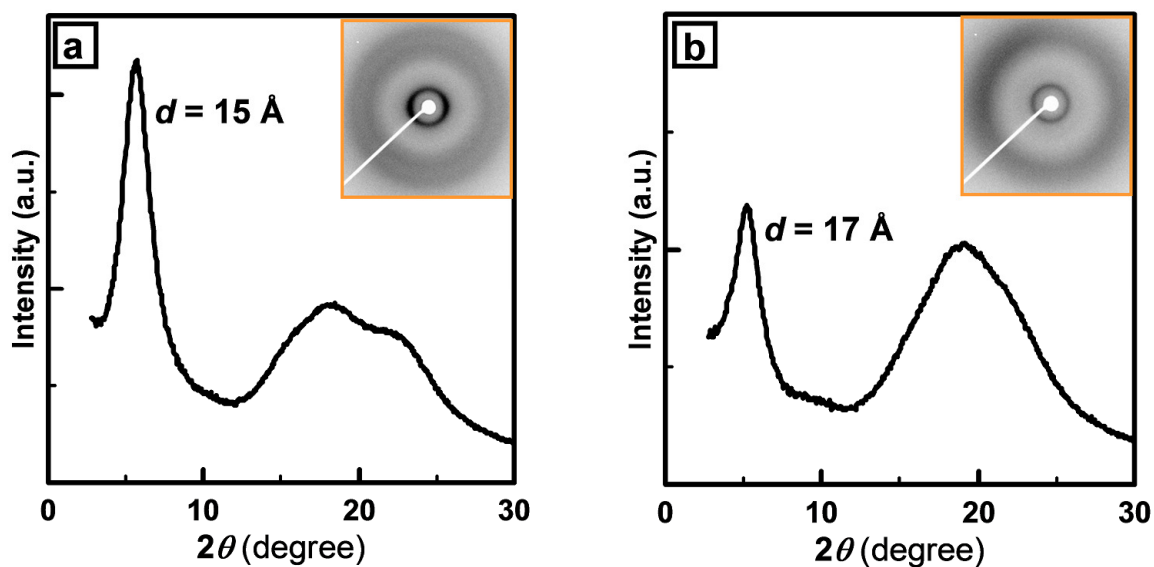


Figure S2. The XRD patterns of (a) (*rac*)-PA2 N-LC film, and (b) (*S*)-D1/(*rac*)-PA2 N*-LC film show reflections describing the polymer interchain distance within the N-LC (5.7° in 2θ) and N*-LC (5.2° in 2θ) domains, respectively. Inset shows the Laue pattern of the polymers.

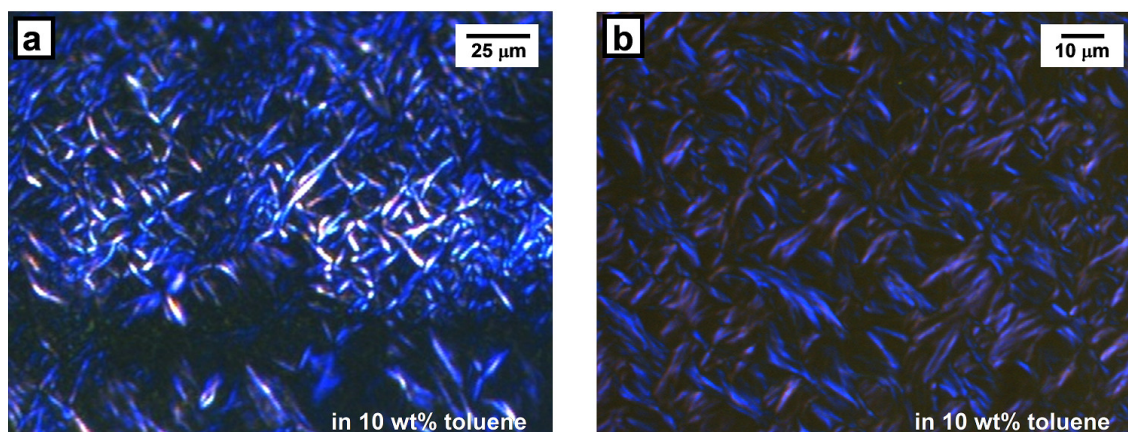


Figure S3. POM image of (a) **(S)-PA3**, and (b) **(S)-D1** doped **(rac)-PA3** (10 wt%) in 10 wt% lyotropic LC solution in toluene showing a fan like texture of a short pitch N*-LC phase.

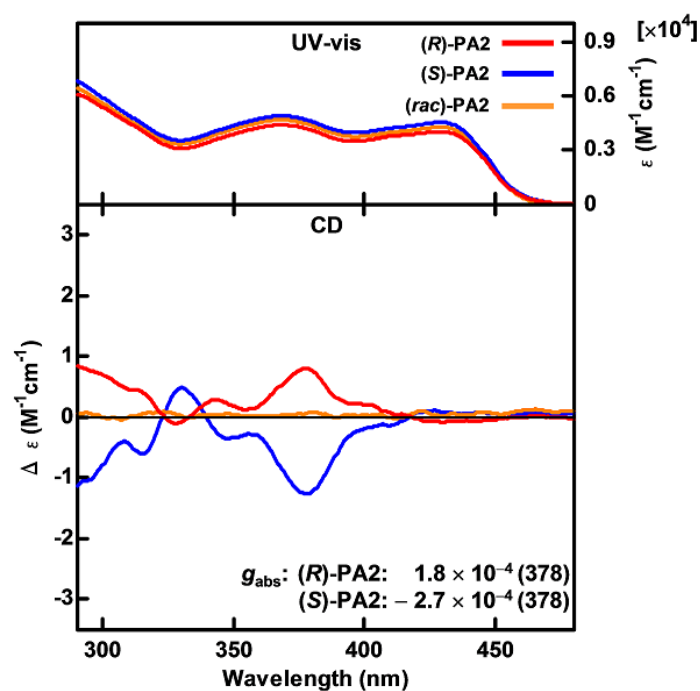


Figure S4. UV-vis (upper) and CD spectra (lower) of **PA2** in toluene solution ($c = 1.2 \times 10^{-4}$ M).

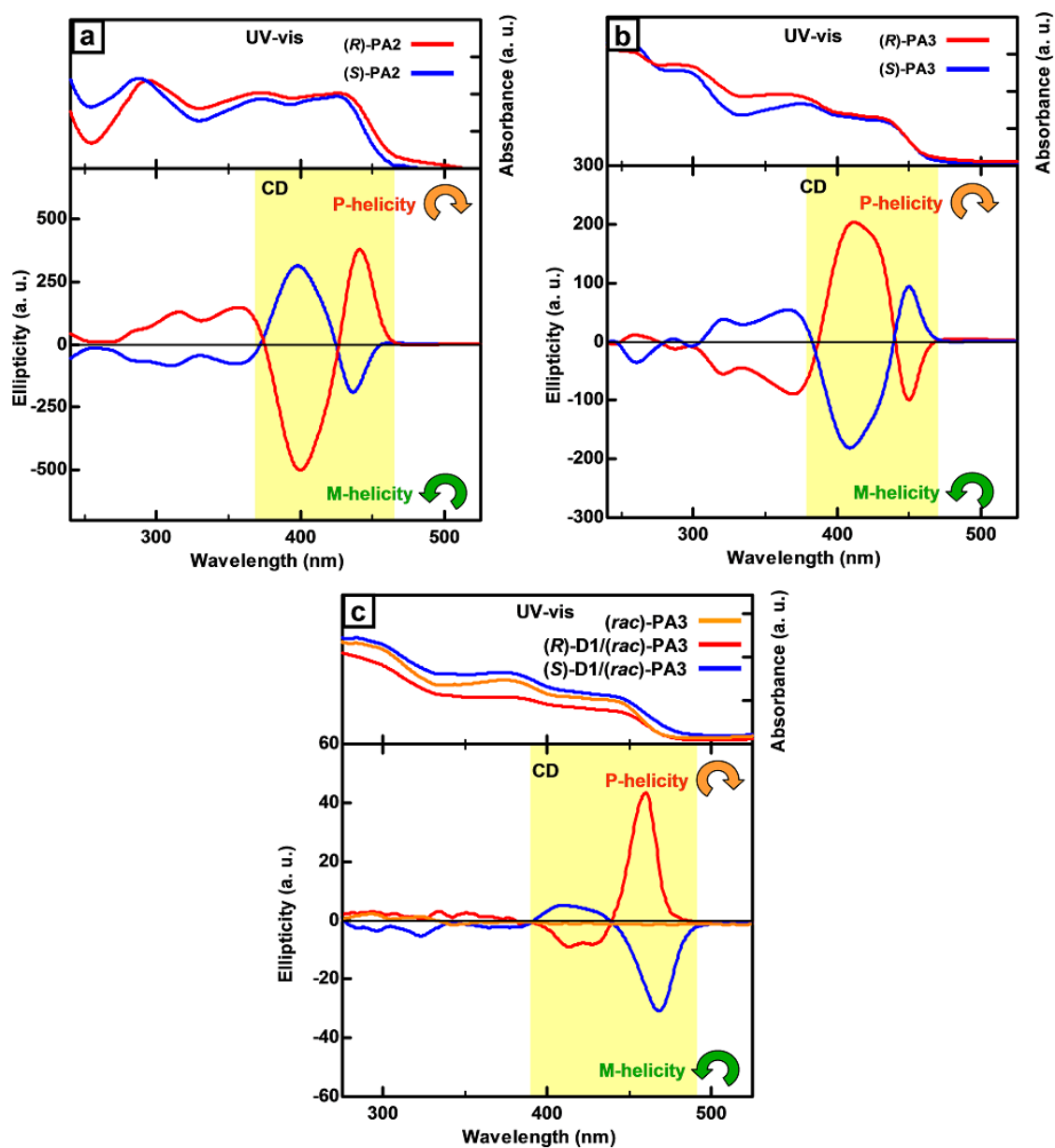


Figure S5. UV-vis (upper) and CD spectra (lower) of (a) (R)-/(S)-PA2 cast film, (b) (R)-/(S)-PA3 cast film, and (c) (R)-/(S)-D1 doped (rac)-PA3 (10 wt%) N*-LC film.

Table S1. Absorption dissymmetry factors (g_{abs}) of the *di*-substituted LCPAs in cast film and N*-LC film.

	$g_{\text{abs}}(\text{wavelength/ nm})^a$
(<i>R</i>)-PA2	$3.7 \times 10^{-2} (445)^b$
(<i>S</i>)-PA2	$-2.4 \times 10^{-2} (440)^b$
(<i>R</i>)-PA3	$-4.6 \times 10^{-3} (450)^b$
(<i>S</i>)-PA3	$7.6 \times 10^{-3} (451)^b$
(<i>R</i>)-D1/(<i>rac</i>)-PA3	$8.0 \times 10^{-4} (461)^c$
(<i>S</i>)-D1/(<i>rac</i>)-PA3	$-2.1 \times 10^{-3} (471)^c$

^aWavelength at which g_{abs} was evaluated

^bIn cast film, ^cin N*-LC film

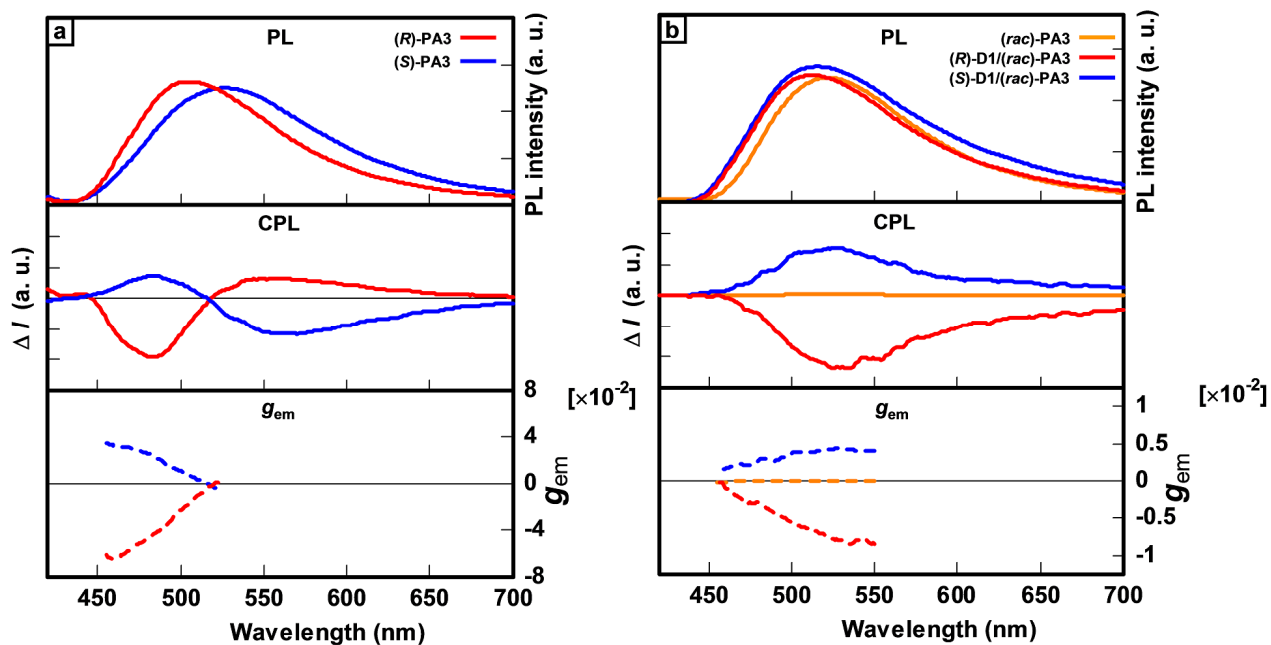


Figure S6. PL (upper), CPL spectra (middle), and g_{em} (lower) spectra of (a) (*R*)-/(*S*)-PA3 N*-LC film, and (b) (*R*)-/(*S*)-D1 doped (*rac*)-PA3 (10 wt%) N*-LC film.

The measurements were performed with excitation using unpolarized light at 367 nm.

Table S2. Emission dissymmetry factors (g_{em}) of the *di*-substituted LCPAs in N*-LC films.

	$g_{\text{em}}(\text{wavelength/ nm})^a$
(R)-PA3	-6.4×10^{-2} (458)
(S)-PA3	3.5×10^{-2} (456)
(R)-D1/(rac)-PA3	-8.4×10^{-3} (535)
(S)-D1/(rac)-PA3	4.2×10^{-3} (535)

^aWavelength at which g_{em} was evaluated

REFERENCES

- (1) (a) M. Grell, D. D. C. Bradley, *Adv. Mater.* **1999**, *11*, 895–905. (b) M. Schadt, *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379. (c) Emeis, C. A.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1967**, *1* (4), 129–132. (d) Dyreklev, P.; Berggren, M.; Inganäs, O.; Andersson, M. R.; Wennerström, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43–45. (e) Liu, J.; Su, H.; Meng, L.; Zhao, Y.; Deng, C.; Ng, J. C. Y.; Lu, P.; Faisal, M.; Lam, J. W. Y.; Huang, X.; Wu, H.; Wong, K. S.; Tang, B. Z. *Chem. Sci.* **2012**, *3*, 2737–2747.
- (2) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119* (41), 9909–9910.
- (3) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118* (20), 4908–4909.
- (4) Oda, M.; Nothofer, H. G.; Lieser, Scherf, U.; Meskers, S. C. J.; Neher, D. *Adv. Mater.* **2000**, *12*, 362–365.
- (5) (a) Chen, S. H.; Conger, B. M.; Mastrangelo, J. C.; Kende, A. S.; Kim, D. U. *Macromolecules* **1998**, *31*, 8051–8057. (b) Wilson, J.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830–6831. (c) Oda, M.; Nothofer, H. G.; Scherf, U.; Sunjic, V.; Richter, D.; Regenstein, W.; Neher, D. *Macromolecules* **2002**, *35*, 6792–6798. (d) Satrijo, A.; Meskers, S. C. J.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 9030–9031. (e) Watanabe, K.; Osaka, I.; Yorozuya, S.; Akagi, K. *Chem. Mater.* **2012**, *24*, 1011–1024. (f) Watanabe, K.; Iida, H.; Akagi, K. *Adv. Mater.* **2012**, *24*, 6451–6456.
- (6) (a) Goto, H. *Macromolecules* **2007**, *40*, 1377–1385. (b) Haraguchi, S.; Numata, M.; Li, C.; Nakano, Y.; Fujiki, M.; Shinkai, S. *Chem. Lett.* **2009**, *38* (3), 254–255.
- (7) Thermotropic LCs exhibit phase transitions as a function of temperature, while

lyotropic LCs exhibit phase transitions as a function of concentration of the LC molecules in a solvent. The nematic LC (N-LC) has a mesophase where the LC molecules have no positional ordering but align along one direction. The N*-LC has an orientation ordering similar to the N-LC, but the director of each domain rotates along a helical axis resulting in a right-handed (clockwise) or left-handed (counter-clockwise) screw structure.

- (8) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P.; Wendorff, J. H. *Adv. Mater.* **2003**, *15*, 282–287.
- (9) Pollmann, P.; Mainusch, K. J.; Stegemeyer, H. Z. *Phys. Chem. (Leipzig)* **1976**, *103*, 295–309.
- (10) (a) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506–508. (b) Grell, M.; Oda, M.; Whitehead, K. S.; Asimakis, A.; Neher, D.; Bradley, D. D. C. *Adv. Mater.* **2001**, *13*, 577–580.
- (11) Il'chishin, I. P.; Tikhonov, E. A.; Tishchenko, V. G.; Shpak, M. T. *JETP Lett.* **1981**, *32*, 24–27.
- (12) Furumi, S. *Chem. Rec.* **2010**, *10*, 394–408.
- (13) (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683–1686. (b) Akagi, K.; Piao, G.; Kaneko, S.; Higuchi, I.; Shirakawa, H.; Kyotani, M. *Synth. Met.* **1999**, *102*, 1406–1409. (c) Akagi, K.; Guo, S.; Mori, T.; Goh, M.; Piao, G.; Kyotani, M. *J. Am. Chem. Soc.* **2005**, *127*, 14647–14654. (d) Akagi, K. *Polym. Int.* **2007**, *56*, 1192–1199.
- (14) Iida, H.; Nakamura, A.; Inoue, Y.; Akagi, K. *Synth. Met.* **2003**, *135*, 91–92.
- (15) (a) Green, M. M.; Park, J. W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138–3154. (b) Siekmeyer, M.;

- Steinmeier, H.; Zugenmaier, P. *Makromol. Chem.* **1989**, *190*, 1037–1045. (c) Robinson, C.; Ward, J. C. *Nature* **1957**, *180*, 1183–1184. (d) Tsujita, Y.; Yamanaka, I.; Takizawa, A. *Polymer J.* **1979**, *11*, 749–754. (e) Livolant, F.; Bouligand, Y. *J. Phys.* **1986**, *47*, 1813–1827. (f) Bawden, F. C.; Pirie, N. W.; Bernal, J. D.; Fankuchen, I. *Nature* **1936**, *138*, 1051–1052. (g) Dogic, Z.; Fraden, S. *Phys. Rev. Lett.* **1997**, *78*, 2417–2420.
- (16) (a) Lam, J. W. Y.; Tang, B. Z. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 2607–2629. (b) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799–5867.
- (17) (a) Kwak, G.; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Chem. Mater.* **2007**, *19*, 3654–3661. (b) Kwak, G.; Minakuchi, M.; Sakaguchi, T.; Masuda, T.; Fujiki, M. *Macromolecules* **2008**, *41*, 2743–2746. (c) Tsuchihara, K.; Fukushima, T. *Macromolecules* **2009**, *42*, 5453–5460. (d) Lee, D.; Kim, H.; Suzuki, N.; Fujiki, M.; Lee, C.-L.; Lee, W.-E.; Kwak, G. *Chem. Commun.* **2012**, *48*, 9275–9277.
- (18) San Jose, B. A.; Matsushita, S.; Moroishi, Y.; Akagi, K. *Macromolecules* **2011**, *44*, 6288–6302.
- (19) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470. (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46–49. (c) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380–2382. (d) Williamson, A. W. *J. Chem. Soc.* **1852**, *4*, 229–239.
- (20) *Textures of Liquid Crystals*; Dierking, I.; Wiley-VCH: Weinheim, 2003.
- (21) The length of the **PA2** nonyloxy phenyl side chain was calculated using molecular mechanics calculations. The side chain with the nonyloxy phenyl moiety has a length (L_1) computed as 15 Å. The XRD peak distance of 15 Å observed in the (*S*)-**PA2** N*-LC film can be assigned as the average polymer interchain distance approximate to that of the side chain length, $d \sim L_1$, within the N*-LC domain. XRD analysis on the N-LC film

of **(rac)-PA2** and N*-LC film of **(S)-D1/(rac)-PA2** showed similar XRD profiles (Figure S2), which suggest that the measured distances of 15–17 Å can be correlated to the polymer interchain distance—regardless of the LC phase. The observed XRD patterns are similar to the XRD profiles of other reports of PDPA showing lyotropic liquid crystallinity.^{17a,b}

(22) It was observed that the N*-LC phase of **(S)-PA2** and **(S)-D1/(rac)-PA2**, have different helical half-pitches of 1.5 and 2.0 μm , respectively (Figure 1a,2b). This shows that the N*-LC phase of **(S)-PA2** has a more twisted helical ordering on a microscopic level, given the same lyotropic LC concentration. This difference can be attributed to the type of the chiral dopant used. In the N*-LC phase of **(S)-PA2**, the chiral dopant is the chiral nonyloxy moiety with an asymmetric type chirality. On the other hand, for the N*-LC phase of **(S)-D1/(rac)-PA2** the chiral dopant **(S)-D1** has an axial type chirality. In the N*-LC phase of **(S)-D1/(rac)-PA2**, the chiral dopant is in between the nematic LC layers where it directs the layers into a helical arrangement.

(23) (a) Shukla, A.; Mazumdar, S. *Phy. Rev. Lett.* **1999**, *19*, 3944–3947. (b) Hidayat, R.; Fujii, A.; Ozaki, M.; Teraguchi, M.; Masuda, T.; Yoshino, K. *Synth. Met.* **2001**, *119*, 597–598. (c) Shukla, A.; Ghosh, H.; Mazumdar, S. *Synth. Met.* **2001**, *116*, 87–90. (d) Ghosh, H.; Shukla, A.; Mazumdar, S. *Phys. Rev. B.* **2000**, *19*, 12763–12774. (e) Vardeny, Z. V., Korovyanko, O. In *Handbook of Conducting Polymers, Conjugated Polymers*, 3rd ed.; Skotheim, T. A.; Reynolds, J. R.; Eds. CRC press: New York, **2007**; pp. 22-1–22-74.

(24) For the preparation of **D1**-doped **(rac)-PA2** and **(rac)-PA3** N*-LC films, the **(R)-/(S)-D1** chiral dopant at 10 wt%, was added to the polymers and then the solution was dissolved in toluene (5–10 wt%) to form a lyotropic LC state. The lyotropic LC

solution was cast onto a quartz plate, which was then exposed under toluene vapor and allowed to dry slowly at room temperature.

(25) It is expected that in low concentration solutions of PDPA in toluene, the polymer main chains will lose the cooperative ordering of the LC phase and will behave like an isotropic liquid. To verify this we measured the UV-vis and CD spectra of *(rac)*-/*(R)*-/*(S)*-**PA2** in low concentration solution (1.2×10^{-4} M) in toluene. The spectra on Figure S4 reveals monosignate Cotton effects that reflect the intrachain helicity of **PA2**, similar to **PA2** in chloroform solution (Figure 4b).

(26) CD measurements in cast films and N*-LC films were taken on all the four possible orientations (horizontal and vertical) of the quartz plates and the results were compared. This procedure was performed to check for sample orientation dependence of the CD measurements. CD results of the samples showed no sample orientation dependence.

(27) (a) Harada, N.; Nakanishi, K. In *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*. University Science Books: California, **1983**. (b) Berova, N.; Nakanishi, K. In *Circular Dichroism: Principles and Applications*, 2nd Edition.; Berova, N.; Nakanishi, K.; Woody, R. Eds. John Wiley and Sons, Inc : New York, **2000**; Chapter. 12, 337–382.

(28) For all cast films and N*-LC films, the linear dichroism was much less than 0.01, which discounts that the large *g*-values are due to measurement artifacts. In addition, measurements were taken on all the four possible orientations (horizontal and vertical) and no orientation dependence was apparent.

**Part III: Chirality Inversion and Switching of
Circularly Polarized Luminescence of Chiral
Conjugated Polymers**

Chapter 4**Inversion of Chirality and Circularly Polarized Luminescence of
Poly(*para*-phenyleneethynylene) Derivatives bearing Chiral Moieties through
Solvent Induced Aggregation****ABSTRACT:**

We have synthesized poly(*para*-phenyleneethynylene) (PPE) derivatives having two chiral moieties in both side chains and characterized their solvent induced chiroptical properties. In varying ratios of chloroform and methanol solvents, the PPE aggregate exhibited a remarkable inversion of Cotton effects of circular dichroism (CD) and circularly polarized luminescence (CPL) spectra. We have revealed a facile way of chiral inversion of CPL in PPE through solvent induced aggregation and investigated the nature of the helical structures present in the aggregate state.

1. Introduction

Inversion of main chain chirality in optically active polymers without changing the configuration of stereocenters is a phenomenon seldom observed. Although most polymers adopt helical conformations in solution and/or in the solid state,¹ optical activity can only be observed when the polymers are prepared in an enantioselective way.

Chiral inversion in π -conjugated systems and polymers by changing the nature of the

polymer environment without affecting a single stereocenter have been extensively reported.² Some reported examples are changes in chirality with changes in temperature,³ pH,⁴ salt concentrations,⁵ and changes in the handedness of the chiral complex,⁶ and chiral solvent used.⁷ One facile way to change the handedness of conjugated polymers is through changing the polarity of its solvent environment during solvent induced aggregation. This method has been reported in conjugated polymers such as regioregular polythiophene (PT),⁸ poly(*p*-phenylenevinylene) (PPV),⁹ and PPE copolymers having peptiptycene groups.¹⁰

One interesting application of chiral inversion of conjugated polymers is the ability to exhibit circularly polarized luminescence (CPL) and control its handedness. Control of the handedness of CPL from polyfluorene^{7a,b} and polysilanes^{7c} by changing the handedness of the chiral solvent used have been reported. The handedness of the CPL of PPV films organized in aggregate state has been reported as well.^{9b}

PPE is a fluorescent conjugated polymer having good planarity and can easily form into supramolecular π -stacked assemblies in aggregate state. In this research, various PPE derivatives with chiral moieties were synthesized. The structural effects on the helical assembly behavior of the PPE aggregates were examined. We focused on the photoluminescent (PL), chiroptical, and CPL properties of the PPE derivatives. In this study we demonstrate that chiral PPE derivatives exhibit chiral inversion in chirality and CPL through solvent induced aggregation. The PPEs exhibited absorption (g_{abs}) and emission dissymmetry factors (g_{em}) values up to the order of 10^{-2} in aggregate state. In solvent induced aggregate state, the PPE derivatives exhibited excellent fluorescent properties with good quantum yield values unlike other conjugated polymer aggregates that typically exhibit fluorescence self-quenching in the aggregate state. The novel

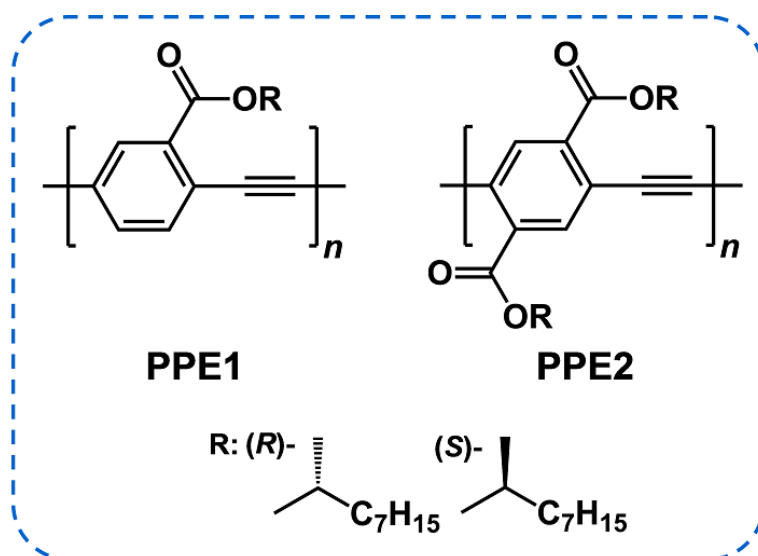
chiral inversion of CPL of the synthesized PPE aggregates may be attractive materials for optoelectronic devices and applications using circularly polarized optical materials.

2. Results and Discussion

2.1. Synthesis and Characterization of Polymers

Various poly(*para*-phenyleneethynylene) (PPE) derivatives having chiral moieties were synthesized (Scheme 1). The two PPE derivatives have 4-nonyloxy chiral moieties with either, (*R*)-, or (*S*)- handedness. **PPE1** has a single chiral moiety while **PPE2** has two chiral moieties.

Scheme 1. Structures of the poly(*para*-phenyleneethynylene) (PPE) derivatives.



The synthesis routes of the precursors, monomers, and polymers are given in Scheme S1 at the supporting figures section. The monomers of the PPE derivatives and the chiral dopants were synthesized using chemical reactions, such as Sonogashira-Hagihara coupling,^{11a,b} Mitsunobu reaction,^{11c} and Steglich esterification reaction.^{11d} The monomers were polymerized via Sonogashira-Hagihara coupling

using tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{TPP})_4$) as catalyst. The polymerization reaction was conducted at 55°C under an argon atmosphere using tetrahydrofuran (THF) as solvent and diisopropylamine (DIPA) as co-solvent. The polymerization proceeded for 24 h before washing the polymer in methanol (MeOH) under constant stirring for another 24 h. The precipitated polymers were then subsequently washed in acetone for 24 h and dried under vacuum.

The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were measured using gel permeation chromatography (GPC) and calibrated using a polystyrene (PS) standard. The GPC results showed that the polymers have M_n values ranging from 15,400 to 17,700 and M_w/M_n values ranging from 1.7 to 2.0 (Table 1).

Table 1. Weight-average (M_w), number-average (M_n) molecular weights, dispersion degree (M_w/M_n), and degree of polymerization (D.P.) of the PPE derivatives.

	M_n	M_w	M_w / M_n	D.P. ^a
(R)-PPE1	17,700	33,000	1.9	66
(S)-PPE1	15,500	26,900	1.7	58
(R)-PPE2	17,600	34,500	2.0	40
(S)-PPE2	15,400	27,700	1.8	35

^a Degree of Polymerization

2.2. Absorption and Photoluminescence

To investigate the optical properties of the PPEs, we examined the absorption (UV-vis), photoluminescence (PL) spectra, and absolute fluorescence quantum yield (Φ), of the PPEs in solution (CHCl_3 , $c = 5.0 \times 10^{-5}$ M) and as cast films (Table 2).

In solution, **PPE1** exhibits a main chain absorption band measuring approximately 390 nm and a blue-colored emission measuring approximately 430 nm (Figure 1a). **PPE1** in CHCl₃ solution was then drop-casted to form **PPE1** cast film. The **PPE1** cast film showed a bathochromic shift in the absorption band to approximately 437 nm and the green-colored emission band around 500 nm. On the other hand, **PPE2** in solution showed a main chain absorption band and blue-colored emission approximately at 407 nm and 450 nm, respectively (Figure 1b). Similar to **PPE1**, **PPE2** cast film exhibited a red-shift in both absorption and fluorescence spectra at approximately 455 nm and 510 nm, respectively.

Table 2. Spectroscopic data for absorption ($\lambda_{\max}$), fluorescence ($E_{\text{m,max}}$), excitation ($E_{\text{x,max}}$), and quantum yield (Φ) of the PPEs in CHCl₃ and film.

	$\lambda_{\max}$ (nm)		$E_{\text{m,max}}$ (nm)		$E_{\text{x,max}}$ (nm)		Φ (%) ^a	
	In CHCl ₃	film	In CHCl ₃	film	In CHCl ₃	film	In CHCl ₃	film
(R)-PPE1	386	439	429	496	380	378	60	20
(S)-PPE1	390	437	431	494	375	371	64	21
(R)-PPE2	405	457	451	510	410	442	65	85
(S)-PPE2	407	455	454	511	410	442	66	86

^aAbsolute quantum yield measured using Integrating Sphere System

Absolute fluorescence quantum yields (Φ) of the **PPE1** and **PPE2** in solution and in cast film were measured using the integrating-sphere method. The quantum yields of the PPEs in solution range from 60 to 66%, while those in cast film from 20 to 86%.

The optical data suggests that in solution and in cast film, the number of substituted chiral moieties in the PPE main chain do not have a significant effect on the absorption and fluorescence but may have an effect on the helicity of the PPEs in aggregate state.

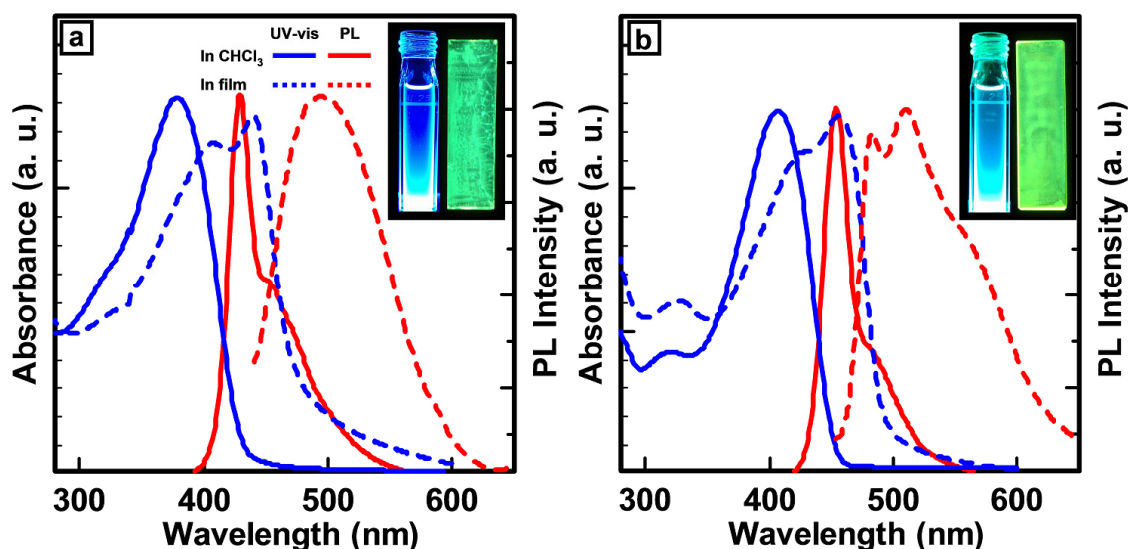


Figure 1. UV-Vis spectra and photoluminescence spectra of (a) **PPE1** and (b) **PPE2** in CHCl_3 and film, inset: PL in solution and cast film.

2.3. Characterization of the Solvent-induced Aggregate State of the PPEs

To investigate the solvent induced aggregation behavior of the PPEs, we conducted absorption and fluorescence spectroscopy of the PPE solutions at various degrees of aggregation. By adding a poor solvent (*i.e.* a solvent in which the polymer is in an aggregate state) to a PPE solution in a good solvent (*i.e.* a solvent in which the polymer is in an expanded and well-dissolved state), it is possible to study the polymers at various degrees of aggregation.

For the PPEs, a mixed solvent system of chloroform (CHCl_3) as good solvent, and methanol (MeOH) as a poor solvent was used. Various **PPE1** and **PPE2** solutions having solvent mixing ratios (from 0 to 95 MeOH %) were prepared ($c = 5.0 \times 10^{-5}$ M).

2.3.1. Absorption and Photoluminescence of the PPE aggregates

The UV-vis spectra of (*S*)-**PPE1** (Figure 2a) showed a main chain absorption band around 390 nm in CHCl_3 solution. At 45% MeOH , the emergence of a shoulder around 430 nm was observed. At higher MeOH %, the shoulder at 430 nm increases,

while the main chain absorption band relative intensity decreases. The absorption band around 430 nm can be assigned as the vibronic band of the **PPE1** aggregates. A picture of **(S)-PPE1** aggregates at various mixing solutions (Figure 2c) shows a change in the solution color from clear (0% MeOH) to yellowish green (95% MeOH) which corresponds to the change of the absorption spectra of **PPE1** in aggregate state.

The photoluminescence (PL) spectra of **(S)-PPE1** (Figure 2b) in CHCl₃ exhibits a blue-colored PL band at 430 nm, originating from the main chain emission, with a shoulder at 450 nm. At higher than 40% MeOH, the main chain PL intensity decreases relative to the 450 nm shoulder PL band. While at 55% MeOH we can observe the emergence of an aggregate green-PL band centered at 510 nm. At 80% MeOH, the main chain PL band disappears and the solution exhibits a green-colored PL originating from the PPE aggregate. A picture of the fluorescence of the **(S)-PPE1** solutions (Figure 2d) shows a change in the fluorescence color from blue (0% MeOH) to blue green (55% MeOH) to green (80% MeOH). Quantum yield (Φ) measurements of the **(S)-PPE1** mixed solutions showed a decrease of quantum yield values from 64% (0% MeOH) to 10% (95% MeOH) (see supporting information, Table S1). The decrease of quantum yield values coincided with the formation of the PPE aggregates. This phenomenon can be associated to non-radiative energy loss brought about by the self-quenching interchain interactions of the PPE π -stacking structures in the aggregate state. This behavior agrees with what is observed in the PL of PPE and conjugated polymers in cast film.^{10,12}

The absorption spectra of **(S)-PPE2** (Figure 2e) showed a main chain absorption band around 410 nm in CHCl₃ solution. At 70% MeOH, a shifting of the main chain absorption band to 425 nm and the emergence of an aggregate absorption peak around

480 nm was observed. At higher MeOH%, the intensity of the aggregate absorption band increases, while the relative intensity of the main chain absorption band decreases. A picture of the (*S*)-PPE2 aggregate solutions at various mixing ratios (Figure 2g) showing a change in the solution color from clear (0% MeOH) to yellowish green (95% MeOH) was observed.

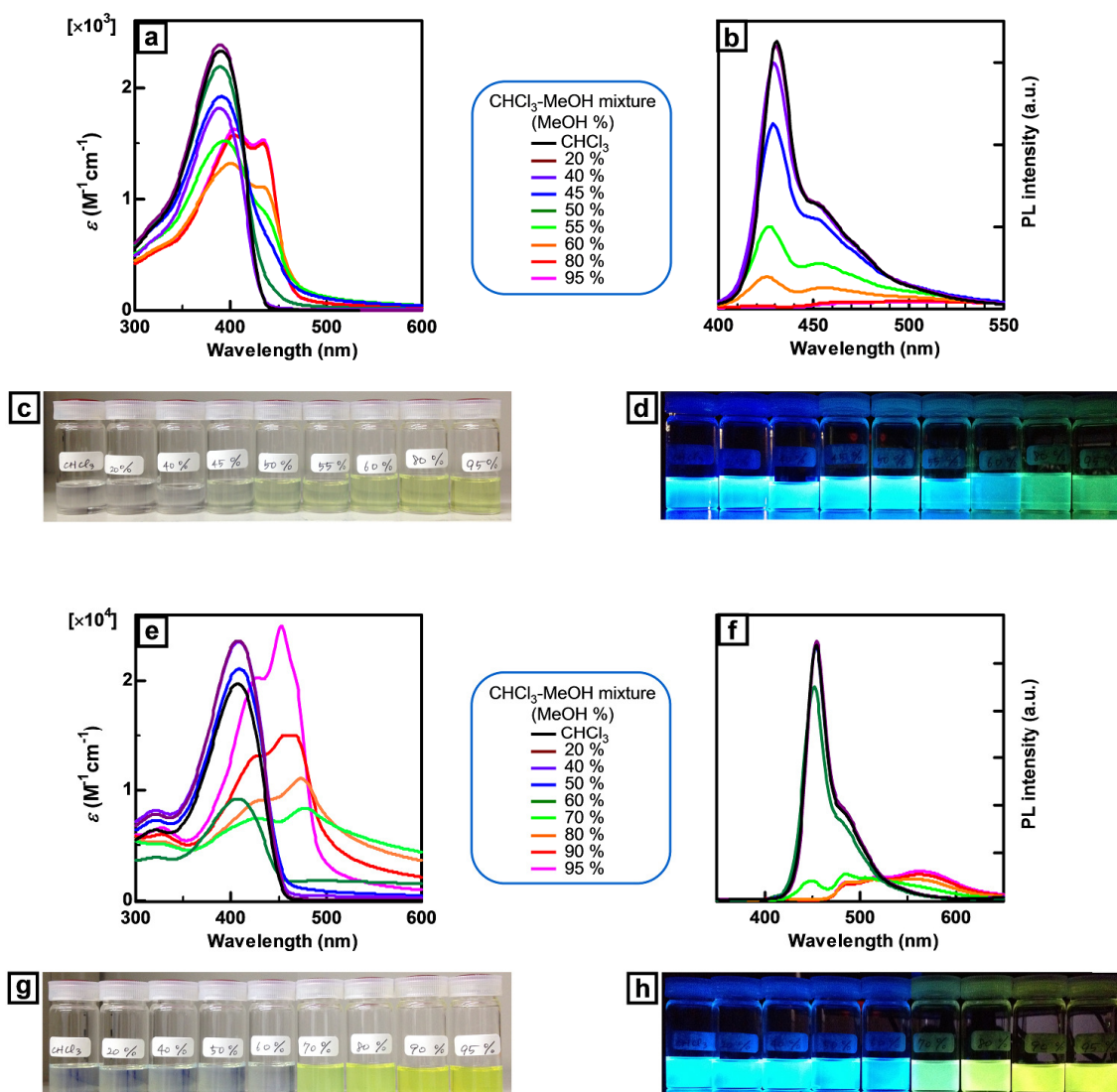


Figure 2. UV-vis, photoluminescence (PL) spectra, photograph, and PL photograph of (*S*)-PPE1 (a), (b), (c), (d), and (*S*)-PPE2 aggregate solutions (e), (f), (g), (h), respectively.

The PL spectra of **(S)-PPE2** (Figure 2f) in CHCl_3 exhibits a blue-colored PL band at 450 nm, with a shoulder at 480 nm. At higher than 60% MeOH, the main chain PL intensity decreases relative to the 480 nm shoulder. While at 80% MeOH we can observe the emergence of an aggregate green-PL band centered at 570 nm. At 80% MeOH, the main chain PL band disappears and the solution exhibits a yellow green-colored PL. A picture of the fluorescence of the **(S)-PPE2** solutions (Figure 2h) shows a change in the fluorescence color from blue (0% MeOH) to yellow green (80% MeOH). Similar to **(S)-PPE1**, **(S)-PPE2** mixed solutions also exhibited a decrease of quantum yield values from 66% (0% MeOH) to 33% (95% MeOH) (Table S1).

2.4. Chiroptical Properties of the Solvent-induced Aggregate State of the PPEs

With the aim to investigate the helical conformation and arrangement of the PPE main chains in an isotropic and aggregate state, we measured the circular dichroism (CD) spectra of the PPE derivatives in a mixed solvent system. The degree of CD was evaluated using absorption dissymmetry factor, g_{abs} . This factor is defined by the following equation: $g_{\text{abs}} = (\epsilon_{\text{L}} - \epsilon_{\text{R}}) / [(\epsilon_{\text{L}} + \epsilon_{\text{R}}) / 2] = \Delta\epsilon / \epsilon$, where $|g_{\text{abs}}| < 2$. The ϵ_{L} and ϵ_{R} are defined as the absorption coefficients of left and right handed polarized light, respectively.

2.4.1. Circular Dichroism of the PPEs aggregates

The CD spectra of **(S)-PPE1** in CHCl_3 (0% MeOH) and in low MeOH solvent solutions showed no Cotton effects. At 45% MeOH, a negative bisignate CD signal centered at the PPE main chain absorption region emerges. At 50% MeOH, the bisignate CD signal was at its maximum with g_{abs} values up to -3.79×10^{-2} at 440 nm (Table S2). Using the exciton coupling theory,¹³ the negative bisignate Cotton effect

suggests that the (*S*)-**PPE1** aggregate forms a left-handed helical π -stacked structure. At higher MeOH% solutions (from 60–80% MeOH), the aggregates exhibit a decrease in CD intensity while maintaining the sign of the bisignate CD signal. At 95% MeOH the CD signal disappeared which suggests that at high MeOH% solutions, the (*S*)-**PPE1** favors a stronger aggregate structure with parallel alignment of polymer chains and the helical structure is lost.¹⁰ The CD spectra of (*R*)-**PPE1** also exhibits the same behavior, but having the opposite sign (Figure S1).

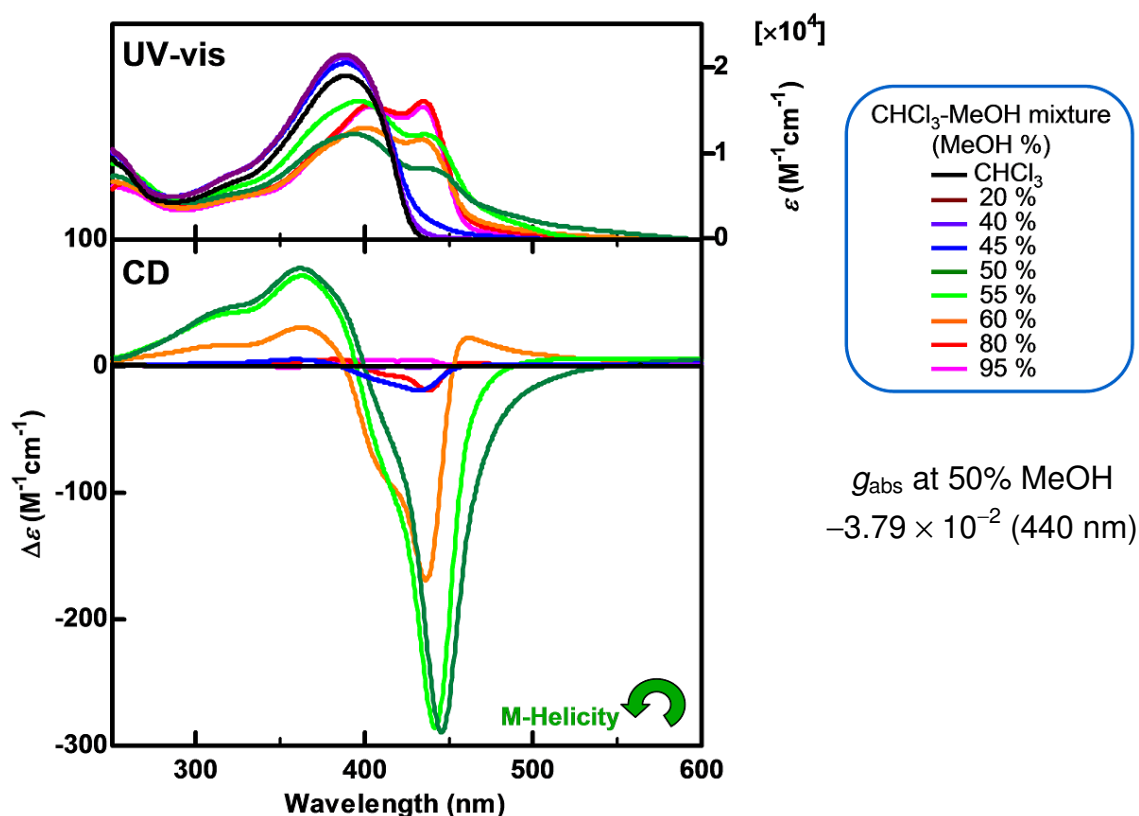


Figure 3. UV-Vis (above), and CD spectra (below) of (*S*)-**PPE1** aggregate solutions.

We then measured the CD spectra of (*R*)-**PPE2** in mixed solvent solutions in order to determine the effect of having two chiral moieties in the side chains to the chiroptical properties and helical arrangement of **PPE2**. The CD spectra of (*R*)-**PPE2** in CHCl_3 (0% MeOH) and in low MeOH solvent solutions showed no Cotton effects. At 60%

MeOH, we can observe the emergence of a negative bisignate CD signal centered at the aggregate absorption region. The emergence of a CD signal coincided with the appearance of the absorption shoulder assigned as the aggregate absorption region. At 70% MeOH, the negative bisignate CD signal was at its maximum with g_{abs} values up to -9.06×10^{-3} and shifted its zero-point crossing to 470 nm corresponding to the main chain absorption region (Table S3). At 80% MeOH, the aggregates show a decrease in CD intensity while maintaining the sign of the bisignate CD signal. At 90% MeOH, we observe an inversion on the CD signal with g_{abs} values up to 9.24×10^{-3} (470 nm) to a positive bisignate CD which suggests that at higher MeOH% the (*R*)-PPE2 aggregates shift to a right handed helical arrangement. At 95% MeOH, the aggregates exhibit a decrease in CD intensity while maintaining the positive bisignate CD signal. The CD spectra of (*S*)-PPE2 also exhibits the same behavior, but having the opposite sign (Figure S2).

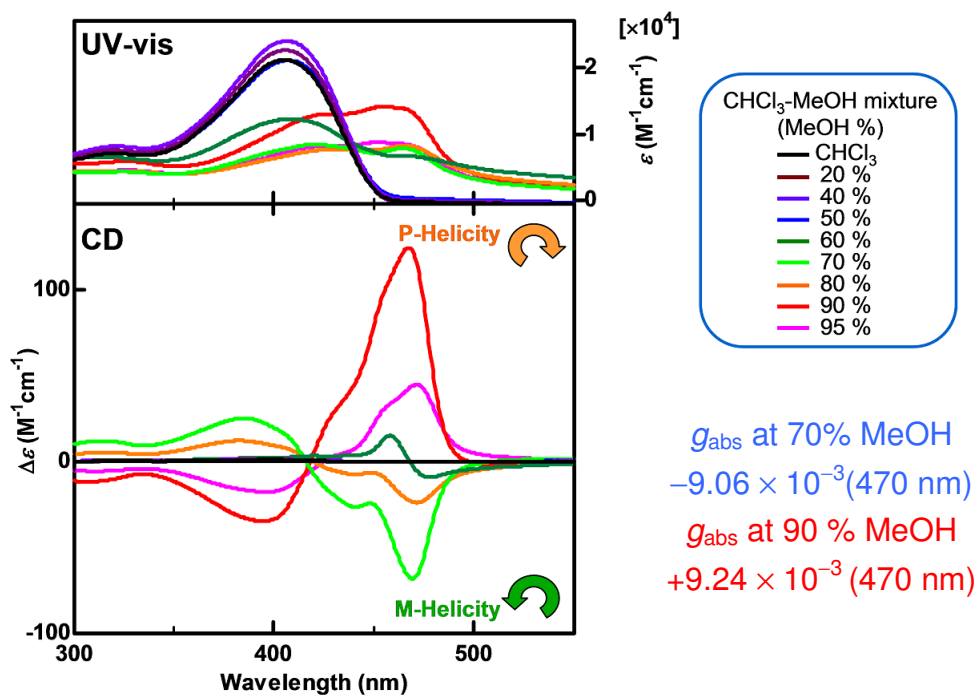


Figure 4. UV-vis (above), and CD spectra (below) of (*R*)-PPE2 aggregate solutions.

Compared to **PPE1**, **PPE2** exhibited chiral inversion through solvent-induced aggregation and exhibited a complex CD signal with composite peaks corresponding to the main chain and aggregate absorption bands. These results persuade us to further investigate the phenomenon of the chiral inversion of **PPE2**.

2.4.2. Circular Dichroism of the PPEs aggregates at varying temperatures and solvent conditions

There have been previous reports of chiral inversion in both supramolecular systems,¹⁴⁻¹⁶ and polymer systems.⁸⁻¹⁰ To investigate whether thermodynamic effects (enthalpy) or kinetic effects (entropy) are responsible for the helical arrangement of the PPE aggregates, we measured the CD spectra of the PPEs in mixed solvent solution at varying temperatures. Such investigations may shed light on the effects of enthalpy, entropy, and the number of chiral moieties on the helical arrangement of the PPE aggregates.

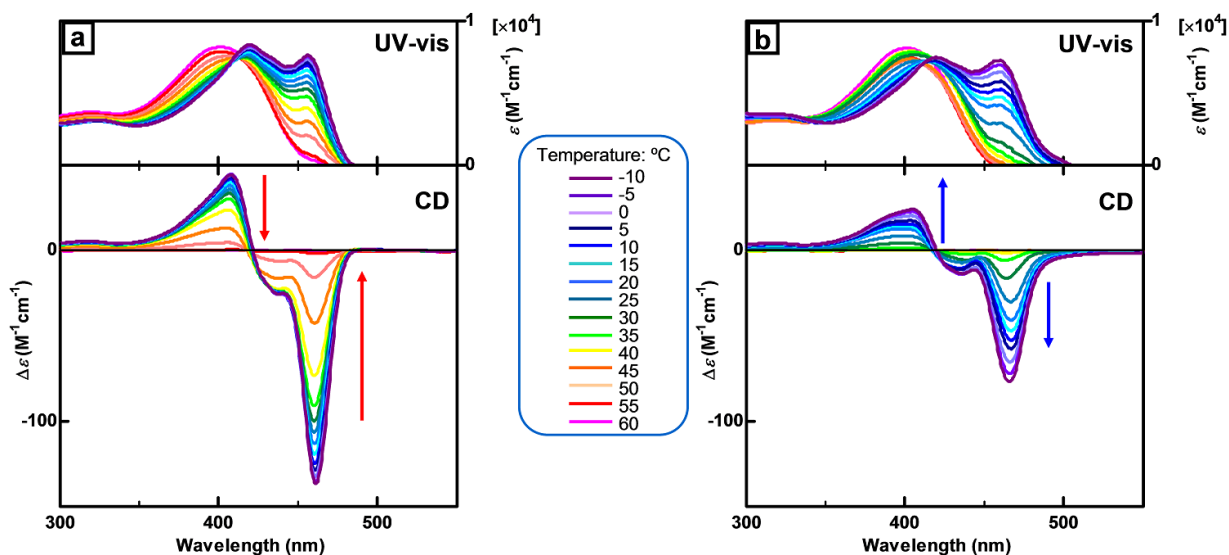


Figure 5. UV-Vis (above), and CD spectra (below) of (*R*)-PPE2 at 70% MeOH in heating (a) and cooling (b) process.

The CD spectra of **(R)-PPE2** at 70% and 90% MeOH, where we observed the highest CD intensities and g_{abs} values having opposite helical sense, were measured at varying temperatures. At 70% MeOH, the CD of the aggregate solution was measured from -10°C to 60°C in the heating process, then back to -10°C in the cooling process (Figure 5). We have observed a decrease in the CD signal and the g_{abs} values (Table S4) as the solution temperature increased until 60°C , where the CD signal disappeared. The disappearance of the Cotton effect at 60°C coincided with the disappearance of the aggregate absorption band in the UV-vis spectra. At the cooling process, we observed the recovery of the CD signal at 40°C and the reemergence of the aggregate absorption band. Towards lower temperatures, the CD signal increased to a maximum at -10°C .

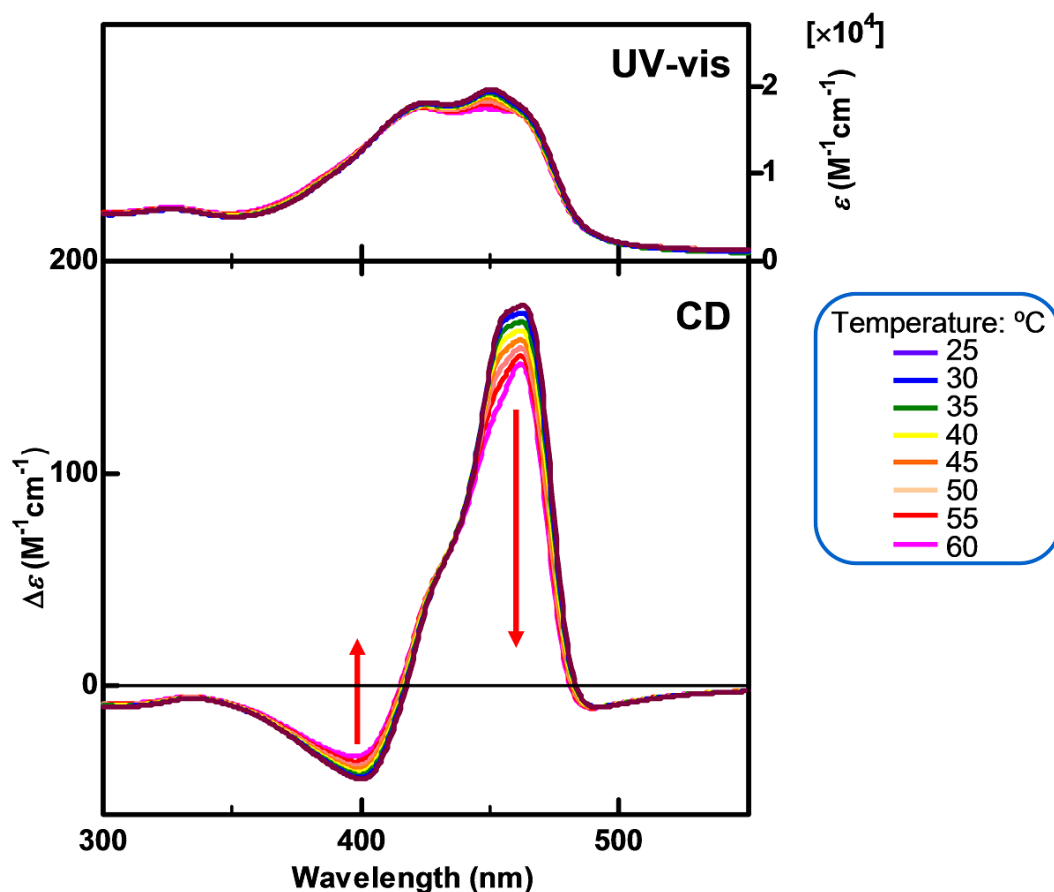


Figure 6. UV-Vis (above), and CD spectra (below) of **(R)-PPE2** at 90% MeOH in heating process.

The CD spectra of **(R)-PPE2** at 90% MeOH was measured and we observed only a slight change in CD intensity and g_{abs} values in the heating process (Figure 6). The UV-vis spectra also shows a minimal change in the relative intensities of the main chain and the aggregate absorption bands.

It can be noted that the CD measurement of **(R)-/(S)-PPE1** in heating also exhibited a decrease in CD intensity and g_{abs} values with the disappearance of the aggregate absorption band at high temperatures (Figure S3). These results suggest that the helical arrangement mechanism of **PPE2** aggregates formed at 70% MeOH is similar to that of **PPE1** formed at 50% MeOH.

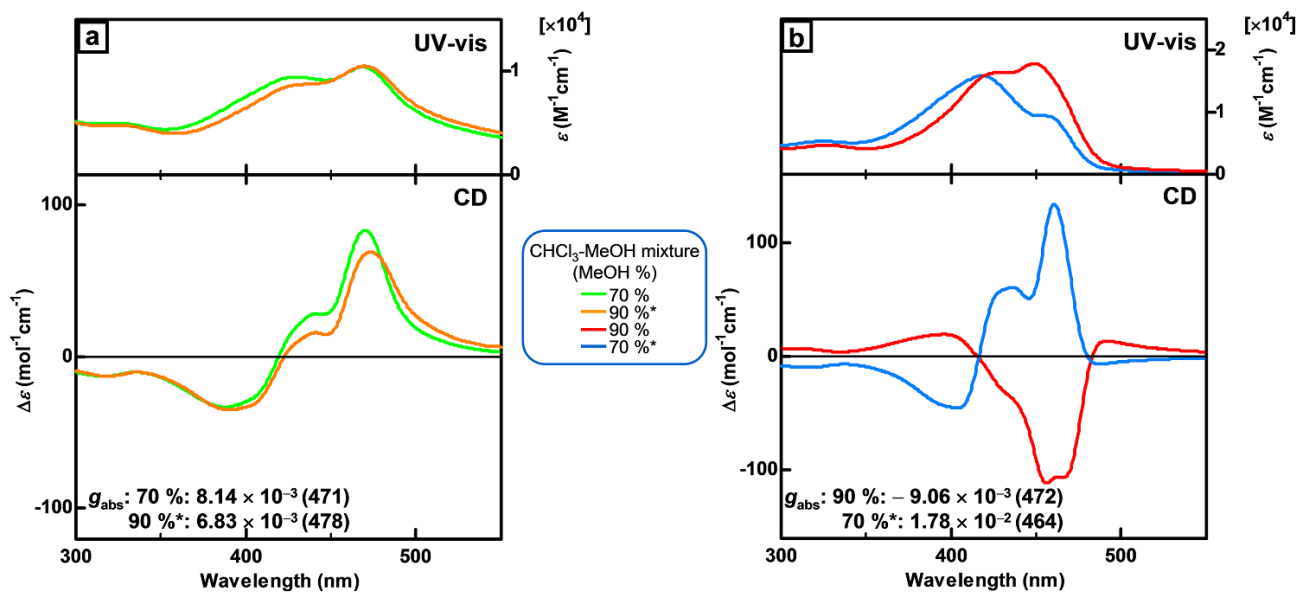


Figure 7. UV-Vis (above), and CD spectra (below) of **(S)-PPE2** at (a) 70% MeOH, 90%* MeOH, and (b) 90% MeOH, 70%* MeOH.

To further investigate the nature of the aggregate formation of **PPE2**, **(S)-PPE2** 70% MeOH solution was prepared then MeOH was added to make a 90%* MeOH solution, furthermore **(S)-PPE2** 90% MeOH solution was prepared and CHCl_3 was added to make a 70%* MeOH solution. The CD spectra of the solutions were then

measured to examine the behavior of the **PPE2** aggregates after a change in solvent environment. It was observed that the CD spectra of (*S*)-**PPE2** 90%* MeOH solution maintained the sign and shape of its bisignate Cotton effects with a no change in the aggregate absorption band (Figure 7a). In contrast, the (*S*)-**PPE2** 70%* MeOH solution showed an inversion of Cotton effects in CD and a decrease in the relative absorption of the aggregate absorption band (Figure 7b). These results suggest that the helical structures of the PPE aggregates at 90% MeOH solution are kinetically trapped during nucleation but change to a more thermodynamically stable aggregate structure when the solvent environment is changed to 70% MeOH. The PPE aggregates at 70% MeOH solution are thermodynamically stable thus even if the solvent environment is changed to 90% MeOH, there is no change in the helical structure of the PPE aggregates.

2.4.3. Proposed model of the Solvent-Induced aggregation of the PPEs

From the CD spectroscopic measurements and investigations, we propose a model describing the chiral inversion behavior of **PPE2** in aggregate state. The bisignate CD signal of (*R*)-**PPE2** at 70% MeOH centered at the polymer main chain absorption band suggests the formation of a helical π -stacked structure (Figure 4). The emergence of an aggregate absorption band which coincides with the bisignate CD signal further supports this. Measurements of the CD spectra of (*R*)-**PPE2** at 70% MeOH at varying temperatures suggest that the aggregation of (*R*)-**PPE2** to a helical π -stacked structure is greatly affected by thermodynamic (enthalpic) effects. At the heating cycle of (*R*)-**PPE2** at 70% MeOH, the helical π -stacked structure is disrupted leading to a decrease in CD signal and decrease of the aggregate absorption band, while cooling the (*R*)-**PPE2** solution recovers the helical π -stacked structure (Figure 8). Furthermore

CD measurements of (*S*)-**PPE2** aggregates that experience a change in solvent environment after nucleation (Figure 7) suggest that the helical π -stacked structure formed at 70% MeOH is thermodynamically stable.

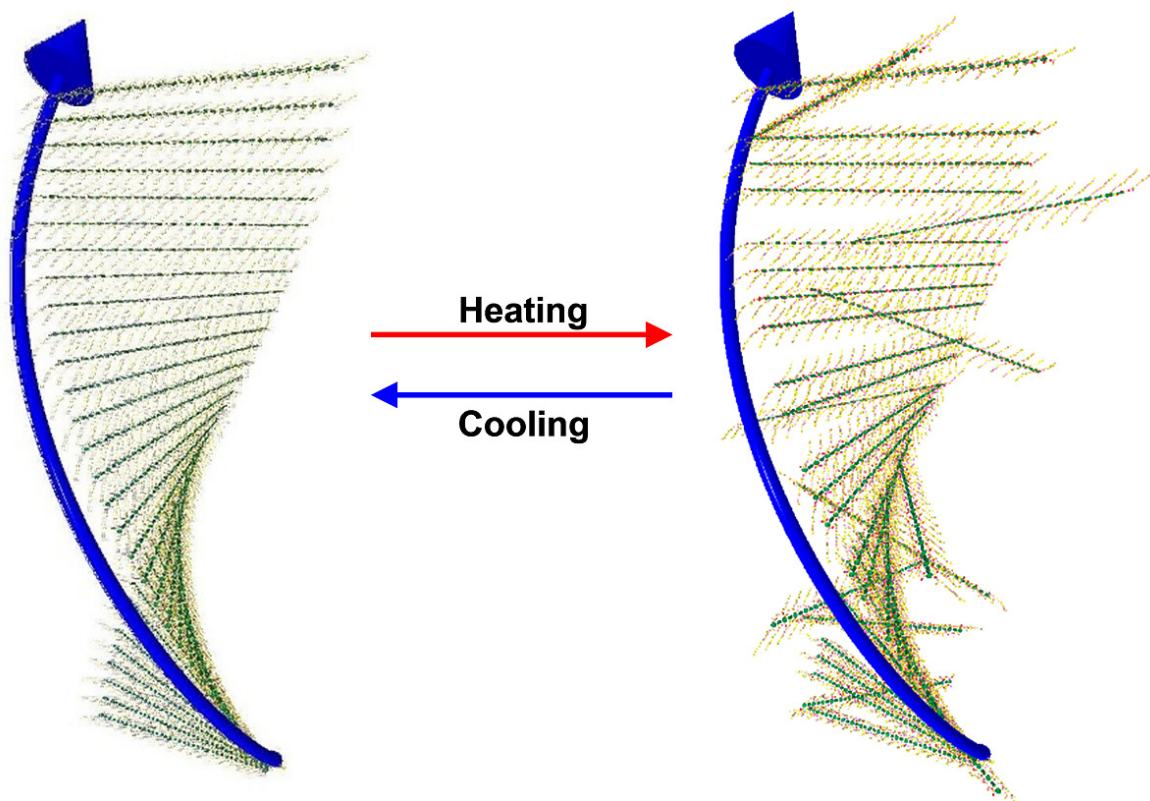


Figure 8. Helical π -stacked model of (*R*)-**PPE2** at 70% MeOH during heating and cooling process.

On the other hand, the CD signal and the aggregate absorption band of (*R*)-**PPE2** at 90% MeOH is only slightly affected by changes in temperature which suggests that the helical arrangement of the **PPE2** aggregates are dominated by kinetic (entropic) effects. At 90% MeOH, the chains of (*R*)-**PPE2** are stacked close together due to the hydrophobic interactions with the poor solvent. In such a state, the (*R*)-**PPE2** polymer chains form into helical bundles (Figure 9a) with a right-handed π -stacked structure at an axis perpendicular to the bundle axis (Figure 9b). The helical bundle consists of

PPE2 main chains closely bound together by π -interactions which makes the helical structure resilient against temperature effects. In addition, (**S**)-**PPE2** aggregates formed at 90% MeOH are locked kinetically into a helical bundles which is kinetically favored due to their closely stacked structure in a poor solvent environment (Figure 7b). From the characterization of the PPE aggregates at various solvent environments, changes in solution temperature, and changes in solvent environment after polymer aggregation we can elucidate that the solvent environment during the nucleation and kinetic and thermodynamic effects play critical roles in determining the helical structure and handedness of the PPE aggregates.

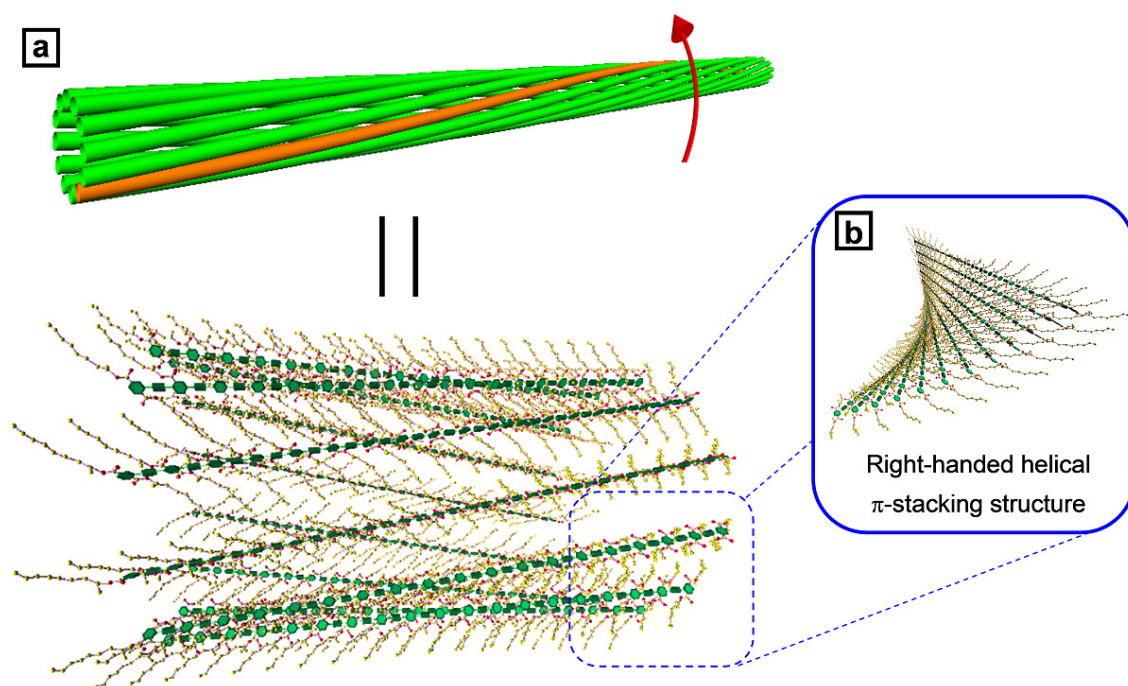


Figure 9. (a) Helical bundle model of (**R**)-**PPE2** at 90% MeOH, (b) right handed π -stacking structure of (**R**)-**PPE2** at an axis perpendicular to the bundle axis.

2.5 Circular Polarized Luminescence of the PPEs aggregates

The CD spectra of the PPEs revealed that the PPE aggregates are arranged in helical π -stacking structures. Since the PPEs exhibit photoluminescence, we investigated the

potential of the PPE aggregates to show CPL.

(R)-/(S)-PPE2 exhibited chirality inversion of the PPE aggregates upon changing of the MeOH% of the mixed solvent solution. Figure 10 shows an interesting inversion of CPL signs at different MeOH% solutions. **(R)-PPE2** at 70% MeOH solution shows a negative CPL band centered around 500 nm with a g_{em} value of -4.55×10^{-3} (491 nm) (Figure 10a, Table S5). At 80% MeOH, **(R)-PPE2** also exhibits a negative CPL with a decrease in the CPL intensity. At 90% MeOH, we observe an inversion of CPL sign where it increases to a maximum intensity at 95% MeOH with a g_{em} value of 1.56×10^{-2} (476 nm).

The CPL spectra of **(S)-PPE2** also exhibits chiral inversion with signs opposite to that of **(R)-PPE2** (Figure 10b). **(S)-PPE2** at 70% MeOH solution shows a positive CPL band centered around 500 nm with a g_{em} value of 1.83×10^{-2} (488 nm) (Table S5), with the CPL band decreasing in intensity at 80% MeOH, and then showing a negative CPL band from 90% MeOH. **(S)-PPE2** at 95% MeOH solution shows a maximum CPL signal g_{em} value of -2.17×10^{-2} (459 nm).

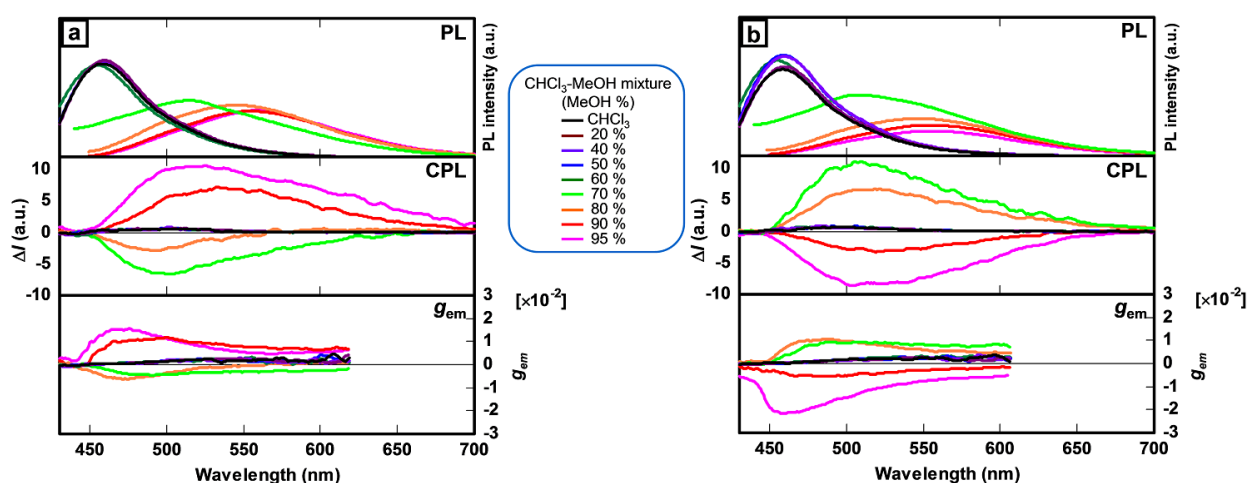


Figure 10. PL (upper), CPL (middle), and g_{em} (lower) spectra of (a) **(R)-PPE2**, and (b) **(S)-PPE2** aggregate solutions.

The CPL spectra of **(R)-/(S)-PPE2** show an inversion of CPL with the g_{em} values and CPL signs agreeing with the signs of the CD spectral data. These results suggest that the CPL bands of **(R)-/(S)-PPE2** were derived from the same source as the CD band, and the helical π -structure between the PPE main chains is responsible for the observed CPL band.

(S)-PPE1 shows CPL at 50% MeOH corresponding to its maximum CD peak. Similar to its CD spectra, **(S)-PPE1** does not show an inversion of chirality (Figure S4).

3.0 Conclusion

We synthesized chiral PPE aggregates that show an interesting phenomena of chiral inversion in the CD and CPL spectra at different solvent conditions. The results suggest that the solvent environment during formation of the PPE aggregates plays a critical role in determining their helical structure and handedness. We put forward a model describing the chiral inversion behavior of **PPE2** in aggregate state. Bisignate Cotton effects centered at the polymer main chain absorption band of **PPE2** in 70% MeOH suggest the formation of a helical π -stacked structure. At 90% MeOH, the chains of **PPE2** are stacked close together due to the hydrophobic interactions with the poor solvent and form into helical bundles. The novel chiral inversion of CPL of the synthesized PPE aggregates may be attractive materials for optoelectronic devices and applications using circularly polarized optical materials.

Acknowledgements

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Chapter 4 Appendix

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1. Experimental Section

1.1. Materials

The chemical reagents we purchased from commercially available sources and were used as received. 2,5-dibromoterephthalic acid, 2,5-dibromobenzoic acid, 2,5-diiodobenzoic acid, and *trans*-dichlorobis(triphenylphosphine)palladium (II) ($\text{PdCl}_2(\text{TPP})_2$) was purchased from Aldrich Co. Ltd. Diethylazodicarboxylate (DEAD), and trimethylsilylacetylene were purchased from Tokyo Kasei Co. Ltd. Copper (I) iodide (CuI) were purchased from Kanto Chemical Co. Ltd. Triphenylphosphine (TPP), (*R*)-(-)-2-nonanol, (*S*)-(+)-2-nonanol and were purchased from Wako Co. Ltd. Tetrabutylammonium fluoride (TBAF), tetrakis(triphenylphosphine)palladium(0)

(Pd(TPP)₄), Diisopropylamine (DIPA), N,N-dimethyl-4aminopyridine (DMAP), dicyclohexylcarbodiimide (DCC), sodium sulfate (Na₂SO₄), triethyl amine (Et₃N), tetrahydrofuran (THF), acetic acid, methanol (MeOH), hexane (*n*-C₆H₁₄), acetone, dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) were purchased from Nacalai Tesque Co. Ltd. All experiments were performed under argon (>99.9995 % purity) atmosphere. THF, DIPA, and Et₃N used were distilled from sodium as a drying agent under argon gas before use.

1.2. Methods

Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either JEOL JNM EX400 400 MHz or JEOL AL-400 400MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from *tetra*-methylsilane (TMS) as an internal standard. Elemental analysis was measured using Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100 and Dionex ICS-1500.

Optical absorption spectra were measured using a JASCO V-570 UV/VIS/NIR spectrometer, and fluorescence spectra were measured using JASCO FP-750 spectrometer with quartz cell (for solution) and quartz plate (for cast film). Absolute fluorescence quantum yield of the polymers was measured using integrating-sphere method at the JASCO FP-6500 spectrometer. Circular dichroism spectra were measured using JASCO J-820 spectropolarimeter. Circularly polarized luminescence was measured using JASCO CPL-200S spectrometer .

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-D (Polymer Laboratories), a

JASCO MD915 UV detector and THF as an eluent at a flow rate of 1.0 mL/min during measurements, where the instrument was calibrated using polystyrene (PS) standard, and were calculated on an 807-IT integrator.

1.3. Syntheses of Monomers and Polymers

The synthesis route of the precursor compounds and monomers (***R***)-/(***S***)-**1** to (***R***)-/(***S***)-**7** and the PPEs (***R***)-/(***S***)-**PPE1–PPE2** are written below:

((***R***)-nonan-2-yl)-2,5-diiodobenzoate ((***R***)-**1**)

((***R***)-nonan-2-yl)-2,5-diiodobenzoate ((***R***)-**1**) was synthesized as follows. Into a 200 mL two-necked flask were added 2,5-diiodobenzoic acid (0.50 g, 1.34 mmol), (***R***)-2-nonanol (0.25 g, 1.74 mmol), *N,N*-dimethyl-4-aminopyridine (DMAP; 0.20 g, 1.60 mmol) under argon gas and dissolved in CH₂Cl₂ (40 mL). The mixture was stirred at room temperature then dicyclohexylcarbodiimide (DCC; 0.33 g, 1.60 mmol) and CH₂Cl₂ (20 mL) was added. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The collected liquid was evaporated and dried under vacuum to give compound (***R***)-**1** (0.59 g, 1.18 mmol) as a colorless oil. Yield = 89%.

Anal. Chemical Formula: (C₁₆H₂₂O₂I₂)_{*n*} (500.16)_{*n*}: C, 38.42; H, 4.43; O, 6.40; Br, 50.75.

Found: C, 38.60; H, 4.42; O, 6.53; I, 50.47.

¹H NMR (400 MHz, CDCl₃, δ): 0.885 (t, 3H, –CH₃), 1.281-1.753 (m, 15H,

–CH₂,–CH₃), 5.161 (sext, 1H, –CH), 7.445 (d, 1H, Ar–H), 7.665 (d, 1H, Ar–H), 8.019 (d, 1H, Ar–H).

¹³C NMR (100 MHz, CDCl₃, δ): 14.09, 19.90, 22.61, 25.43, 29.14, 29.36, 31.75, 35.82, 73.43, 139.03, 140.99, 142.40.

((S)-nonan-2-yl)-2,5-diiodobenzoate ((S)-1)

((S)-nonan-2-yl)-2,5-diiodobenzoate ((S)-1) was synthesized as follows. Into a 200 mL two-necked flask were added 2,5-diiodobenzoic acid (0.50 g, 1.34 mmol), (*R*)-2-nonanol (0.25 g, 1.74 mmol), *N,N*-dimethyl-4-aminopyridine (DMAP; 0.20 g, 1.60 mmol) under argon gas and dissolved in CH₂Cl₂ (40 mL). The mixture was stirred at room temperature then dicyclohexylcarbodiimide (DCC; 0.33 g, 1.60 mmol) and CH₂Cl₂ (20 mL) was added. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The collected liquid was evaporated and dried under vacuum to give compound (S)-1 (0.53 g, 1.05 mmol) as a colorless oil. Yield = 79%.

Anal. Chemical Formula: (C₁₆H₂₂O₂I₂)_n (500.16)_n: C, 38.42; H, 4.43; O, 6.40; Br, 50.75. Found: C, 38.49; H, 4.50; O, 6.42; I, 50.66.

¹H NMR (400 MHz, CDCl₃, δ): 0.885 (t, 3H, –CH₃), 1.281-1.753 (m, 15H, –CH₂,–CH₃), 5.161 (sext, 1H, –CH), 7.445 (d, 1H, Ar–H), 7.665 (d, 1H, Ar–H), 8.019 (d, 1H, Ar–H)

¹³C NMR (100 MHz, CDCl₃, δ): 14.09, 19.90, 22.61, 25.43, 29.14, 29.36, 31.75, 35.82, 73.43, 139.03, 140.99, 142.40.

(*R*)-(nonan-2-yl)-2,5-dibromobenzoate ((*R*)-2)

(*R*)-(nonan-2-yl)-2,5-dibromobenzoate ((*R*)-2) was synthesized as follows. Into a 200 mL two-necked flask were added 2,5-dibromobenzoic acid (1.00 g, 3.57 mmol), (*R*)-2-nonanol (0.62 g, 4.29 mmol), N,N-dimethyl-4aminopyridine (DMAP; 0.52 g, 4.29 mmol) under argon gas and dissolved in CH₂Cl₂ (40 mL). The mixture was stirred at room temperature then dicyclohexylcarbodiimide (DCC; 1.78 g, 6.79 mmol) and CH₂Cl₂ (20 mL) was added. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃ as eluent. The collected liquid was evaporated and dried under vacuum to give compound (*R*)-2 (1.26 g, 3.14 mmol) as a colorless oil. Yield = 88%.

Anal. Chemical Formula: (C₁₆H₂₂O₂Br₂)_n (406.16)_n: C, 47.32; H, 5.46; O, 7.88; Br, 39.35. Found: C, 47.32; H, 5.41; O, 8.13; Br, 39.09.

¹H NMR (400 MHz, CDCl₃, δ): 0.8798 (t, 3H, –CH₃), 0.8621-1.7743 (m, 15H, –CH₂, –CH₃), 5.1617 (sext, 1H, –CH), 7.4306 (d, 1H, Ar–H), 7.4941 (d, 1H, Ar–H), 7.8403 (d, 1H, Ar–H).

¹³C NMR (100 MHz, CDCl₃, δ): 14.07, 19.88, 22.61, 25.40, 29.14, 29.36, 31.75, 35.83, 73.39, 133.59, 134.94, 135.42, 164.43.

(*S*)-(nonan-2-yl)-2,5-dibromobenzoate ((*S*)-2)

(*S*)-(nonan-2-yl)-2,5-dibromobenzoate ((*S*)-2) was synthesized as follows. Into a 200 mL two-necked flask were added 2,5-dibromobenzoic acid (1.00 g, 3.57 mmol), (*S*)-2-nonanol (0.62 g, 4.29 mmol), N,N-dimethyl-4aminopyridine (DMAP; 0.52 g, 4.29

mmol) under argon gas and dissolved in CH_2Cl_2 (40 mL). The mixture was stirred at room temperature then dicyclohexylcarbodiimide (DCC; 1.78 g, 6.79 mmol) and CH_2Cl_2 (20 mL) was added. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound (**S**)-**2** (0.98 g, 2.42 mmol) as a colorless oil. Yield = 67%.

Anal. Chemical Formula: $(\text{C}_{16}\text{H}_{22}\text{O}_2\text{Br}_2)_n$ (406.16) $_n$: C, 47.32; H, 5.46; O, 7.88; Br, 39.35. Found: C, 47.21; H, 5.42; O, 8.01; Br, 39.10.

^1H NMR (400 MHz, CDCl_3 , δ): 0.8798 (t, 3H, $-\text{CH}_3$), 0.8621-1.7743 (m, 15H, $-\text{CH}_2, -\text{CH}_3$), 5.1617 (sext, 1H, $-\text{CH}$), 7.4306 (d, 1H, Ar-H), 7.4941 (d, 1H, Ar-H), 7.8403 (d, 1H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.07, 19.88, 22.61, 25.40, 29.14, 29.36, 31.75, 35.83, 73.39, 133.59, 134.94, 135.42, 164.43.

(*R*)-(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)benzoate ((*R*)-3**)**

(*R*)-(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)benzoate ((*R*)-**3**) was synthesized as follows. Into a 100 mL three-necked flask were added compound (**R**)-**2** (1.00 g, 2.48 mmol), trimethylsilylacetylene (0.74 g, 7.43 mmol), $\text{PdCl}_2(\text{TPP})_2$ (34.7 mg, 0.05 mmol), CuI (4.7 mg, 0.02 mmol), 10 mL Et_3N and 20 mL THF under argon. After continuous stirring, solution was heated to 70 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous

Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, CHCl₃/hexane = 1 : 1 as eluent). The product was evaporated and dried under vacuum to give compound **(R)-3** (1.16 g, 2.64 mmol) as an amber colored oil. Yield = Quantitative.

Anal. Chemical Formula: (C₂₆H₄₀O₂Si₂)_n (440.77)_n: C, 70.85; H, 9.15; O, 7.26; Si, 12.74. Found: C, 70.58; H, 9.33.

¹H NMR (400 MHz, CDCl₃, δ): 0.0580 (s, 18H, –CH₃), 0.8690 (t, 3H, –CH₃), 1.2644-1.7257 (m, 15H, –CH₂–CH₃), 5.1617 (sext, 1H, –CH), 7.4210 (d, 1H, Ar–H), 7.4838 (d, 1H, Ar–H), 7.8292 (d, 1H, Ar–H).

¹³C NMR (100 MHz, CDCl₃, δ): 1.02, 14.06, 19.30, 22.61, 25.43, 29.14, 31.74, 72.51, 102.97, 133.30, 133.97, 134.54.

(S)-(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)benzoate ((S)-3)

(S)-(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)benzoate ((S)-3) was synthesized as follows. Into a 100 mL three-necked flask were added compound **(S)-3** (0.64 g, 1.59 mmol), trimethylsilylacetylene (0.47 g, 4.76 mmol), PdCl₂(TPP)₂ (22.5 mg, 0.03 mmol), CuI (12.1 mg, 0.06 mmol), 10 mL Et₃N and 20 mL THF under argon. After continuous stirring, solution was heated to 70 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl₃ (3×). The organic layer was dried over anhydrous Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, CHCl₃/hexane = 1 : 1 as eluent). The product was evaporated and dried under vacuum to give compound **(S)-3** (0.88 g, 1.99 mmol) as an amber colored oil. Yield = 80.3%.

Anal. Chemical Formula: (C₂₆H₄₀O₂Si₂)_n (440.77)_n: C, 70.85; H, 9.15; O, 7.26; Si,

12.74. Found: C, 71.09; H, 9.15.

^1H NMR (400 MHz, CDCl_3 , δ): 0.0580 (s, 18H, $-\text{CH}_3$), 0.8690 (t, 3H, $-\text{CH}_3$), 1.2644-1.7257 (m, 15H, $-\text{CH}_2$, $-\text{CH}_3$), 5.1617 (sext, 1H, $-\text{CH}$), 7.4210 (d, 1H, Ar-H), 7.4838 (d, 1H, Ar-H), 7.8292 (d, 1H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 1.02, 14.06, 19.30, 22.61, 25.43, 29.14, 31.74, 72.51, 102.97, 133.30, 133.97, 134.54.

(*R*)-di(nonan-2-yl)-2,5-diethynylbenzoate ((*R*)-4)

(*R*)-di(nonan-2-yl)-2,5-diethynylbenzoate ((*R*)-4) was synthesized as follows. Into a 100 mL round-bottom flask were added compound (**(*R*)-3**) (1.16 g, 2.64 mmol), acetic acid (0.32 g, 5.28 mmol), and 30 mL THF. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and TBAF (7.92 g, 7.92 mmol) was added dropwise to the solution in the flask. After continuous stirring for 1 hour, the solution was then evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, CHCl_3 as eluent). The product was evaporated and dried under vacuum to give compound ((*R*)-4) (1.16 g, 3.90 mmol) as an amber colored oil. Yield = Quantitative. Anal. Chemical Formula: $(\text{C}_{20}\text{H}_{24}\text{O}_2)_n$ (296.41) $_n$: C, 81.04; H, 8.16; O, 10.80. Found: C, 80.16; H, 8.21; O, 11.37.

^1H NMR (400 MHz, CDCl_3 , δ): 0.876 (t, 3H, $-\text{CH}_3$), 1.270-1.746 (m, 15H, $-\text{CH}_2$, $-\text{CH}_3$), 3.210 (s, 1H, acetylene), 3.457 (s, 1H, acetylene), 5.172 (sext, 1H, $-\text{CH}$), 7.554 (d, 2H, Ar-H), 8.024 (s, 1H, Ar-H),

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.06, 19.42, 22.61, 25.40, 29.16, 31.74, 71.49, 102.95, 132.31, 134.10, 134.95.

(S)-di(nonan-2-yl)-2,5-diethynylbenzoate ((S)-4)

(S)-di(nonan-2-yl)-2,5-diethynylbenzoate ((S)-4) was synthesized as follows. Into a 100 mL round-bottom flask were added compound ((S)-3) (0.85 g, 1.93 mmol), acetic acid (0.23 g, 3.86 mmol), and 30 mL THF. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and TBAF (5.79 g, 5.79 mmol) was added dropwise to the solution in the flask. After continuous stirring for 1 hour, the solution was then evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, CHCl_3 as eluent). The product was evaporated and dried under vacuum to give compound ((S)-4) (0.25 g, 0.83 mmol) as an amber colored oil. Yield = 43.0%.

Anal. Chemical Formula: $(\text{C}_{20}\text{H}_{24}\text{O}_2)_n$ (296.41) $_n$: C, 81.04; H, 8.16; O, 10.80. Found: C, 79.01; H, 8.03; O, 12.89.

^1H NMR (400 MHz, CDCl_3 , δ): 0.876 (t, 3H, $-\text{CH}_3$), 1.270-1.746 (m, 15H, $-\text{CH}_2, -\text{CH}_3$), 3.210 (s, 1H, acetylene), 3.457 (s, 1H, acetylene), 5.172 (sext, 1H, $-\text{CH}$), 7.554 (d, 2H, Ar-H), 8.024 (s, 1H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.06, 19.42, 22.61, 25.38, 29.12, 31.74, 71.51, 102.90, 132.31, 134.15, 134.94.

(R)-di(nonan-2-yl)-2,5-dibromoterephthalate ((R)-5)

(R)-di(nonan-2-yl)-2,5-dibromoterephthalate ((R)-5) was synthesized as follows. Into a 200 mL three-necked flask were added TPP (1.07 g 4.08 mmol) and 2,5-dibromoterephthalic acid (0.60 g, 1.85 mmol) under argon gas and dissolved in THF (50 mL). In the addition funnel, a mixture of DEAD (2.06 g, 40 wt% in toluene, 4.08 mmol), (S)-(+)-2-nonanol (0.64 g, 4.45 mmol) and 30 mL THF was prepared. After

dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound **(R)-5** (0.89 g, 1.55 mmol) as a colorless oil. Yield = 84%.

Anal. Chemical Formula: $(\text{C}_{26}\text{H}_{40}\text{Br}_2\text{O}_4)_n$ (576.40) $_n$: Calcd. C, 54.18; H, 7.00; Br, 27.72; O, 11.10; Found C, 54.51; H, 7.11; O, 11.53; Br, 26.69.

^1H NMR (400 MHz, CDCl_3 , δ): 0.881 (t, 6H, $-\text{CH}_3$), 1.276-1.723 (m, 30H, $-\text{CH}_2, -\text{CH}_3$), 5.169 (sext, 2H, $-\text{CH}$), 7.954 (s, 2H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.09, 19.88, 22.64, 25.41, 29.18, 31.78, 35.83, 73.87, 136.11.

(S)-di(nonan-2-yl)-2,5-dibromoterephthalate ((S)-5)

(S)-di(nonan-2-yl)-2,5-dibromoterephthalate ((S)-5) was synthesized as follows. Into a 200 mL three-necked flask were added TPP (1.07 g 4.08 mmol) and 2,5-dibromoterephthalic acid (0.60 g, 1.85 mmol) under argon gas and dissolved in THF (50 mL). In the addition funnel, a mixture of DEAD (2.06 g, 40 wt% in toluene, 4.08 mmol), (R)-(-)-2-nonanol (0.64 g, 4.45 mmol) and 30 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and

extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 as eluent. The collected liquid was evaporated and dried under vacuum to give compound **(R)-5** (0.93 g, 1.61 mmol) as a colorless oil. Yield = 87%.

Anal. Chemical Formula: $(\text{C}_{26}\text{H}_{40}\text{Br}_2\text{O}_4)_n$ (576.40) $_n$: Calcd. C, 54.18; H, 7.00; Br, 27.72; O, 11.10; Found C, 54.29; H, 7.01; O, 10.85; Br, 27.48.

^1H NMR (400 MHz, CDCl_3 , δ): 0.881 (t, 6H, $-\text{CH}_3$), 1.276-1.723 (m, 30H, $-\text{CH}_2, -\text{CH}_3$), 5.169 (sext, 2H, $-\text{CH}$), 7.954 (s, 2H, Ar-H)

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.09, 19.88, 22.64, 25.41, 29.18, 31.78, 35.83, 73.87, 136.11

(R)-di(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)terephthalate ((R)-6)

(R)-di(nonan-2-yl)-2,5-bis((trimethylsilyl)ethynyl)terephthalate **((R)-6)** was synthesized as follows. Into a 200 mL three-necked flask were added compound **(R)-5** (0.35 g, 0.61 mmol), trimethylsilylacetylene (0.36 g, 3.64 mmol), $\text{PdCl}_2(\text{TPP})_2$ (8.52 mg, 0.012 mmol), CuI (2.31 g, 0.012 mmol), 5 mL Et_3N and 10 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, $\text{CHCl}_3/\text{hexane} = 1 : 1$ as eluent). The product was evaporated and dried under vacuum to give compound **(R)-6** (0.39 g, 0.63 mmol) as an amber colored oil. Yield = Quantitative.

Anal. Chemical Formula: $(\text{C}_{36}\text{H}_{58}\text{O}_4\text{Si}_2)_n$ (611.03) $_n$: Calcd. C, 70.77; H, 9.57; O, 10.47; Si, 9.19. Found C, 70.49; H, 9.74.

^1H NMR (400 MHz, CDCl_3 , δ): 0.247 (t, 18H, $-\text{CH}_3$), 0.853 (s, 3H, $-\text{CH}_3$), 1.242-1.763 (m, 30H, $-\text{CH}_2-$), 5.159 (sext, 2H, $-\text{CH}$), 7.985 (s, 2H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.28, 20.17, 22.83, 25.69, 29.40, 31.98, 36.10, 73.29, 102.63, 122.69, 135.25, 136.50, 165.04.

(S)-di(nonan-2-yl)-2,5-bis(trimethylsilyl)ethynylterephthalate ((S)-6)

(S)-di(nonan-2-yl)-2,5-bis(trimethylsilyl)ethynylterephthalate ((S)-6) was synthesized as follows. Into a 200 mL three-necked flask were added compound (S)-5 (0.35 g, 0.61 mmol), trimethylsilylacetylene (0.36 g, 3.64 mmol), $\text{PdCl}_2(\text{TPP})_2$ (8.52 mg, 0.012 mmol), CuI (2.31 g, 0.012 mmol), 5 mL Et_3N and 10 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, $\text{CHCl}_3/\text{hexane} = 1 : 1$ as eluent). The product was evaporated and dried under vacuum to give compound (S)-6 (0.39 g, 0.64 mmol) as an amber colored oil. Yield = Quantitative.

Anal. Chemical Formula: $(\text{C}_{36}\text{H}_{58}\text{O}_4\text{Si}_2)_n$ (611.03) $_n$: Calcd. C, 70.77; H, 9.57; O, 10.47; Si, 9.19. Found C, 70.56; H, 9.36

^1H NMR (400 MHz, CDCl_3 , δ): 0.247 (s, 18H, $-\text{CH}_3$), 0.853 (t, 3H, $-\text{CH}_3$), 1.242-1.763 (m, 30H, $-\text{CH}_2-$), 5.159 (sext, 2H, $-\text{CH}$), 7.985 (s, 2H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.28, 20.17, 22.83, 25.69, 29.40, 31.98, 36.10, 73.29, 102.63, 122.69, 135.25, 136.50, 165.04.

(R)-di(nonan-2-yl)-2,5-diethynylterephthalate ((R)-7)

(R)-di(nonan-2-yl)-2,5-diethynylterephthalate ((R)-7) was synthesized as follows.

Into a 100 mL round-bottom flask were added compound **(R)-6** (0.20 g, 0.33 mmol), acetic acid (0.04 g, 0.66 mmol), and 10 mL THF. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and TBAF (0.26 g, 0.98 mmol) was added dropwise to the solution in the flask. After continuous stirring for 30 m, the solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous Na_2SO_4 . The solution was evaporated and purified by open column chromatography (silica gel, $\text{CHCl}_3/\text{hexane} = 1 : 1$ as eluent). The product was evaporated and dried under vacuum to give compound **((R)-7)** (0.16 g, 0.34 mmol) as an amber colored oil. Yield = Quantitative.

Anal. Chemical Formula: $(\text{C}_{30}\text{H}_{42}\text{O}_4)_n$ (466.66) $_n$: Calcd. C, 77.21; H, 9.07; O, 13.71. Found: C, 72.03; H, 9.40; O, 15.66.

^1H NMR (400 MHz, CDCl_3 , δ): 0.877 (t, 3H, $-\text{CH}_3$), 1.288-1.763 (m, 30H, $-\text{CH}_2, -\text{CH}_3$), 3.495 (s, 2H, acetylene), 5.201 (sext, 2H, $-\text{CH}$), 8.111 (s, 2H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.10, 20.21, 22.68, 25.72, 29.41, 31.99, 36.50, 73.40, 103.41, 123.10, 134.89, 135.25, 165.32.

(S)-di(nonan-2-yl)-2,5-diethynylterephthalate ((S)-7)

(S)-di(nonan-2-yl)-2,5-diethynylterephthalate ((S)-7) was synthesized as follows. Into a 100 mL round-bottom flask were added compound **(S)-6** (0.20 g, 0.33 mmol), acetic acid (0.04 g, 0.66 mmol), and 10 mL THF. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and TBAF (0.26 g, 0.98 mmol) was added dropwise to the solution in the flask. After continuous stirring for 30 m, the solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with CHCl_3 (3 $\times$). The organic layer was dried over anhydrous

Na₂SO₄. The solution was evaporated and purified by open column chromatography (silica gel, CHCl₃/hexane = 1 : 1 as eluent). The product was evaporated and dried under vacuum to give compound ((*S*)-**7**) (0.09 g, 0.20 mmol) as an amber colored oil. Yield = 62%.

Anal. Chemical Formula: (C₃₀H₄₂O₄)_n (466.66)_n: Calcd. C, 77.21; H, 9.07; O, 13.71. Found: C, 77.01; H, 9.19; O, 12.95.

¹H NMR (400 MHz, CDCl₃, δ): 0.877 (t, 3H, -CH₃), 1.288-1.763 (m, 30H, -CH₂,-CH₃), 3.495 (s, 2H, acetylene), 5.201 (sext, 2H, -CH), 8.111 (s, 2H, Ar-H).

¹³C NMR (100 MHz, CDCl₃, δ): 14.11, 20.21, 22.71, 25.72, 29.40, 32.06, 36.50, 73.40, 103.40, 123.06, 134.10, 135.34, 165.30.

(*R*)-PPE1

(*R*)-PPE1 was synthesized as follows. Into a schlenk flask were added compound (**(*R*)-1**) (0.1 g, 0.20 mmol), (**(*R*)-4**) (0.06 g, 0.20 mmol), 0.7 mL THF, and 1.5 mL DIPA (Diisopropylamine) under argon. Into a second schlenk flask were CuI (1.14 mg, 6.00 μmol), Pd(TPP)₄ (6.93 mg, 6.0 μmol), and 0.8 ml THF. After continuous stirring for 1 hour, the solution in the second flask was added to the first via syringe then the solution was heated to 55 °C and left overnight. The mixture was cooled to room temperature, dissolved with CHCl₃ and was added dropwise to 500 mL of methanol under stirring. The polymer precipitate was stirred for 24 h, filtered, then washed again in 500 ml of acetone for 24 h. The polymer was then filtered and dried in vacuo. A yellowish amber colored solid was obtained with a yield of 15.1% (8.7 mg, 0.03 mmol). *M*_w. 17,600 *M*_w/*M*_n. 1.9 (GPC, PS calibration).

Anal. Chemical Formula: (C₁₈H₂₂O₂)_n (286.41)_n: Calcd. C, 79.68; H, 9.15; O, 11.17; Found C, 72.88; H, 7.98; O, 10.91.

^1H NMR (400 MHz, CDCl_3 , δ): 0.885 (br, 3H, $-\text{CH}_3$), 1.255-1.753 (br 15H, $-\text{CH}_2, -\text{CH}_3$), 5.225 (br, 1H, $-\text{CH}$), 7.673 (br, 1H, Ar-H), 8.169 (br, 1H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.10, 19.35, 22.56, 22.61, 25.39, 29.11, 32.08, 73.10, 133.11, 134.09, 135.20.

(S)-PPE1

(S)-PPE1 was synthesized as follows. Into a schlenk flask were added compound **(S)-1** (0.1 g, 0.20 mmol), **(S)-4** (0.06 g, 0.20 mmol), 1 mL THF, and 1.5 mL DIPA under argon. Into a second schlenk flask were CuI (0.99 mg, 5.2 μmol), $\text{Pd}(\text{TPP})_4$ (6.01 mg, 5.2 μmol), and 1ml THF. After continuous stirring for 30 minutes, the solution in the second flask was added to the first via syringe then the solution was heated to 55 $^\circ\text{C}$ and left overnight. The mixture was cooled to room temperature and was added dropwise to 500 mL of methanol under stirring. The polymer precipitate was stirred for 24 h, filtered, then washed again in 500 ml of acetone for 24 h. The polymer was then filtered and dried in vacuo. A yellowish amber colored solid was obtained with a yield of 60.0% (0.06 g, 0.24 mmol). M_w . 15,500 M_w/M_n . 1.7 (GPC, PS calibration).

Anal. Chemical Formula: $(\text{C}_{18}\text{H}_{22}\text{O}_2)_n$ (286.41) $_n$: Calcd. C, 79.68; H, 9.15; O, 11.17; Found C, 71.10; H, 9.97; O, 8.98.

^1H NMR (400 MHz, CDCl_3 , δ): 0.885 (br, 3H, $-\text{CH}_3$), 1.255-1.753 (br, 15H, $-\text{CH}_2, -\text{CH}_3$), 5.225 (br, 1H, $-\text{CH}$), 7.673 (br, 1H, Ar-H), 8.169 (br, 1H, Ar-H).

^{13}C NMR (100 MHz, CDCl_3 , δ): 14.10, 19.33, 22.52, 22.59, 25.39, 29.12, 32.10, 73.25, 133.13, 134.10, 135.20.

(R)-PPE2

(R)-PPE2 was synthesized as follows. Into a schlenk flask were added compound **(R)-1** (0.1 g, 0.17 mmol), **(R)-4** (0.0081 g, 0.17 mmol), 1 mL THF, and 1.5 mL DIPA

under argon. Into a second schlenk flask were CuI (0.99 mg, 5.20 μ mol), Pd(TPP)₄ (6.01 mg, 5.20 μ mol), and 0.8 ml THF. After continuous stirring for 1 hour, the solution in the second flask was added to the first via syringe then the solution was heated to 55 °C and left overnight. The mixture was cooled to room temperature, dissolved with CHCl₃ and was added dropwise to 500 mL of methanol under stirring. The polymer precipitate was stirred for 24 h, filtered, then washed again in 500 ml of acetone for 24 h. The polymer was then filtered and dried in vacuo. A yellowish amber colored solid was obtained with a yield of 15.3% (0.012 g, 0.026 mmol). M_w , 17,600 M_w/M_n , 2.0 (GPC, PS calibration).

Anal. Chemical Formula: (C₂₉H₄₄O₄)_n (456.67)_n: Calcd. C, 76.27; H, 9.71; O, 14.01; Found C, 74.58; H, 9.49; O, 12.14.

¹H NMR (400 MHz, CDCl₃, δ): 0.847 (br, 3H, -CH₃), 1.225-1.748 (br, 30H, -CH₂, -CH₃), 5.224 (br, 2H, -CH), 8.308 (br, 2H, Ar-H).

¹³C NMR (100 MHz, CDCl₃, δ): 14.09, 20.09, 22.64, 25.53, 29.21, 31.81, 36.04, 73.02, 134.80, 136.10, 164.26.

(S)-PPE2

(S)-PPE2 was synthesized as follows. Into a schlenk flask were added compound (S)-1 (0.1 g, 0.17 mmol), (S)-4 (0.0081 g, 0.17 mmol), 1 mL THF, and 1.5 mL DIPA under argon. Into a second schlenk flask were CuI (0.99 mg, 5.20 μ mol), Pd(TPP)₄ (6.01 mg, 5.20 μ mol), and 0.8 ml THF. After continuous stirring for 1 hour, the solution in the second flask was added to the first via syringe then the solution was heated to 55 °C and left overnight. The mixture was cooled to room temperature, dissolved with CHCl₃ and was added dropwise to 500 mL of methanol under stirring. The polymer precipitate was stirred for 24 h, filtered, then washed again in 500 ml of

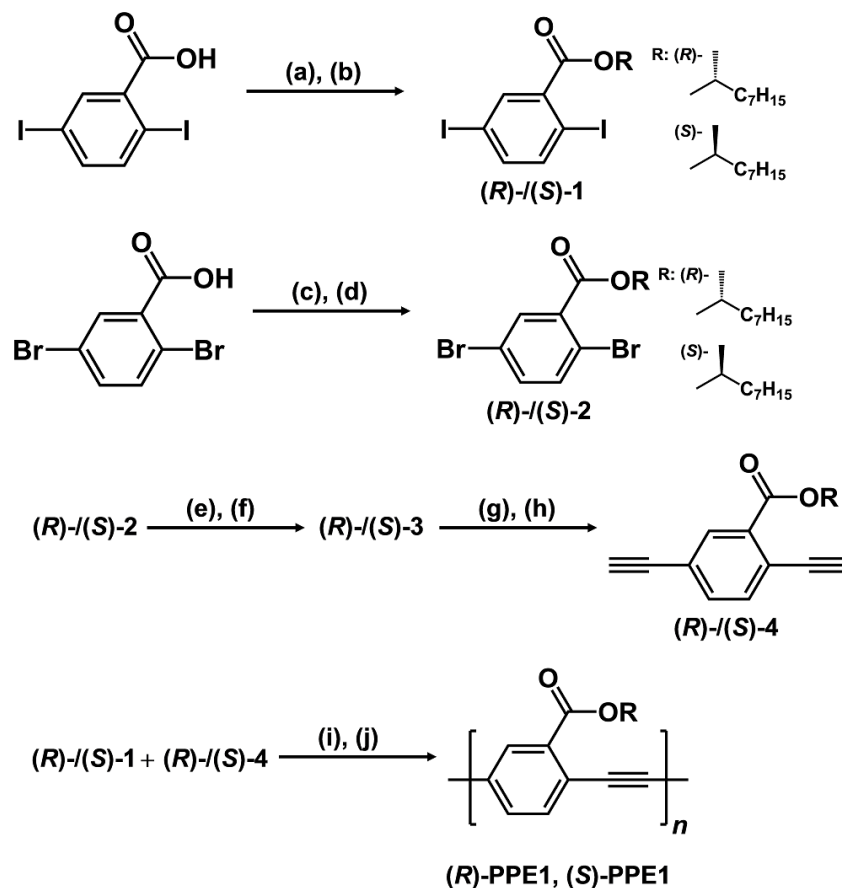
acetone for 24 h. The polymer was then filtered and dried in vacuo. A yellowish amber colored solid was obtained with a yield of 22.3% (0.018 g, 0.04 mmol). M_w . 15,400 M_w/M_n . 1.8 (GPC, PS calibration).

Anal. Chemical Formula: $(C_{29}H_{44}O_4)_n$ (456.67) $_n$: Calcd. C, 76.27; H, 9.71; O, 14.01; Found C, 73.76; H, 8.90; O, 14.40.

1H NMR (400 MHz, $CDCl_3$, δ): 0.847 (br, 3H, $-CH_3$), 1.225-1.748 (br, 30H, $-CH_2, -CH_3$), 5.224 (br, 2H, $-CH$), 8.308 (br, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.09, 20.09, 22.64, 25.53, 29.21, 31.81, 36.04, 73.02, 134.80, 136.10, 164.26.

2. Supporting Figures

Scheme S1. Synthetic routes of polymers.^a

^aConditions: **PPE1**: (a,b) (R)/(S)-2-nonanol, DMAP, DCC, CH₂Cl₂, r.t., 24 h; 89% for (R)-1 and 79% for (S)-1;

(c,d) (R)/(S)-2-nonanol, DMAP, DCC, CH₂Cl₂, r.t., 24 h; 88% for (R)-2 and 67% for (S)-2;

(e,f) (R)-2, (S)-2, TMS-acetylene₂, PdCl₂(TPP)₂, CuI, Et₃N, THF, 70 °C, 24 h; quantitative for (R)-3 and 80% for (S)-3;

(g,h) (R)-3, (S)-3, acetic acid, TBAF, THF, rt, 24 h; quantitative for (R)-4 and 43% for (S)-4;

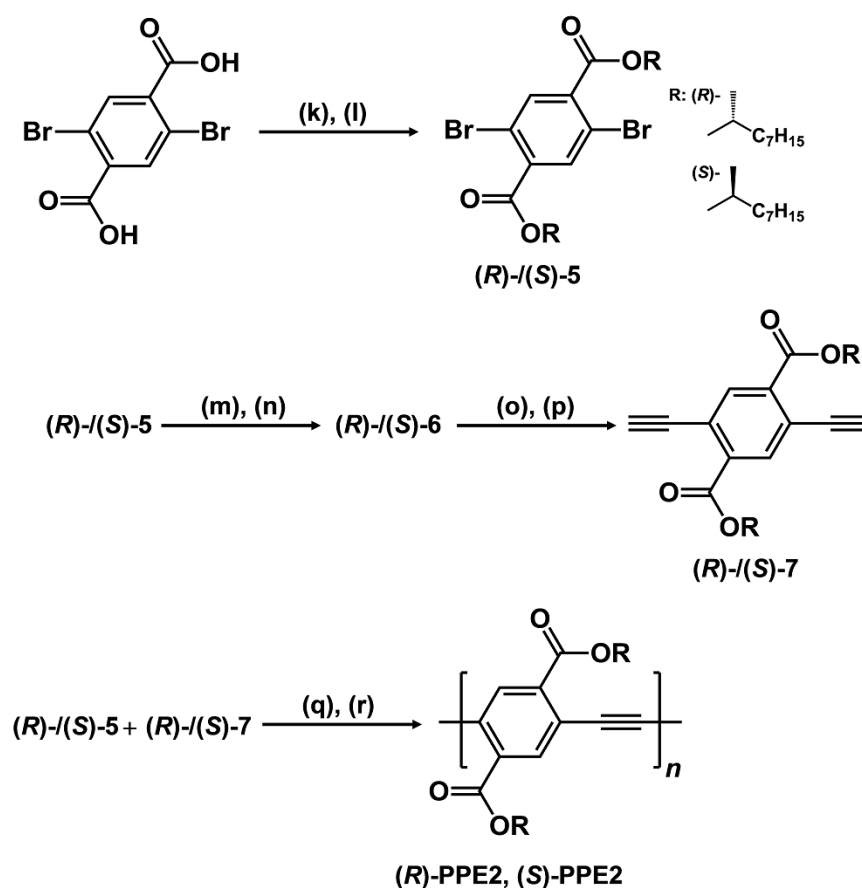
(i,j) (R)-1 & (R)-4, (S)-1 & (S)-4, Pd(TPP)₄, CuI, DIPA, THF, 55 °C, 24 h; 15% for (R)-PPE1 and 60% for (S)-PPE1.

DMAP = N,N-dimethyl-4aminopyridine

DCC = dicyclohexylcarbodiimide

TBAF = tetrabutylammonium fluoride

DIPA = diisopropylamine



PPE2: (k,l) (S)/(R)-2-nonanol, DEAD, TPP, THF, r.t., 24 h; 84% for (R)-5 and 87% for (S)-5;

(m,n) (R)-5, (S)-5, TMS-acetylene₂, PdCl₂(TPP)₂, CuI, Et₃N, THF, 65 °C, 24 h; quantitative for (R)-6 and quantitative for (S)-6;

(o,p) (R)-6, (S)-6, acetic acid, TBAF, THF, rt, 24 h; quantitative for (R)-7 and 62% for (S)-7;

(q,r) (R)-5 & (R)-7, (S)-5 & (S)-7, Pd(TPP)₄, CuI, DIPA, THF, 55 °C, 24 h; 15% for (R)-PPE2 and 22% for (S)-PPE2.

DEAD = diethylazodicarboxylate

TPP = triphenylphosphine

Table S1. Quantum Yield measurements of (S)-PPE1 and (S)-PPE2 aggregate solutions.

Φ (%) ^a	CHCl ₃	20 % ^b	40 %	45 %	50 %	55 %	60 %	70 %	80 %	90 %	95 %
(S)-PPE1	64	63	62	57	48	36	21	–	9	–	10
(S)-PPE2	66	65	64	–	66	–	65	35	31	33	33

^aAbsolute quantum yield measured using Integrating Sphere System^bMeOH % (v/v)**Table S2.** Absorption dissymmetry factors (g_{abs}) measurements of (R)-PPE1 and (S)-PPE1 aggregate solutions at 440 nm.

MeOH ratio (%)	(R)-PPE1	(S)-PPE1
CHCl ₃	–	–
20 %	–	–
40 %	–	-2.21×10^{-3}
45 %	–	-7.67×10^{-3}
50 %	6.09×10^{-3}	-3.79×10^{-2}
55 %	5.20×10^{-3}	-2.90×10^{-2}
60 %	3.54×10^{-3}	-1.48×10^{-2}
80 %	6.80×10^{-4}	-1.25×10^{-3}
95 %	1.50×10^{-4}	-3.20×10^{-4}

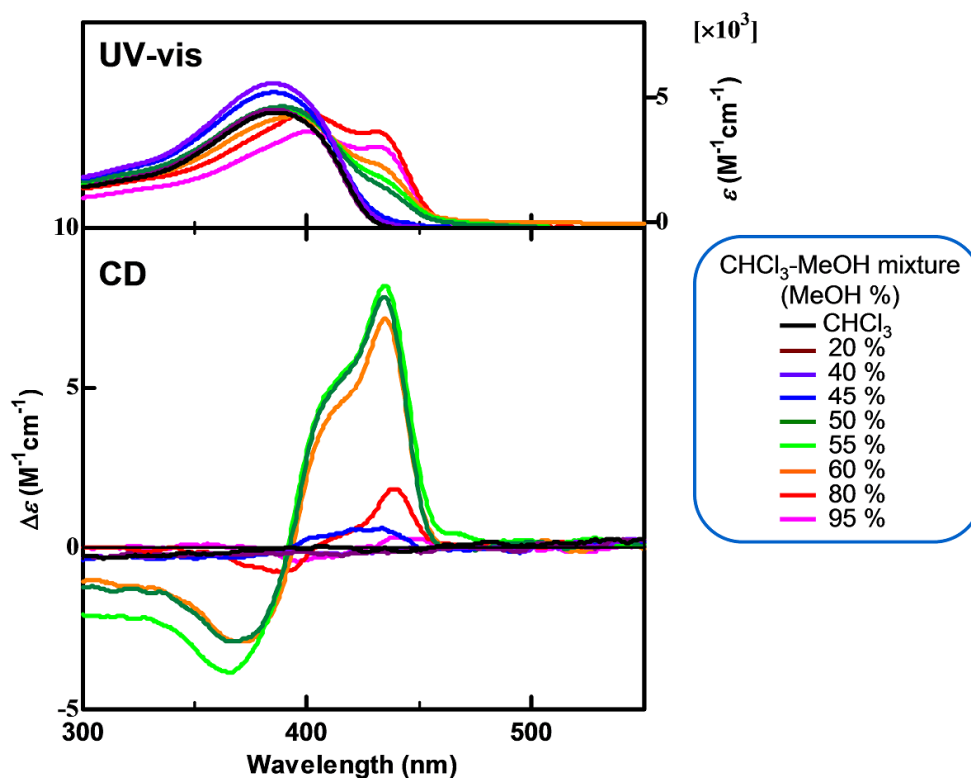


Figure S1. UV-Vis (above), and CD spectra (below) of *(R)*-PPE1 aggregate solutions.

Table S3. Absorption dissymmetry factors (g_{abs}) measurements of *(R)*-PPE2 and *(S)*-PPE2 aggregate solutions at 470 nm.

MeOH ratio (%)	<i>(R)</i> -PPE2	<i>(S)</i> -PPE2
CHCl_3	—	—
20 %	—	—
40 %	—	—
50 %	—	—
60 %	-5.13×10^{-3}	-6.40×10^{-4}
70 %	-9.06×10^{-3}	3.32×10^{-3}
80 %	-3.07×10^{-3}	5.95×10^{-3}
90 %	9.24×10^{-3}	-1.26×10^{-2}
95 %	5.64×10^{-3}	-2.54×10^{-2}

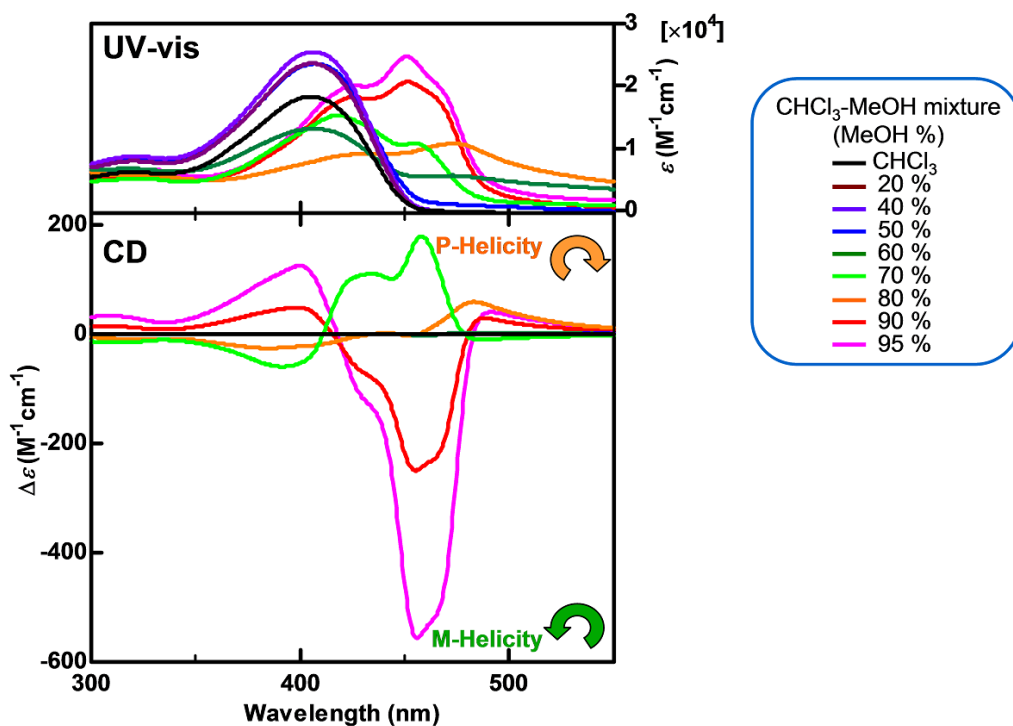
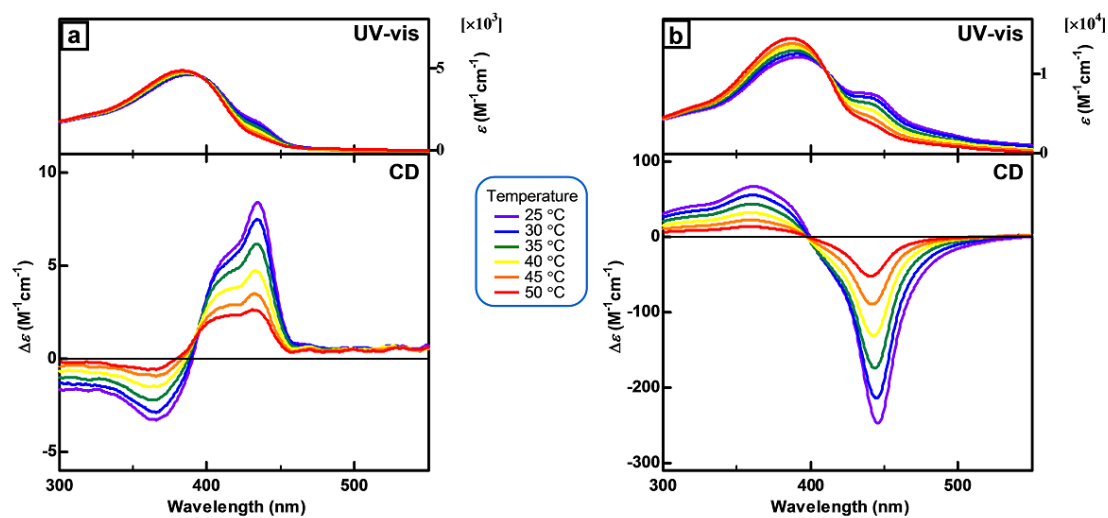


Figure S2. UV-Vis (above), and CD spectra (below) of (*S*)-PPE2 aggregate solutions.



Temperature (°C)	(<i>R</i>)-PPE1 (55% MeOH)	(<i>S</i>)-PPE1 (50% MeOH)
25°C	5.20×10^{-3}	-3.49×10^{-2}
30°C	5.04×10^{-3}	-3.24×10^{-2}
35°C	4.59×10^{-3}	-2.93×10^{-2}
40°C	4.08×10^{-3}	-2.51×10^{-2}
45°C	3.55×10^{-3}	-2.06×10^{-2}
50°C	3.13×10^{-3}	-1.42×10^{-2}

Figure S3. UV-Vis (above), and CD spectra (below) of (a) (*R*)-PPE1 at 55% MeOH and (b) (*S*)-PPE1 at 50% MeOH in heating process. (c) g_{abs} values of (*R*)-/(*S*)-PPE1.

Table S4. Absorption dissymmetry factors (g_{abs}) measurements of (R)-PPE2 aggregate solutions at 470 nm in heating and cooling process.

Temperature (°C) (Heating)	(R)-PPE2 (70% MeOH)	(R)-PPE2 (90% MeOH)	Temperature (°C) (Cooling)	(R)-PPE2 (70% MeOH)	(R)-PPE2 (90% MeOH)
– 10°C	-2.31×10^{-2}	–	40°C	-4.37×10^{-3}	–
– 5°C	-2.34×10^{-2}	–	35°C	-8.84×10^{-3}	–
0°C	-2.40×10^{-2}	–	30°C	-1.47×10^{-2}	–
5°C	-2.40×10^{-2}	–	25°C	-1.31×10^{-2}	–
10°C	-2.38×10^{-2}	–	20°C	-1.20×10^{-2}	–
15°C	-2.47×10^{-2}	–	15°C	-1.24×10^{-2}	–
20°C	-2.57×10^{-2}	–	10°C	-1.24×10^{-2}	–
25°C	-2.73×10^{-2}	1.05×10^{-2}	5°C	-1.21×10^{-2}	–
30°C	-2.94×10^{-3}	1.04×10^{-2}	0°C	-1.22×10^{-2}	–
35°C	-3.19×10^{-3}	1.03×10^{-2}	–5°C	-1.24×10^{-2}	–
40°C	-3.16×10^{-3}	1.00×10^{-2}	–10°C	-1.26×10^{-2}	–
45°C	-3.13×10^{-3}	9.80×10^{-3}			
50°C	-2.25×10^{-3}	9.59×10^{-3}			
55°C	-1.14×10^{-3}	9.36×10^{-3}			
60°C	–	9.09×10^{-3}			

Table S5. Emission dissymmetry factors (g_{em}) measurements of (R)-/(S)-PPE2 aggregate solutions (measured wavelength in parenthesis).

MeOH ratio (%)	(R)-PPE2	(S)-PPE2
CHCl ₃	2.65×10^{-3} (527)	2.65×10^{-3} (560)
20 %	2.27×10^{-3} (527)	2.73×10^{-3} (549)
40 %	2.83×10^{-3} (548)	2.70×10^{-3} (540)
50 %	2.61×10^{-3} (542)	3.26×10^{-3} (566)
60 %	3.14×10^{-3} (555)	3.43×10^{-3} (564)
70 %	-4.55×10^{-3} (491)	1.83×10^{-2} (488)
80 %	-6.32×10^{-3} (475)	1.06×10^{-2} (488)
90 %	1.17×10^{-2} (499)	-5.66×10^{-2} (474)
95 %	1.56×10^{-2} (476)	-2.17×10^{-2} (459)

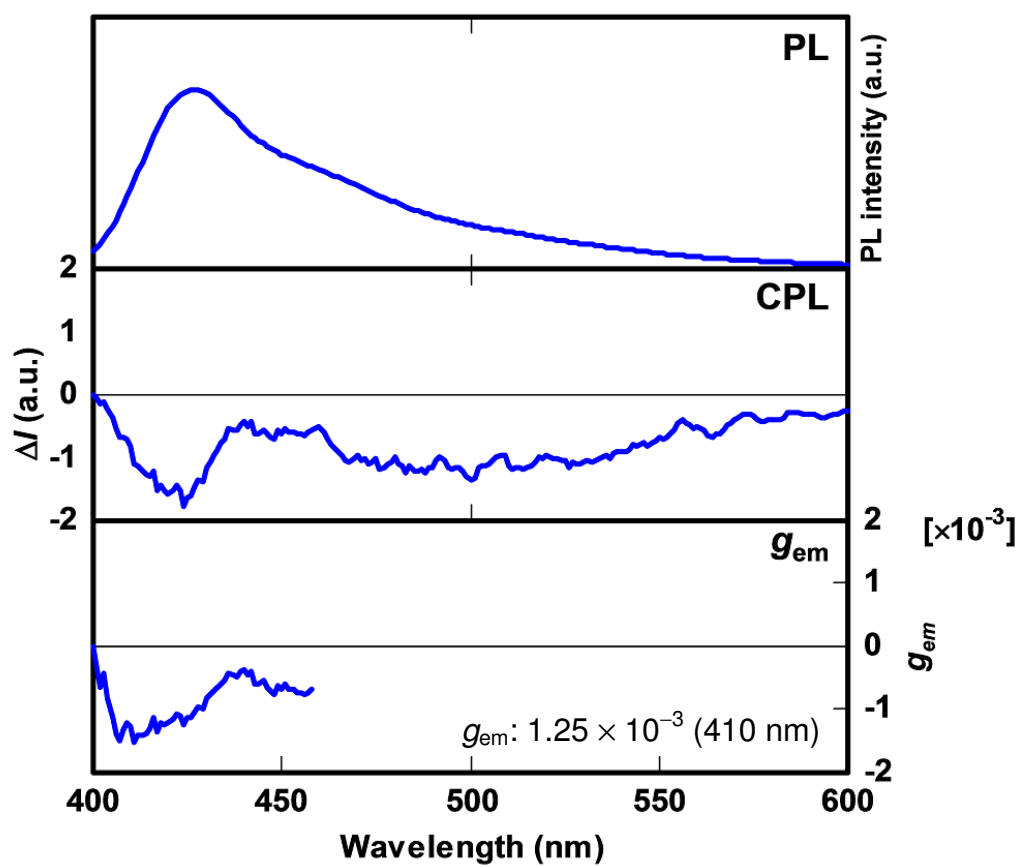


Figure S4. PL (upper), CPL (middle), and g_{em} (lower) spectra of (S)-PPE1 in 50% MeOH solution

REFERENCES

- (1) Wulff, G. *Angew. Chem.* **1989**, *101*, 22–38.
- (2) Janssen, H. M.; Meijer, E. W. *Macromolecules* **1997**, *30*, 8129–8138.
- (3) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385–387.
- (4) Okamoto, Y.; Nakano, T.; Ono, E.; Hatada, K. *Chem. Lett.* **1991**, *20*, 525–528.
- (5) (a) Pohl, F. M.; Jovin, T. M. *J. Mol. Biol.* **1972**, *67*, 375–396. (b) Cosstick, R.; Eckstein, F. *Biochemistry* **1985**, *24*, 3630–3638.
- (6) Li, C.; Numata, M.; Takeuchi, M.; Shinkai, S. *Chem Asian J.* **2006**, *1*, 95–101.
- (7) (a) Kawagoe, Y.; Fujiki, M.; Nakano, Y. *New J. Chem.*, **2010**, *34*, 637–647. (b) Nakano, Y.; Lui, Y.; Fujiki, M. *Polym. Chem.*, **2010**, *1*, 460–469. (c) Nakano, Y.; Ichiyanagi, F.; Naito, M.; Yang, Y.; Fujiki, M. *Chem. Commun.*, **2012**, *48*, 6636–6638.
- (8) (a) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157–160. (b) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702–6704. (c) Goto, H.; Okamoto, Y.; Yashima, E. *Macromolecules* **2002**, *35*, 4590–4601. (d) Koeckelberghs, G.; Cornelis, D.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1132–1136.
- (9) (a) Satrijo, A.; Swager, T. M. *Macromolecules* **2005**, *38*, 4054–4057. (b) Satrijo, A.; Meskers, S. C. J.; Swager, T. M. *J. Am. Chem. Soc.*, **2006**, *128*, 9030–9031.

- (10) Zahn, S; Swager, T. M. *Angew. Chem. Int. Ed.* **2002**, *41*, 4225–4230.
- (11) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467–4470. (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46–49. (c) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380–2382. (d) Neises, B.; Steglich, W. *Angew. Chem. Int. Ed.* **1978**, *17*, 522–524.
- (12) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030–1034.
- (13) (a) Harada, N.; Nakanishi, K. In *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*. University Science Books: California, **1983**. (b) Berova, N.; Nakanishi, K. In *Circular Dichroism: Principles and Applications*, 2nd Edition.; Berova, N.; Nakanishi, K.; Woody, R. Eds. John Wiley and Sons, Inc : New York, **2000**; Chapter. 12, 337–382.
- (14) Jyothish, K.; Hariharan, M., Ramaiah, D. *Chem. Eur. J.* **2007**, *13*, 5944–5951.
- (15) Lohr, A.; Lysetska, M.; Whrthner, F. *Angew. Chem. Int. Ed.* **2005**, *44*, 5071–5074.
- (16) Yamada, T.; Nagata, Y.; Suginome, M. *Chem. Commun.*, **2010**, *46*, 4914–4916.

Chapter 5**Photoswitchable, Helically π -Stacked Assemblies of Poly(*para*-phenylene)****Derivatives Bearing Photoresponsive Chiral End-groups****ABSTRACT:**

We synthesized poly(*para*-phenylene) (PPP) derivatives bearing photoresponsive chiral dithienylethene (DE*) end-groups, which induced chirality in the PPP main chain. In the assembled state, photoisomerization of the chiral DE* end-groups from the open to closed form changed the handedness of the helically π -stacked structures. The circular dichroism spectra of mixed solvent solutions and cast films of the PPP assemblies exhibited bisignate Cotton effects in the absorption region associated with the polymer main chain; these features indicate the presence of helically π -stacked structures. The conformation change of the chiral DE* end-groups, from the open to closed form, led to a helical inversion of the PPP π -stacked assemblies. Furthermore, the chiral transcription of achiral poly(bithiophenethiophene) by assembled chiral PPP was demonstrated. The chirally transcribed PBTT showed helical inversion with the photoisomerization of the PPP chiral DE* end-groups. We present the first report of helical inversion of a conjugated polymer using a photoresponsive moiety. These photoresponsive PPP assemblies can be used in dynamic optical memory systems and functional chiroptical devices.

1. Introduction

Many researchers have brought about chiral inversions in π -conjugated systems and polymers by changing the nature of the polymer environment without affecting their stereocenters.¹ These changes in chirality have been generated by varying parameters such as the temperature,² pH,³ and salt concentration.⁴ One facile way to change the handedness of conjugated polymers is to incorporate a photoresponsive chiral moiety within their structures.

Photoresponsive compounds have been widely researched and, due to their fast switching abilities, ease of synthesis, and versatility, have been used in a variety of applications. Introduction of photoresponsive moieties in π -conjugated systems have made possible the switching of optoelectronic properties of conducting polymers,⁵ photoinduced aggregates,⁶ and supramolecular assemblies.⁷ They have been also used for the dynamic switching of linearly polarized luminescence (LPL)⁸ and circularly polarized luminescence (CPL)⁹ and in the development of molecular nanomachines,¹⁰ phototunable chiral nematic LCs,¹¹ and phototunable photonic bandgap materials.¹²

Azobenzenes, sterically overcrowded stilbenes, spiropyrans, azulenes, and fluorenes are examples of well-studied photochromic molecules that show reversible changes in their molecular structure and absorption spectrum upon photo- and/or thermal induction.¹³ Chiral compounds having an azobenzene moiety have been used as chiral dopants due to their photochemical *trans*–*cis* isomerization behavior.¹⁴ Although easy to synthesize, the azo group has low fatigue resistance and is thermally unstable.

Meanwhile, dithienylethene (DE) derivatives, which are also able to undergo conformational changes between the open and closed forms via photoisomerization, are resistant to fatigue and are thermally stable. Therefore, it is advantageous to employ

these derivatives in photochromic materials compared to other photoresponsive compounds.^{13b,15}

Herein, we report the synthesis of poly(*para*-phenylene) (PPP) derivatives that have photoresponsive chiral DE* end-groups. These end-groups induced chirality in the main PPP chains. We demonstrated that in the assembled state, the photoisomerization of the chiral DE* end-groups from the open to the closed form leads to a change in the helicity of the π -stacked structures. Furthermore, the chiral transcription of achiral poly(bithiophenethiophene) (PBTT) by chiral PPP in the assembled state was also demonstrated. The chirally transcribed PBTT showed helical inversion upon the photoisomerization of the chiral DE* end-groups of PPP.

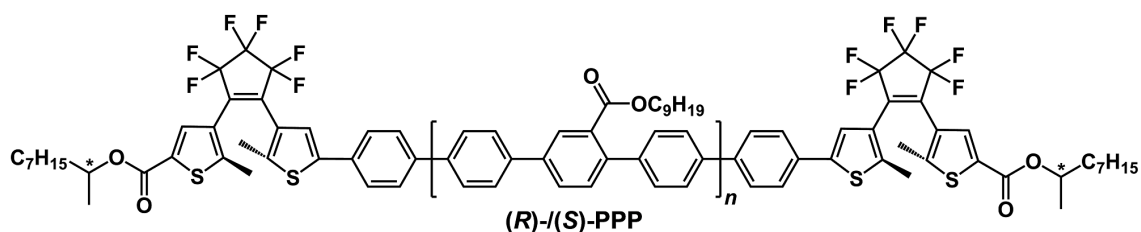
To the best of our knowledge, this paper is the first report of chirality inversion of a helically π -stacked conjugated polymer through the photoisomerization of a chiral photoresponsive moiety. Such assemblies could be attractive for use in optoelectronic devices and optical memory systems.

2. Results and Discussion

2.1. Synthesis and Characterization of the Polymers

Poly(*para*-phenylene) derivatives bearing photoresponsive chiral dithienylethene end-groups were synthesized (Scheme 1). The PPP main chain was substituted with a *n*-nonyloxycarbonyl moiety, and the photoresponsive chiral DE* end-groups were substituted with a chiral nonyloxycarbonyl moiety possessing either (*R*)- or (*S*)-handedness ((*R*)- or (*S*)-PPP, respectively).

The synthetic routes to the precursors, photoresponsive chiral DE* end-groups, monomers, and polymers are given in Scheme S1 at the supporting figures section.



Scheme 1. Structure of the chiral PPP derivatives bearing photoresponsive chiral DE* endgroups.

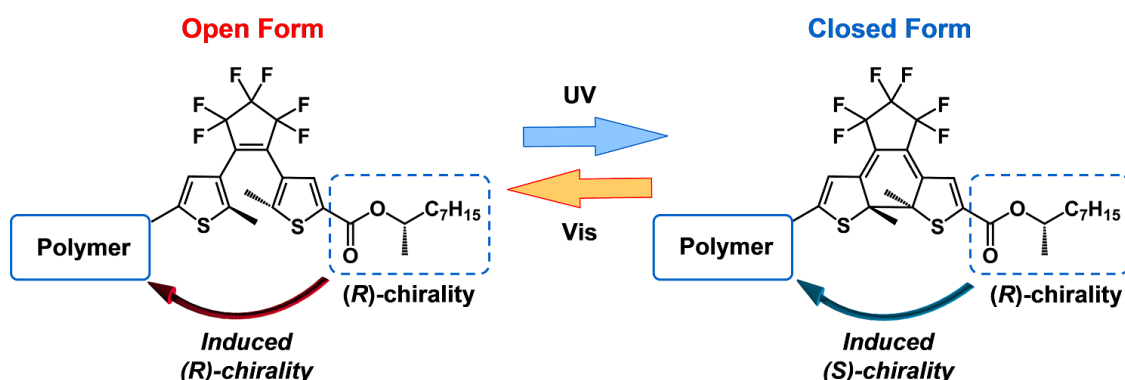
Briefly, the monomers *n*-nonyl-2,5-dibromobenzoate and 4,4'-biphenyldiboronic acid bis(trimethylene glycol) cyclic ester and the **(R)-/(S)-Br-DE*** end-groups were copolymerized via a Suzuki coupling reaction in which tetrakis(triphenylphosphine)palladium(0) (Pd(TPP)₄) was used as the catalyst. The polymerization was conducted at 80 °C under an argon atmosphere using tetrahydrofuran (THF) and water as the solvent system. The reaction proceeded for 24 h, and then the polymer was washed in water under constant stirring for an additional 24 h. Next, the precipitated polymers were filtered and subsequently washed in methanol (MeOH) for 24 h. Finally, they were dried under vacuum.

The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were measured using gel permeation chromatography (GPC) (calibrated using a polystyrene (PS) standard). According to the GPC results, the M_n of the polymers ranged from 4,200 to 4,600 and had M_w/M_n values of 1.1 and degrees of polymerization between 10 and 11 (Table S1).

2.2. Photoswitching behavior of the chiral PPPs

The chirality of the synthesized PPPs bearing photoswitchable chiral DE* end-groups could be switched using UV and visible light. In the case of **(R)-PPP** bearing photoswitchable DE* with (*R*)-chirality, the chirality of the main chain could be

controlled by changing the conformation of the chiral DE* end-groups. Upon irradiation with UV light (254 nm), the end-groups adopted a closed conformation, which induced (*S*)-chirality in the PPP main chain. Conversely, upon irradiation with visible light, the DE end-groups adopted an open conformation, which induced (*R*)-chirality in the PPP main chain (Scheme 2).



Scheme 2. Photoisomerization of the chiral DE* endgroups leads to a switching of chirality of the PPP main chain.

The photoisomerization of the chiral DE* end-groups of (*R*)-/(*S*)-PPP was examined via ^1H NMR (in CDCl_3) (Figure S1). Two broad signals were observed at 1.95 and 2.00 ppm, and these peaks were assigned to the methyl protons at the 5,5' substitution position of the dithienylethene moiety in its open form. When the system was irradiated with UV light ($\lambda = 254$ nm, 4 W), photoisomerization occurred and two new broad signals at 2.21 and 2.25 ppm appeared, which corresponded to the methyl protons at the 5,5' substitution position of the dithienylethene moiety in its closed form. The integrated intensities of the proton signals indicated that 84 % and 83 % of the open forms were converted to the closed forms in the photostationary states (PSS) of (*R*)-PPP and (*S*)-PPP, respectively. The PSS is defined as $\{[\text{closed form}]/([\text{open form}] + [\text{closed form}])\} \times 100$.^{15a,c} After subsequent irradiation of the systems with visible

light ($\lambda > 400$ nm, 100 W), the only signals observed were those of the open form. The values of conversion of the PSS of **(R)/(S)-PPP** were similar to those of the chiral DE* end-group precursors, **(R)/(S)-Br-DE*** (Table S2). Note that because the closed form is not completely formed after irradiation with UV light, we will refer to the mixture of structures obtained as the closed form/PSS from here on out.

The UV-vis absorption and circular dichroism (CD) spectra of the chiral DE* end-group precursors, **(R)/(S)-Br-DE***, in a solution of chloroform (CHCl_3) do not show absorption peaks indicative of the open forms of the compound in the visible range (Figure 1a). Upon irradiation of **(R)/(S)-Br-DE*** with UV light, the closed forms/PSSs exhibit absorption peaks and monosignate Cotton effects around 550 nm (Figure 1b). These bands originate from the extended conjugation between the thiophene rings and the six-membered ring that bridges them in the closed form of the molecule. The DE functional group photoisomerizes quickly, is highly stable, and resists fatigue upon repeated irradiation with UV and visible light. The **(R)-Br-DE***

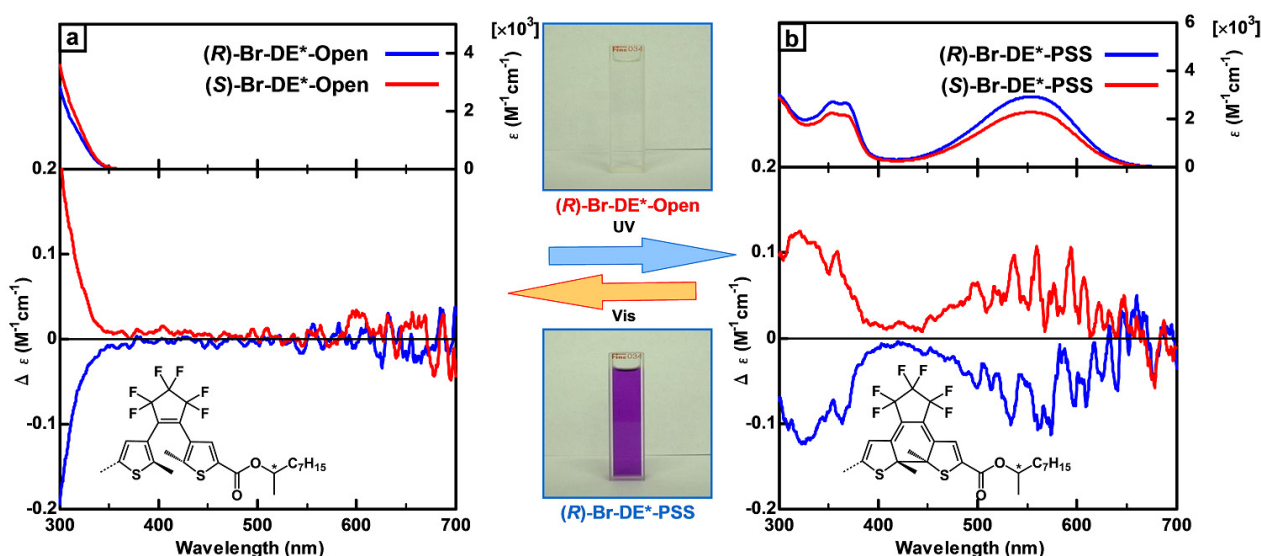


Figure 1. UV-vis (upper) and CD (lower) spectra of **(R)/(S)-Br-DE*** (CHCl_3 solution) in (a) open form and (b) PSS. Photograph of **(R)-Br-DE*** solution in open form (center top) and PSS (center bottom).

solution shows photochromic behavior when the conformation of the photoresponsive chiral end-group changes.

Furthermore, a CHCl_3 solution of **(R)-/(S)-PPP** shows photochromic behavior upon irradiation with UV light due to the emergence of an absorption peak at 600 nm, which is indicative that the chiral DE^* end-groups are in the closed form (Figure 2). When the chiral DE^* end-groups are in the open form, the UV-vis spectrum reveals an absorption peak at 340 nm from the PPP main chain. When the end-groups are in the closed form, a shoulder band emerges between 360 nm and 420 nm and the absorption peak of the end-groups are also present at 600 nm. The extended π -conjugation between the closed form of the chiral DE^* end-groups and the PPP main chain leads to a bathochromic shift of the peak from 550 nm to 600 nm.

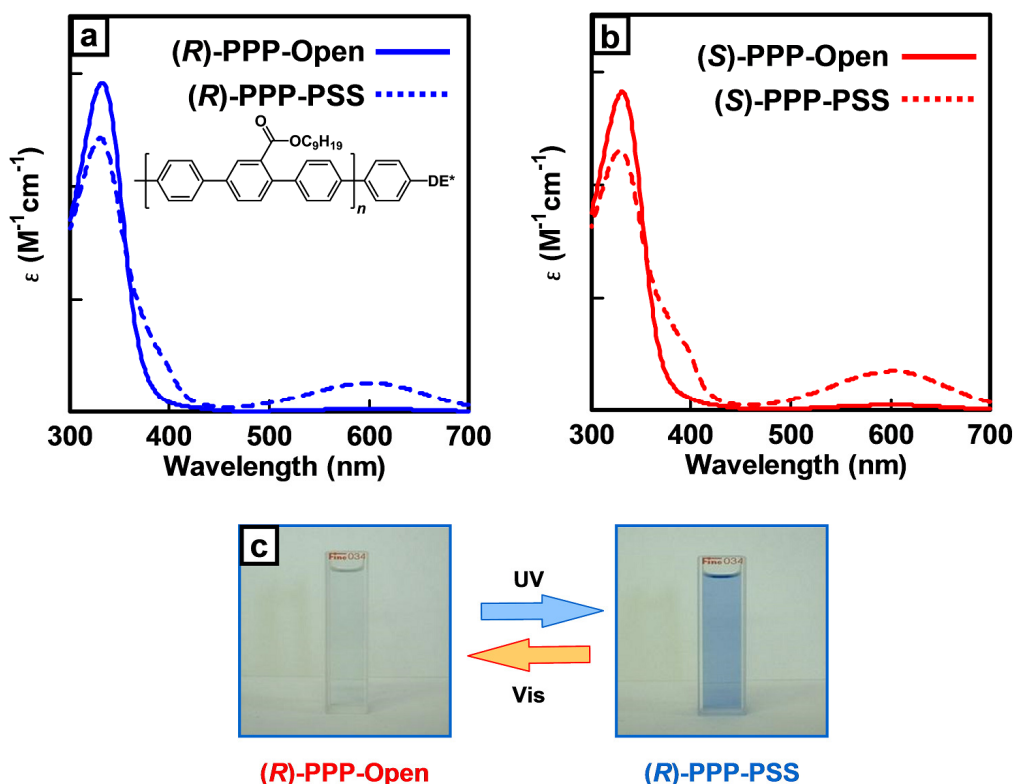


Figure 2. (a) UV-vis spectra of (a) **(R)-PPP** and (b) **(S)-PPP** (CHCl_3 solution) in open form and PSS. (c) Photograph of **(R)-PPP** solution in open form (left) and PSS (right).

It has been reported that the CD spectra of CHCl_3 solutions of aromatic conjugated polymers substituted with chiral nonyloxycarbonyl moieties, such as poly(thiophene) or poly(phenylthiophene), exhibit monosignate Cotton effects. These effects are due to the transfer of chirality from the chiral side chains to the main chain via “through bond interactions”.¹⁶ In contrast, the CD spectra of CHCl_3 solutions of **(R)-/(S)-PPP** in both the open and closed forms did not exhibit Cotton effects. These results suggest that the PPP main chain does not form an intrachain one-handed helical structure in solution, likely because the chiral centre is located on the end-group, far from the PPP main chain. This distance makes intrachain chiral induction difficult.

2.3 Helical Switching of the PPPs in Assembled State

In solution, **(R)-/(S)-PPP** do not exhibit Cotton effects. However, in the assembled state, the polymers can exhibit helically π -stacked structures. For instance, highly planar thiophene-based aromatic conjugated copolymers, such as poly(diphenylenethiophene), have been reported to adopt helically π -stacked structures in the assembled state.¹⁶ Thus, we investigated whether PPP could form helically π -stacked structures in the assembled state (either in a mixed solvent or a cast film system).

First, **(R)-/(S)-PPP** was dissolved in CHCl_3 and exposed to either UV or visible light to obtain the open or closed form of the chiral DE* end-groups. Then, a poor solvent (i.e., methanol (MeOH)) was added to the solution (CHCl_3 :MeOH, 1:1 v/v) and polymer assemblies were formed. The absorption and CD spectra of the polymer assemblies were measured.

The CD spectra of **(R)-/(S)-PPP** revealed bisignate Cotton effects in the region

associated with the PPP main chain, which suggests that helically π -stacked structures are formed in the assembled state (Figure 3). π -stacked assemblies of (*R*)-/(*S*)-PPP switch chirality upon photoisomerization of the chiral DE* end-groups. Exciton coupling theory¹⁷ indicates that the open form of (*R*)-PPP has *P*-helicity and a right-handed helically π -stacked structure, while the closed form/PSS of (*R*)-PPP has *M*-helicity and a left-handed helically π -stacked structure (Figure 3a). Assemblies of (*S*)-PPP also switched chirality between the open (*M*-helicity) and closed form (*P*-helicity) with opposite handedness relative to (*R*)-PPP (Figure 3b).

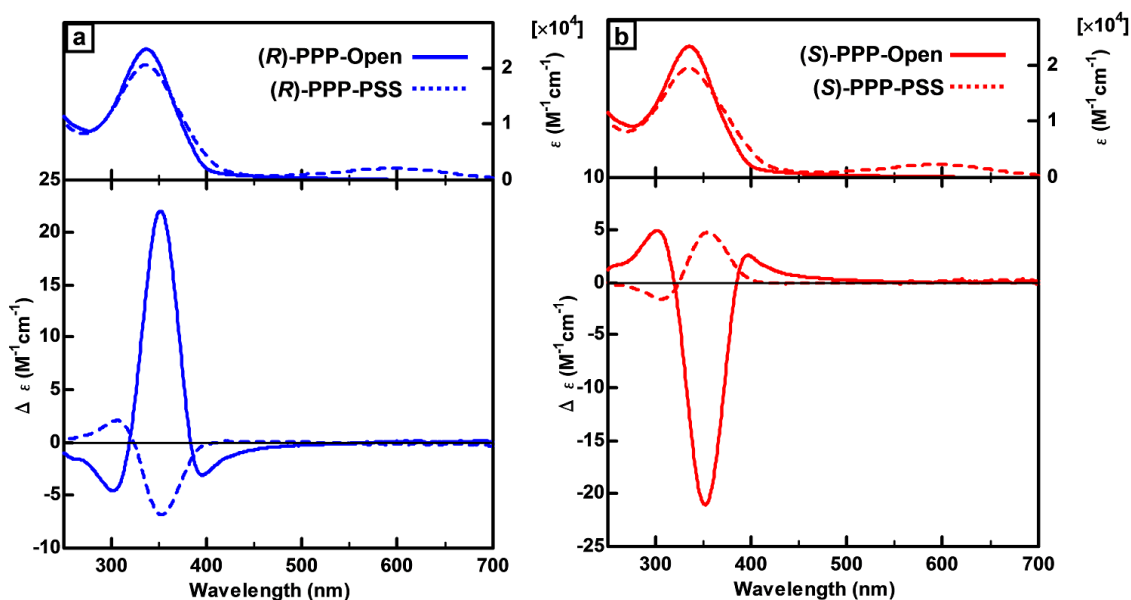


Figure 3. UV-vis (upper) and CD (lower) spectra of (a) (*R*)-PPP and (b) (*S*)-PPP assembled state (CHCl_3 :MeOH, 1:1 v/v solution) in open form and PSS.

It should be noted that the Cotton effects of the open and closed forms of the (*R*)-/(*S*)-PPP assemblies were not symmetric, as the open form showed a larger intensity compared to the closed form. These results are related to the degree of conversion of the end-groups from the open to the closed form. Photoresponsive DE molecules show varying degrees of conversion from the open to closed form depending on their molecular structures as well as conditions including temperature and solvent

environment.^{15a,b,18} In other words, when **(R)-/(S)-PPP** in its open form is exposed to UV light and photoisomerization occurs, not all of the chiral DE* end-groups are converted to the closed form. A difference in the chiral induction strength was observed for the open and closed forms of the chiral DE* end-groups in PPP because not all of the end-groups are converted. Furthermore, the open form of the chiral DE* end-group has a more bulky conformation, which induces a more twisted helically π -stacked structure. Figure 4 shows a schematic model of the formation of helical π -stacked assemblies of **(R)-PPP** having either left- or right-handed helical sense in open form or closed form/PSS, respectively.

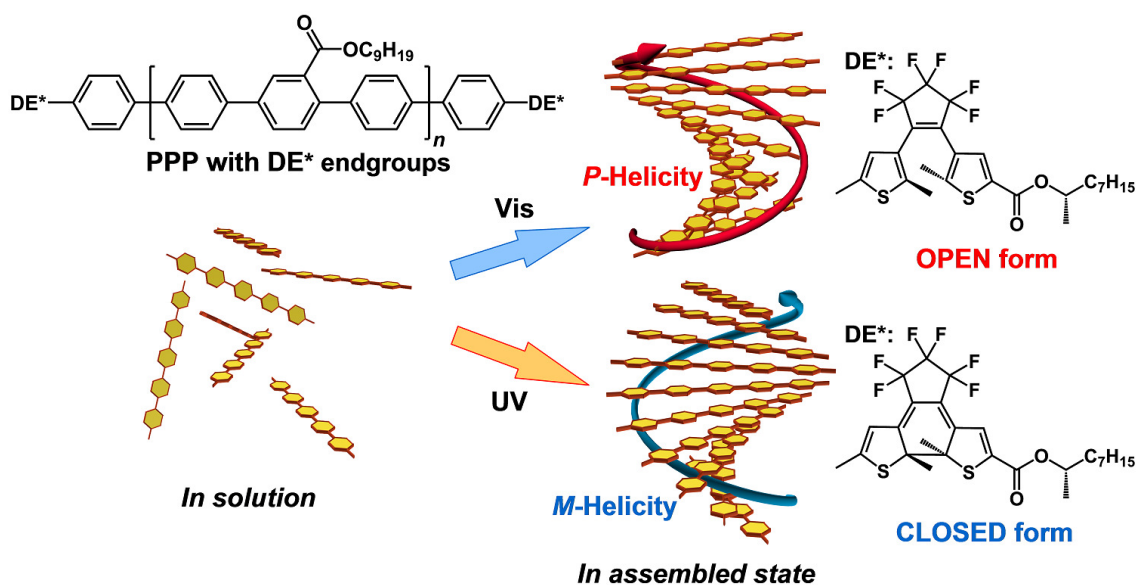


Figure 4. Schematic model of the helically π -stacked assemblies of **(R)-PPP** exhibiting opposite helical sense upon photoisomerization of the chiral DE* end-groups.

After the formation of the **(R)-/(S)-PPP** assemblies in the mixed solvent, subsequent photoisomerization of the chiral DE* end-groups from either the PSS to the open form or vice versa did not cause a significant change in the CD spectra of system (Figure S2). Such behavior was also observed with **(R)-PPP** cast films (Figure S3). During the

formation of the polymer assemblies, the handedness of the helically π -stacked structures was determined by the chirality of the DE* end-groups. In the assembled state, strong interchain interactions maintain the handedness of the helically π -stacked structures, which prevent the chiral inversion of the DE* end-groups.

2.4 Helical Switching of Achiral PBTT in Assembled State through Chiral Transcription

We observed that **(R)-/(S)-PPP** form helically π -stacked structures in the assembled state in both mixed solvent solutions and cast films. Furthermore, we investigated the potential for the induction of chirality in an achiral polymer by chiral PPP through chiral transcription. First, **(R)-/(S)-PPP** was dissolved in CHCl_3 and was either exposed to UV or visible light to select the open or closed form of the chiral DE* end-groups. Then, an achiral polymer, poly(bithiophenethiophene) (**PBTT**), was added to the solution at a 1:1 mole ratio. The polymer mixture was then drop-cast onto a quartz substrate, and the CD spectra of the resulting film was measured.

The CD spectrum of the **(R)-PPP-Open/PBTT** cast film shows bisignate Cotton effects from 250 nm to 400 nm and from 450 nm to 700 nm that are associated with the absorption of the main chain of PPP and PBTT, respectively (Figure 5a). The **(R)-PPP-PSS/PBTT** cast film shows bisignate Cotton effects associated with the PPP and PBTT absorption bands having opposite handedness relative to **(R)-PPP-Open/PBTT**. Likewise, **(S)-PPP-Open/PBTT** and **(S)-PPP-PSS/PBTT** show bisignate Cotton effects having opposite handedness relative to their **(R)-PPP/PBTT** counterparts (Figure 5b). The CD results indicate that chiral transcription occurred in the achiral PBTT through the formation of helically π -stacked

structures consisting of chiral PPP and achiral PBTT.

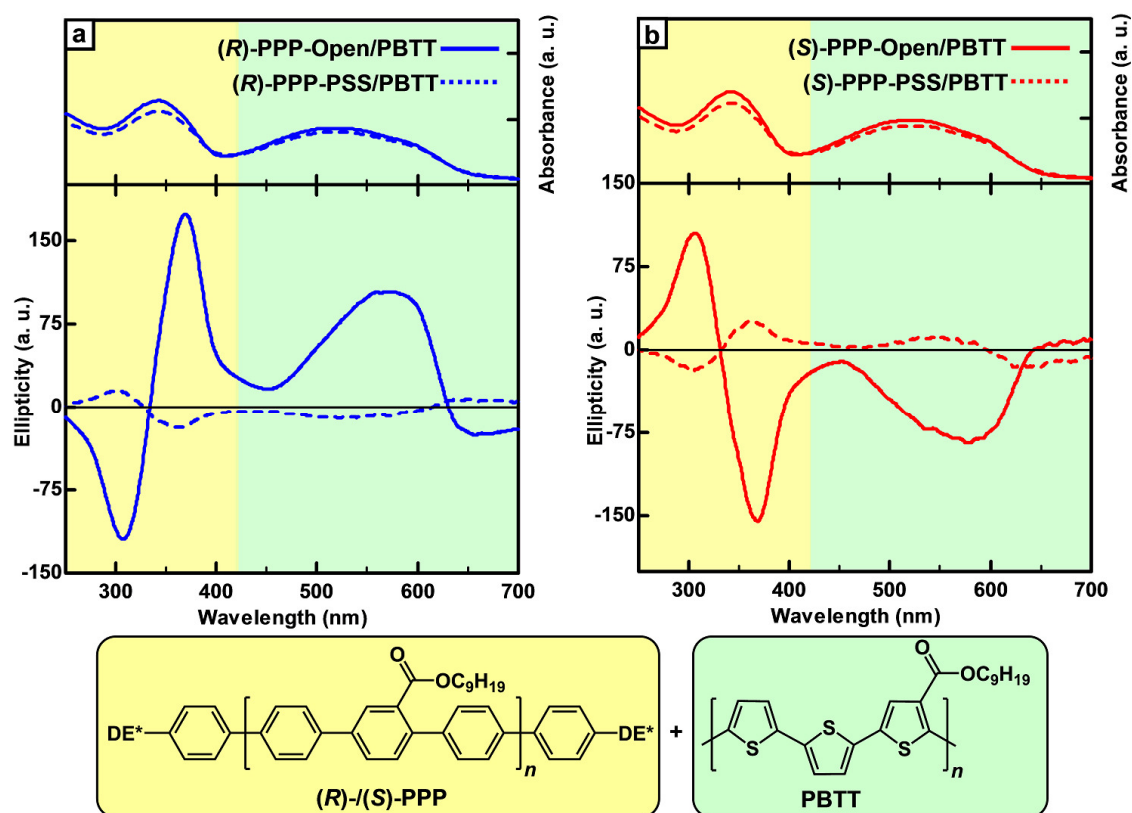


Figure 5. UV-vis (upper) and CD (lower) spectra of (a) **(R)-PPP/PBTT** cast film, and (b) **(S)-PPP/PBTT** cast film in open form and PSS. Shaded regions represent absorption regions of PPP (yellow) and PBTT (green).

Similar to **(R)-/(S)-PPP** system, the CD spectra of the **(R)-/(S)-PPP-Open/PBTT** system show larger intensities compared to those of **(R)-/(S)-PPP-PSS/PBTT**. These differences are also related to the degree of conversion of the DE moieties and the stronger chiral induction of the open form of the chiral DE* end-groups.

3.0 Conclusion

Novel photoresponsive PPP derivatives have been synthesized by introducing chiral, photoisomerizable DE* end-groups to the PPP main chain. In the assembled state,

helical inversion of the π -stacked structures was observed upon photoisomerization of the chiral DE* end-groups. Furthermore, we reported the chiral transcription of the achiral PBTT through the formation of helically π -stacked assemblies consisting of photoresponsive chiral PPP and achiral PBTT. We show, for the first time, the inversion of the chirality of a conjugated polymer through the photoisomerization of its chiral end-groups. These dynamic, photoresponsive PPP assemblies can potentially be used in the development of dynamic optical memory systems and functional chiroptical devices.

Acknowledgements

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Chapter 5 Appendix

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1. Experimental Section

1.1. Materials

The chemical reagents were purchased and used as received. Octafluorocyclopentene, chlorotrimethylsilane, 2-methylthiophene, and 2,5-dibromobenzoic acid were purchased from Aldrich Co. Ltd. Diethylazodicarboxylate (DEAD), 4-4' biphenyldiboronic acid, and 1-3 propanediol were purchased from Tokyo Kasei Co. Ltd. Triphenylphosphine (TPP), (*R*)-(-)-2-nonanol, (*S*)-(+)-2-nonanol, and 1-nonanol were purchased from Wako Co. Ltd. Tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{TPP})_4$), Br_2 , sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), magnesium sulfate (Mg_2SO_4), sodium

bicarbonate (NaHCO_3), anhydrous sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}$), *n*-BuLi, tetrahydrofuran (THF), acetic acid (CH_3COOH), hydrochloric acid (HCl), methanol (MeOH), ethanol (EtOH), hexane (*n*- C_6H_{14}), acetonitrile, dichloromethane (CH_2Cl_2), and chloroform (CHCl_3) were purchased from Nacalai Tesque Co. Ltd. All experiments were performed under an argon atmosphere (> 99.9995 %). The THF and CH_2Cl_2 were distilled using sodium and sodium hydride as the drying agents, respectively, under argon gas before use.

1.2. Methods

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using either a JEOL JNM 270 MHz, Bruker AVANCE-600 600 MHz, or JEOL AL-400 400 MHz NMR spectrometer. Chemical shifts were represented in parts per million downfield from *tetra*-methylsilane (TMS) (the internal standard). Elemental analysis was performed using a Perkin-Elmer 2400CHN elemental analyser, Yanako CHN Corders (MT-3, MT-5 and MT-6), a JSL JM-10, a Mitsubishi chemical analytech AQF-100, and a Dionex ICS-1500.

Optical absorption spectra were measured using a Hitachi U-3500 UV/VIS/NIR spectrometer and a JASCO V-570 UV/VIS/NIR spectrometer. Circular dichroism spectra were taken using a JASCO J-720 and J-820 spectropolarimeter.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a PLgel 5 μm MIXED-D (Polymer Laboratories), a JASCO MD915 UV detector and THF as the eluent (flow rate = 1.0 mL/min). The instrument was calibrated using a polystyrene (PS) standard and calculations were made using a 807-IT integrator.

1.3. Syntheses of Monomers and Polymers

The synthesis route of the precursor compounds, monomers, polymers are written below:

3,5-dibromo-2-methylthiophene (1)

3,5-dibromo-2-methylthiophene (**1**) was synthesized as follows. Into a 500 mL three-necked flask were added 2-methylthiophene (26.5 g, 270 mmol) under argon gas and dissolved in acetic acid (100 mL) and dichloromethane (CH_2Cl_2) (100 mL). The mixture was stirred and the flask was placed into an ice bath and then covered with aluminum foil. Inside the addition funnel, 30 mL of bromine solution was dissolved in acetic acid (30 mL) and CH_2Cl_2 (30 mL) was added dropwise into the solution for 1 hr. The solution is then allowed to stir under ice bath for 2 hr and the reaction flask is then removed from the ice bath and allowed to stir for 12 hrs. Excess anhydrous sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$) was added to the reaction solution and stirred for 30 minutes. The residue was washed with Na_2CO_3 aqueous solution and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Mg_2SO_4 and the crude product was then purified by open column chromatography using hexane as eluent. The collected liquid was evaporated to give a yellow liquid. Fractional distillation was performed to remove elemental sulfur giving (**1**) (54.4 g, 217 mmol) as a yellow liquid. Yield = 80%. Anal. Chemical Formula: $(\text{C}_5\text{H}_4\text{Br}_2\text{S})_n$ (253.84) $_n$: C, 23.5; H, 1.6. Found: C, 22.5; H, 1.68. ^1H NMR (270 MHz, CDCl_3): δ = 2.33 (s, 3H, Th- CH_3), 6.85 (s, H, Th- H). ^{13}C NMR (400 MHz, CDCl_3): δ = 14.8, 108.5, 108.7, 132.1, 136.0.

1,2-Bis(5-trimethylsilyl-2-methyl-3-thienyl)hexafluorocyclopentene (2)

1,2-Bis(5-trimethylsilyl-2-methyl-3-thienyl)hexafluorocyclopentene (2) was synthesized as follows. Into a 500 mL three-necked flask was added (1) (33.9 g, 132 mmol) under argon gas and dissolved in THF (120 mL). The mixture was stirred and the flask was placed into a dry ice bath (dry ice/ethanol, $-78\text{ }^{\circ}\text{C}$). Inside the addition funnel, 54 mL (140 mmol) of *n*-BuLi (2.6 M in hexane) was added dropwise into the solution for 1 hr. The solution is then allowed to stir under the dry ice bath for 10 min. Inside the next addition funnel, 16.8 mL (132 mmol) of chlorotrimethylsilane dissolved in THF (50 mL) was added dropwise into the solution for 10 min. The solution is then allowed to stir for 90 min. Furthermore inside the next addition funnel, 54 mL (140 mmol) of *n*-BuLi (2.6 M in hexane) was added dropwise into the solution for 30 min and is then allowed to stir for 10 min. Finally inside the next addition funnel, octofluorocyclopentene (14.0 g, 66 mmol) was dissolved in THF (50 mL) was added dropwise into the solution for 90 min and is then allowed to stir for 2 hrs. The reaction flask is then removed from the dry ice bath and the solution was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Mg_2SO_4 and the crude product (brown color) was then purified by open column chromatography using hexane as eluent. The collected liquid was evaporated to give a yellow liquid. Recrystallization in acetonitrile was performed giving (2) (18.6 g, 36 mmol) as a white crystal. Yield = 55%. Anal. Chemical Formula: $(\text{C}_{21}\text{H}_{26}\text{F}_6\text{S}_2\text{Si}_2)_n$ (512.72) $_n$: C, 49.19; H, 5.11. Found: C, 49.12; H, 5.13. ^1H NMR (270 MHz, CDCl_3): δ = 0.26 (s, 18H, Si- CH_3), 1.90 (s, 6H, Th- CH_3), 7.05 (s, 2H, Th- H). ^{13}C NMR (270 MHz, CDCl_3): δ = 14.1, 111.0, 116.1, 136.4, 126.5, 133.9, 138.6, 146.8.

1,2-Bis(5-bromo-2-methyl-3-thienyl)hexafluorocyclopentene (3)

1,2-Bis(5-bromo-2-methyl-3-thienyl)hexafluorocyclopentene (**3**) was synthesized as follows. Into a 300 mL three-necked flask were added (**2**) (6.02 g, 11.7 mmol) under argon gas and dissolved in CH₂Cl₂ (15 mL). The mixture was stirred and the flask was placed into an ice bath and then covered with aluminum foil. Inside the addition funnel, 0.12 mL of bromine solution was dissolved in CH₂Cl₂ (5 mL) was added dropwise into the solution for 1 hr. The solution is then allowed to stir under ice bath for 1 hr and the reaction flask is then removed from the ice bath. Excess anhydrous sodium thiosulfate (Na₂S₂O₃·H₂O) was added to the reaction solution and stirred for 30 minutes. The residue was washed with water and extracted with CHCl₃ (3×). The residue was dried over anhydrous Na₂SO₄ and the crude product was then purified by open column chromatography using hexane as eluent. The collected liquid was evaporated to giving (**3**) (5.90 g, 1.12 mmol) as a white crystal. Yield = 96%. Anal. Chemical Formula: (C₁₅H₈Br₂F₆S₂)_n (526.15)_n: C, 34.2; H, 1.5. Found: C, 34.2; H, 1.7. ¹H-NMR (600 MHz, CDCl₃): δ = 1.88 (s, 6H, Th-CH₃), 7.01 (s, 2H, Th-H). ¹³C-NMR (600 MHz, CDCl₃): δ = 14.4, 110.1, 110.8, 115.8, 125.2, 129.1, 135.6, 143.3.

1-(5bromo-2-methyl-3-thienyl)-2-(2-methyl-5-carboxylicacid-3-thienyl)hexafluorocyclopentene (4)

1-(5bromo-2-methyl-3-thienyl)-2-(2-methyl-5-carboxylicacid-3-thienyl)hexafluorocyclopentene (**4**) was synthesized as follows. Into a 500 mL three-necked flask was added (**3**) (5.26 g, 10 mmol) under argon gas and dissolved in THF (300 mL). The mixture was stirred and the flask was placed into a dry ice bath (dry ice/ethanol, -78°C). Inside the addition funnel, 3.9 mL (10.14 mmol) of *n*-BuLi (2.6 M in hexane) was added

dropwise into the solution for 30 min. The brown colored solution is then allowed to stir under the dry ice bath for 10 min. Next CO₂ bubbling through the reaction solution was performed for 30 min. Furthermore the reaction flask is then removed from the ice bath and CO₂ bubbling of the solution continued for 90 min. Quenching was performed by adding excess HCl to the reaction flask and was consequently washed with water and CHCl₃ (3×). The solution was dried over Na₂SO₄ and the crude product was then purified by open column chromatography using CHCl₃:MeOH (10:1) as eluent. The collected liquid was evaporated giving **(4)** (3.54 g, 7.2 mmol) as a white crystal. Yield = 72%. Anal. Chemical Formula: (C₁₆H₉BrF₆O₂S₂)_n (491.26)_n: C, 39.1; H, 1.8. Found: C, 39.1; H, 2.1. ¹H NMR (600 MHz, CDCl₃): δ = 1.72 (s, 3H, Th-CH₃), 1.86 (s, 3H, Th-CH₃), 6.99 (s, 1H, Th-H), 7.78 (s, 1H, Th-H). ¹³C NMR (600 MHz, CDCl₃): δ = 14.1, 14.8, 110.4, 110.7, 115.7, 125.0, 129.0, 135.5, 143.3.

1-(5-bromo-2-methyl-3-thienyl)-2-[5-((*R*)-methyloctyloxy)carbonyl-2-methyl-3-thienyl]hexafluorocyclopentene ((*R*)-Br-DE*)

1-(5-bromo-2-methyl-3-thienyl)-2-[5-((*R*)-methyloctyloxy)carbonyl-2-methyl-3-thienyl]-hexafluorocyclopentene ((*R*)-Br-DE*) was synthesized as follows. Into a 300 mL three-necked flask were added **(4)** (0.101 g, 0.206 mmol), (*S*)-2-nonanol (0.147 g, 1.02 mmol) and TPP (0.265 g, 1.01 mmol) under argon gas and dissolved in THF (50 mL). In the addition funnel, a mixture of DEAD (0.435 g, 40 wt% in toluene, 1.00 mmol) and 10 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. After evaporation of the solvent, the residue was washed with

water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CHCl_3 :Hexane (1:2) as eluent. The collected liquid was evaporated and dried under vacuum to give compound **(R)-Br-DE*** (0.097 g, 0.157 mmol) as a light yellow liquid. Yield = 76% Anal. Chemical Formula: $(\text{C}_{25}\text{H}_{27}\text{BrF}_6\text{O}_2\text{S}_{22})_n$ (617.50) $_n$: C, 48.63; H, 4.41. Found: C, 49.39; H, 4.69. ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (s, 3H, DE-COOCH(CH_3)(CH_2) $_6$ - CH_3), 1.00–1.71 (m, 15H, DE-COOCH(CH_3)(CH_2) $_6$ - CH_3), 1.86 (s, 1H, in DE Th- CH_3), 1.99 (s, 1H, in DE Th- CH_3), 5.06–5.11 (m, 1H, DE-COOCH(CH_3)(CH_2) $_6$ - CH_3), 7.02 (s, 1H, in DE Th- H), 7.71 (s, 1H, in DE Th- H). ^{13}C -NMR (400 MHz, CDCl_3): δ = 14.0, 14.4, 14.8, 20.0, 22.6, 25.3, 29.1, 29.4, 31.7, 35.9, 56.8, 72.7, 110.1, 122.5, 125.0, 125.3, 129.0, 132.5, 148.1, 160.7.

1-(5-bromo-2-methyl-3-thienyl)-2-[5-((S)-methyloctyloxy)carbonyl-2-methyl-3-thienyl]hexafluorocyclopentene ((S)-Br-DE*)

1-(5-bromo-2-methyl-3-thienyl)-2-[5-((S)-methyloctyloxy)carbonyl-2-methyl-3-thienyl]-hexafluorocyclopentene ((S)-Br-DE*) was synthesized as follows. Into a 300 mL three-necked flask were added **(4)** (0.101 g, 0.206 mmol), (*R*)-2-nonanol (0.147 g, 1.02 mmol) and TPP (0.265 g, 1.01 mmol) under argon gas and dissolved in THF (50 mL). In the addition funnel, a mixture of DEAD (0.435 g, 40 wt% in toluene, 1.00 mmol) and 10 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3 $\times$). The residue was dried over anhydrous Na_2SO_4

and the crude product was then purified by open column chromatography using CHCl_3 :Hexane (1:2) as eluent. The collected liquid was evaporated and dried under vacuum to give compound (**S**)-**Br-DE*** (0.094 g, 0.149 mmol) as a light yellow liquid. Yield = 74%. Anal. Chemical Formula: $(\text{C}_{25}\text{H}_{27}\text{BrF}_6\text{O}_2\text{S}_{22})_n$ (617.50) $_n$: C, 48.63; H, 4.41. Found: C, 48.94; H, 4.44. ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (s, 3H, DE-COOCH(CH₃)(CH₂)₆-CH₃), 1.00–1.70 (m, 15H, DE-COOCH(CH₃)(CH₂)₆-CH₃), 1.86 (s, 1H, in DE Th-CH₃), 1.99 (s, 1H, in DE Th-CH₃), 5.07–5.11 (m, 1H, DE-COOCH(CH₃)(CH₂)₆-CH₃), 7.02 (s, 1H, in DE Th-H), 7.71 (s, 1H, in DE Th-H). ^{13}C -NMR (400 MHz, CDCl_3): δ = 14.1, 14.4, 14.9, 20.0, 22.6, 25.3, 29.1, 29.4, 31.7, 35.9, 72.7, 110.1, 125.0, 125.3, 129.0, 132.5, 143.1, 148.1, 160.8.

***n*-Nonyl-2,5-dibromobenzoate (5)**

n-Nonyl-2,5-dibromobenzoate (**5**) was synthesized as follows. Into a 300 mL three-necked flask were added 2,5-dibromobenzoic acid (2.79 g, 10 mmol), 1-nonanol (1.45 g, 10 mmol), and TPP (2.62 g, 13.9 mmol) under argon gas and dissolved in THF (15 mL). In the addition funnel, a mixture of DEAD (4.44 g, 40 wt% in toluene, 10.2 mmol) and 10 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. After evaporation of the solvent, the residue was washed with water and extracted with CHCl_3 (3×). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using CH_2Cl_2 :Hexane (1:1) as eluent. The collected liquid was evaporated and dried under vacuum to give compound (**5**) (3.58 g, 8.81 mmol) as a light yellow liquid. Yield =

88%. Anal. Chemical Formula: $(C_{16}H_{22}Br_2O_2)_n$ (406.16) $_n$: C, 47.32; H, 5.46. Found: C, 47.55; H, 5.51. 1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (s, 3H, Ph-COO(CH₂)₈-CH₃), 1.24–1.80 (m, 14H, Ph-COOCH₂(CH₂)₇-CH₃), 4.35 (t, 2H, J = 6.8 Hz, Ph-COOCH₂(CH₂)₇-CH₃), 7.52 (m, 1H, Ph-*H meta* to -COOC₉H₁₉), 7.67 (m, 1H, Ph-*H para* to -COOC₉H₁₉), 8.00 (m, 1H, Ph-*H ortho* to -COOC₉H₁₉). ^{13}C -NMR (400 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.0, 28.5, 29.2, 29.4, 31.8, 66.2, 120.1, 120.8, 133.9, 134.0, 135.1, 135.5, 164.8.

4,4'-biphenyldiboronic acid bis(trimethylene glycol) cyclic ester (6)

4,4'-biphenyldiboronic acid bis(trimethylene glycol) cyclic ester (6) was synthesized as follows. Into a 300 mL two-necked flask were added 4,4'-biphenyldiboronic acid (11.7 g, 11.7 mmol), 1,3-propanediol (2.05 g, 26.9 mmol) under argon gas and dissolved in CH_2Cl_2 (200 mL). After dissolving the reagents under constant stirring, the flask was heated to 40°C for 48 hrs. After evaporation of the solvent, the residue was recrystallized at ethanol. The crystals were filtered and dried under vacuum to give compound (6) (2.64 g, 8.2 mmol) as white crystals. Yield = 70%. Anal. Chemical Formula: $(C_{18}H_{20}B_2O_4)_n$ (312.97) $_n$: C, 67.2; H, 6.3. Found: C, 66.9; H, 6.14. 1H NMR (600 MHz, $CDCl_3$): δ = 2.06 (quint, J = 5.5 Hz, 4H, -CH₂*para* to -B), 4.17 (t, J = 5.5 Hz, 8H, -CH₂*meta* to -B), 7.61 (d, J = 8.3 Hz, 4H, Ph-*H meta* to -BO₂(CH₂)₃), 7.83 (d, J = 8.3 Hz, 4H, Ph-*H ortho* to -BO₂(CH₂)₃). ^{13}C -NMR (600 MHz, $CDCl_3$): δ = 27.4, 61.9, 126.4, 131.7, 133.9, 143.1.

(R)-PPP

(R)-PPP was synthesized as follows. Into a schlenk flask were added (5) (0.102 g,

0.25 mmol), (**6**) (0.097g, 0.30 mmol), and (**R**)-**Br-DE*** (0.093 g, 0.15 mmol) under argon gas and dissolved in THF (35 mL). After dissolving the reagents under constant stirring, tetrakis(triphenylphosphine)palladium(0) (Pd(TPP)₄) (0.0058 g, 0.005 mmol), NaHCO₃ (0.420 g, 5.0 mmol), and water (20 mL) was added to the reaction mixture. The flask was then heated to 80°C for 24 hrs. The mixture was cooled to room temperature and was added dropwise to 500 mL of water under stirring. The polymer precipitate was stirred for 24 h, which was then filtered and dried in vacuo. The polymer aggregates were then subsequently washed in 500 mL of methanol and and dried in vacuo. A green solid was obtained (0.0884 g). M_w . 5,200 M_w/M_n . 1.1 (GPC, PS calibration). Yield = 47 %, Elemental Analysis,¹⁹ ¹H NMR (400 MHz, CDCl₃): δ = 0.74–0.96 (br, 6H, DE-COOCH(CH₃)(CH₂)₆-CH₃, Ph-COO(CH₂)₈-CH₃), 1.00–1.45 (br, 19H, DE-COOCH(CH₃)(CH₂)₆-CH₃, Ph-COOCH₂(CH₂)₇-CH₃), 1.96–2.10 (br, 6H, in DE Th-CH₃), 4.07–4.20 (br, 2H, Ph-COOCH₂(CH₂)₇-CH₃), 5.10–5.13 (br, 1H, DE-COOCH(CH₃)(CH₂)₇-CH₃), 7.32–7.49 (br, 2H, in DE Th-H), 7.49–8.10 (br, 15H, Ph-H). ¹³C NMR (400 MHz, CDCl₃): δ = 14.1, 14.6, 14.9, 20.0, 22.6, 25.4, 25.8, 28.3, 29.1, 29.3, 29.4, 31.7, 31.8, 35.9, 65.4, 72.7, 125.5, 125.9, 126.4, 126.6, 127.1, 127.3, 127.4, 128.2, 128.7, 128.9, 129.3, 131.1, 131.8, 132.1, 132.4, 132.7, 142.1, 148.2, 160.9, 168.9.

(S)-PPP

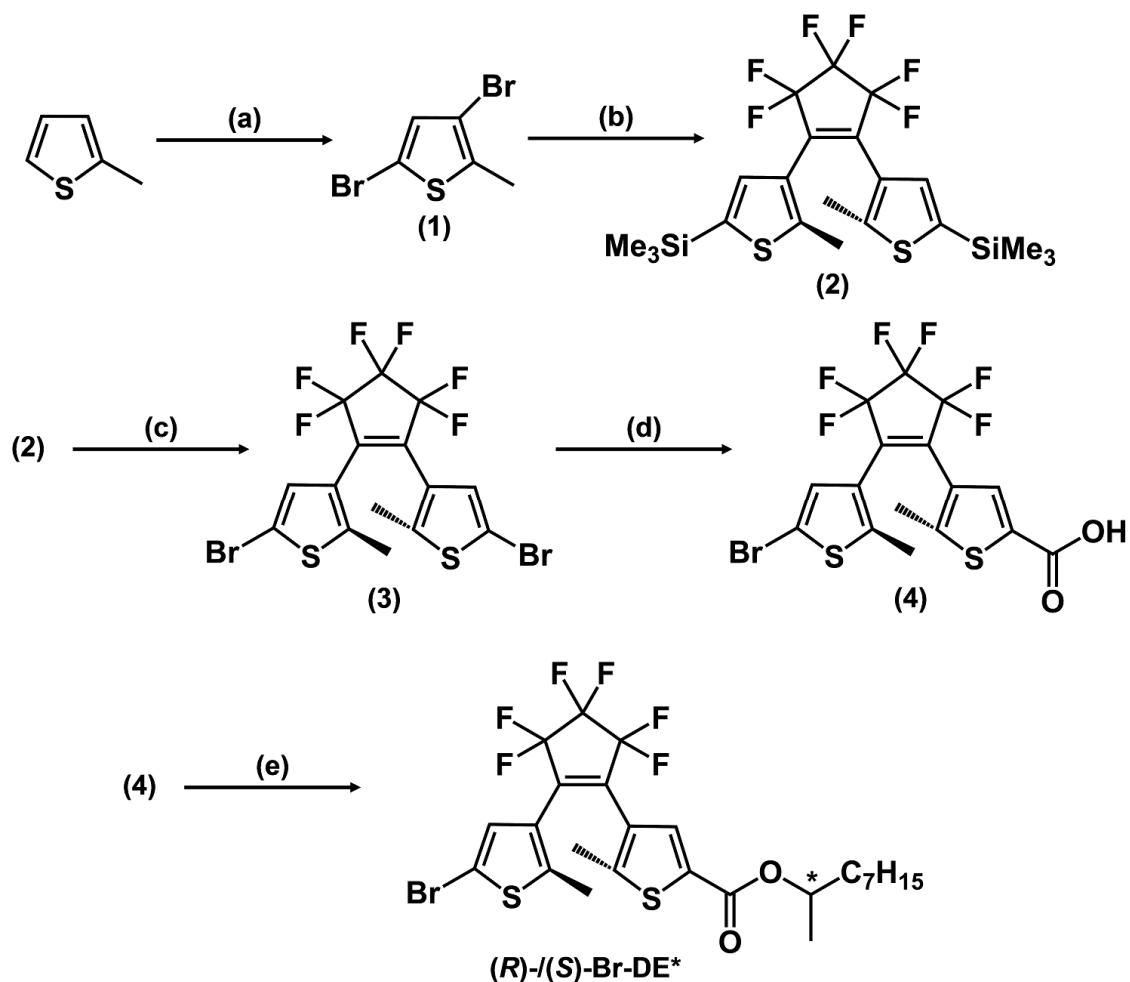
(S)-PPP was synthesized in a similar way as (R)-PPP. Polymerization yielded a green solid (0.0914 g). M_w . 4,800 M_w/M_n . 1.1 (GPC, PS calibration). Yield = 49 %, Elemental Analysis,¹⁹ ¹H NMR (400 MHz, CDCl₃): δ = 0.75–0.95 (br, 6H, DE-COOCH(CH₃)(CH₂)₆-CH₃, Ph-COO(CH₂)₈-CH₃), 1.00–1.50 (br, 19H,

DE-COOCH(CH₃)(CH₂)₆-CH₃, Ph-COOCH₂(CH₂)₇-CH₃, 1.96–2.01 (br, 6H, in DE Th-CH₃), 4.07–4.20 (br, 2H, Ph-COOCH₂(CH₂)₇CH₃), 5.08–5.12 (br, 1H, DE-COOCH(CH₃)(CH₂)₇-CH₃), 7.30–7.50 (br, 2H, in DE Th-*H*), 7.50–8.00 (br, 15H, Ph-*H*). ¹³C NMR (400 MHz, CDCl₃): δ = 14.1, 14.6, 20.0, 22.6, 25.4, 25.8, 28.3, 29.2, 29.4, 35.9, 65.4, 72.7, 125.5, 125.9, 126.4, 126.6, 127.3, 127.4, 128.2, 128.9, 129.3, 131.1, 131.9, 132.4, 132.7, 160.9.

***poly*(bithiophenethiophene) (PBTT)**

PBTT was synthesized as described at a previous report.¹⁶

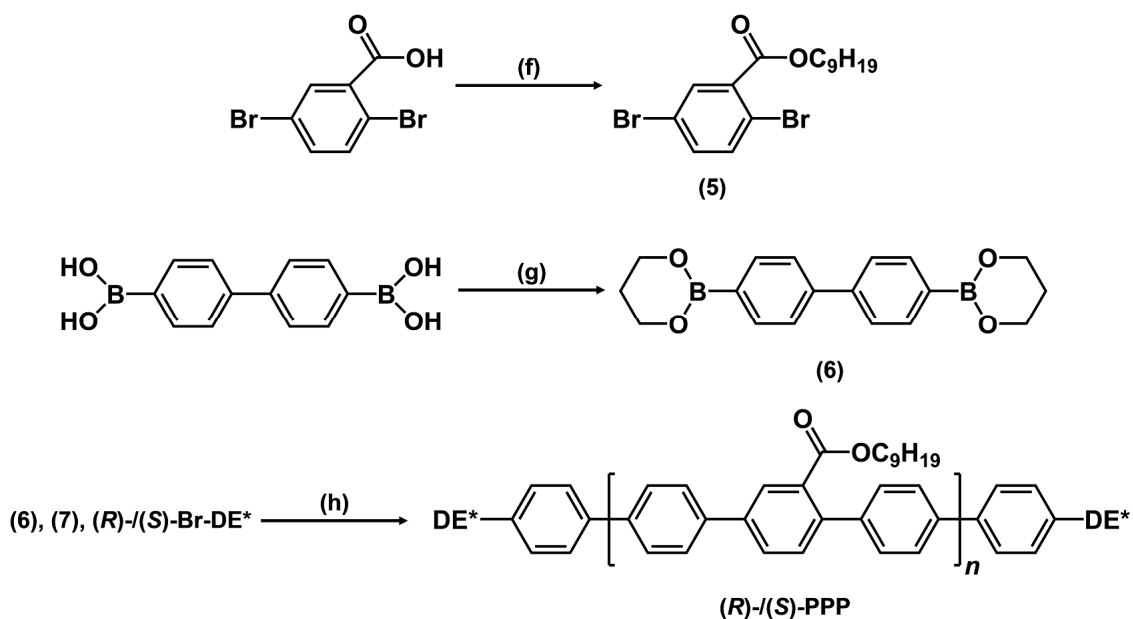
2. Supporting Figures

Scheme S1. Synthetic routes of precursors, monomers, polymers.^{a,b}

^aConditions: (*R*)-/(*S*)-Br-DE*: (a) Br₂, CH₃COOH, CH₂Cl₂, 0 °C, 12 h; 80% for **1**; (b) **1**, chlorotrimethylsilane, *n*-BuLi, octafluorocyclopentene, THF, -78 °C, 2 h; 57% for **2**; (c) **2**, Br₂, CH₂Cl₂, 0 °C, 1 h; 74% for **3**; (d) **3**, *n*-BuLi, octafluorocyclopentene, THF, -78 °C, 1 h; 74% for **4**; (e) (*S*)-2-nonanol/(*R*)-2-nonanol, DEAD, TPP, THF, 24 h; 76% for (*R*)-Br-DE* and 74% for (*S*)-Br-DE*.

DEAD = diethylazodicarboxylate

TPP = triphenylphosphine



^bConditions: **(R)-/(S)-PPP**: (f) 1-nonanol, DEAD, TPP, THF, 24 h; 88% for **5**; (g) 4,4'-biphenyldiboric acid, CH₂Cl₂, 0 °C, 48 h; 70% for **6**; (h) **5**, **6**, **(R)-/(S)-Br-DE***, Pd(TPP)₄, NaHCO₃, THF, 24 h; 70% for **(R)-PPP**, 61% for **(S)-PPP**.

Table S1. Results of polymerizations of the chiral PPP derivatives.

	M_n	M_w	M_w / M_n	D.P. ^{a,b}
(R)-PPP	4,600	5,200	1.1	11(33)
(S)-PPP	4,200	4,800	1.1	10(30)

^a DP: Degree of Polymerization, stands for the quantity of the repeating unit

^b The values in the parenthesis are the average number of aromatic rings in the main chain

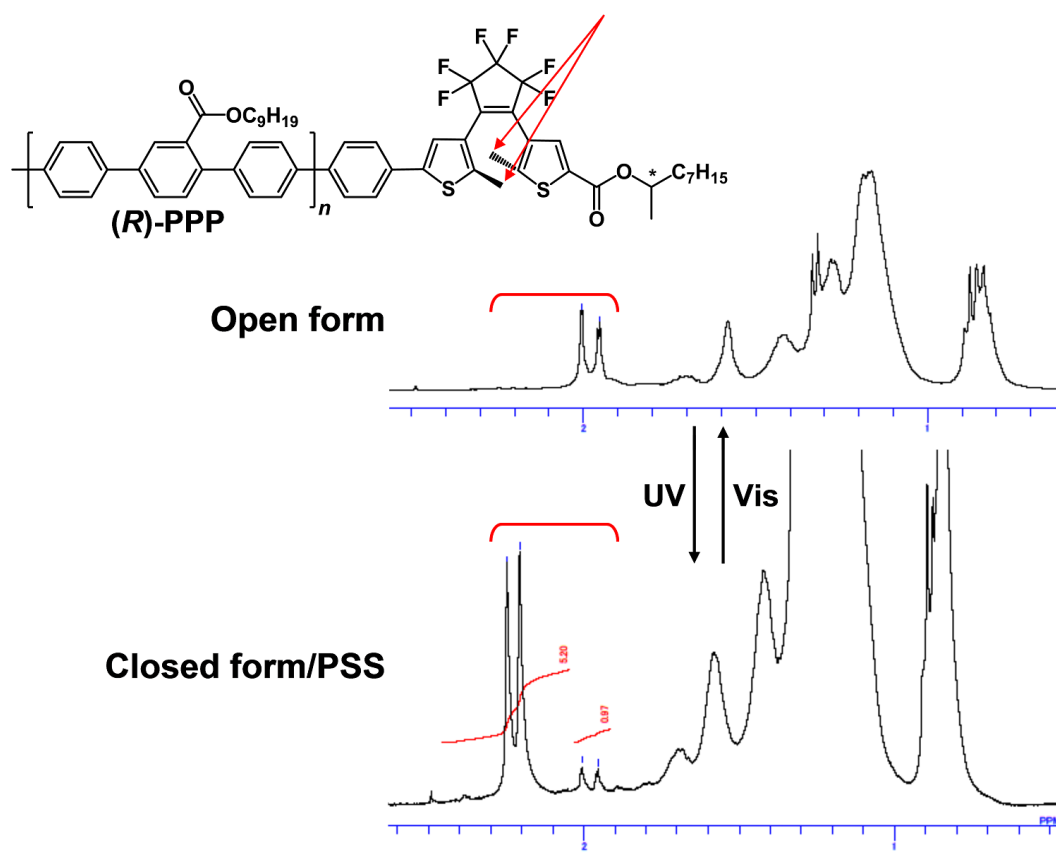


Figure S1. ^1H NMR spectra of **(R)-PPP** in the open form (top) and in the closed form/PSS (bottom) in CDCl_3 .

Table S2. Degrees of conversion of **(R)-/(S)-PPP** and the chiral DE* end-group precursors at the photostationary state (PSS).

Degree of conversion ^a	
(R)-PPP	84 %
(S)-PPP	83 %
(R)-Br-DE*	83 %
(S)-Br-DE*	84 %

^a measured at the photostationary state (PSS) upon exposure to UV light ($\lambda=254\text{nm}$, 4W) at 4 hrs.

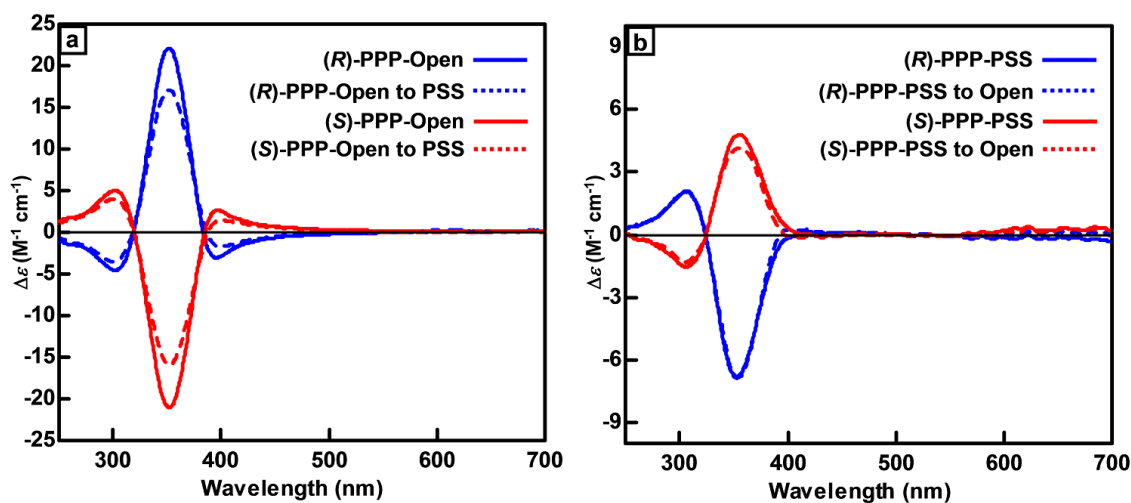


Figure S2. CD spectra of (R)-(S)-PPP in the aggregated state: (a) in the open form followed by exposure to UV light (transition: from open form to PSS) and (b) in the PSS followed by exposure to visible light (transition: from PSS to open form).

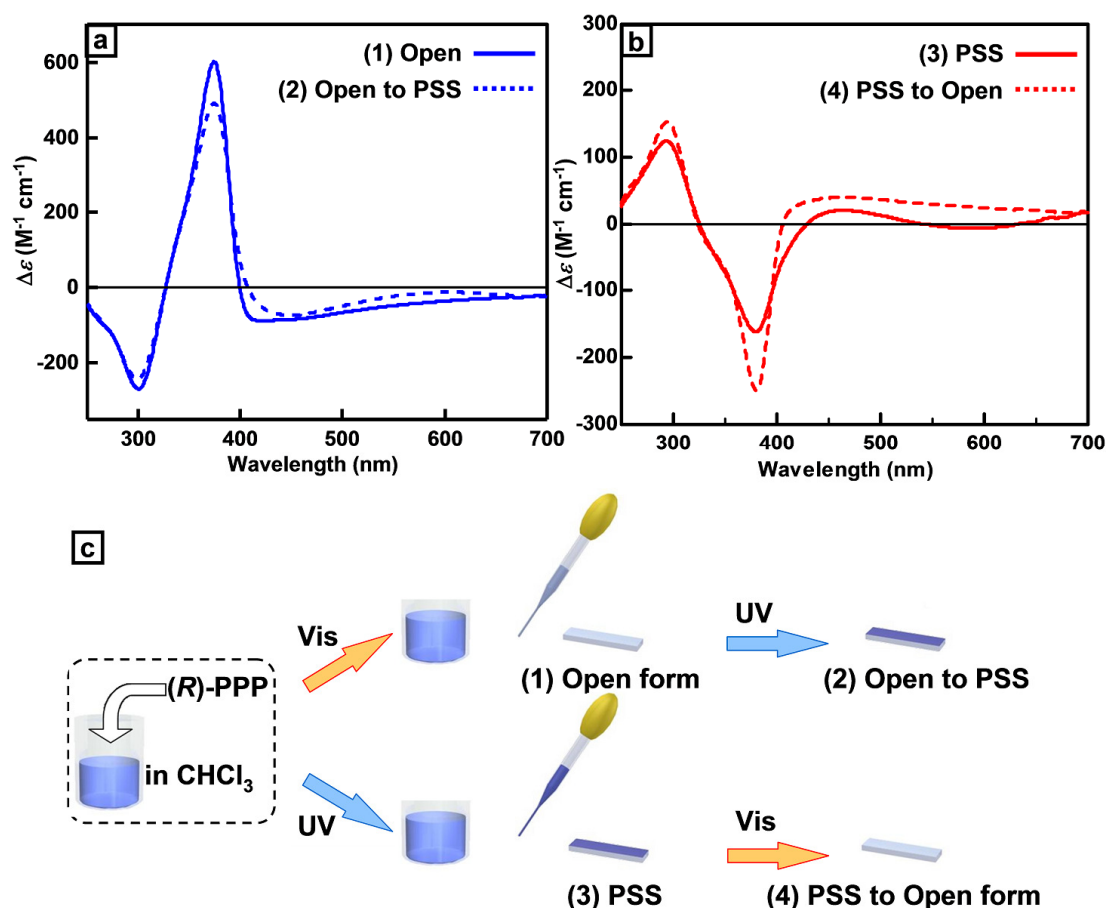


Figure S3. CD spectra of (R)-PPP cast film in (a) the open form (1), followed by exposure to UV light (2), and in (b) PSS (3), followed by exposure to visible light (4). (c) Schematic diagram of the subsequent photoisomerizations of (R)-PPP cast films.

REFERENCES

- (1) Janssen, H. M.; Meijer, E. W. *Macromolecules* **1997**, *30*, 8129–8138.
- (2) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385–387.
- (3) Okamoto, Y.; Nakano, T.; Ono, E.; Hatada, K. *Chem. Lett.* **1991**, *20*, 525–528.
- (4) a) Pohl, F. M.; Jovin, T. M. *J. Mol. Biol.* **1972**, *67*, 375–396; b) Cosstick, R.; Eckstein, F. *Biochemistry* **1985**, *24*, 3630–3638.
- (5) Harvey, P. H.; Tovar, J. D. *Polym. Chem.* **2011**, *2*, 2699–2706
- (6) Fukaminato, T.; Irie, M. *Adv. Mater.* **2006**, *18*, 3225–3228.
- (7) Yagai, S.; Iwai, K.; Karatsu, T.; Kitamura, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 9679–9683.
- (8) a) Hayasaka, H.; Tamura, K.; Akagi, K. *Macromolecules* **2008**, *41*, 2341–2346; b) Akagi, K. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2463–2485.
- (9) Hayasaka, H.; Miyashita, T.; Tamura, K.; Akagi, K. *Adv. Funct. Mater.* **2010**, *20*, 1243–1250.
- (10) a) Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759; b) Vicario, J.; Feringa, B. L. *Nature* **2006**, *440*, 163.
- (11) Hayasaka, H.; Miyashita, T.; Nakayama, M.; Kuwada, K.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 3758–3765.
- (12) a) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *379*, 506–508; b) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P.; Wendorff, J. H. *Adv. Mater.* **2003**, *15*, 282–287; c) Wang, Y.; Urbas, A.; Li, Q. *J. Am. Chem. Soc.* **2012**, *134*, 3342–3345.

- (13) a) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789–1816; b) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001.
- (14) a) Pieraccini, S.; Masiero, S.; Spada, G. P.; Gottarelli, G. *Chem. Commun.* **2003**, 598–599; b) Kawamoto, M.; Aoki, T.; Wada, T. *Chem. Commun.* **2007**, 930–932; c) Li, Q.; Green, L.; Venkataraman, N.; Shiyanovslaya, I.; Khan, A.; Urbas, A.; Doane, J. W. *J. Am. Chem. Soc.* **2007**, *129*, 12908–12909.
- (15) a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; b) Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792; c) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309.
- (16) Watanabe, K.; Osaka, I.; Yorozuya, S.; Akagi, K. *Chem. Mater.* **2012**, *24*, 1011–1024.
- (17) a) Harada, N.; Nakanishi, K. In *Circular Dichroic Spectroscopy: Exciton Coupling in Organic Stereochemistry*; University Science Books: California, 1983; b) Berova, N.; Nakanishi, K. In *Circular Dichroism: Principles and Applications*, 2nd ed. (Berova, N.; Nakanishi, K.; Woody, R., Eds.; John Wiley and Sons, Inc.: New York, 2000, *12*, 337–382.
- (18) Irie, M.; Sayo, K. *J. Phys. Chem.* **1992**, *96*, 7671–7674
- (19) Elemental analysis on (*R*)-/(*S*)-PPP with end-capped moieties was not performed. The relative elemental composition values of the polymer main chain and the end-cap moieties vary widely as a result of the distribution of polymer chain lengths and molecular weights. Thus, elemental analysis would not be an accurate measure of sample purity.

Chapter 6**Dynamic Switching of Circularly Polarized Luminescence of
Di-Substituted Polyacetylene by Selective Transmission through a
Thermotropic Chiral Nematic Liquid Crystal****ABSTRACT:**

We have demonstrated the dynamic switching of circularly polarized luminescence (CPL) of chiral *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) from left-to-right-handed CPL and vice-versa through the selective transmission of CPL across a thermotropic chiral nematic liquid crystal (N*-LC) phase. By combining a chiral *di*-LCPA CPL emitting film with a N*-LC cell and tuning the selective reflection band of the N*-LC phase to coincide with the CPL emission band, we constructed a CPL switchable cell. The phase change associated with the thermotropic N*-LC cell at varying temperatures leads to a change in selective transmission of CPL which enables dynamic switching of CPL. We anticipate that CPL switchable devices might find applications in switchable low threshold lasers and optical memory devices.

1. Introduction

Circularly polarized luminescence (CPL) of organic and polymeric materials has attracted considerable interest in photonic devices, such as light-emitting diodes, optical amplifiers, and optical information storage.^{1,2} Various chiral liquid crystalline fluorescent conjugated polymers exhibiting CPL functionalities have been reported.^{2–5} The well-defined chiral packing of the liquid crystalline main chain as well chiral interchain interactions lead to reports of emission dissymmetry factors (g_{em}) values of up to orders of 10^{-1} . Recently, we have reported the synthesis of chiral *di*-substituted liquid crystalline polyacetylene (*di*-LCPA) showing a highly ordered lyotropic chiral nematic liquid crystal (N*-LC) phase showing g_{em} values of up to -2.3×10^{-1} .⁶

One unique and important optical property of the N*-LC helical structures is the "selective reflection of circularly polarized light" which was employed to achieve high degrees of CPL.⁷ When N*-LCs are sandwiched between a pair of substrates with anchoring surfaces, the helical axis is spontaneously oriented perpendicular to the substrate surface. In this alignment, the N*-LCs show an intrinsic optical texture, the so-called planar or Grandjean texture.⁸ When CPL propagates into a planar-aligned N*-LC cell along the helical axis, the N*-LC molecules can reflect CPL having the same helical handedness as the N*-LC phase at λ_{max} . On the other hand, CPL with opposite helical handedness to the N*-LC phase transmits through the planar N*-LC cell without light reflection. The center of the CPL reflection band, λ_{max} , is related to the helical pitch, p , of the N*-LC phase as defined by: $\lambda_{max} = np$, where n is the index of refraction of the LCs.

A common method to prepare a N*-LC phase is to add a chiral dopant to a nematic LC (N-LC) host. Upon the addition of a chiral dopant, chirality is induced to the

N-LC hosts to form to a N*-LC phase. In order to construct a N*-LC phase having selective reflection in the visible light range, a helical pitch in the order of several hundred nanometers is necessary. *Tetra*-LC substituted binaphthyl derivatives, chiral dopants having large helical twisting powers (β_M), have shown selective reflection in the visible light range.⁹

The selective reflection properties of N*-LCs have been utilized in various areas of research such as the preparation glassy N*-LC films embedded with chromophores having high degrees of CPL,¹⁰ photonic crystals exhibiting low-threshold lasing,¹¹ and N*-LC mixtures with photochemically tunable CPL.¹²

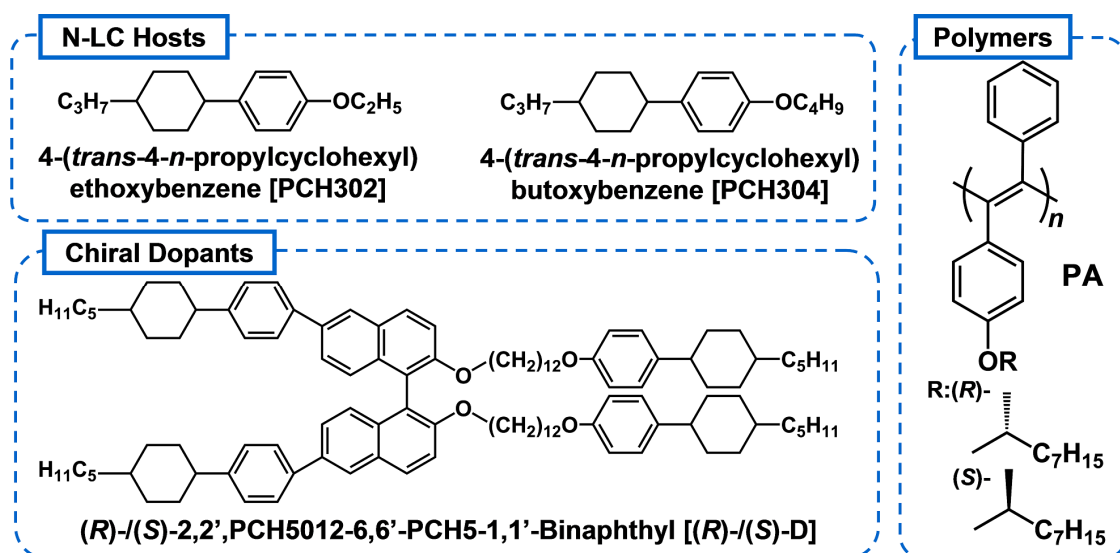
Recently, switching functionalities in CPL such as poly(phenyleneethynylene) aggregates exhibiting chiral inversion of CPL at varying solvent conditions were reported.¹³ In addition, dynamic switching between fluorescence and quenching of CPL from poly(bithienylene-phenylene)s having photoresponsive diarylethene moieties has also been reported.¹⁴ Further developing the concept of dynamic switching of CPL, we utilized the selective reflection property and thermotropic liquid crystallinity of N*-LCs as a dynamic thermally responsive material to enable dynamic chiral switching of CPL originating from chiral *di*-LCPA.

In this work, a CPL switchable cell was prepared consisting of a CPL emitting film, chiral *di*-LCPA, combined with a thermoresponsive N*-LC cell. The N*-LC cell was prepared so that the selective reflection range of the N*-LC coincides with the CPL wavelength of the *di*-LCPA film. Through the phase change of the thermotropic N*-LC cell at different temperatures, we present dynamic switching of CPL. Furthermore, the selective transmission of CPL across the N*-LC phase enables the amplification of CPL originating from *di*-LCPA to show high degrees of g_{em} .

2. Results and Discussion

2.1. Synthesis of the Polymers, LC Hosts, and Chiral Dopants

We synthesized room temperature nematic LC N-LC hosts, **PCH 302** and **PCH 304**, having phenylcyclohexyl mesogen cores and *n*-ethyloxy or *n*-butyloxy tails, respectively. *Tetra*-LC-substituted binaphthyl derivatives, **(R)-D** and **(S)-D**, having high β_M , were adopted as chiral dopants to prepare a N*-LC phase with the selective reflection band within the visible range of light. The synthesis of **(R)-/(S)-D** was described in a previous report.⁹ Two chiral *di*-LCPA derivatives, **(R)-PA** and **(S)-PA**, having a poly(diphenylpolyacetylene) main chain structure and 4-nonyloxy phenyl groups with either (*R*)-, or (*S*)-handedness in their side chains were polymerized using a WCl_6 catalyst in a metathesis polymerization reaction as described in a previous report.⁶ The structures of the synthesized N-LC hosts, chiral dopants, and chiral *di*-LCPAs are shown in Scheme 1.



Scheme 1. Synthesized nematic LC (N-LC) hosts: **PCH 302**, **PCH 304**; Chiral dopants: **(R)-/(S)-D**; and *Di*-substituted liquid crystalline polyacetylene: **(R)-/(S)-PA**.

2.2. Preparation and Liquid Crystallinity of the CPL Switchable Cell

A N*-LC phase consisting of **PCH 302**, **PCH 304**, and **(S)-D** in 100:100:2.2 mole ratio was prepared and injected into a cell consisting of two sandwiched quartz slides with a 35 μ m polyimide spacer. **(R)-PA** was dissolved in toluene at 10wt % to form a lyotropic N*-LC solution, which is casted to a quartz slide to prepare a CPL emitting layer. The left-handed **(S)-N*-LC** cell is placed beside the **(R)-PA** CPL emitting layer to form a CPL switchable cell (Figure 1a). A CPL switchable cell having opposite handedness consisting of a **(R)-N*-LC** cell with **(S)-PA** CPL emitting layer was also prepared.

Polarizing optical microscopy (POM) images of the prepared **(S)-N*-LC** cell at room temperature revealed a Grandjean texture characteristic of a planar N*-LC phase (Figure 1b).⁸ Upon heating to 36°C, the N*-LC phase transforms into an isotropic phase. Cholesteryl oleyl carbonate is a N*-LC molecule known to have a left-handed helical sense, and is utilized as a LC standard for a miscibility test with the prepared N*-LCs.¹⁵ The miscibility test method is based on the observation of the mixing area between the N*-LC and the LC standard using POM, where the helical sense of the LC standard is known. As shown in the supporting figures section; Figure S1a, the mixture of **(R)-N*-LC** and cholesteryl oleyl carbonate revealed a discontinuity in the mixing area of the two N*-LC phases. In the contact region of the two N*-LC phases, we observe that the striations characteristic of the N*-LC phase is lost yielding an LC texture corresponding to a N-LC phase. In contrast, the mixture of **(S)-N*-LC** and cholesteryl oleyl carbonate showed no change in optical texture, where the N*-LC phase was maintained in the mixing area (Figure S1b).

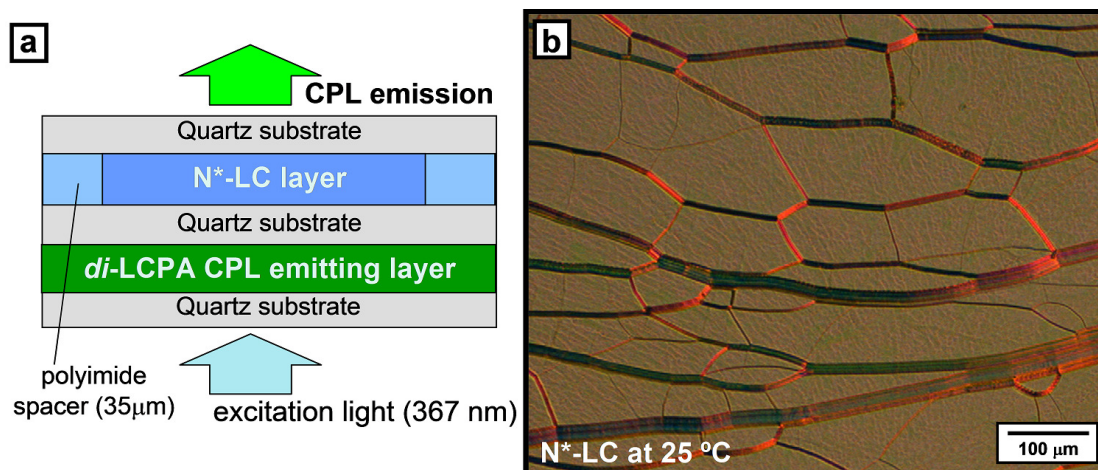


Figure 1. (a) Schematic diagram of the CPL switchable cell (b) POM image of (S)-N*-LC cell at 25°C showing a planar Grandjean texture.

2.3. Selective Reflection Band and Photoluminescence Spectra

After verifying the helical sense of the prepared N*-LC cells through a miscibility test, the selective reflection band of the prepared N*-LC cells were measured from their absorption spectra. The PL spectra of the *di*-LCPA CPL emitting film was also measured to verify the overlap between the CPL emission band of *di*-LCPA and the selective reflection band of the prepared N*-LC cells.

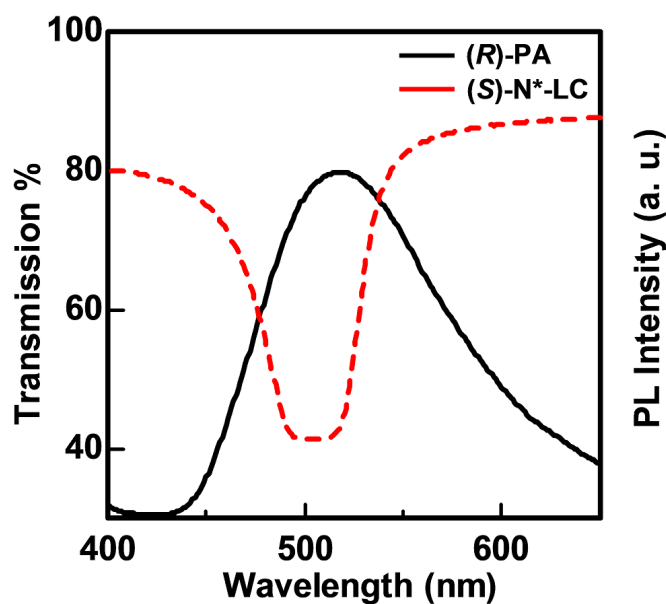


Figure 2. Photoluminescence (PL) emission (black) of (R)-PA film upon excitation at 367 nm and the transmission spectra (red) of the (S)-N*-LC cell showing the selective reflection band.

The PL spectra of **(R)-PA** shows a green colored PL band centered at 515 nm while the absorption spectra of the **(S)-N*-LC** cell shows a selective reflection band from 460 to 530 nm centered at 505 nm coinciding with the PL band of the CPL emitting film (Figure 2). The PL and absorption spectra of **(S)-PA** and the prepared **(R)-N*-LC** cell were also measured (Figure S2).

2.4. Dynamic Switching of the Circularly Polarized Luminescence

The CPL spectra of the CPL switchable cell made from **(R)-PA/(S)-N*-LC** was measured. The schematic diagram showing the CPL switching mechanism is described at Figure 3. Upon excitation with monochromatic light at 367 nm, the **(R)-PA** CPL emitting film emits both left- and right-handed CPL, but it is predominantly left-handed CPL (i). At room temperature, the **(S)-N*-LC** cell selectively reflects left-handed CPL (ii) and only right-handed CPL is transmitted (iii) (Figure 3a). The transmitted right-handed CPL signal was observed at the CPL spectra (Figure 3c).

At 40°C, the helical arrangement of the N*-LC phase is lost and becomes a disordered isotropic phase where the selective reflection of left-handed CPL does not occur (iv). At this state, the predominantly left-handed CPL from the **(R)-PA** CPL emitting film is transmitted (v) (Figure 3b). The transmitted left-handed CPL signal was observed at the CPL spectra (Figure 3c).

The degree of CPL was evaluated by the emission dissymmetry factor, g_{em} . The emission dissymmetry factor is defined as $g_{em} = (I_L - I_R) / [(I_L + I_R) / 2] = \Delta I / I$, where $|g_{em}| < 2$. The I_L and I_R are defined as the intensities of left and right handed polarized lights, respectively. At room temperature, we observed the amplification of right-handed

CPL originating from the *di*-LCPA film through the selective transmission of right-handed CPL at the (S)-N*-LC phase. The amplified right-handed CPL showed g_{em} values of nearly pure CPL with values up to -1.79 . At 40°C , the predominantly left-handed CPL showed g_{em} values an order lower at $+1.25 \times 10^{-1}$.

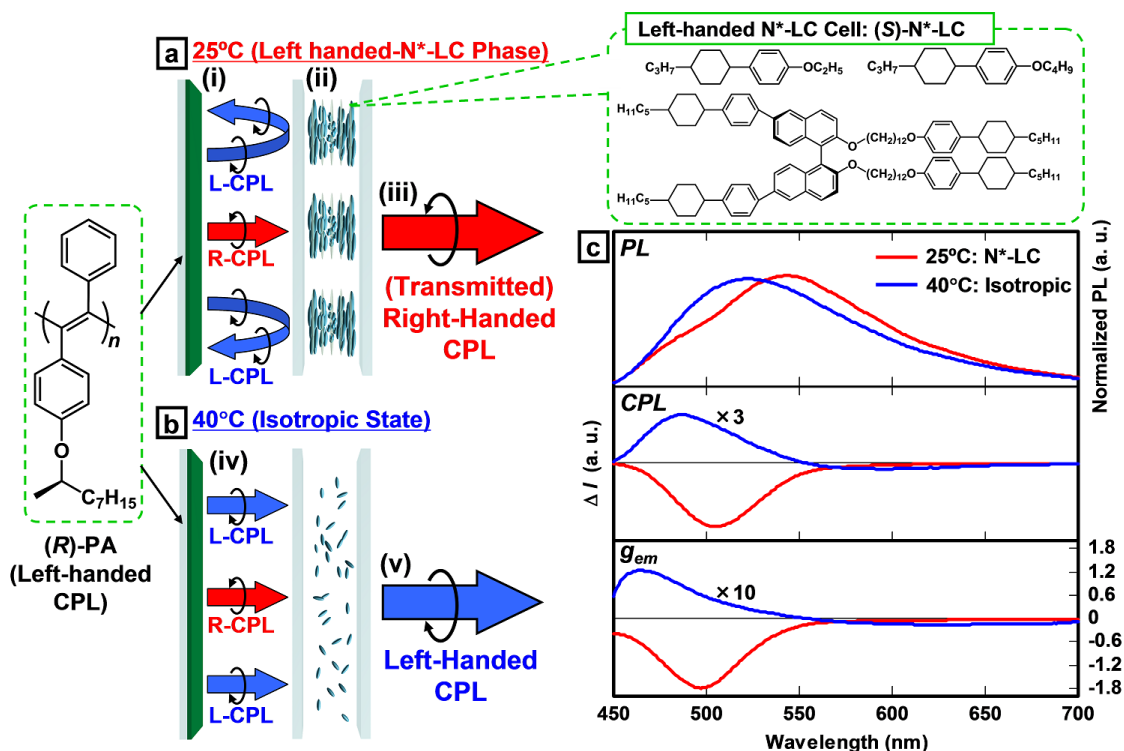


Figure 3. Schematic diagram of the (R)-PA/(S)-N*-LC CPL switchable cell. (a) At 25°C , (i) the (R)-PA film emits predominantly left-handed CPL, (ii) the (S)-N*-LC cell selectively reflects left-handed CPL, and (iii) only right-handed CPL is transmitted leading to amplification of right-handed CPL. (b) At 40°C , (iv) the (S)-N*-LC cell becomes an isotropic phase and selective reflection of CPL does not occur, thus (v) predominantly left-handed CPL is transmitted. (c) the PL (upper), CPL (middle), and g_{em} (lower) spectra of (R)-PA/(S)-N*-LC CPL switchable cell at 25°C (red) and 40°C (blue).

The CPL spectra of the CPL switchable cell consisting of a (R)-N*-LC cell with (S)-PA CPL emitting layer were also measured and exhibited similar results. The CPL spectra of the (S)-PA/(R)-N*-LC CPL switchable cell shows handedness opposite to

(*R*)-PA/(*S*)-N*-LC CPL switchable cell (Figure S3). At room temperature the amplified left-handed CPL showed g_{em} values up to +1.77, while at 40 °C the predominantly right-handed CPL from the (*S*)-PA film has a g_{em} value of -1.46×10^{-1} . The g_{em} values of the CPL switchable cells are summarized at Table 1.

Table 1. Emission dissymmetry factors (g_{em}) of the CPL switchable cells.

	Temperature	$g_{em}(\text{wavelength/ nm})^a$
(R)-PA/(S)-N*-LC	25°C	– 1.79 (497)
	40°C	+ 1.24×10^{-1} (464)
(S)-PA/(R)-N*-LC	25°C	+ 1.77 (510)
	40°C	– 1.46×10^{-1} (460)

^awavelength at which g_{em} was evaluated

3.0 Conclusion

It was confirmed that thermotropic N*-LCs are excellent materials for the switching and amplification of CPL originating from chiral *di*-LCPA film. The emission of CPL originating from *di*-LCPA film within the selective reflection band of the N*-LC cell enables the selective reflection of CPL leading to CPL amplification and CPL switching upon a change of phase by the thermotropic N*-LC cell. We anticipate that this concept could be extended further to other liquid crystal systems exhibiting selective reflection, such as ferroelectric liquid crystals and blue liquid crystal phases, in order to achieve faster dynamic switching and selective reflection of CPL in three dimensions. The synergistic incorporation of chiral fluorescent conjugated polymers as CPL materials with the dynamic switching functionality of liquid crystals might lead to the emergence of next generation switchable low threshold lasers and optical memory devices.

Acknowledgements

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Chapter 6 Appendix

Table of Contents

1. Experimental Section

1.1. Methods

2. Supporting Figures

1. Experimental Section

1.1. Methods

The microscope observation was carried out under crossed nicols using a Carl Zeiss Axio Imager M1M polarizing microscope equipped with a Carl Zeiss AxioCam MRc5 digital camera and a Linkam TH600PM and L600 heating and cooling stage with temperature control.

Optical absorption spectra were measured using a JASCO V-570 UV/VIS/NIR spectrometer and fluorescence spectra were measured using JASCO FP-750 spectrometer. Circularly polarized luminescence was measured using JASCO CPL-200S spectrometer with a TTM-204 temperature controller.

Cholesteryl oleyl carbonate was purchased from Aldrich Co. Ltd. The 35 μ m polyimide tape used as a spacer was purchased from Nitto Tape, Co. Ltd.

2. Supporting Figures

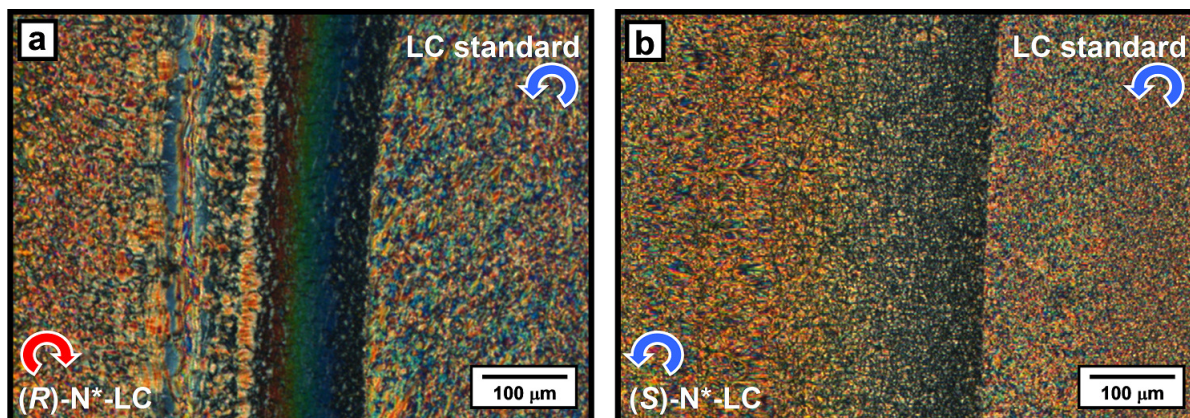


Figure S1. POM image of the miscibility test between the left-handed LC standard **cholesteryl oleyl carbonate** (right side) and (a) right-handed **(R)-N*-LC** showing discontinuity between the N*-LC phases, and (b) left-handed **(S)-N*-LC** showing a continuous N*-LC phase.

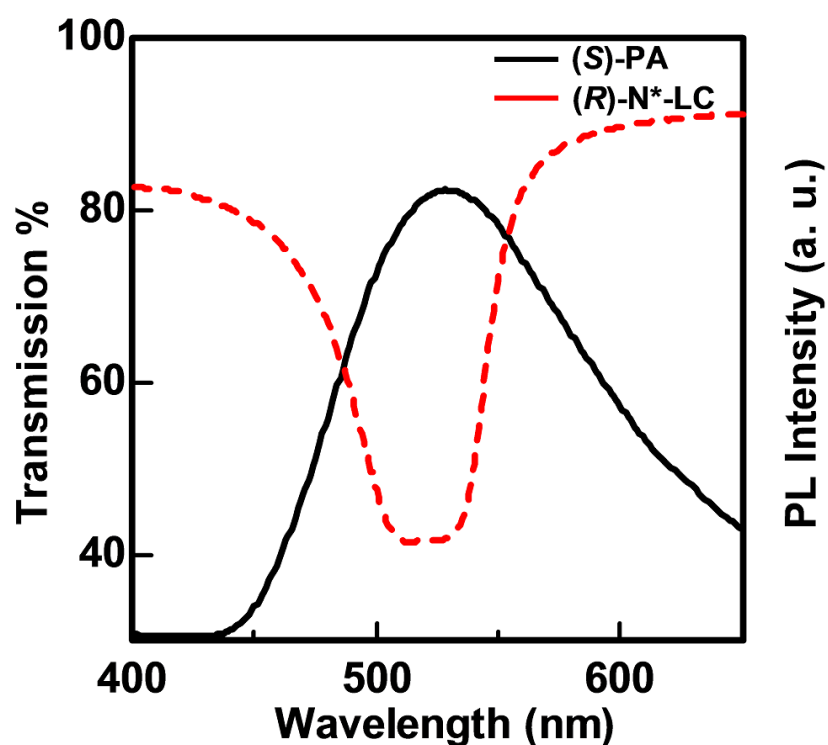


Figure S2. Photoluminescence (PL) emission (black) of **(S)-PA** film upon excitation at 367 nm and the transmission spectra (red) of the **(R)-N*-LC** cell showing the selective reflection band.

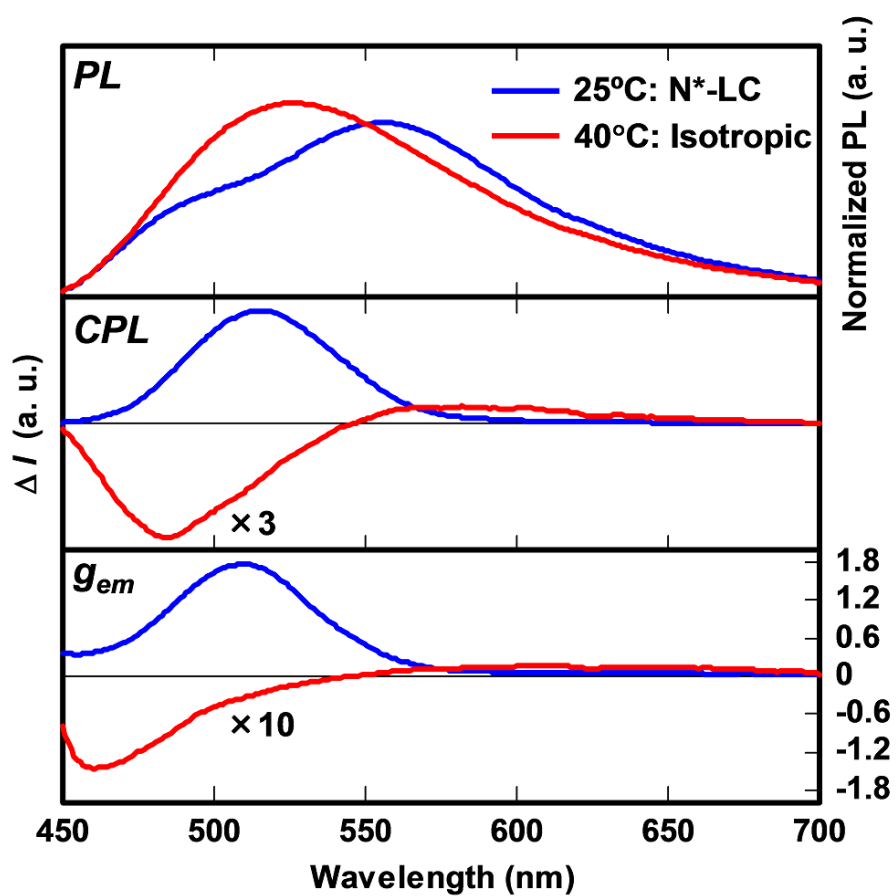


Figure S3. PL (upper), CPL (middle), and g_{em} (lower) spectra of (S)-PA/(R)-N*-LC CPL switchable cell at 25°C (blue) and 40°C (red).

REFERENCES

- (1) (a) M. Grell, D. D. C. Bradley, *Adv. Mater.* **1999**, *11*, 895–905. (b) M. Schadt, *Annu. Rev. Mater. Sci.* **1997**, *27*, 305–379. (c) Emeis, C. A.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1967**, *1* (4), 129–132. (d) Dyreklev, P.; Berggren, M.; Inganäs, O.; Andersson, M. R.; Wennerström, O.; Hjertberg, T. *Adv. Mater.* **1995**, *7*, 43–45. (e) Liu, J.; Su, H.; Meng, L.; Zhao, Y.; Deng, C.; Ng, J. C. Y.; Lu, P.; Faisal, M.; Lam, J. W. Y.; Huang, X.; Wu, H.; Wong, K. S.; Tang, B. Z. *Chem. Sci.* **2012**, *3*, 2737–2747.
- (2) Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1997**, *119* (41), 9909–9910.
- (3) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118* (20), 4908–4909.
- (4) Oda, M.; Nothofer, H. G.; Lieser, Scherf, U.; Meskers, S. C. J.; Neher, D. *Adv. Mater.* **2000**, *12*, 362–365.
- (5) (a) Chen, S. H.; Conger, B. M.; Mastrangelo, J. C.; Kende, A. S.; Kim, D. U. *Macromolecules* **1998**, *31*, 8051–8057. (b) Wilson, J.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830–6831. (c) Oda, M.; Nothofer, H. G.; Scherf, U.; Sunjic, V.; Richter, D.; Regenstein, W.; Neher, D. *Macromolecules* **2002**, *35*, 6792–6798. (d) Satrijo, A.; Meskers, S. C. J.; Swager, T.

- M. *J. Am. Chem. Soc.* **2006**, *128*, 9030–9031. (e) Watanabe, K.; Osaka, I.; Yorozuya, S.; Akagi, K. *Chem. Mater.* **2012**, *24*, 1011–1024.
- (6) San Jose, B. A.; Matsushita, S.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 19795–19807.
- (7) De Vries, H. *Acta. Crystallogr.* **1951**, *4*, 219–226.
- (8) *Textures of Liquid Crystals*; Dierking, I.; Wiley-VCH: Weinheim, 2003.
- (9) Goh, M.; Kyotani, M.; Akagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 8519–8527.
- (10) (a) Chen, S. H.; Katsis, D.; Schmid, A. W.; Mastrangelo, J. C.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506–508. (b) Grell, M.; Oda, M.; Whitehead, K. S.; Asimakis, A.; Neher, D.; Bradley, D. D. C. *Adv. Mater.* **2001**, *13*, 577–580.
- (11) (a) Furumi, S. *Chem. Rec.* **2010**, *10*, 394–408. (b) Coles, H.; Morris, S. *Nat. Photonics* **2010**, *4*, 676–685.
- (12) (a) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P.; Wendorff, J. H. *Adv. Mater.* **2003**, *15*, 282–287. (b) Vijayaraghavan, R. K.; Abraham, S.; Akiyama, H.; Furumi, S.; Tamaoki, N.; Das, S. *Adv. Funct. Mater.* **2008**, *18*, 2510–2517.
- (13) (a) Satrijo, A.; Swager, T. M. *Macromolecules* **2005**, *38*, 4054–4057. (b) Satrijo, A.; Meskers, S. C. J.; Swager, T. M. *J. Am. Chem. Soc.*, **2006**, *128*, 9030–9031.
- (14) Hayasaka, H.; Miyashita, T.; Tamura, K.; Akagi, K. *Adv. Funct. Mater.* **2010**, *20*,

1243–1250.

(15) Akagi, K. *Polym. Int.* **2007**, 56, 1192–1199.

General Conclusion

In **Chapter 1**, functionality tunable *mono*-substituted PA copolymers bearing LC and chiral moieties were synthesized. The copolymers show a stable SmA phase up to 50:50* in feeding mole ratio of LC and chiral monomers. It was found that the copolymerization method is a facile way to prepare a stable smectic mesophase and impart chirality to the mesophase. The synthesized *mono*-PA copolymers could be potential photorefractive materials because of the electroclinic properties associated with the SmA* phase.

In **Chapter 2**, *di*-substituted liquid crystalline PA derivatives represented by poly(alkylphenylacetylene)s [PAPAs] and poly(diphenylacetylene)s [PDPAAs] were synthesized and their thermal and optical properties were evaluated. The polymers exhibit enantiotropically thermotropic or lyotropic liquid crystallinity. The origin of emission of substituted PAs was elucidated and fluorescent trends such as emission color and quantum yield was also investigated. It was found that the macroscopically aligned films of the *di*-LCPAs emit linearly polarized luminescence (LPL) by virtue of the functionalities associated with liquid crystallinity and fluorescence. The mechanism of LPL of the *di*-LCPAs with respect to the polymer structure, alignment type, and emission color was elucidated.

In **Chapter 3**, chiral *di*-LCPA derivatives were synthesized that show a highly ordered lyotropic N*-LC phase, thereby giving rise to a high degree of circular polarization.

The PDPA main chain structure of the *di*-LCPAs, along with chirality induced with either chiral nonyloxy phenyl moieties or chiral dopants, allows the formation of a highly ordered lyotropic N*-LC phase. It was found that the highly ordered lyotropic N*-LC phase is indispensable for the generation of CPL with high g_{em} values. In addition to having the highest values of CPL in aliphatic conjugated polymers, our approach represents an attractive alternative to thermotropic LC systems for the development of LC-based optoelectronic devices and future applications that utilize circularly polarized optical materials.

In **Chapter 4**, chiral PPE aggregates that show an interesting phenomena of chiral inversion in the CD and CPL spectra at different solvent conditions were synthesized. The results suggest that the solvent environment during formation of the PPE aggregates plays a critical role in determining their helical structure and handedness. A model describing the chiral inversion behavior of chiral PPE in aggregate state was put forward. Bisignate Cotton effects centered at the polymer main chain absorption band of PPE in 70% MeOH suggest the formation of a helical π -stacked structure. At 90% MeOH, the chains of PPE are stacked close together due to the hydrophobic interactions with the poor solvent and form into helical bundles. The novel chiral inversion of CPL of the synthesized PPE aggregates may be attractive materials for optoelectronic devices and applications using circularly polarized optical materials.

In **Chapter 5**, novel photoresponsive PPP derivatives have been synthesized by introducing photoresponsive chiral dithienylethene (DE*) endgroups to the PPP main chain. The helical inversion of π -stacking structures with the photoisomerization of the

chiral DE* endgroups were observed in assembled state. Furthermore, the chiral transcription of achiral PBTT through the formation of helical π -stacking assemblies consisting of photoresponsive chiral PPP and achiral PBTT was reported. This is the first report of a conjugated polymer showing inversion of chirality through the photoisomerization of the chiral endgroups. The dynamic photoresponsive functionality of the synthesized PPP assemblies have potential applications in the development of dynamic optical memory systems and functional chiroptical devices.

In **Chapter 6**, the emission of CPL originating from *di*-LCPA film within the selective reflection band of the N*-LC cell enables the selective reflection of CPL leading to CPL amplification and CPL switching upon a change of phase by the thermotropic N*-LC cell. The synergistic incorporation of chiral fluorescent conjugated polymers as CPL materials with the dynamic switching functionality of liquid crystals might lead to the emergence of next generation switchable low threshold lasers and optical memory devices.

List of Publications

Chapter 1

Competitive and Constructive Structural Effects of Liquid Crystalline and Chiral Units on the Functional Properties of *Mono*-Substituted Polyacetylene Copolymers

San Jose, B. A.; Matsushita, S.; Akagi, K. *to be submitted*

Chapter 2

Di-substituted Liquid Crystalline Polyacetylene Derivatives That Exhibit Linearly Polarized Blue and Green Emissions

San Jose, B. A.; Matsushita, S.; Moroishi, Y.; Akagi, K. *Macromolecules*. **2011**, *44*, 6288–6302.

Chapter 3

Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on *Di*-substituted Polyacetylene Derivatives That Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence

San Jose, B. A.; Matsushita, S.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 19795–19807.

Chapter 4

Inversion of Chirality and Circularly Polarized Luminescence of Poly(*para*-phenyleneethynylene) Derivatives bearing Chiral Moieties through Solvent Induced Aggregation

San Jose, B. A.; Suzuki, S.; Matsushita, S.; Akagi, K. *to be submitted*

Chapter 5

Photoswitchable, Helically π -Stacked Assemblies of Poly(*para*-phenylene) bearing
Photoresponsive Chiral End-groups

San Jose, B. A.; Tada, N.; Ashibe, T.; Yorozya, S.; Akagi, K. *submitted/under review*

Chapter 6

Dynamic Switching of Circularly Polarized Luminescence of *Di*-substituted
Polyacetylene by Selective Transmission through a Thermotropic Chiral Nematic
Liquid Crystal

San Jose, B. A.; Yan, J.; Akagi, K. *to be submitted*

Other Publications

Liquid Crystalline Polyacetylene Derivatives with Advanced Electrical and Optical
Properties (*Chapter 2 and Chapter 3 Research Theme: Review Article*)

San Jose, B. A.; Akagi, K. *Polym. Chem.* **2013**, 5144–5161.

Books

1. “液晶性を有する二置換ポリアセチレン誘導体の合成と性質”、有機電子デバイスのための導電性高分子の物性と評価、シーエムシー出版、
松下哲士、サンホセベネディクトアルセナ、赤木和夫、(2012)

(*Chapter 2 Research Theme: Book Chapter Contribution*)

2. "Self-Assembled Liquid Crystalline Conjugated Polymers: Synthesis, Development, and their Advanced Electro-Optical Functionalities", Book Chapter in: *Nanoscience with Liquid Crystals: From Self-Organized Nanostructures to Applications*. Li, Q. Ed. Springer Publishing, Inc., San Jose, B. A.; Akagi, K. (2014)
(Chapter 2 and Chapter 3 Research Theme: Book Chapter Contribution, in press)

List of Presentations

International Conferences:

(1) Poster presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis of Liquid Crystalline *Di*-Substituted Polyacetylene Derivatives with Blue-Light Emission” **18th Iketani Conference**, Awaji, Japan, October 21–23, 2008.

(2) Oral presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis of Liquid Crystalline *Di*-Substituted Polyacetylene Derivatives with Blue-Light Emission” **Seoul University-Kyoto University One Day Workshop**, Korea, November 21, 2008.

(3) Oral presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis and Functionality of Liquid Crystalline *Di* -Substituted Polyacetylene Derivatives” **5th International Symposium on Microscale Chemistry/5th Philippine Chemistry Congress**, Subic Bay, Zambales, Philippines, April 8–10, 2010.

(4) Poster presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Chiral Polyacetylene Derivatives Bearing Liquid Crystalline Moieties with Polarized Functionality” **The International Conference on Science and Technology of Synthetic Metals 2010 (ICSM 2010)** Kyoto, Japan, July 4–9, 2010.

List of Presentations

(5) Poster presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Chiral Polyacetylene Derivatives Bearing Liquid Crystalline Moieties with Circularly Polarized Luminescence” **Joint Workshop on Functional Synthetic Metals**, Busan, Korea, November 20, 2010.

(6) Oral presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Circularly Polarized Luminescence of *Di*-Substituted Polyacetylene through the Formation of a Chiral Nematic Liquid Crystal Phase” **29th National Philippine Physics Congress**, University of the Philippines-Diliman, Manila, Philippines, October 24–26, 2011.

(7) Oral presentation: San Jose, B.; Yan, J.; Akagi, K. “Dynamic Switching of Circularly Polarized Light through Selective Reflection in a Thermotropic Chiral Nematic Liquid Crystal Phase” **31th National Philippine Physics Congress**, University of San Carlos, Cebu, Philippines, October 23–25, 2013.

Domestic Conferences:

(1) Oral Presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis of Liquid Crystalline *Di*-Substituted Polyacetylene Derivatives with Blue-Light Emission” **57th SPSJ Symposium on Macromolecules**, Osaka, September 24–26, 2008.

(2) Poster Presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis of Liquid Crystalline *Di*-Substituted Chiral Polyacetylene Derivatives with Blue-Light Emission” **58th SPSJ Annual Meeting**, Kobe, May 27–29, 2009

(3) Oral Presentation: San Jose, B.; Matsushita, S.; Moroishi, Y.; Akagi, K. “Synthesis of Chiral Polyacetylene Derivatives Bearing Liquid Crystalline Moieties with Polarized Functionality” **58th SPSJ Symposium on Macromolecules**, Kumamoto, September 16–18, 2009.

(4) Oral Presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Circularly Polarized Luminescence of *Di*-Substituted Polyacetylene through the Formation of a Chiral Nematic Liquid Crystal Phase” **59th SPSJ Symposium on Macromolecules**, Sapporo, September 15–17, 2010.

(5) Oral Presentation: Suzuki, S.; San Jose, B.; Matsushita, S.; Akagi, K. “Synthesis and Properties of Poly(*para*-phenyleneethynylene) (PPE) Derivatives with Chiral Substituents in Side Chains” **61th SPSJ Annual Meeting**, Yokohama, March 29–31, 2012.

(6) Poster Presentation: Suzuki, S.; San Jose, B.; Matsushita, S.; Akagi, K. “Chirality Inversion and Circularly Polarized Luminescence of Poly(*para*-phenyleneethynylene) Derivatives bearing Chiral Moieties through Solvent Induced Aggregation” **61th SPSJ Symposium on Macromolecules**, Nagoya, September 19–21, 2012.

(7) Oral Presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on Disubstituted Polyacetylene Derivatives That Exhibit High Dissymmetry Factors in Circularly Polarized Luminescences” **62th SPSJ Annual Meeting**, Kyoto, May 29–31, 2013.

List of Presentations

(8) Oral Presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Lyotropic Chiral Nematic Liquid Crystalline *Di*-substituted Polyacetylene Derivatives that exhibit Circularly Polarized Luminescence” **2013 JLCC Symposium**, Osaka University, September 8–10, 2013

List of Honors, Awards, and Scholarships

Synthetic Metals Young Scientist Award, ICSM 2010

Poster Presentation: San Jose, B.; Matsushita, S.; Akagi, K. “Chiral Polyacetylene Derivatives Bearing Liquid Crystalline Moieties with Polarized Functionality”

The International Conference on Science and Technology of Synthetic Metals 2010 (ICSM 2010) Kyoto, Japan, July 4–9, 2010.

Monbukagakusho (Japanese Government) Research Student Scholarship

Research Student, April 2007-March 2008

Master's Course, April 2008-March 2010

Doctorate Course, April 2010-March 2013

Japan Student Services Organization (JASSO) Honors Scholarship

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