

Studies on Molecular Systems with Electron
Conjugation by Wide-range Spectroscopy
Complex

Koo Yun Hee

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Preface

In the investigation on the organic π -conjugated material, spectroscopic methods have been utilized as versatile tools both for the analysis of structure and optoelectronic properties in these materials. Each spectroscopical method provides distinct information on the materials in investigation, hence, the selection and the combination of the method to reveal the property of the materials become important.

In this work, various kinds of π -conjugated materials in condensed phases are investigated with the extensive analysis of the data from steady and time-resolved spectroscopic techniques to elucidate the structural and electronic properties of these materials. In first two chapters, examples of how the spectroscopic analysis can be used to elucidate the characteristics in the condensed phase π -conjugated materials will be given with the conjugated polymer and expanded porphyrin in condensed phase and in third chapter, newly developed spectroscopic technique circularly polarized light time-resolved microwave conductivity (CPL-TRMC) to investigate spin-dependence will be introduced and demonstrated with the chiral perylenediimide and the carbon nanotube composite film.

Contents

Preface	I
Contents	II
General Introduction	1
Chapter 1. Spectroscopic characterization of the morphological characteristics of the crystalline Poly(3-hexylthiophene) cube	32
Chapter 2. Electrical conductivity switching in Tetrathiafulvalene-annulated expanded porphyrin by protonation induced close π -stacking	49
Chapter 3. Circularly polarized light induced microwave conductivity measurement on chiral PDI/SWCNT composite	71
Conclusion	101
List of Publications	103
Acknowledgement	105

General Introduction

1. Spectroscopic methods

Spectroscopy, which is the field that studies the electromagnetic waves interacting with the matter, has been versatile tool for the analysis for the materials both in quantitative and qualitative ways.¹ The practice of the spectroscopy is done by measuring the emitted, transmitted or reflected electromagnetic waves from the matter and analyzing the intensity and the frequency to reveal the properties of the matters. One of the fundamental principles that governs the study of interaction between light and matter is Beer-Lambert law which describes the attenuation of radiation in the matter as equation:

$$P = P_0 e^{-\alpha x} \quad (1)$$

where P_0 , P , α , x are the incident radiant power, the radiation power passing the matter, the absorptivity and the path length, respectively.² The absorptivity expressed as complex number can explain the absorbance and the reflection of the radiation, which allows the measurement of radiation emitted from the matter as a way to elucidate the properties of the matter. The emission from the matter can be divided into elastic and inelastic, depending whether the energy of incident radiation is conserved or not, respectively. The spectroscopic method that utilizes the elastic scattering of the light is providing the information on the structure and the morphology of the materials, on the other hand, the method that utilizes the inelastic scattering is giving the information on the energy levels in the materials, calculated from the change in the frequency of the radiation emitted from the matters. Another way to categorize the spectroscopic methods would be resonant and dissipative. In resonant spectroscopic methods, radiation that is corresponding to the energy level of the materials will interact with the matter to elucidate properties of the materials and in dissipative spectroscopic methods, energy loss in the system is tracked to reveal the properties of the materials. All of the frequency range of the electromagnetic waves are possible to be employed to investigate the structural and the optoelectronic properties of the materials, from gamma-ray to radiowave and each frequency

range can be utilized to lead to different quantum transitions of the matters. Alongside the steady-state techniques, time-resolved spectroscopic techniques were also developed to track the photophysical processes of the materials with different frequency ranges of excitation and probe waves. In this section, steady-state and time-resolved spectroscopical techniques which were used in the work will be introduced for the qualitative assessment of the materials.

1-1. Absorption spectroscopy in ultraviolet-visible-near-infrared (UV-vis-NIR) region

Absorption spectroscopy in UV-vis-NIR region has been a fundamental tool for the spectroscopical analysis of the materials. UV-vis region of the electromagnetic wave corresponds to the electronic transition of the molecule; thus this technique provides the information on the energy of the electronic states of the material. Conjugated materials tend to have absorption in longer wavelength region due to the extension of the conjugation which leads to the smaller bandgap.³ In materials with highly extended conjugation, electronic transitions can be reside in the NIR region. Absorption spectroscopy often becomes a basis for the experimental design and the interpretation of the other spectroscopic methods and can be paired with the chemical or electrochemical titration to inspect the redox-induced change in the electronic transitions of the materials.

In absorption spectroscopy, absorbance is calculated from the intensity of the transmitted light to the incident light. The relationship between the intensity of the incident and transmitted light, transmittance, and absorbance can be expressed as following equation:

$$A = -\log T = -\log \frac{I}{I_0} \quad (2)$$

where A , T , I_0 and I stands for the absorbance, the transmittance, the intensitiy of incident light and intensity of the transmitted light, respectively. Relationship between the concentration and the absorbance of molecules in the dilute solution state can be explained by the Beer-Lambert law, which is described in equation (1).

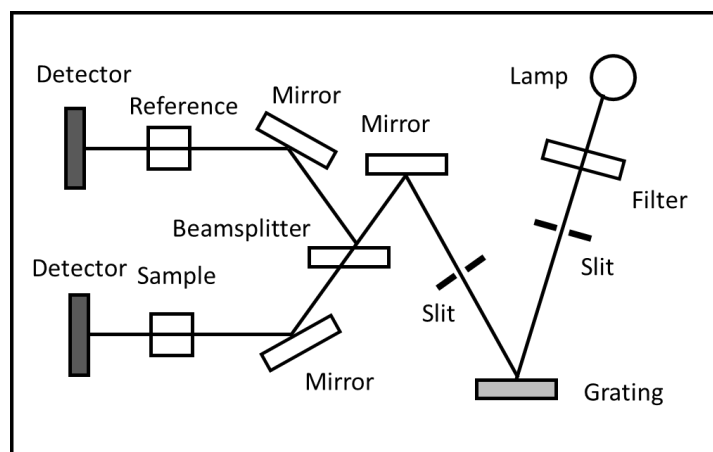


Figure 1. Schematics of the UV-vis-NIR instrument (double beam)

Typical instrument for the absorption spectroscopy is depicted in Figure 1. It consists of light sources, wavelength selectors, sample holders, detectors and signal processors. For UV range, deuterium or hydrogen arc lamps are employed and for visible-NIR range, xenon or tungsten lamps are used as continuum sources. Light generated by the lamps are guided through the wavelength selector, which uses gratings or prisms to separate each wavelength component and selected wavelength is passed through the sample holder to measure the transmittance. For detection, photomultiplier tube (PMT) or photodiode can be employed.

1-2. Electronic circular dichroism spectroscopy

Electromagnetic wave consists of electric field and magnetic field which are perpendicularly oscillating with each other. If the electric field vector oscillates in one plane, the light is linearly polarized. On the other hand, the electric vector can also rotate through propagating direction drawing circle in one period of a wave. Two different directions of the rotation are available, one with clockwise and one with counterclockwise, which is expressed as right-circularly polarized (RCP) and left-circularly polarized (LCP) light, respectively. These two different circular polarizations of the light will represent two different spin-angular momentum of the light. Circularly polarized light will interact with the chiral material differently as the circularly polarized light itself is also chiral.

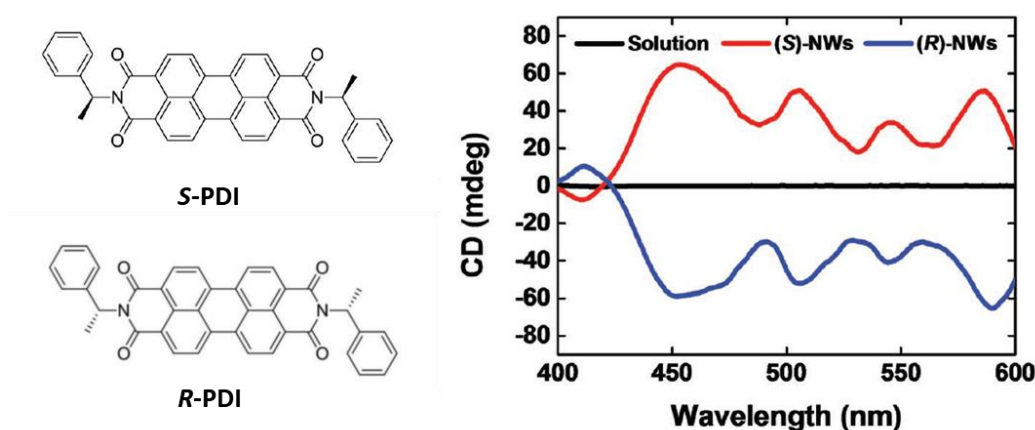


Figure 2. CD spectra of *R/S*-perylenediimide nanowires showing cotton signal.⁴

Circular dichroism (CD) is defined as differential absorption of LCP and RCP light. This phenomenon was found by Jean-Baptiste Biot, Augustin Fresnel and Aime Cotton.⁵ CD can be calculated by measuring the absorption of the LCP and RCP and taking the difference between them. The CD value is calculated by following equation:

$$\Delta A = A_L - A_R = (\varepsilon_L - \varepsilon_R)cl \quad (3)$$

where A_L and A_R are the absorbance of left- and right-handed light and ε_L and ε_R are the molar absorptivity of the left- and right-handed light, respectively. CD value is usually expressed as elipsity for the historical reasons and can be interconverted to the differential absorption by equation:

$$\theta = 3298.2 \Delta A \quad (4)$$

CD spectra are sometimes explained by the Cotton effect, which is first discovered by Aime Cotton.⁶ If the CD increases as the wavelength increases, it is called the positive Cotton effect and if the CD decreases, it is called negative Cotton effect. Enantiomers will interact oppositely to the circular polarization, yielding CD spectra with mirror image to the wavelength axis.

Owing to the inherent chirality of the building blocks for the biomolecules, CD spectroscopy was often employed for the structural analysis of the biomolecules such as DNA and proteins.^{7,8} It has been an important technique for the analysis of the secondary structure of proteins.^{7,9} In recent days, CD spectroscopy is widely used for the assessment of the chiral materials for the spintronic applications.¹⁰⁻¹²

Sometimes the materials can exhibit apparent CD, if the materials has ordered structure. This extrinsic effect arises from the existence of linear dichroism (LD) and the linear birefringence (LB), which will be present in the oriented sysetms.¹³ This effect will result in the orientation dependence in the CD spectrum, often even flips the sign of the CD spectra. The observed CD value can be expressed by following equation:

$$CD_{obs} = CD_{true} + (LD' \cdot LB - LD \cdot LB') \quad (5)$$

where CD_{obs} and CD_{gen} is the observed CD and the genuine CD and LD' and LB' are the linear dichroism and the linear birefringence measured with the rotation of the sample to the optical axis by 45° , respectively. LD' and LB' terms are reversed when the sample is flipped by 180° , thus the genuine CD without orientation dependence can be calculated by taking average of the CD spectra measured with flip of the sample orientation.¹⁴

The instrumentation of the CD is largely similar to the UV-vis-NIR absorption spectrometer; however, it has some major differences for generating and guiding circularly polarized light to the sample. Conversion between the LCP and RCP will be performed with the modulator element with piezoelectric element which will convert the ellipticity of the light by applying the mechanical stress to the quartz plate. For the wavelength selection, prisms are adopted instead of the gratings to preserve the polarization of the light.

1-3 Raman spectroscopy

Raman spectroscopy is a spectroscopic method measuring inelastically scattered light to identify vibrational energy modes of the materials. When the material is irradiated with the strong light source, it will be excited to the virtual states when the excitation wavelength is away from the absorption band. When the material relaxes down to ground state, it can relax down to the vibrational level which is different from the original state. This inelastic scattering is called Raman scattering and by calculating the frequency difference to the excitation light, the energy of the vibrational level of the materials can be obtained (Figure 3).¹⁵

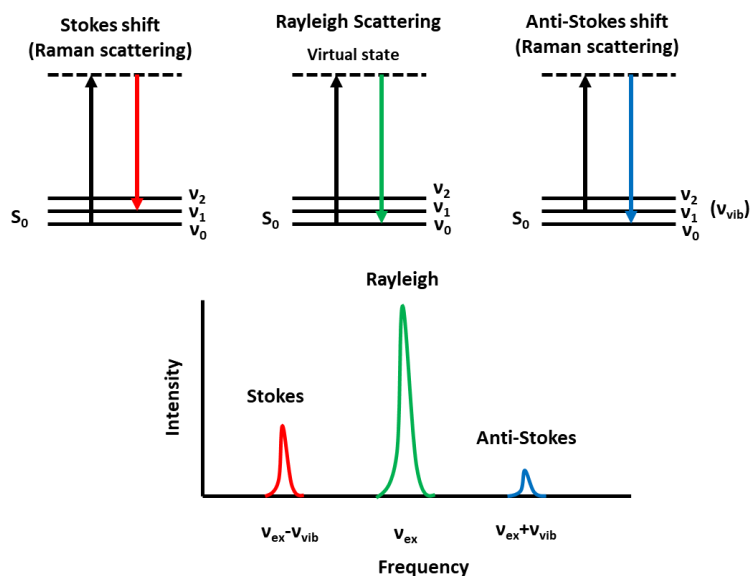


Figure 3. Schematics for Rayleigh scattering and Stokes and anti-Stokes shift of Raman scattering.

Along with infrared (IR) spectroscopy, this method gives the information on the vibrational energy levels of the materials. The selection rule, however, are different for the IR and Raman spectroscopy: Raman scattering requires the change in the polarizability while IR absorption requires net change in the permanent dipole moment during the vibration. Thus, the Raman spectroscopy is sensitive to the symmetric vibrations while the IR spectroscopy is sensitive to the asymmetric or bending motion of the materials. Being sensitive to the symmetric vibrations, Raman spectroscopy has been useful tool for the structural analysis of the carbon-based materials. Raman bands from sp^2 carbons are strong enough for the sensitive structural analysis, allowing analysis of the defect and the orientation of the layers.¹⁶⁻¹⁷

In order to increase the sensitivity, resonance Raman spectroscopy scheme can be applied which uses incident photon energy of close to the electronic transitions of the materials. Resonance to the electronic energy level of the materials will increase the sensitivity greatly in several order of magnitudes and additional selectivity can be achieved by selective enhancement of vibrational modes that are from the parts of the materials that are undergoing electronic transition.¹⁸

Lasers are generally used as the light source for the Raman spectroscopy owing to their high intensity and monochromatic wavelength. The target material will be irradiated with the

laser beam and scattered light will be collected with focusing lens. After removing the Rayleigh scattering by the band-pass filter and the spectrograph will be recorded with the monochromator and the detector system.

1-4. X-ray diffraction spectroscopy

X-ray diffraction spectroscopy measures the diffracted X-ray from the crystalline compounds to analyze the structure of the sample. This technique was discovered by von Laue in 1912, and has been a useful tool for the analysis of the various kinds of solid samples. In X-ray diffraction spectroscopy, the sample material is irradiated with the X-ray with differing the glancing angle 2θ and the intensity of the X-ray reflected back from the sample will be recorded. The X-ray will be reflected when they hit the nuclei in the atoms that comprises the crystal and diffracted to give diffraction patterns. The relationship between the reflected beam and the lattice parameters can be expressed as Bragg's law (Figure 4):

$$n\lambda = 2d \sin \theta \quad (6)$$

where the λ , d and θ are the X-ray wavelength, the separation in the lattice plane, the Bragg angle which is half of the glancing angle, respectively and n is integer number for the n th order reflection.¹⁹

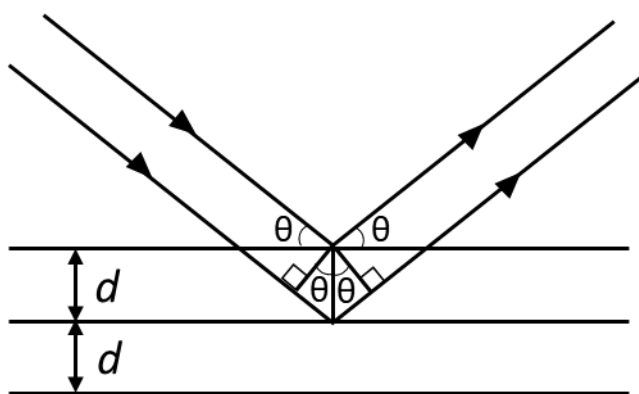


Figure 4. Schematics for Bragg diffraction

X-ray crystallography has been used for identifying the molecular structure in the

crystals, which has been a powerful tool for the analysis even for the macromolecules like proteins. Powder X-ray has been versatile tool for identification of the crystals and the crystalline domain size analysis of the sub-micrometer crystallites. Scherrer's formula describes the relationship between the size for the crystallite and the full-width half-maximum (FWHM) of the peaks, which can be written as:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (7)$$

where τ , K , λ , β , θ are the mean size of the crystalline domains, the shape factor and the line broadening calculated from FWHM of the peaks.²⁰⁻²¹

1-5. Transient absorption spectroscopy

Transient absorption (TA) spectroscopy is a time-resolved technique which utilizes the UV-vis pump beam to excite the material and probe continuum to track the absorption change with time. It has been a versatile tool for the analysis of the photophysics and photochemistry of the various types of materials. This spectroscopic technique can track the spectral signal of the excited-state species with in time-resolved manner, providing rich information on the photophysical processes in the material. Femtosecond and nanosecond transient absorption instrumentations were most widely used, which have the time resolution for femtosecond to nanosecond in femtosecond TA and from nanosecond to microsecond for nanosecond TA. Femtosecond TA can be used for tracking early time evolution of the photophysical processes such as radiative and nonradiative decay from first singlet state, charge separation and energy transfer and Nanosecond TA can track charge recombination, decay of the triplet state and sometimes the delayed fluorescence. Both the techniques also can be combined to get a full picture of the excited state dynamics of the materials.

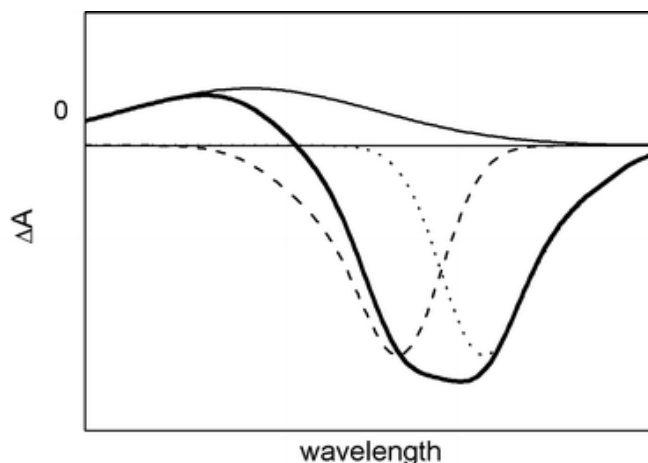


Figure 5. Spectral features that can be observed in the differential absorption spectra measured by TA spectroscopy: ground-state bleach (dashed line), stimulated emission (dotted line), excited-state absorption (thin line), sum of these contributions (bold line).²²

Several different photophysical processes can contribute to the differential absorption measured in the TA, and these can be analyzed to reveal the photophysics and photochemistry of the materials (Figure 5). There are four possible contribution which can be seen in differential absorption spectra: (1) ground-state bleach (GSB), (2) excited state absorption (EA) (3) stimulated emission (SE) (4) product absorption.²² (1) Ground-state bleach (GSB) is coming from the depletion of the number of the molecules in the ground state. GSB is shown as negative signal at the spectral range where the steady-state absorption of the molecule locates. (2) Excited state absorption (EA) is absorption from the transiently generated excited state species from photoexcitation with the pump beam. EA is shown as positive signal in the differential absorption spectra. (3) Stimulated emission (SE) to the ground state also can be induced by the probe pulse when it passes through the excited species generated by the pump pulse. Because this process will increase the intensity of the light which reaches to the detector, SE will be shown as negative signal in the spectral region where fluorescence emission can be observed in steady-state measurements. (4) Product absorption can be also observed when the photochemical processes are present in the system. This will be observed in similar manner to the EA, as positive signal in the spectra.

Because the transient absorption spectra contain spectral signal from all the transiently generated species, interpretation of the spectra requires the information of the absorption peak of transient species. The steady-state spectroscopic methods such as absorption emission

spectroscopy as well as the spectroelectrochemistry or the redox titration can be utilized to find out the location of the spectral features of GSB, SE, EA from charge separated species and sometimes the other time-resolved techniques such as time-resolved photoluminescence can be valuable in the identification of the photophysical process that accompanies emission. By comparing the spectral features and the decay time constant, spectral features can be assigned to the specific photophysical processes. Global or target analysis can be also utilized for the identification and assignment of the transient species, by separating spectral features for each decay component.

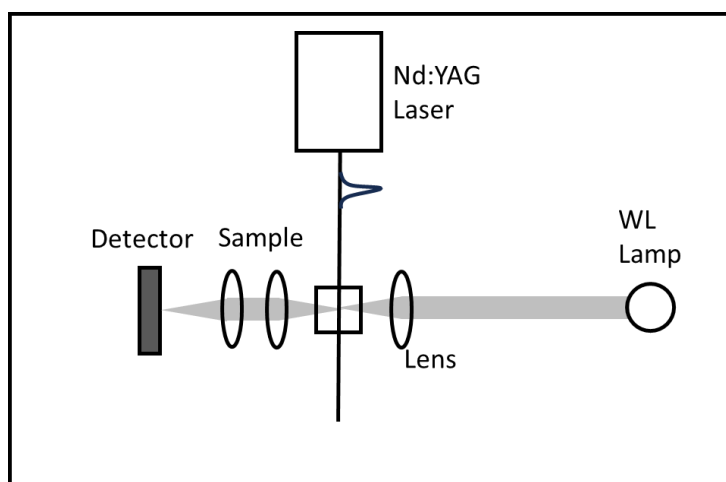


Figure 6. Instrumentation for the nanosecond transient absorption spectroscopy (ns-TA)

Nanosecond transient absorption spectroscopy employ lamp for the probe and the absorbance of the sample with and without pump pulse is recorded to calculate the differential absorption (Figure 6). Fluorescence from the pump excitation can be ruled out by taking pump-only and the dark signal with following equation:

$$\Delta A = -\log \left(\frac{I_{\text{pump-probe}} - I_{\text{pump}}}{I_{\text{probe}} - I_{\text{dark}}} \right) \quad (8)$$

where $I_{\text{pump-probe}}$, I_{pump} , I_{probe} and I_{dark} are the intensity of the signal calculated with both pump and probe, pump only, probe only and without any light source, respectively. For detection system for the nanosecond transient absorption, Streak camera is often adopted in the ns-TA instrumentation to obtain two-dimensional spectra of time and wavelength.

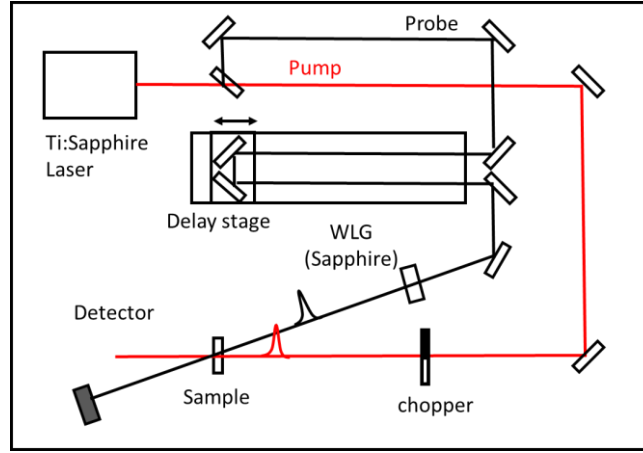


Figure 7. Instrumentation for the femtosecond transient absorption spectroscopy (fs-TA). Unmarked optics are the mirrors.

Instrumentation for the femtosecond transient absorption spectroscopy (fs-TA) employs different strategy to the ns-TA, as the response time of the detector cannot reach fs-ps time range. In order to make time delay between the pump and probe beams with ultrafast time duration, probe white-light continuum pulse is generated from the small portion of the pump pulse and guided to the mechanical delay to generate fs to ns time delay between pump and probe pulses (Figure 7).

1-6. Flash-photolysis time-resolved microwave conductivity

Time-resolved microwave conductivity (TRMC) is a technique which utilizes microwave as a probe for measuring the complex conductivity of the material. In this method, microwave resonant cavity is utilized for the complex conductivity measurement. The theory regarding on complex permittivity analysis with a resonant cavity was proposed by Slater, where the relationship between quality factor of the cavity and complex conductivity can be expressed as:

$$\Delta\left(\frac{1}{Q}\right) - i\frac{2\Delta f_0}{f_0} = \frac{F}{\omega\epsilon_0}\Delta\tilde{\sigma} \quad (9)$$

where $Q, f_0, F, \omega, \varepsilon_0$ and $\tilde{\sigma}$ are the quality factor, the resonance frequency, the geometric factor, the angular frequency of electromagnetic wave, and the permittivity of the vacuum, respectively.²³ The Q value is defined by following equation:

$$\frac{1}{Q} = \frac{P}{\omega_0 W} \quad (10)$$

where P, W and ω_0 are the energy loss per unit time, stored energy in the cavity and the angular resonance frequency of the cavity. The time averaged W and P in the cavity can be expressed as the equation on the electric field as follows:

$$\langle W \rangle = \frac{\varepsilon' E_0^2}{2}, \quad \langle P \rangle = \frac{1}{2} \omega \varepsilon' \tan \delta E_0^2 \quad (11)$$

and Q can be expressed as when ω_0 is close to ω :

$$\frac{1}{Q} = \frac{\langle P \rangle}{\omega_0 \langle W \rangle} = \frac{\omega}{\omega_0} \tan \delta \approx \tan \delta = \frac{\sigma}{\omega \varepsilon'} \quad (12)$$

Thus, the conductivity σ change in the material is proportional to the change in the reciprocal of Q . The reciprocal of the quality factor Q_L of the loaded cavity can be expressed as reciprocal sum of the quality factor Q_U of the unloaded cavity and quality factor Q_C from coupling of the cavity and the waveguide:

$$\frac{1}{Q_L} = \frac{1}{Q_U} + \frac{1}{Q_C} \quad (13)$$

When the sample is inserted to the cavity, the complex reflection coefficient of r of the cavity can be expressed as following equation from Tomonaga's description.²⁴⁻²⁵

$$r = \frac{\omega_0/Q_C}{(\omega - \omega_0) + i(\frac{\omega_0}{2Q_L})} + i \quad (14)$$

The complex conjugate of complex reflection coefficient can be expressed as follows:

$$R = r \cdot r^* = \frac{P_r}{P_i} = \frac{\left(\frac{2\Delta\omega}{\omega_0}\right)^2 + \left(\frac{1}{Q_U} - \frac{1}{Q_C}\right)^2}{\left(\frac{2\Delta\omega}{\omega_0}\right)^2 + \left(\frac{1}{Q_U} + \frac{1}{Q_C}\right)^2} \approx \frac{\left(\frac{1}{Q_U} - \frac{1}{Q_C}\right)^2}{\left(\frac{1}{Q_U} + \frac{1}{Q_C}\right)^2} \quad (15)$$

The conductivity change due to the sample can be written as a term of Q :

$$\Delta \frac{1}{Q} = \frac{1}{Q_U'} - \frac{1}{Q_U} \quad (16)$$

Then the change in the energy loss in the cavity can be written as:

$$\begin{aligned} \frac{\Delta P_r}{P_i} &= \frac{\left(\frac{1}{Q_U} + \Delta \frac{1}{Q} - \frac{1}{Q_C}\right)^2}{\left(\frac{1}{Q_U} + \Delta \frac{1}{Q} + \frac{1}{Q_C}\right)^2} - \frac{\left(\frac{1}{Q_U} - \frac{1}{Q_C}\right)^2}{\left(\frac{1}{Q_U} + \frac{1}{Q_C}\right)^2} \\ &\approx \frac{4\left(\frac{1}{Q_U} - \frac{1}{Q_C}\right)\frac{1}{Q_C}}{\left(\frac{1}{Q_U} + \frac{1}{Q_C}\right)^3} \Delta \frac{1}{Q} = \mp 2Q_L \left(\frac{1}{\sqrt{R}} \pm 1\right) \Delta \frac{1}{Q} = A\Delta\sigma \end{aligned} \quad (17)$$

where A is the sensitivity factor. Thus, change dielectric loss in the cavity can be converted to the change in the conductivity.

Pioneering work based on this technique is pulse-radiolysis (PR)-TRMC invented by Warman, which uses electron beam to ionize the sample to generate free carriers.²⁶⁻²⁸ Flash-photolysis (FP)-TRMC, on the other hand, uses laser pulse for carrier injection by inducing exciton dissociation to the carriers. In FP-TRMC measurement, dielectric loss from microwave cavity is monitored after photogeneration of the carriers to track the local motion of the charge carriers.²⁹⁻³¹ Owing to the non-contact nature, this method can be readily used for the samples with various morphologies including powder, film, crystals, solution, etc., without device fabrication process. Also, high-sensitivity of FP-TRMC allows the conductivity measurements of the organic semiconducting methods, which usually have lower conductivity compared to the inorganic semiconducting materials. Since TRMC is a technique for tracking local motion of the carriers, combined with the conductivity measurements methods which tracks long-range motion of carriers in bulk such as field-effect transistor (FET) measurement or time-of-flight (TOF) to track the effect of the morphology of the sample. Sometimes FP-TRMC methods also can be paired to the other time-resolved spectroscopic techniques like TA for the assignment of the conductive species contributing to the conductivity transients.

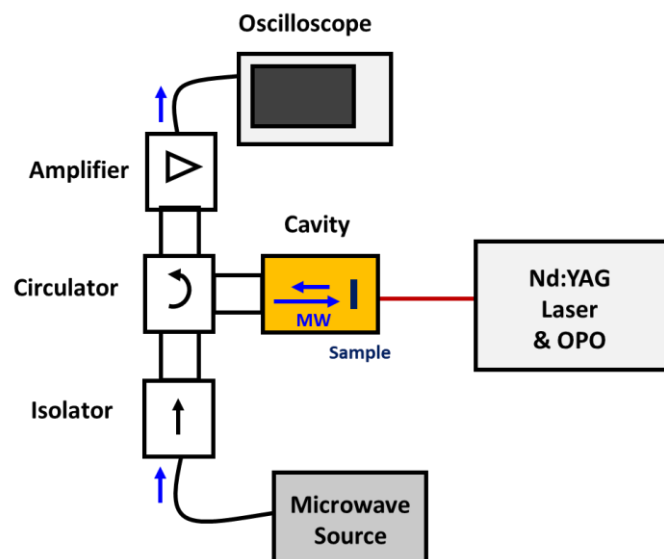


Figure 8. Schematics of TRMC instrumentation.

Typical FP-TRMC instrumentation is depicted in Figure 8. Microwave is generated by the microwave source and guided through the cavity and the reflected microwave power is tracked to calculate the conductance of the sample. For the microwave source, Gunn oscillator or signal generator can be used and generated microwave will be guided to the resonance cavity. The reflected microwave from the cavity is guided to the amplifier and detector passing circulator which rotates only the loss of reflected microwave will be recorded by the oscilloscope.

2. Target materials

2-1. Conjugated polymers

Conjugated polymers are polymers which are made with unsaturated building blocks which are connected together with single bonds which have π character. These types of polymers can have the extended conjugation through the backbone structure and conducting pathway can be formed through this extended conjugation. Conjugated polymers share the advantages of the polymeric materials, that it can be used at low-cost large-scale solution processing and flexible film formation.³²⁻³³ These properties make conjugated polymers as promising candidates for organic semiconducting materials and several different designs of the

conjugated polymers were suggested in past years. Some of the examples of monomers that are used as building blocks of the conjugated polymers are shown in Figure 9.

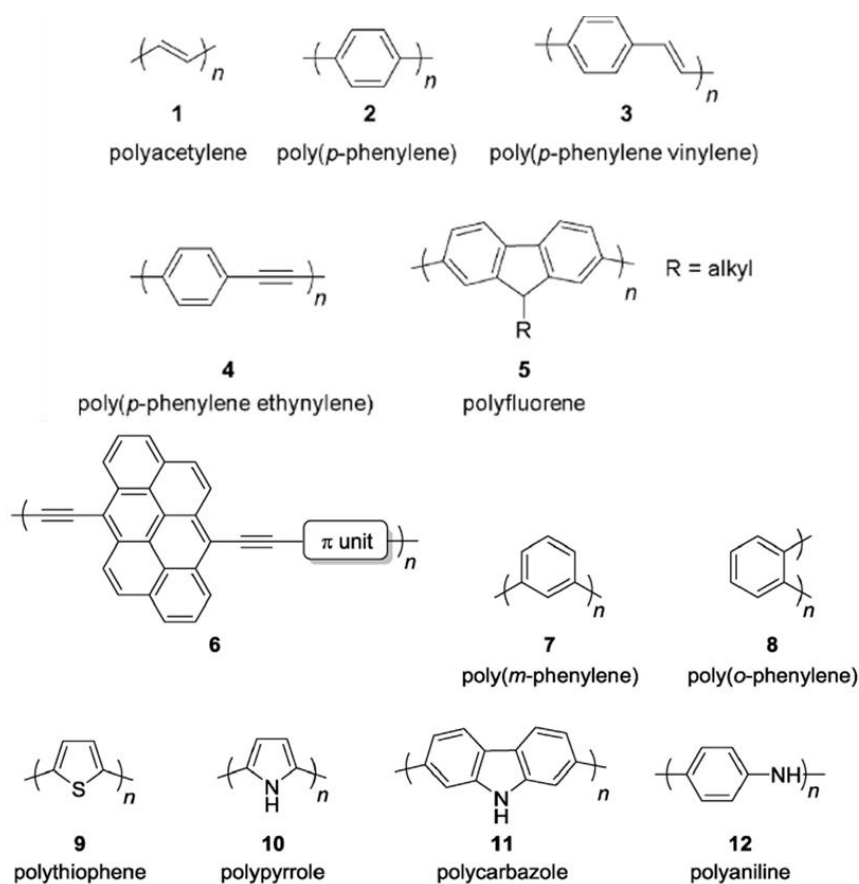


Figure 9. Examples of the structures of representative conjugated polymers.³⁴

When the conjugated polymers are fabricated to the films, it will form the mixture of crystalline and amorphous domain. Crystalline domain will show ordered stacking of polymer chains, which can be both intra- and inter-chain stack and amorphous domains will reside between the crystalline domains. These mesoscale morphologies have critical impact on the transporting properties of the polymer films, which will be changing with the size, ratio, and orientation of the domains. Morphology of the conjugated polymer films can be engineered both in the molecular and supramolecular aspects. Molecular aspects contain the control of regioregularity in polymerization and control on the molecular weight and its dispersion of the polymers. Regioregular polymers tend to yield better stacking between the monomers hence

leading to the formation of films with higher crystallinity. The relationship of between the regioregularity and the charge carrier mobility was investigated with poly-3-hexylthiophene (P3HT) and higher mobility was observed for regioregular P3HT compared to the regiorandom P3HT about two to three orders of magnitude.³⁵ The relationship with molecular weight and the transporting properties was extensively examined on P3HT by several researchers that the mobility generally increases with the molecular weight of the P3HT and similar trends were also observed for other polymers.³⁷⁻⁴¹ This trend can be explained by longer electrical conducting pathway provided by longer chain and better inter-crystallite charge transport in amorphous region, which was formulated by the field-effect transistor studies and the pulse-radiolysis (PR)-TRMC studies.^{36-37, 42} Dependence of the molecular weight dispersion was also examined with the P3HT films. The ratio of the high molecular weight contents generally increases the charge carrier mobility, by forming tie-chains in the amorphous domain.⁴³

In supramolecular aspects of polymer film fabrication, selection of the fabrication methods and the fabrication condition will greatly impact the morphology of the film. Several different methods including drop-casting, spin-coating, dip-coating and blade coating can be used to fabricate the polymer film.⁴⁴⁻⁴⁷ Choice of the condition, such as solvent, concentration and processing time and thermal or solvent annealing will change the morphology of conjugated polymer films.⁴⁸

Morphology of the conjugated polymer films can be examined with several different methods. Along with the microscopic techniques like Scanning electron microscope (SEM) and tunneling electron microscope (TEM), spectroscopical techniques were adopted for the analysis of the morphology. X-ray based techniques were widely used for the characterization of the crystalline domain size and the orientation. Powder XRD measurement can be employed to calculate the crystalline domain size, as explained in the above section using Scherrer's equation. Grazing-incidence wide-angle X-ray scattering (GIWAXS) and near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy can be applied to get information on the orientation of crystalline domain at the surface and the bulk, respectively.⁴⁹⁻⁵⁰

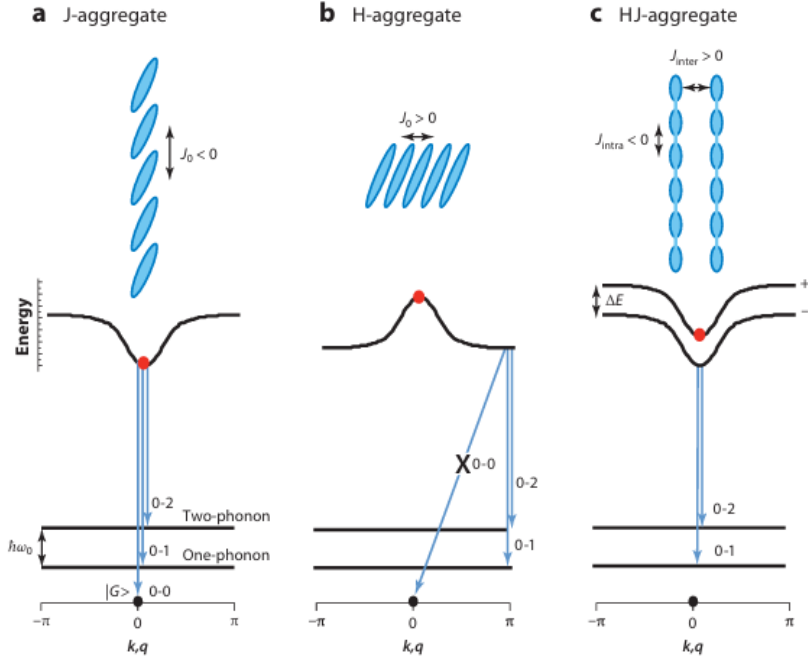


Figure 10. (a) H- and (b) J- aggregate interaction and (c) the conjugated molecule expressed as HJ-aggregate.⁵¹

Vibronic structures of the absorption and fluorescence can be also used for the analysis of the morphology, as they convey the information on the stacking of the polymer. This interaction was formulated by H-J aggregate model made by Spano, which interprets interchain and intrachain interaction as H and J-like interaction of the aggregates, respectively (Figure 10).⁵¹⁻⁵² H-like interaction will suppress the 0-0 vibronic peak intensity while J-like interaction will enhance the 0-0 vibronic peak intensity in the absorption and fluorescence spectra. P3HT can be explained weakly interacting H aggregate model which accounts interchain electron delocalization but neglecting intrachain exciton motion. In this model, absorbance of P3HT can be expressed as a function of photon energy by following equation:

$$A(E) \propto \sum_{m=0} \left(\frac{S^m}{m!} \right) \times \left(1 - \frac{W e^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n! (n-m)} \right)^2 \times \exp \left(\frac{(E - E_{0-0} - mE_p)^2}{2\sigma^2} \right) \quad (18)$$

where W is exciton bandwidth, S is Huang-Rhys factor, E_p is effective energy of main vibrational mode, E_{0-0} is 0-0 transition energy and σ is Gaussian linewidth. The 0-0 and 0-1 vibronic peak ratio in absorption can be expressed as following equation when a Huang-Rhys factor of unity is assumed:

$$\frac{I_A^{0-0}}{I_A^{0-1}} \approx \left(\frac{1 - 0.24W/\hbar\omega_0}{1 + 0.073W/\hbar\omega_0} \right)^2 \quad (19)$$

Where $\hbar\omega_0$ is the energy of the intramolecular vibration coupled to the electronic transition. W is related to the conjugation length that an increase in conjugation length will result the decrease in W and the number of repeating units can be estimated from the data from the oligomers.⁵³⁻⁵⁴

2-2 Expanded porphyrins

Porphyrins is the molecule composed with four pyrrole subunits connected in coplanar structure to form square-planar skeleton. Porphyrins and its derived structures are found in many biological systems which will participate to the electron transfer reaction owing to its low LUMO and high HOMO energy. Porphyrins are aromatic compounds that have 18 π electrons which follows Hückel's rule on the aromaticity with $[4n+2]$ electrons, and the electronic properties of the porphyrin were formulated by Gouterman which is explained by interaction of four π frontier orbitals of degenerate two HOMO and LUMO, leading to the strong Soret (or B) band from allowed transition at 500 nm and relatively weak Q band transition from forbidden transition at 600 nm (Figure 11).⁵⁵

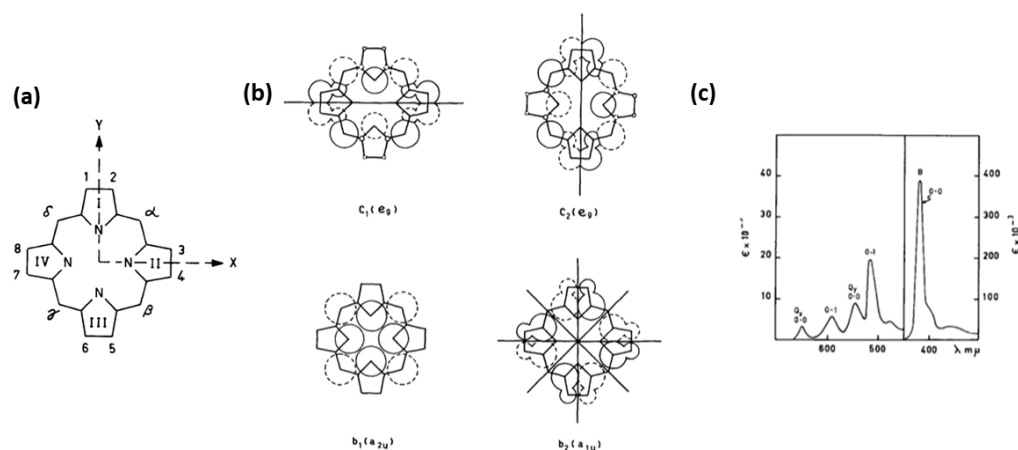


Figure 11. (a) Basic skeleton, (b) frontier orbitals and (c) absorption spectrum of porphyrin.⁵⁵

Expanded porphyrins are porphyrin-like molecules with the increased number of pyrrolic units, defined more precisely by Sessler and Seidel as “macrocycles that contain

pyrrole, furan, thiophene and other heterocyclic subunits linked together either directly or through one or more spacer atoms in such a manner that the internal ring pathway contains a minimum of 17 atoms".⁵⁶ Since the first expanded porphyrin sapphyrin was discovered by Woodward et.al, in 1966, expanded porphyrins with different number of pyrrolic units up to hexadecaphyrin was synthesized.⁵⁷⁻⁶² Core-modified expanded porphyrins which has pyrrole units substituted with the other heterocycles such as thiophene and furan and expanded carbaporphyrinoids with carbocyclic units N-confused pyrroles were also synthesized and reported.⁶³⁻⁷⁰ Porphyrin and some examples of the expanded porphyrins are depicted in Figure 12.

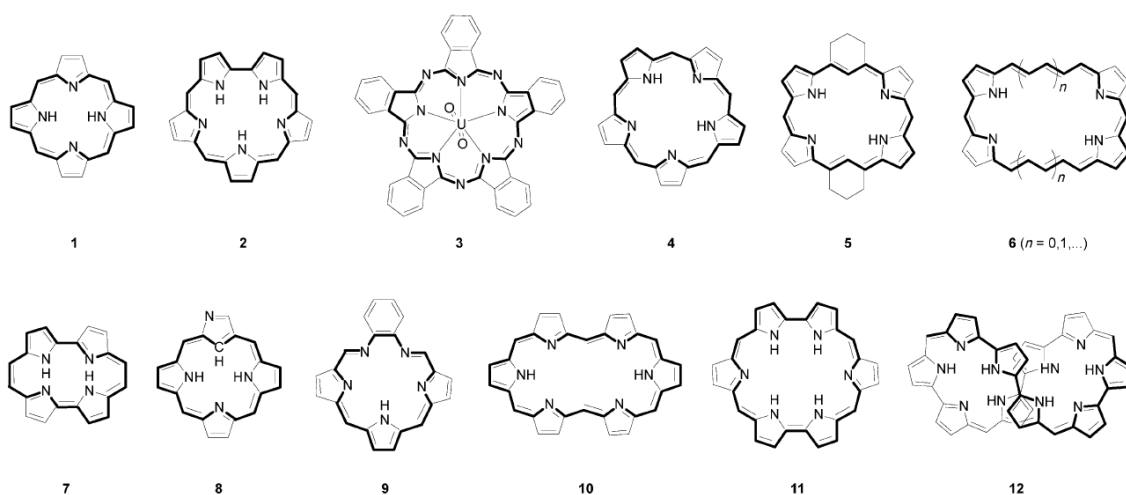


Figure 12. Examples of the expanded porphyrins⁵⁶

Owing to the extended conjugation through the expanded backbone, expanded porphyrins have smaller bandgap compared to the original porphyrin, which leads to red-shifted absorption spectra. Depending on the number of the pi electrons in the conjugated pathway, these expanded porphyrins can be $[4n+2]$ Hückel aromatic or $[4n]$ Hückel antiaromatic. Expanded porphyrins with Hückel aromaticity generally have similar electronic structure to the porphyrins with Q-like and Soret-like bands while red-shifted spectrum, while the Hückel antiaromatic expanded porphyrins show smeared band with at the longer wavelength region from the forbidden transition to the lowest singlet excited state.⁷¹⁻⁷²

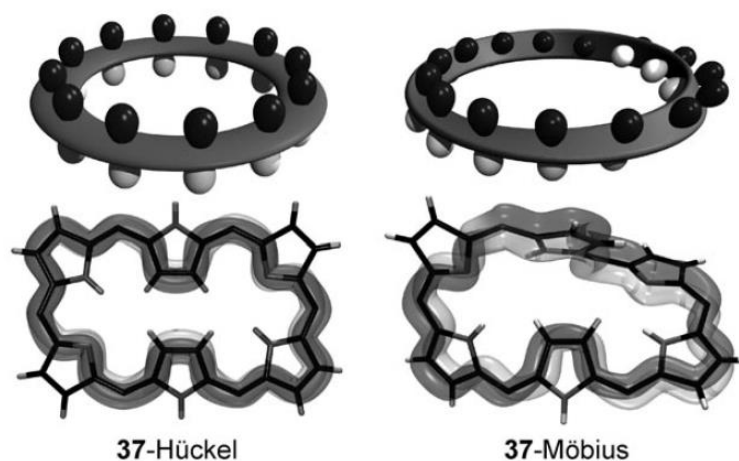


Figure 13. Hückel and Möbius conformation of hexaphyrins.⁷⁶

The flexibility of the backbone structure from the expansion allows the expanded porphyrins to adopt twisted conformation such as Möbius and figure-eight conformation (Figure 13).^{66, 72-76} The change in the conformation leads to completely different electronic properties in these expanded porphyrins. If the expanded porphyrins adopt Möbius conformation, Möbius aromaticity which has opposite pi electron counting rule to the Hückel aromaticity that molecules with $[4n]$ electrons in conjugation path will be aromatic can be achieved.⁷⁷⁻⁷⁸ Extensive tilting to the figure-eight may cause the loss of the aromaticity and sometimes lead to the nonaromatic properties in the molecules.⁷⁹ Conformation of the expanded porphyrins can be controlled by several means, including metal coordination, protonation, and bridge-formation in the center of the molecule.⁷⁹⁻⁸⁰

2-3 Carbon nanotubes

Carbon nanotubes (CNTs) are carbon allotropes which is composed of sp^2 carbons rolled in tubular shape. CNT was first discovered by Iijima in 1991, synthesized by arc evaporation method.⁸¹ Carbon nanotubes can be seen as graphene sheets rolled into cylindrical shape after it is cut into the rectangular shape. Depending on the choice of the chiral vectors to roll the graphene sheet, carbon nanotubes can form three different types of the structure. Chirality in graphene sheet described as (n,m) is described in Figure 14. If $m = 0$, the CNT will have zigzag structure and if $n = m$, the carbon CNT will have armchair structure. In other cases,

it will be a chiral CNT which can have enantiomer with mirror image.⁸² The electronic property it exhibits will vary depending on their structure that the armchair CNT will be metallic and in other cases, it will be semiconducting. If the $n-m$ for semiconducting tubes are the multiples of 3, it will be a small-bandgap semiconductor and if it is not, it will be large-bandgap semiconductor.⁸³

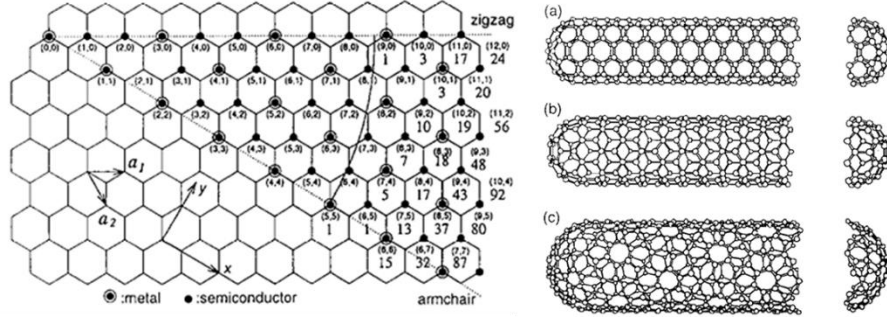


Figure 14. Chirality index in carbon nanotubes and the three different structural types of carbon nanotubes. (a) armchair ($n = m$), (b) zigzag ($m = 0$) and (c) chiral.⁸²

Optical properties of the carbon nanotube will be governed by its unique electronic structure. Being a 1D material, distribution of the density of states in carbon nanotubes is not continuous but have discontinuous peaks. This is called Van Hove singularity and result in the sharp and strong absorption peaks from the dipole allowed E_{nn} transitions.⁸⁴ The energy of this Van hove singularities is strongly dependent on the chirality index (n, m) of the CNT. Kataura plot which plots the diameter versus the electronic transition energy shows this clearly: oscillation in transition energy observed in CNTs in similar diameter range, indicating stronger influence of chirality index to the diameter of CNT.⁸⁵

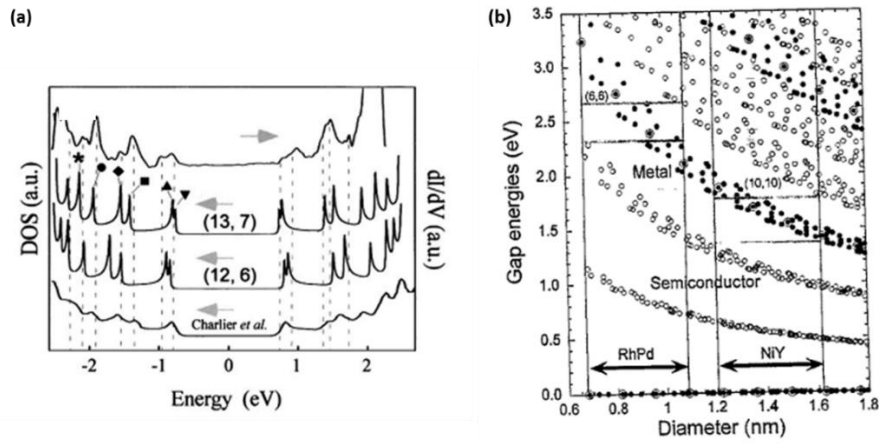


Figure 15. (a) Density of states of CNTs and (b) Kataura plot.^{84, 85}

CNTs will exhibit the strong Raman peaks, which were found to be a useful tool for the analysis of the carbon nanotube.⁸⁶ Radial breathing mode (RBM) located around 100-350 cm^{-1} can be a measure for the diameter of the CNTs as RBM mode frequency is

$$\nu_{RBM} = 234/d + 10 \quad (19)$$

for SWCNTs where d is the diameter of the carbon nanotube. The ratio between G mode which is originating from the planar vibration mode in graphite-like material ($\sim 1580 \text{ cm}^{-1}$) and D mode which is originating from graphite-like carbons from structural defects ($\sim 1350 \text{ cm}^{-1}$) can be used as a measure for the defects or functionalization of the CNTs.

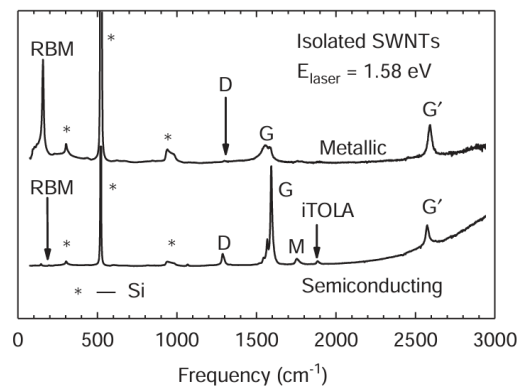


Figure 15. Raman spectra of the metallic and semiconducting SWCNTs.⁸⁶

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Chapter 1

Spectroscopic characterization of the morphological characteristics of the crystalline poly(3-hexylthiophene) cube

Abstract

Conjugated polymer crystals are expected to be an ideal platform for achieving the highest density-of-state of electrons in valence and conduction bands. Facile protocol to prepare crystalline particles P3HT-CP of poly(3-hexylthiophene) (P3HT) was developed and the property and the stability of the P3HT-CP particles were investigated. Formation of the ordered structure in P3HT-CP has been observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and clear cube structure of polymer crystals with the sharp edges were identified. Further investigation with the spectroscopic techniques including powder X-ray diffraction (PXRD), UV-vis electronic absorption spectroscopy suggests existence of long-range ordering with the large contribution of the crystalline domain in the particles. The stability of the P3HT-CP particles was confirmed by electronic absorption spectra of P3HT-CP dispersion and the thin-film of P3HT-CP, that the signs of deformation was not observed after casting crystals to the substrate.

Introduction

Poly(3-hexylthiophene) (P3HT) has been a benchmark polymeric material in modern optoelectronic applications such as thin film transistors (TFTs)^{87,88} and organic photovoltaics (OPVs)^{88,89} by long-lasting active debates on its structure-property relationship. In the solid-state structures of P3HT, regioregular P3HT (rr-P3HT), which features almost exclusively head-to-tail coupling between 3-hexylthiophene units, tends to form crystalline and/or amorphous mixed domains, whereas regiorandom P3HT (rra-P3HT) dominantly exhibits amorphous domains. The crystalline/amorphous morphology results in the distinctive optical/electrical properties such as optical/electrical bandgaps^{90,91} or bulk charge-carrier mobilities.^{36,87, 92-93} These morphological features therefore impact on the device performance. For example, the shift in the energy levels of P3HT crystalline domain conduction and valence bands with respect to those of P3HT amorphous domain, can modulate a free energy driving force (ΔG_{ET}) to a counterpart in photoinduced electron/hole transfer event, a key parameter for photon-to-charge conversion processes in OPV materials.^{91,94} In addition, exciton delocalization in polymer crystalline domains can effectively contribute to the dissociation of bound geminate electron-holepairs and eventually to free charge-carrier generation, contrasting to amorphous polymer domains with preferred localized excitons, resulting in geminate electron-hole recombination.⁹⁵⁻⁹⁹ In this regard, polymer crystalline domains can prove to be an effective structure to overcome low-dielectric disadvantage for free charge-carrier generation.

In spite of the potentials of polymer crystalline structures in modulating polymer optoelectric properties and hence device performance, their fabrication engineering is still a challenging task. During thin-film fabrication, the control of the crystalline structure formation such as the size or shape of crystallites and amorphous portions is limited. Alternatively, several crystallite formation strategies in solution-phase before film-deposition have been proposed.¹⁰⁰⁻¹¹² In this report, The author fabricated highly crystalline P3HT particles (P3HT-CPs) with angular shapes and sharp particle edges, utilizing an antisolvent slow-diffusion method. These P3HT-CPs feature pre-deposition condensed phase structures with particle dimensions spanning from 100nm to micron size scale. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterization results of the P3HT-CPs suggest well-ordered packing between polymer backbones along the (100) direction and substantially suppressed polymer amorphous fractions. Electronic absorption spectroscopic results reveal that the pre-

deposition structures can be transferred to a thin-film state without additional structural development or deformation of the crystalline structures.

Experimental

Synthesis of Regioregular-P3HT (rr-P3HT)

The rr-P3HT in this study was synthesized by the Grignard metathesis (GRIM) method, employing 2,5-dibromo-3-hexylthiophene in the presence of Ni(dppp)Cl₂, which was proven to be an effective synthetic route for the high-degree of regioregularity.^{87,113-114} To a 100 mL oven dried round bottom flask was added 2,5-dibromo-3-hexylthiophene (2 g, 6.13 mmol) in anhydrous THF (61 mL) under argon atmosphere. Isopropyl magnesium chloride lithium chloride complex solution (4.95 mL, 6.44 mmol, 1.3 M in THF) was then added and the resulting mixture was stirred at room temperature. After being stirred for 1 h, Ni(dppp)Cl₂ (52.5 mg, 0.0969 mmol) prepared in a N₂ glove box was dissolved in THF (6 mL) and added to the reaction mixture to initiate the polymerization. After 3 h at room temperature, the polymerization was quenched by adding methanol and the precipitated solids were then obtained. Polymer was purified by Soxhlet extraction in acetone, hexane and chloroform. The chloroform fraction was concentrated under reduced pressure. The concentrate was precipitated in methanol and filtered. The resulting polymer was dried in a vacuum oven at ambient air, and the desired purple solid was obtained. (700 mg, 69% yield). ¹H NMR (CDCl₃, 300 MHz): δ 6.98 (s, 1H), 2.85 (t, 2H, $J = 7.8$ Hz), 1.68 (br, 2H), 1.37 (br, 6H), 0.91 (t, 3H, $J = 6.9$ Hz). Data are consistent with those reported in the literature.^{115,116}

P3HT-CP and control particle preparation

P3HT crystalline particles (P3HT-CPs) were prepared by an antisolvent slow-diffusion method. A small vial containing 1 ml of chlorobenzene (CB) solution of rr-P3HT (1.0 mg/ml concentration) was kept in a larger sealed vial with antisolvent n-hexane (HX) (1 ml) with the 1:1 CB and HX volume ratio. With a higher vapor pressure and low density of HX (17.1 kPa at 21 °C and 0.6606 g/cm³; CB 1.27 kPa at 21 °C and 1.1075g/cm³), P3HT CB solution absorbed HX, and the volume of P3HT solution slowly increased (Figure 17a).¹¹⁷ As P3HT does not dissolve in HX, the slow diffusion of HX into CB leads to formation of P3HT aggregation seeds. After 3 days, all n-hexane within the larger vial was introduced in the small vial containing rr-P3HT chlorobenzene solution, and the interface of the solution turned to dark orange color due to the formation of P3HT-CPs at the interface. At 3 days, 1 ml of n-hexane was added to larger vial. With further mixing n-hexane with CB solution over next 4 days, the entire P3HT solution (1:2 volume ratio of CB:HX) turned to purple/brown color. (Figures 1a

and S3) The solution which contains P3HT-CPs was centrifuged (Beckman Coulter, Microfuge 16) 2 times at the same conditions of 6659 g for 30 min to remove single chain P3HT in supernatant. The first centrifugation of 1:2 volume ratio of CB/HX was conducted with 6659 g (30 min.). After elimination of supernatant (orange color; individual rr-P3HT chain), the mixed solvent of toluene/hexane (1:1.4 ratio) was added to P3HT-CPs which were separated by the first centrifugation as shown in Figure 17a. The second centrifugation was conducted with 6659 g (30 min.) to remove the remaining individual P3HT polymers in the supernatant. After elimination of supernatant, the separated P3HT-CPs were redispersed in toluene/n-hexane/1-propanol for further characterization and optical spectroscopic experiments. (0.4:0.5:0.1 volume ratio). 1-Propanol was added to substitute the highly volatile n-hexane antisolvent, allowing the author to stabilize P3HT-CP dispersion in the solution free from re-dissolving and/or adsorption onto the surfaces of vials/optical cells. The reference P3HT particles were prepared by the quick injection of HX antisolvent into rr-P3HT CB solution, followed by the same particle separation process using centrifugation, and redispersion in the same solvent toluene:n-hexane:1-propanol (0.4:0.5:0.1 vol. ratio) mixture.

¹H and ¹³C NMR

¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer. Chemical shifts are reported as δ values relative to internal SiMe₄ or chloroform (δ 0.00 for ¹H).

Gel-permeation chromatography (GPC)

GPC measurements were carried out on a Shimadzu liquid S5 chromatography system using THF as an eluent with a flow rate of 1.0 mL/min. Column temperature was set at 40 °C and polystyrene standards were used for molecular weight analyses. Molecular weight and polydispersity of rr-P3HT were calculated to be $M_w = 9.4 \text{ kg mol}^{-1}$ and 1.43, respectively.

Scanning electron microscopy (SEM)

The samples for SEM were prepared by drop-cast of P3HT particles (dispersed in toluene/hexane/1-propanol mixed solvents) on silicon wafer. The images were recorded on a JEOL JSM-7500F microscope with the accelerating voltages of 15 kV.

Transmission electron microscopy (TEM)

TEM images were obtained using a JEOL JEM-F200 at 80 kV.

Powder X-ray diffraction (PXRD)

PXRD was measured on a Rigaku Miniflex 600. Diffraction patterns were recorded over a range of 2° – 40° 2θ . Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 15 mA and 40 kV is used with Bragg–Brentano geometry. A scan rate of $0.5^{\circ}/\text{min}$ was used for all scans for both detectors with a slit width of 0.2. For each sample, the quartz substrate background was subtracted from the diffraction pattern. The spectral line broadening (β) is corrected to consider the instrumental line broadening, using the following relationship, $\beta^2 = \beta_t^2 - \beta_i^2$, where β_t is the experimentally obtained line broadening and β_i is the instrumental line broadening, which was obtained using standard material Si powder. Contribution from strain broadening was not significant as the (100) peak appears at a smaller angle ($\sim 5.4^{\circ}$).

UV-vis absorption spectroscopy

Diffuse transmittance spectra were measured using an ultraviolet-visible (UV-vis) spectrophotometer (U-3900, Hitachi, Japan), equipped with a 60 mm BaSO₄-coated integrating sphere in order to avoid spectral distortion from relatively large particle dimension of $0.1\sim 1 \mu\text{m}$. The measurements of UV-vis absorption spectra were carried out on either quartz (or glass) substrate for thin-film samples or in a 2-mm path-length quartz optical cell for polymer-dispersion samples. For all measurements, corrections for the transmittance of a blank substrate or an optical cell with solvent were made prior to each measurement.

Results and discussion

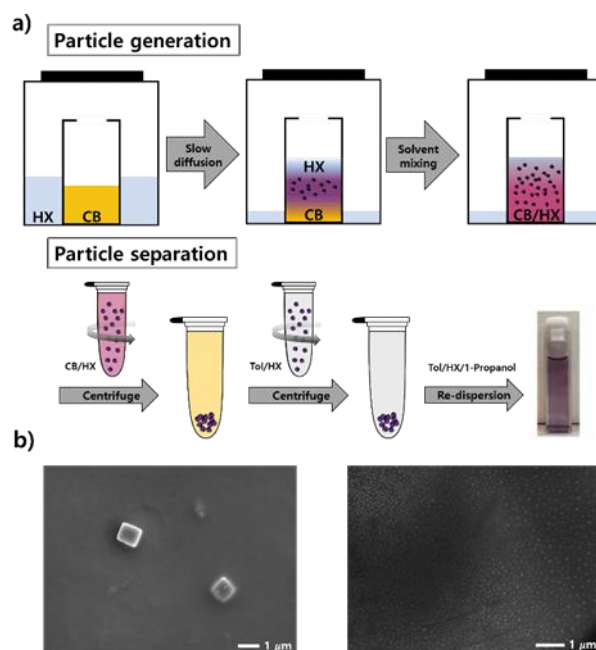


Figure 17. a) The summary of P3HT-CP preparation using the antisolvent slow-diffusion method described in the text. b) Representative SEM images of P3HT-CPs.

Figures 17b and S2 show the morphology of P3HT-CPs observed by scanning electron microscopy (SEM), as well as an image of the reference P3HT particles (Figure S3). The particle shapes of P3HT-CPs represented in Figures 17b and S2 exhibit homogeneous cubic structures with smooth-flat surfaces and sharp particle edges, suggesting well-ordering of P3HT backbones in the particles. Although their particle sizes appear to vary in the range from 0.1~1 μm , their characteristic features of flat surface, sharp particle edge, and cubic shape contrast unambiguously to the reference P3HT particles. The reproducibility of P3HT-CP formation was confirmed in multiple batches with the identical protocol.

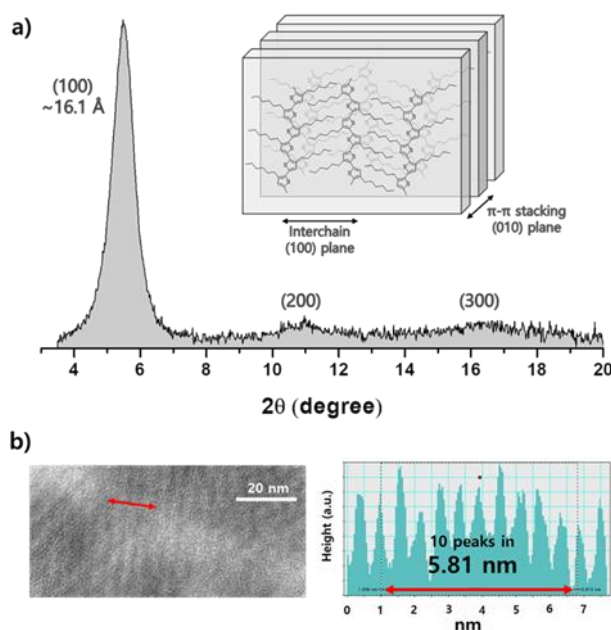


Figure 18. P3HT-CP morphological characterization: a) schematic representation of polymer packing behavior and the PXRD profile of the thin-film prepared from P3HT-CPs; b) representative TEM images showing electron diffraction patterns.

Figure 18 displays the structural characterization of P3HT-CPs. The PXRD profile for the drop-cast film from the P3HT-CP dispersion is shown in Figure 2a. The respective PXRD 2θ peaks at 5.48° , 11.01° , and 16.36° attribute to the (100), (200), and (300) reflections. The corresponding d -spacing (d_{100}) is calculated to be $16.1 \text{ \AA}$ from the Bragg equation, consistent with the previous interlayer spacing in well-ordered P3HT lamellar structures.^{104,114,118} The intensive (100) peak suggest that the highly crystalline nature of the resulting P3HT-CPs. The coherent domain size of the (100) plane, assumed as the crystallite size (L_{100}) is approximated by Scherrer's formula (equation 7) where K , λ , θ are the 0.9, $1.5418 \text{ \AA}$, 5.48° , respectively. The value of L_{100} is estimated to be 9.2 nm which is comparable to that of highly crystalline nanowires.¹⁰⁴

This P3HT-CP intra-crystallite structure was further investigated using transmission electron microscope (TEM) measurements. The representative TEM images of P3HT-CPs in Figures 18b show the clear electron diffraction (ED) patterns extending over 100 nm through the conjugation and the stacking direction. These results suggests the presence of the long-range ordering in P3HT-CP and possibly the suppressed formation of amorphous domains.

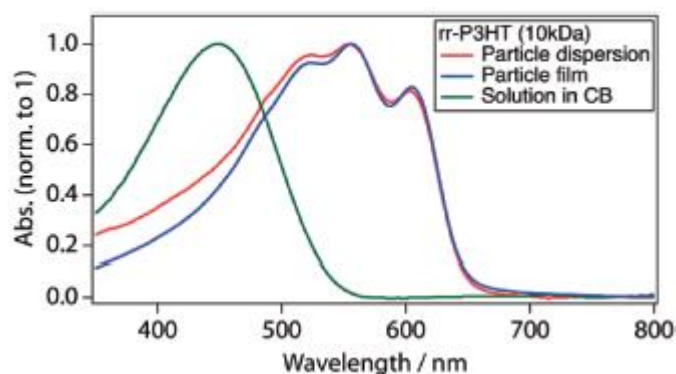


Figure 19. Normalized electronic absorption spectra of a) the P3HT-CP dispersion in toluene/HX/1-propanol (0.4:0.5:0.1 vol. ratio) (red), the drop-casted film on a quartz plate from the P3HT-CPs dispersion (blue), and rr-P3HT solution in chlorobenzene (green).

Structural evolution or deformation of P3HT-CPs during solvent evaporation was examined using electronic absorption spectroscopy. The representative electronic absorption spectra of both P3HT-CP dispersion in toluene:n-hexane:1-propanol (0.4:0.5:0.1 volume ratio) mixture (red) and the drop-cast P3HT-CPs thin-film (blue) in Figure 19 are almost identical and therefore verify that additional structural formation during solvent drying is minimal. This absorption spectrum of the dispersed P3HT-CPs (red in Figure 19) clearly displays the suppressed $S_0 \rightarrow S_1$ transition of isolated rr-P3HT chains at ~ 450 nm (green in Figure 19), and reveals the vibronic progressions from about 490 nm to 610 nm, characteristics of intrachain planarization and interchain $\pi\pi$ interactions upon rr-P3HT aggregation (crystalline domain) formation, consistent with electron microscopic results.^{89-90,119}

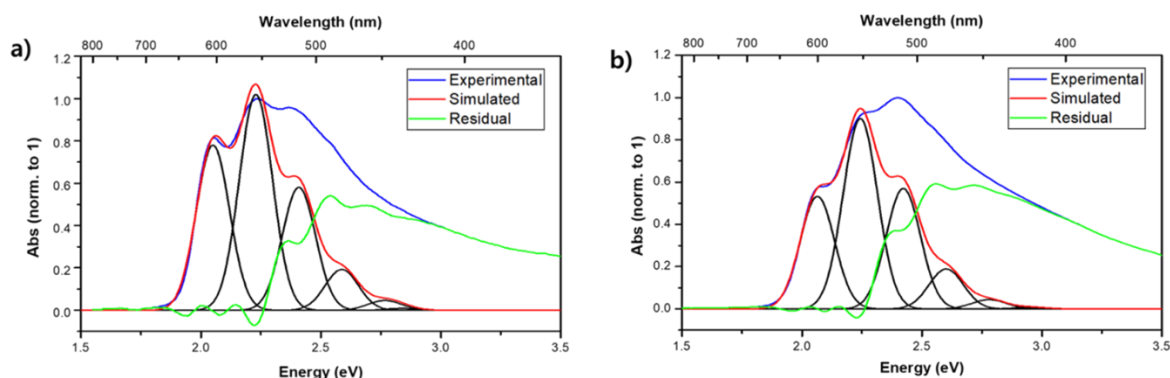


Figure 20. Normalized absorbance spectra (solid blue) and the fit from the weakly-coupled H-aggregate model (black) of a) the P3HT-CP dispersion and b) the control P3HT particle dispersion prepared by the antisolvent quick-injection method.

The absorption spectra of the dispersion of P3HT-CP as well as the control P3HT particle were further analysed within the context of the weakly-coupled H-aggregate model developed by Spano et. al. (Figure 20).^{51,52} The exciton bandwidth W were calculated with the equation 18 by taking S as unity and E_p to be 0.179 eV assuming that the dominant vibrational mode which couples to the electronic transition is the C=C symmetric stretching. The values of W were obtained to be 73.7 meV for P3HT-CP dispersion, contrasting to the W (139.7 meV) for the aforementioned control P3HT particle dispersion (Figure 20b). This reduced 73.7 meV of W in P3HT-CP is consistent with the previous prediction between W and the number of interacting thiophene repeat units (N) of approximately 50.⁵³⁻⁵⁴ TEM data show large number of interacting thiophene repeating units (Figures 18b and S2). Given the M_w of 9.4 kg mol⁻¹ for the used rr-P3HT, it can be presumed that the whole chain stacks side-by-side, and consequently P3HT-CP exhibits dominant crystallite-formation.

Conclusion

In conclusion, conjugated polymer particles based on P3HT with high regioregularity (>97%) were prepared and the crystalline polymer particle formation and separation protocols using a slow antisolvent-diffusion method and centrifugation were developed. The SEM, TEM, and PXRD results evince that these particles exhibit sharp particle edge, extraordinary molecular ordering over 100 nm from high crystallinity and consequently suppressed amorphous domain formation. The UV-vis spectroscopic analysis suggests P3HT-CP particles remain stable during transfer process from dispersion to the solid-state, without structural deformation. This P3HT-CPs potentially can be a useful model system to investigate the role of crystalline domains in exciton and carrier dynamics as well as the correlation between condensed-phase structure and electric properties in low-dielectric materials.

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Chapter 1 Appendix

1-116 P3HT

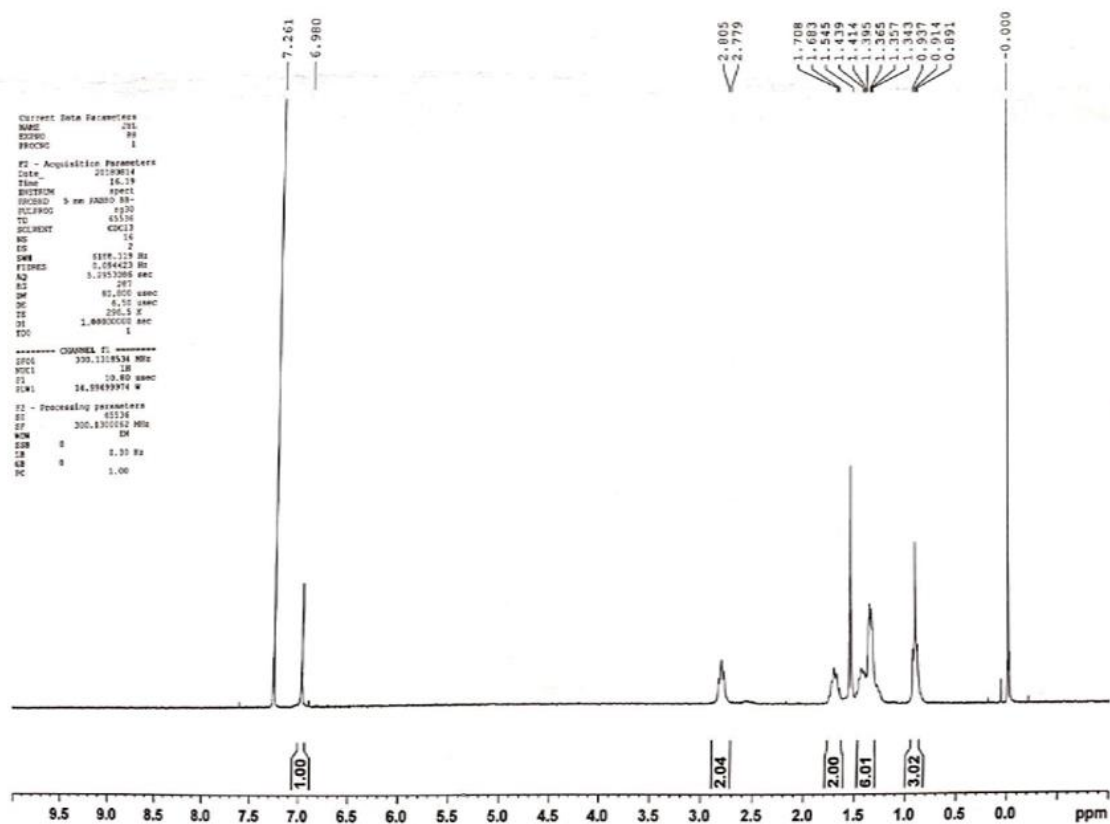


Figure S1. ^1H NMR of P3HT.

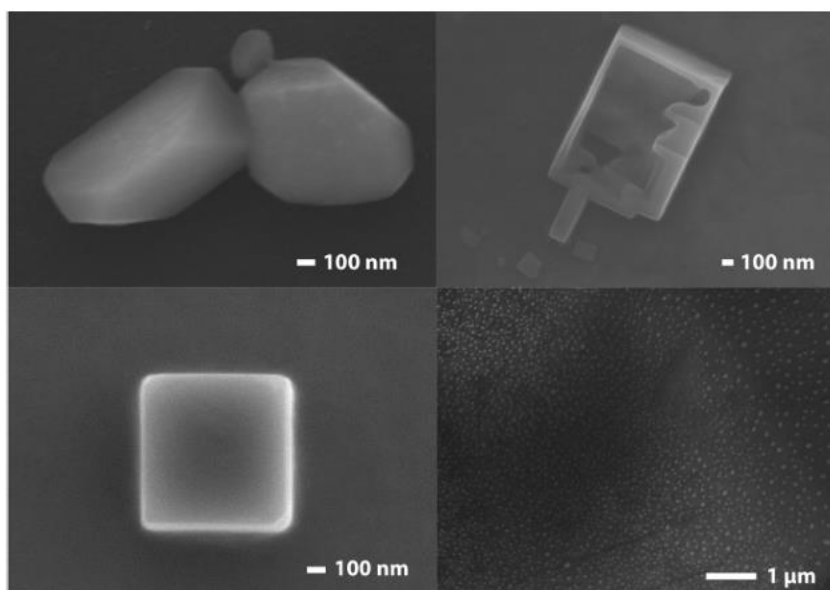


Figure S2. Representative SEM images of P3HT-CPs obtained by antisolvent slow-diffusion method.

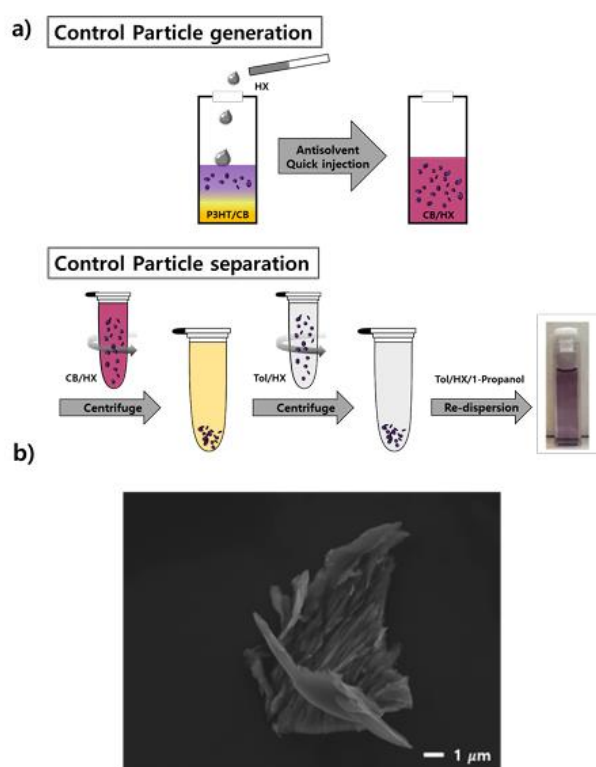


Figure S3. a) The summary of control P3HT particle prepared by quick injection. b) Representative SEM image of control P3HT particle.

Chapter 2

Electrical conductivity switching in Tetrathiafulvalene-annulated expanded porphyrin by protonation induced close π -stacking

Abstract

In the design of the condensed phase materials with molecules, control on the packing structure in solid state play a key role in controlling the properties of the materials. The packing structure of the materials can be modified by not only by the modification on the molecular structure itself, but also with indirect ways such as protonation. In this work, protonation induced packing structure and electrical conductivity of tetrathiafulvalene-annulated expanded porphyrin derivative **TTF₂-Rub** was investigated. Upon protonation, huge change in the conformation was observed between **TTF₂-Rub** and **H₂TTF₂-Rub²⁺**, which leads to the close packing of tetrathiafulvalene (TTF) units in the solid state. Protonation induced conductivity change was investigated through the flash-photolysis time resolved conductivity (FP-TRMC) and photocurrent measurements for the **TTF₂-Rub** and **H₂TTF₂-Rub²⁺** and the leap in electrical conductivity from insulating in neutral **TTF₂-Rub₂** to conductive in deprotonated **H₂TTF₂-Rub²⁺** was observed. This sharp modification to the conductivity could be attributed to the shorter intermolecular distance and an efficient π orbital delocalization between TTF moieties in the solid-state of protonated compounds.

Introduction

Tetrathiafulvalene (TTF)-based molecular materials have attracted much attention in light of their rich chemistry such as facile redox reactions, conductivity, nonlinear optical properties, and magnetic properties in recent days.¹²⁰⁻¹²³ A TTF moiety is well-known to be involved in rich redox chemistry that several TTF derivatives can exist in stable redox states.¹²⁴⁻¹²⁵ The stacked mono-cationic TTF radical ($\text{TTF}^{+\bullet}$), di-cationic TTF (TTF^{2+}), and the mixed-valence species have been often expected to show switching of electrical conductivity in their condensed phases. Counter-anions of oxidation reagents near the TTF moieties were, however, indispensable for the charge compensation in the redox states, which often hinder their tightly bound alignments of TTFs, and hence disrupts electronic conductive pathways. In recent years, the synthetic chemistry of TTF and its analogous has been received renewed interests due to the wide tunability of electronic properties observed in TTF-annulated macrocyclic systems such as calixpyrroles, porphyrins, and expanded porphyrins.¹²⁶⁻¹²⁷ Among these, studies of TTF-hybridized expanded porphyrins having more than four pyrrole rings are relatively unexplored.¹²⁸ Here, the author reports the synthesis, characterization, and comparison of structural and electrical properties of meso-mesityl substituted benzo-TTF-annulated tetrathiarubyrin **TTF₂-Rub** and its di-protonated form **H₂TTF₂-Rub²⁺**. Tetrathiarubyrin was employed as 26 π macrocyclic aromatic core with well-defined protonation site and rigid structure attributed from core-modification of four pyrrole rings in rubyrin to thiophenes.¹²⁹⁻¹³² As shown in Figure 21, meso-mesityl-substituted core-modified [26]rubyrin **1** and benzo-TTF-annulated [26]rubyrin **Rub** and benzo-TTF-annulated [26]rubyrin **TTF₂-Rub** were newly synthesized and fully characterized by ¹H, ¹³C, and mass-spectrometry (Figure 22). Compound **TTF₂-Rub** consists of a 26 π -tetrathiarubyrin core, capable of accepting two protons and two annulated benzo-TTF units. The former and latter can be recognized as an electron-accepting and donating moiety, respectively. Both the complex **TTF₂-Rub** and **H₂TTF₂-Rub²⁺** can thus be considered as the D-A-D diads but differed by the electron accepting strength of the rubyrin core.^{128,133-135}

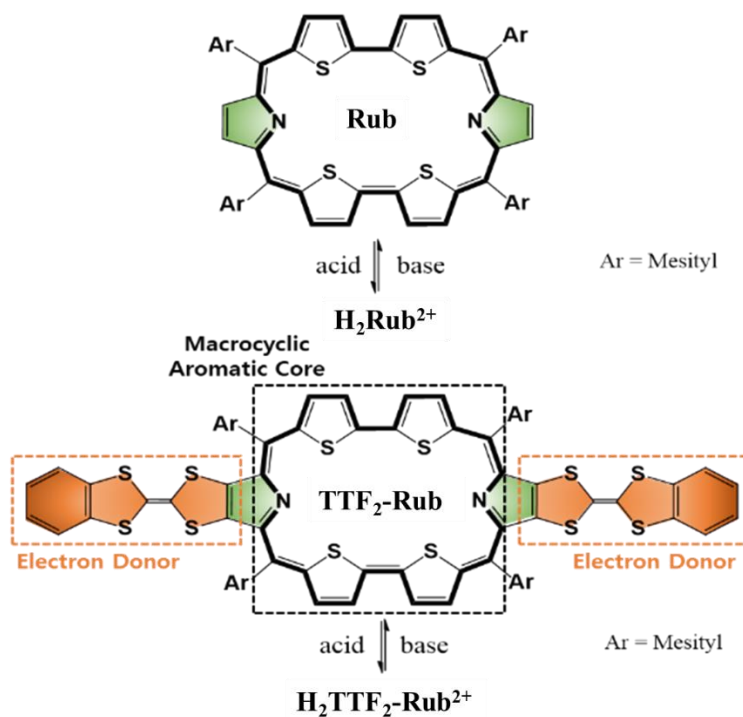


Figure 21. Molecular structures of tetrathiarubyrin **Rub** and benzo-TTF-annulated tetrathiarubyrin **TTF₂-Rub**. Bold bonds in the molecular structures represent the expected macrocyclic conjugation pathways.

Experimental

Synthesis

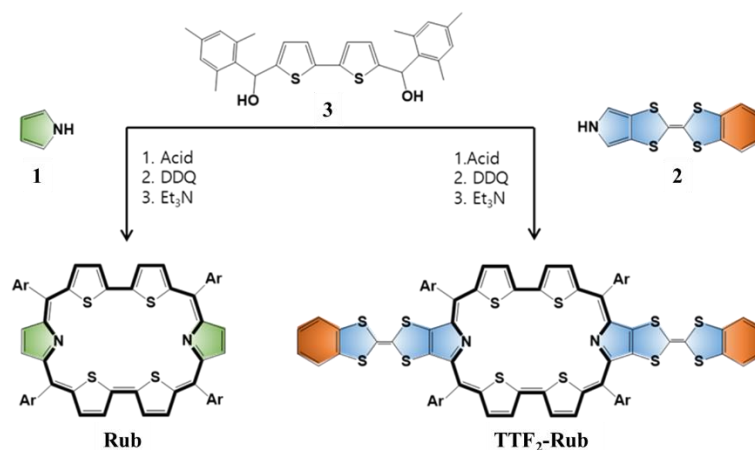


Figure 22. Synthesis of **Rub** and **TTF₂-Rub**.

A dichloromethane solution (350 mL) of the corresponding pyrrole (**1**, 1 mmol) and Benzo-TTF-pyrrole (**2**, 1 mmol), respectively, and bithiophene diols (**3**, 1 mmol) was degassed for 30 min by bubbling with argon before addition of a catalytic amount of p-toluenesulfonic acid (pTsOH) (0.25 mmol). Then the reaction mixture was stirred for 12h at room temperature. DDQ (2 mmol) was then added to the mixture and stirred further for 15 min in air, followed by neutralization with triethylamine (0.1 mmol). The resulting solution was evaporated and followed by stirring with NaOH 1M for 1h. The crude product was obtained by filtered and washed with hexane and MeOH. The desired compound **Rub** was purified over silica gel and eluted with THF:hexane (1:6). and compound **TTF₂-Rub** was eluted with chloroform:hexane (3:1).

Pyrrole tetrathiarubyrin (1) Yield :10%; ¹H NMR (500 MHz, CD₂Cl₂, 25°C, TMS) δ[ppm]: 11.74 (d, 4H, 4.8Hz), 10.41 (d, 4H, 4.7Hz), 8.96 (s, 8H), 7.56 (s, 8H), 2.81 (s, 12H), 2.06 (s, 24H). ¹³C NMR (126 MHz, CDCl₃, 25°C, TMS) δ[ppm]: 154.1, 141.5, 140.4, 139.1, 138.4, 136.7, 134.6, 134.5, 130.4, 129.7, 128.2, 21.3, 21.0. High resolution MALDI-TOF-MS: m/z calcd for [C₆₄H₅₄N₂S₄]⁺H⁺: 981.4028; found: 981.3122.

Benzo-TTF-annulated tetrathiarubyrin (2) Yield: 11%; ¹H NMR (500 MHz, CD₂Cl₂, 25°C, TMS) δ[ppm]: 11.74 (d, 4H, 5.1Hz), 10.34 (d, 4H, 4.9 Hz), 7.58 (s, 8H), 7.30 (dd, 4H, 5.5, 3.1Hz), 7.12 (d, 4H, 20.6Hz), 2.81 (s, 12H), 1.91 (s, 24H); ¹³C NMR (126 MHz, CDCl₃, 25°C,

TMS) δ [ppm]: 159.9, 144.4, 143.6, 141.9, 139.8, 139.2, 139.0, 137.1, 136.9, 134.8, 130.8, 129.8, 128.2, 125.7, 121.83, 105.2, 21.8, 21.4. High resolution MALDI-TOF-MS: m/z calcd for $[\text{C}_{80}\text{H}_{58}\text{N}_2\text{S}_{12}]\text{H}^+$: 1434.1258; found: 1434.1251.

X-ray Diffraction Measurements

X-ray diffraction was measured on a Rigaku Miniflex 600. Diffraction patterns were recorded over a range of 2° – 40° 2θ . Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 15 mA and 40 kV is used with Bragg–Brentano geometry. A scan rate of $0.5^\circ/\text{min}$ was used for all scans for both detectors with a slit width of 0.2. The spectral line broadening (β) is corrected to consider the instrumental line broadening, using the following relationship, $\beta^2 = \beta_t^2 - \beta_i^2$, where β_t is the experimentally obtained line broadening and β_i is the instrumental line broadening, which was obtained using the standard material Si powder.

Flash-Photolysis Time-resolved Microwave Conductivity Measurements

Transient photoconductivity was measured by a FP-TRMC setup. Polycrystalline neutral **TTF₂-Rub** and **H₂TTF₂-Rub²⁺** were deposited onto quartz substrate, and laminated with Scotch® tape as gas-barrier which was transparent against excitation light sources at 355 nm. All the crystals were back-excited through quartz substrate. A resonant cavity with $Q \sim 2500$ was used to obtain a high degree of sensitivity in the conductivity measurement. Probing microwave frequency was set at $\sim 9.1 \text{ GHz}$, such that the electric field of the microwave was sufficiently small not to disturb the translational motion of charge carriers. The observed value of photoconductivity converted to the product of the quantum yield f and the sum of charge-carrier mobilities $\Sigma\mu$ by $\phi\Sigma\mu = \Delta\sigma (eI_0F_{\text{light}})^{-1}$, where e , I_0 , F_{light} and $\Delta\sigma$ are the unit charge of a single electron, incident photon density of excitation laser (photons per m^2), a correction factor (m^{-1}) and a transient photoconductivity, respectively. The sample was set at the point of electric field maximum in a resonant cavity. FP-TRMC experiments were performed at room temperature.

Single-crystal X-ray structure determination

Single-crystal X-ray crystallographic analyses were performed at SPring-8 beam line BL40XU using Si (111) monochromated synchrotron radiation ($0.81088 \text{ \AA}$) with Rigaku Saturn 724+ CCD detector. Single crystals of **TTF₂-Rub** suitable for X-ray diffraction studies were analyzed by a 724+ CCD detector using synchrotron radiation at beamline BL40XU ($\lambda = 0.81088 \text{ \AA}$) of SPring-8 (Hyogo, Japan). The structures of **TTF₂-Rub** were solved by direct

methods and refined by the full-matrix least squares method. The position of all non-hydrogen atoms was found from difference Fourier electron density maps and refined anisotropically. All calculations were performed using Rigaku “Crystal Structure” crystallographic software packages or Yadokari-XG (Wakita, Nemoto et al., 2009) and illustrations were drawn by ORTEP. These crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-2090994 for compound **TTF₂-Rub** respectively. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational calculations

All calculations were carried out using the Gaussian 16 Revision A.03 program suite.¹³⁶ All structures were fully optimized without any symmetry restriction starting from crystal structures and used without any further modification after optimization. All the calculations were performed using density functional theory (DFT) method at B3LYP/6-31G(d) level.¹³⁷

Results and Discussions

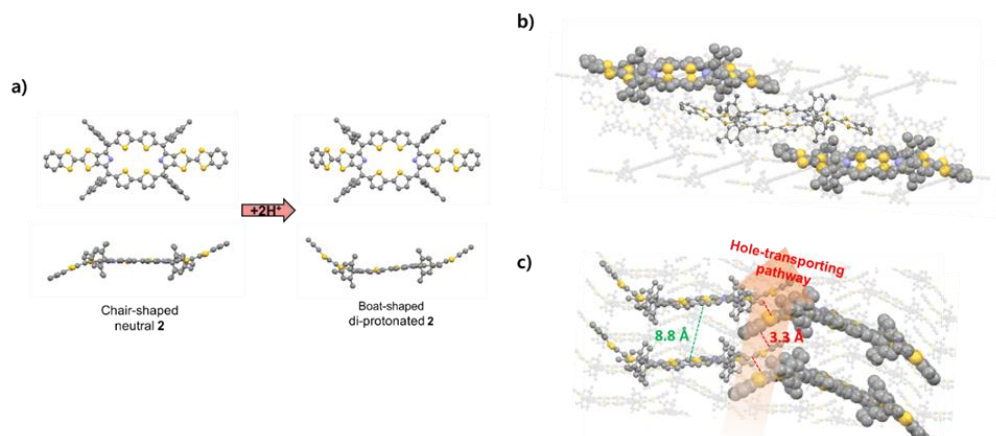


Figure 23. a) X-ray crystal structures of neutral and di-protonated **TTF₂-Rub**. All the hydrogen, solvent molecules, and counter anions of acid are omitted for clarity. Single crystal packing structures of b) neutral and c) di-protonated **TTF₂-Rub**.

To investigate differences in the solid-state structural properties between the complex **Rub** and **TTF₂-Rub**, X-ray single crystallographic analyses for these two compounds were performed (Figure 23). Single crystal of neutral **TTF₂-Rub** was obtained by slow diffusion of diethyl ether into a solution of **TTF₂-Rub** in CH₂Cl₂, while that of **H₂TTF₂-Rub²⁺** was obtained in the presence of the excess amount of trifluoroacetic acid (TFA) under the same solvent condition. Crystal structures of **TTF₂-Rub** and **H₂TTF₂-Rub²⁺** were confirmed by single crystal X-ray diffraction (SC-XRD) analyses. While rubyrin core moieties in both **TTF₂-Rub** and **H₂TTF₂-Rub²⁺** adopts a nearly planar geometry, conformation of TTF moieties in these two crystals show significant differences. As shown in Figure 1a, two benzo-TTF units of **H₂TTF₂-Rub²⁺** were oriented to the same direction with respect to rubyrin core (boat-shape) while those of neutral **2** adopt opposite direction (chair-shape). The protonated form **H₂TTF₂-Rub²⁺** displays the effective π - π stacking between benzo-TTFs with short intermolecular distances between stacked benzo-TTF of ca. 3.4 Å, while close contacts between two neighbouring benzo-TTF moieties were not found in the case of neutral **TTF₂-Rub**. Crystal structure for monoprotonated species **HTTF₂-Rub⁺** was also Identified, however, enough amounts of single crystals of **HTTF₂-Rub⁺** could not be isolated for other measurements.

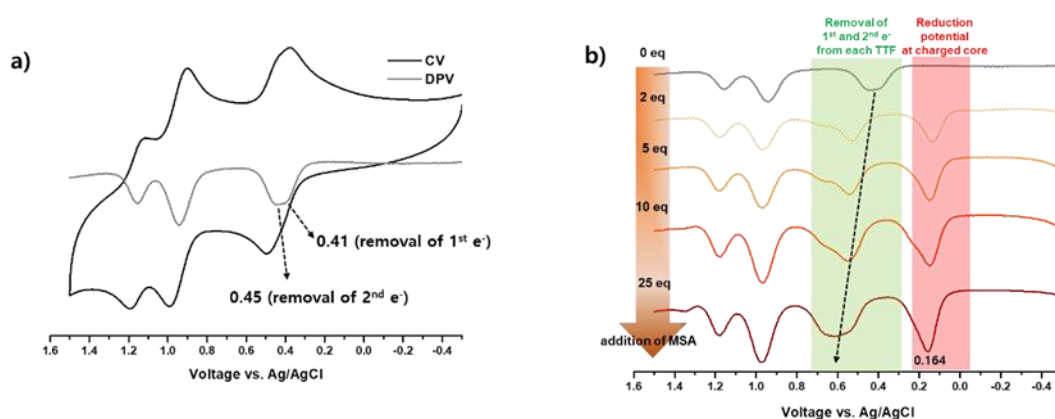


Figure 24. a) Cyclic and differential pulse voltammograms of neutral **TTF₂-Rub** recorded in CH₂Cl₂ containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. b) Electrochemical titrations and changes of DPVs upon addition of MSA. Working, reference, and counter electrodes were glassy carbon, Ag/AgCl, and platinum wire, respectively.

To investigate changes in electrochemical properties of **TTF₂-Rub** upon protonation, cyclic and differential pulse voltammetric analyses on **TTF₂-Rub** were performed in CH₂Cl containing 0.5 M of tetrabutylammonium hexafluorophosphate. with incremental additions of MSA. As shown in Figure 24a, the first and second oxidation of **TTF₂-Rub** appeared at 0.41 and 0.45 V (vs Ag/AgCl). These two consecutive oxidation processes can be assigned to one electron oxidation from each benzo-TTF moiety in **TTF₂-Rub**. The rationale for this assignment comes from the first oxidation potential of benzo-TTF-pyrrole **TTF** (Figure S7) and molecular orbitals and their energy levels calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set (Figure S11a). No evidence of reduction was seen for either **TTF₂-Rub** or **TTF** upon scanning down to -0.5 V in the absence of acid. However, upon adding MSA to 2 mM CH₂Cl₂ solutions of **TTF₂-Rub**, a new reduction wave at 0.164 V in DPV appears and this band continues to grow as MSA is added and then becomes saturated at ca. 25 equivalents. A similar electrochemical behavior was also observed for compound 1 upon adding MSA (Figure S8). This process can be thus assigned to a reduction event involving the protonated rubyrin core. It also indicates that the di-protonated form of **TTF₂-Rub** possesses a significantly more electron-deficient rubyrin core compared to neutral **TTF₂-Rub**, likely leading to stronger intramolecular electron transfer interactions between the benzo-TTFs to positively charged macrocyclic aromatic core (Figure 24b). Accordingly, the first and second

oxidation potentials were positively shifted due to more electron-deficient nature induced by protonation.

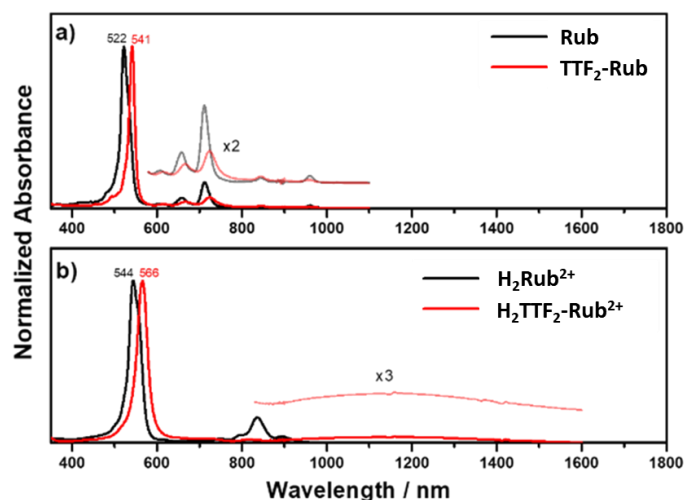


Figure 25. UV/Vis/NIR absorption spectral changes from a) neutral to b) di-protonated **Rub** (black lines) and **TTF₂-Rub** (red lines).

The steady-state electronic absorption spectra of neutral and di-protonated **Rub** and **TTF₂-Rub** were recorded in CH₂Cl₂ (Figure 25). Neutral **Rub** and **TTF₂-Rub** exhibited the typical optical features of aromatic porphyrinoid which are often described as B-like and Q-like bands coming from core four-orbital interaction.¹³⁸⁻¹⁴⁵ The absorption spectra of neutral **Rub** and **TTF₂-Rub** exhibit sharp and intense B-like bands at 522 and 541 nm, respectively, and five Q-like bands at almost the same wavelengths as shown in Figure 25a. Interestingly, neutral **TTF₂-Rub** showed very weak absorption tailing up to 1100 nm (Figure S9). The red-shifted B-like band and absorption tailing in the NIR region in neutral **TTF₂-Rub** in comparison to those of non-annulated **Rub** are due to the strong electronic coupling between the macrocyclic aromatic core and the peripheral benzo-TTF moieties. The absorption tail can be attributed to the charge transfer (CT) transitions from benzo-TTFs to aromatic core.^{125,128} TDDFT calculation of neutral **TTF₂-Rub** predicts the vertical transitions at 939, 942, 978, and 990 nm which are from HOMO-1 and HOMO on benzo-TTF to LUMO and LUMO+1 on the core moiety (Figure S11b,c), supporting intramolecular CT transitions in the regime. Upon addition of excess MSA, **H₂TTF₂-Rub²⁺** exhibited a bathochromic shift of B-like band at 566

nm, associated with an enhancement of the NIR CT transition, while **H₂Rub²⁺** only showed bathochromic shift of B- and Q- like bands (Figure 25b). This increase in extinction coefficient of the NIR absorption band ($\epsilon = 6.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 1170 nm) suggests **H₂TTF₂-Rub²** has the stronger intramolecular CT nature compared to neutral counterpart.

To study electronic nature of **TTF₂-Rub** and **H₂TTF₂-Rub²⁺**, analysis on the NMR spectra were done. Upon adding methanesulfonic acid (MSA) into 1 mM solution of **TTF₂-Rub** in CD₂Cl₂ (Figure S5), the nullification of the NMR signals at 7.11 and 7.30 ppm (Hc and Hd in Figure S4) which were assigned to the benzo-TTF protons was observed. This could be attributed to spin localization at benzo-TTF moieties.

The powder X-ray diffraction (PXRD) pattern of the single crystal of neutral is in good accordance with the simulated one from single-crystal X-ray crystallography. However, PXRD pattern of the di-protonated single crystal shows some possibility of incomplete isolation of single crystal of **H₂TTF₂-Rub²⁺** from mixture of single crystals of protonated species. Although di-protonated crystals might be not completely isolated, significant increase in conductivity could be assigned to formation of TTF stack upon protonation (Figure S12).

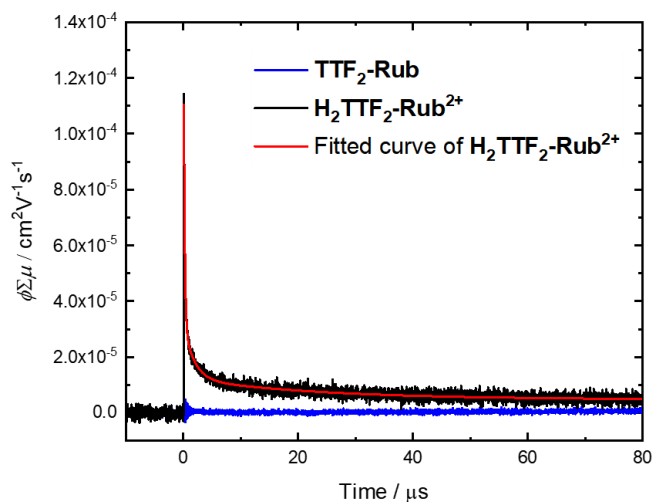


Figure 26. Kinetic traces of photoconductivity transients of single crystals of neutral and di-protonated **TTF₂-Rub** recorded by FP-TRMC measurements.

To investigate the impact of packing structures in electrical conductivities of **TTF₂-Rub** and **H₂TTF₂-Rub²⁺**, the transient electronic conductivities were measured by flash-photolysis time-resolved microwave conductivity (FP-TRMC) technique in their single-crystal states.^{28,30-31,146} The observed photoconductivity transients were shown in Figure 26. The vertical axis $\phi\Sigma\mu$ represents the product of the photogeneration efficiency of the free charge carriers (ϕ) and the sum of the mobilities of the positive and negative charge carriers ($\Sigma\mu = \mu_+ + \mu_-$). The single crystal of **H₂TTF₂-Rub²⁺** showed a clear photoconductivity transient (the maximum $\phi\Sigma\mu = 1.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$: determined as a pre-exponential factor of the following multi-exponential decay analysis) with triple exponential decay with the time constants of $1.7 \times 10^{-7} \text{ s}$ (83.7%), $1.7 \times 10^{-6} \text{ s}$ (11.9%) and $2.3 \times 10^{-5} \text{ s}$ (4.4%), which is in a striking contrast to neutral **TTF₂-Rub** exhibiting negligible photoconductivity transient upon exposure to the identical light pulses at 355 nm.

To estimate ϕ_{max} , the author performed a DC mode photocurrent measurement using a comb-type interdigitated gold electrode on a glass substrate (Figure S14).^{28,147} The photocurrent transients of **H₂TTF₂-Rub²⁺** and poly(9,9'-dioctylfluorene) (PDOF) are scaled with the applied bias voltage up to $2 \times 10^4 \text{ V cm}^{-1}$ (Figures S14-15), giving ϕ_{max} value of single-crystal **H₂TTF₂-Rub²⁺** as 5×10^{-4} . $\Sigma(\mu_+ + \mu_-)$ can be calculated to be $0.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, showing a markedly increase in charge carrier mobility in **H₂TTF₂-Rub²⁺** compared to neutral **TTF₂-Rub**. Protonation impacts on crystal structure significantly, and the transformation into one-dimensional π - π stack of benzo-TTF radicals with small intermolecular distance secures highly conductive pathways in **H₂TTF₂-Rub²⁺** while no such effective π - π interactions observed in neutral **TTF₂-Rub**.

Conclusion

In summary, benzo-TTF-annulated [26]rubicin and its diprotonated form were prepared, and investigated their spectroscopic and electronic properties. Electrical conductivity change upon packing structure change could be induced by simple protonation of TTF-annulated core-modified expanded porphyrin derivative. Enhanced photoconductivity from the single-crystal of **H₂TTF₂-Rub²⁺** compared to neutral **TTF₂-Rub** could be attributed to the one-dimensional hole-transporting pathways which consists of closely formed π - π stack of benzo-TTF in the single crystal of **H₂TTF₂-Rub²⁺**. The author thus believes that present combination of protonation induced IET-based redox and structural changes in TTF annulated expanded porphyrin derivatives could emerge as a powerful tool in the search for new type of organic electronic materials with stimulus-controlled electrically conductive materials.

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Chapter 2 Appendix

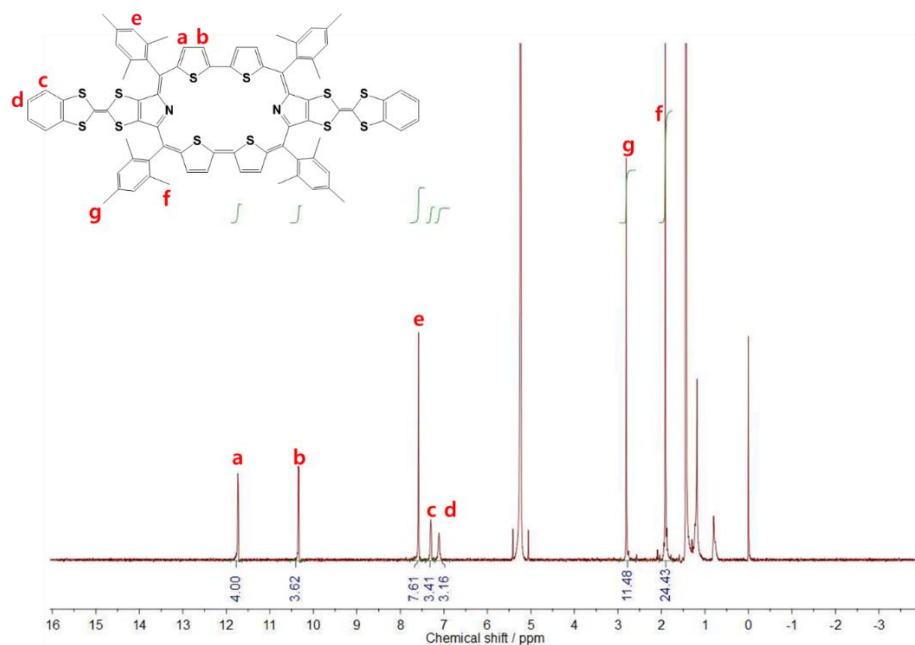


Figure S4. ¹H NMR spectrum of neutral **TTF₂-Rub** recorded at room temperature in CD₂Cl₂.

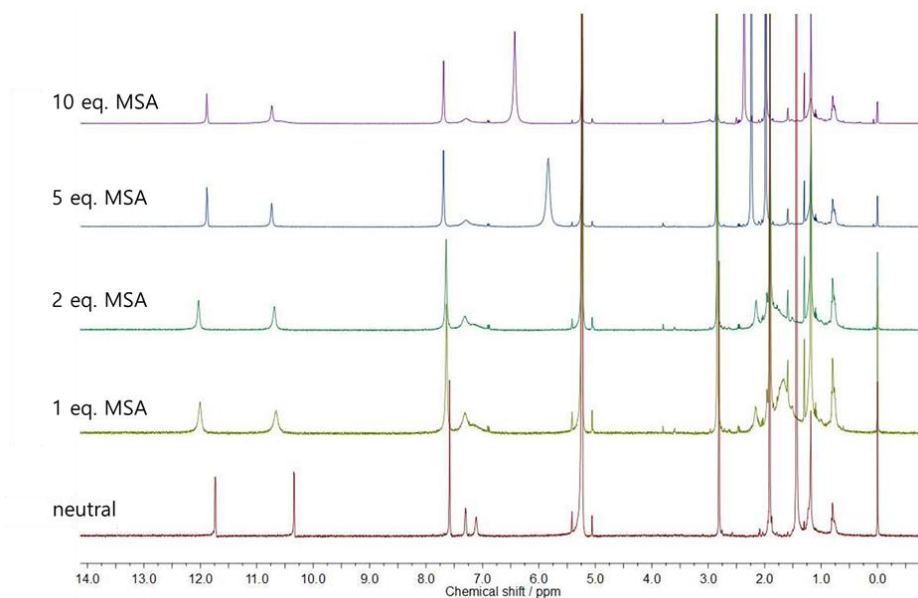


Figure S5. ¹H NMR spectral change of **TTF₂-Rub** upon addition of MSA.

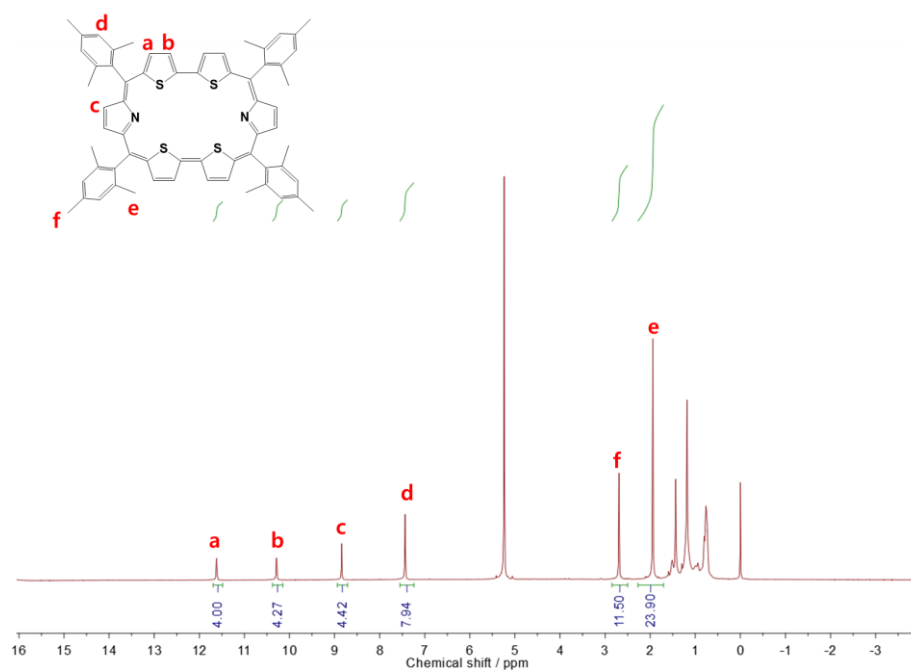


Figure S6. ^1H NMR spectrum of neutral **Rub** recorded at room temperature in CD_2Cl_2 .

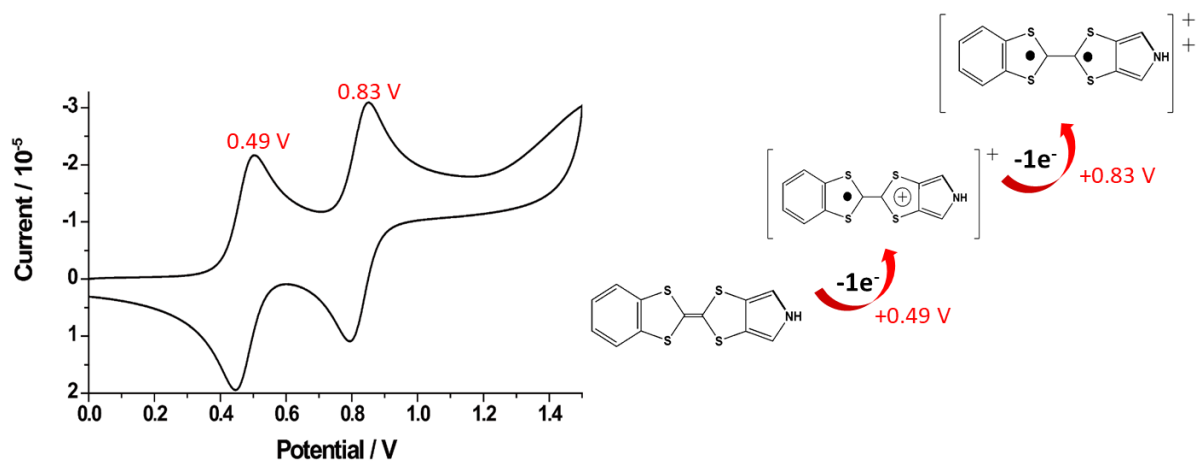


Figure S7. Cyclic voltammogram of precursor **TTF₂-Rub** recorded in CH_2Cl_2 containing 0.1 M tetrabutylammonium phosphate as a supporting electrolyte. Working, reference, and counter electrodes were glassy carbon, Ag/AgCl, and platinum wire, respectively.

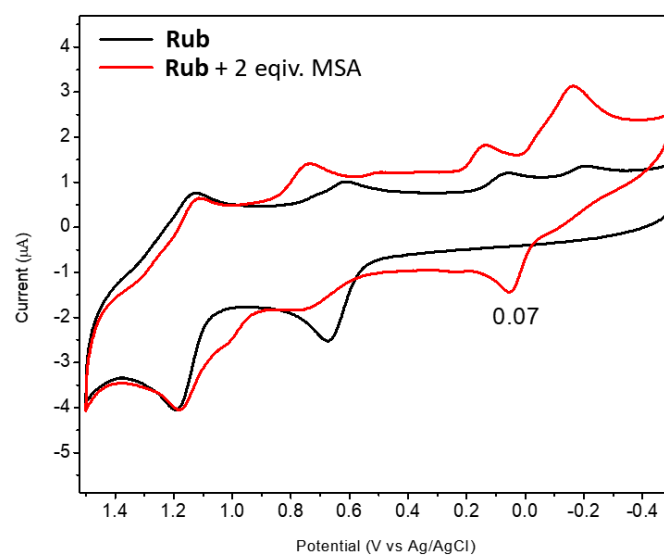


Figure S8. Cyclic voltammogram of **Rub** and **H₂Rub²⁺** recorded in CH₂Cl₂ containing 0.1 M tetrabutylammonium phosphate as a supporting electrolyte. Working, reference, and counter electrodes were glassy carbon, Ag/AgCl, and platinum wire, respectively.

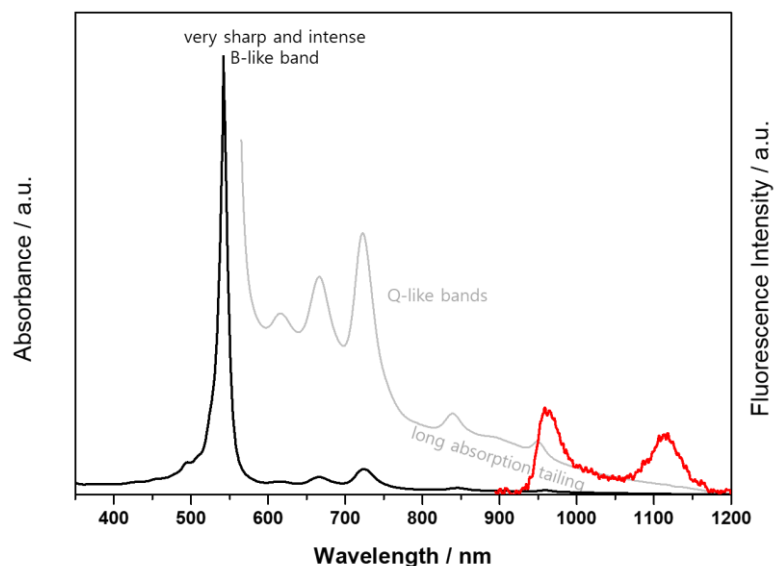


Figure S9. Steady-state absorption and fluorescence spectra of neutral **TTF₂-Rub** recorded in CH₂Cl₂.

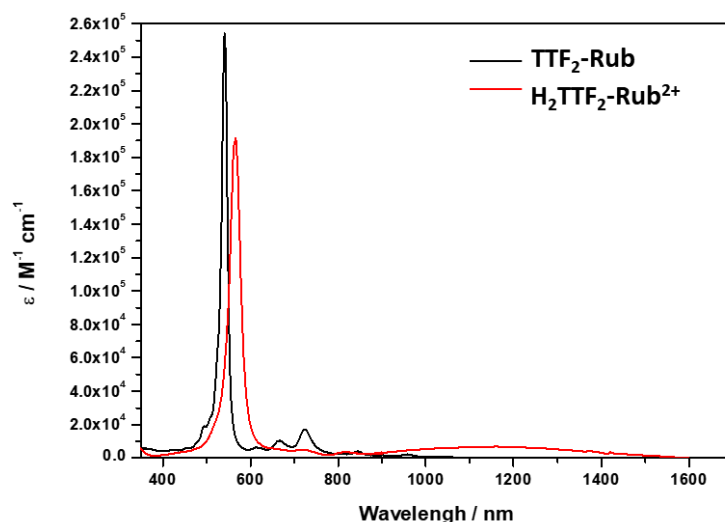


Figure S10. Steady-state absorption spectra of neutral and protonated **TTF₂-Rub** recorded in CH₂Cl₂.

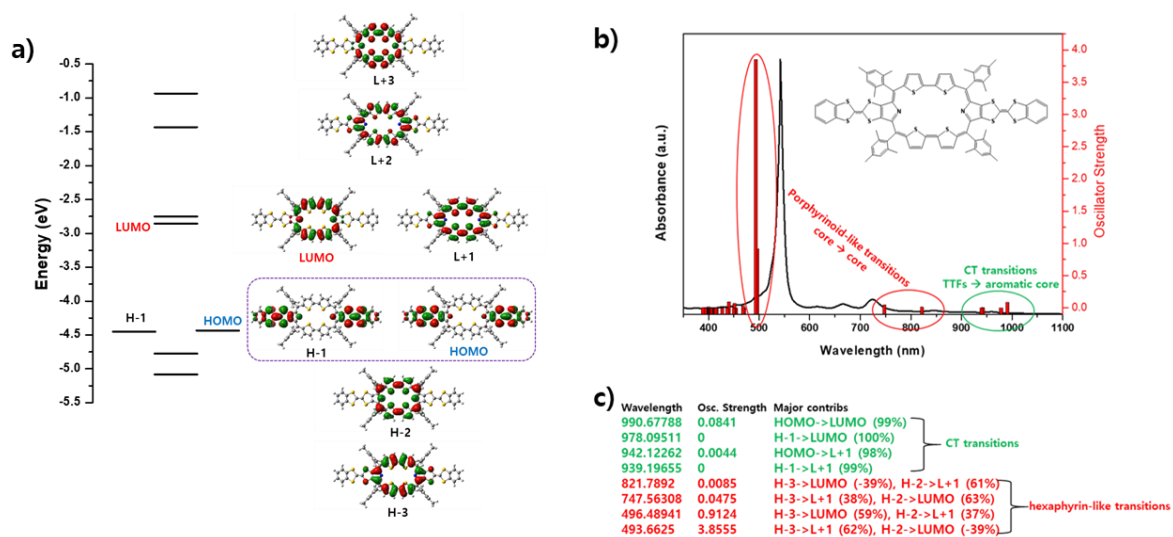


Figure S11. a) Energy level diagrams and molecular orbitals, b) calculated vertical transitions and steady-state absorption spectrum, and c) major transitions of neutral **TTF₂-Rub** calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set.

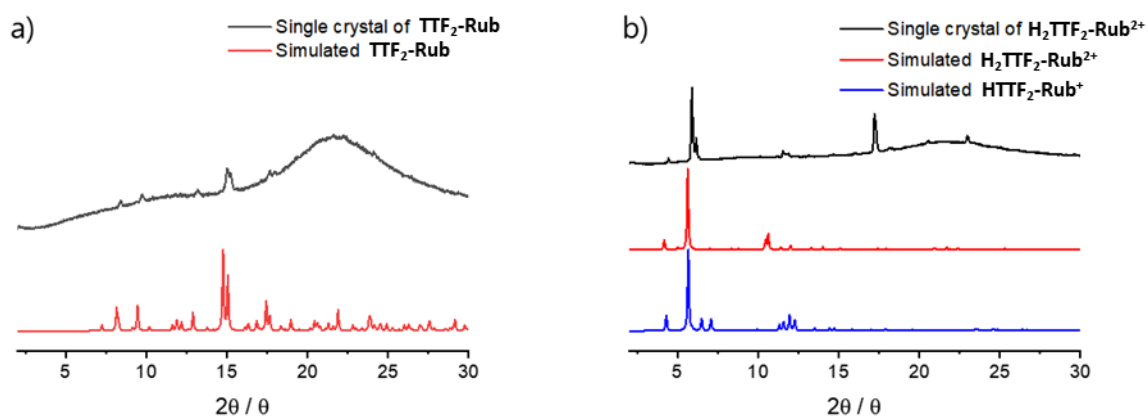


Figure S12. Experimental and simulated XRD profiles of (a) neutral **TTF₂-Rub** and (b) **H₂TTF₂-Rub²⁺**

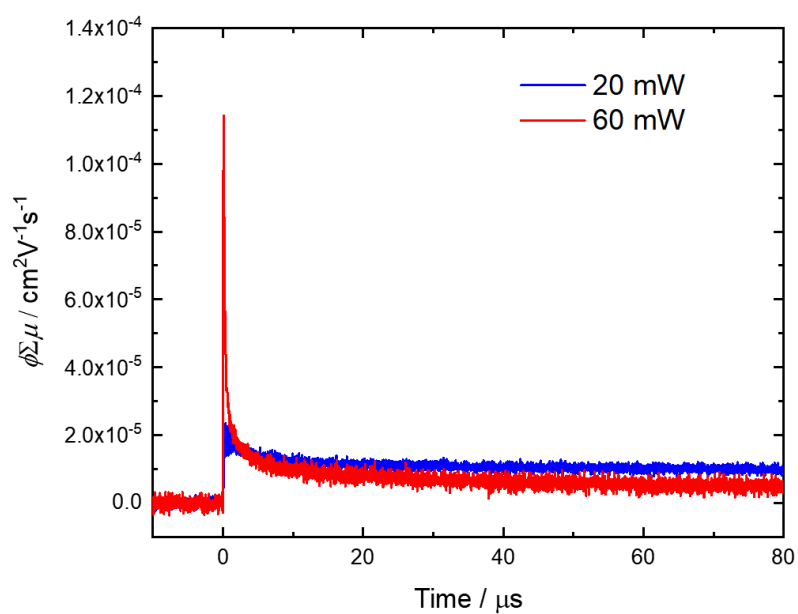


Figure S13. Power dependence of TRMC traces of **H₂TTF₂-Rub²⁺**

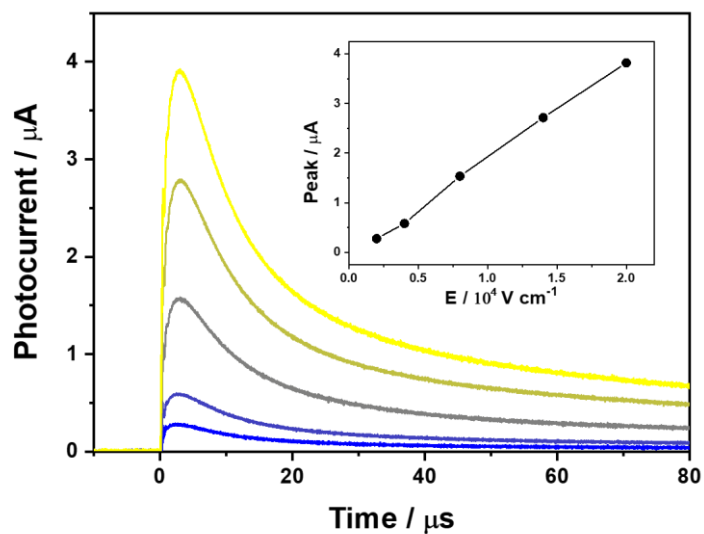


Figure S14. Photocurrent transients of drop casted $\text{H}_2\text{TTF}_2\text{-Rub}^{2+}$ upon exposure to 355 nm laser. The applied bias, E , was increased from the blue to yellow. The inset shows peak photocurrent intensity vs E .

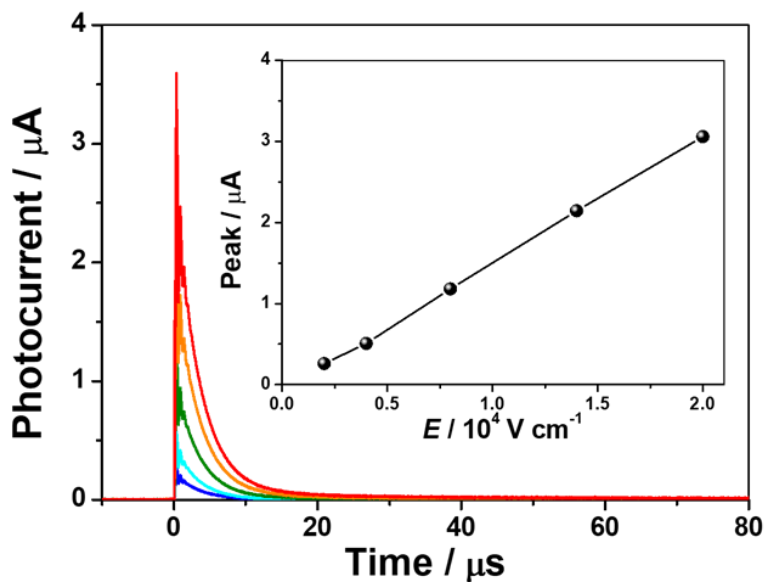


Figure S15. Photocurrent transients of drop-casted PDOF upon exposure to 355 nm laser. The applied bias, E , was increased from the blue to red. The inset shows the peak photocurrent intensity vs E .

Chapter 3

Circularly polarized light induced microwave conductivity measurement on chiral PDI/SWCNT composite

Abstract

In this work, CPL-TRMC (Circularly Polarized Light-Time Resolved Microwave Conductivity) for investigation of the CPL-dependent photo-induced charge carrier dynamics in chiral materials with chiroptical properties is developed and examined with chiral perylenediimide (PDI) and single-walled carbon nanotube (SWCNT) composite. Chiral *R*- or *S*-PDI molecular thin films were paired with handedness-sorted (6,5) and (11,-5) SWCNT films to compose donor(D)-acceptor(A) system for spin-dependent charge separation process, and the D-A system was examined through linear and circular polarization dependent steady-state and time-resolved measurements. The *R*-PDI-(6,5) film exhibited strong enhancement in circular dichroism (CD), and revealed a reversed transient conductivity signal, relative to the polarity of CD, in CPL-TRMC measurement upon excitation of the E_{11} state, which is interpreted as arising from a spin-dependent initial charge separation process. Through linear polarization dependent flash photolysis TRMC and circular polarization resolved femtosecond transient absorption, the author could deduce that sub-ps inter-tubular charge separation upon E_{11} excitation in SWCNT was responsible for the spin-dependent photoconductivity transients observed in CPL-TRMC measurements.

Introduction

Recent developments in spintronics shed light on chiral materials for the application of electron spins as well as the spin-dependent charge transport. Various types of chiral materials encompassing biological systems, synthetic organic and inorganic chemistry have been suggested, and their charge/spin transport properties were examined through several different spin injection methods.^{11,148-150} Spin injection by ferromagnetic electrodes is a primary choice in spintronic device operation, and a variety of structures have been designed to enable efficient and quantitative spin injection into target materials.¹⁵¹ Adopting ferromagnetic electrodes for spin injection requires device fabrication processes, and interfacial issues between ferromagnets and target materials are often critical for optimizing device operation.¹⁵²⁻¹⁵³

Photoionization by circularly polarized light (CPL) can be utilized for contact-free spin injection into target materials through spin-dependent excitation of the electrons.¹⁵⁴⁻¹⁵⁵ Spin-polarized photoelectron spectroscopy (PES) under CPL illumination has been used to evaluate the spin selectivity of electrons transmitted through chiral materials, and photo-current measurement under CPL illumination has been often the choice for spin-selective transport and spin-selective charge transfer in chiral organic and inorganic materials.^{4,148,156} In both of the techniques the contact issues are critical to the quantitative assessment of spin selectivity and transport, leading to strong demand for alternative methods utilizing non-contact modes.

Time-resolved spectroscopy techniques with CPL excitation have been demonstrated as complete non-contact assessments of spin-dependent charge transport chiral materials and heterostructures. Dependence of charge transfer rate on spin-selective excitation was clearly observed using a time-resolved fluorescence (TR-FL).¹⁵⁷ The spin polarization of radical pairs formed by electron transfer could be calculated using the time-resolved electron paramagnetic resonance (TR-EPR) spectroscopic system in donor-acceptor dyad systems with chiral components.¹⁵⁸ These recently developed spectroscopic approaches can reveal mechanistic insights into the spin-dependent charge transfer processes. For comprehensive understanding of the total landscape of spin-dependent charge transfer processes, direct methods for tracking the local motion of the electrons with high sensitivity are highly desirable.¹⁵⁹

Electronic conductivity can be measured not only by conventional direct current (DC) techniques, but also as optical conductivity in terms of a material's complex permittivity. One of the representative optical conductivity techniques is the time resolved microwave

conductivity (TRMC) technique, based on Drude-Zhener modeling of the frequency dependent dielectric constant.¹⁶⁰ Flash photolysis (FP)-TRMC is a completely contactless technique, both in the photo-carrier injection step and for monitoring the resulting electrical conductivity with the microwave probe.^{29-30,161} Herein, The author employs CPL as an excitation light source to design a novel contactless technique for assessing inherent spin-dependent electron transport, which the author terms CPL-induced time-resolved microwave conductivity (CPL-TRMC).

Donor-acceptor heterojunctions featuring single-walled carbon nanotubes (SWCNTs) with single chirality and handedness were chosen for demonstration of the CPL-TRMC system, owing to their high conductivity, well-defined handedness, and concomitant distinct optical anisotropy in their electronic transitions. Electronic transitions of chirality sorted SWCNT can be predicted from the chirality indices (n,m) of the SWCNTs and pure enantiomers show, both theoretically and experimentally, alternating CD signs upon progression of E_{ii} transitions which are optically allowed transitions for the electric field of the light parallel to the axis of the nanotube.¹⁶²⁻¹⁶³ SWCNTs can give strong TRMC signals upon photoexcitation via the direct band-gap excitation, the prerequisite for CPL-TRMC in the present work, due to the relatively large Onsager distance for the initial electron-hole pairs in SWCNT and a high free charge carrier yield of ~6% in isolated semiconducting SWCNTs.¹⁶⁴ The high carrier mobilities in SWCNTs should allow the author to detect evident signatures of CPL excitation in the differential transient conductivity.¹⁶⁵⁻¹⁶⁶ Successful demonstration of spin-dependent charge separation upon CPL illumination of a SWCNT/perovskite bilayer further suggests the possibility of detecting spin-dependent charge separation with CPL-TRMC.¹⁵⁶

In this work, The author demonstrates the successful establishment of the CPL-TRMC measurement system with SWCNT as a material platform, showing spin-dependent charge transfer in the SWCNTs. The total landscape of charge-spin relationship in SWCNT film upon charge injection through CP photoexcitation has been elucidated by the combination of CPL-TRMC and femtosecond transient absorption.

Experimental

Chirality separation of SWCNTs

(6,5) and (11,-5) SWCNTs were prepared by single-chirality enantiomer separation of CoMoCAT SWCNT using stepwise elution gel chromatography with triple surfactant system of sodium cholate, sodium dodecyl sulfate, and sodium lithocholate.¹⁶⁷⁻¹⁷⁰ Randomly-oriented SWCNT films were deposited by vacuum filtration on filter membrane and transferred to quartz plates for optical measurements.¹⁷¹⁻¹⁷²

Synthesis of *R/S*-PDI

R- and *S*-PDI was synthesized by following a literature procedure.⁴ The successful synthesis was confirmed by NMR (JEOL AL-400). Tetrahydrofuran (THF) was purchased from Nacalai Tesque and used without further purification. *R/S*-PDI films and SWCNT/PDI composite films were prepared by drop casting 50 μ L of *R/S*-PDI 1mg/mL THF solution onto quartz plates and SWCNT films, respectively.

UV-Vis-NIR Absorption and Circular Dichroism (CD) Spectroscopy

UV-Vis-NIR absorption spectra and CD spectra were obtained from JASCO 1700 CD spectrometer. Baseline was taken with the quartz plate used for film fabrication. The mask was made with the thick paper to cover the part without samples.

Raman Spectroscopy

Raman spectra was obtained from JASCO NRS-4100 Raman spectrometer with a backscattering configuration. CW DPSS laser (532 nm) was used for the excitation. Laser power of 0.6 mW was used for *R*-PDI-(6,5) and 6.2 mW was used for *R*-PDI, pristine (11,-5), and washed *R*-PDI-(6,5) samples. Exposure of 1 sec and beam size of $\sim 1 \mu\text{m}$ were used for all measurements. Peak positions were corrected with Si as a reference in same measurement conditions.

Linear/circular polarization resolved Flash-photolysis time resolved microwave conductivity (FP-TRMC)

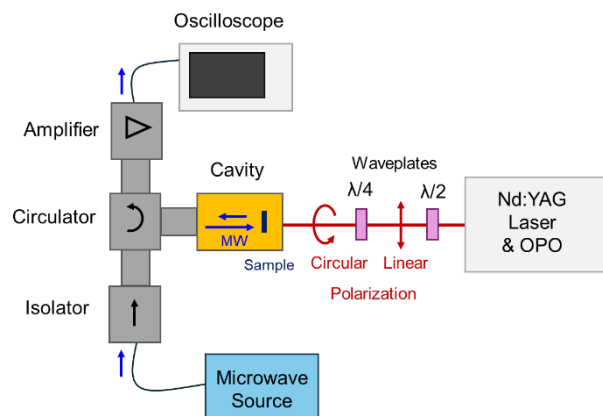


Figure 27. Schematics of CPL-TRMC setup. Nd/YAG lasers with optical parametric oscillator (OPO) are used for the excitation light sources at 355, 580 and 1020 nm. A Gunn diode oscillator or microwave signal generator was employed as a microwave source with the tuning range of 100kHz~43.5GHz at 1-100 mW.

FP-TRMC experiments were carried out as follows. For 355 nm pulsed photoinjection measurements, pulses were generated by third-harmonic generation with the photon density of 0.9×10^{15} photons cm^{-2} from Spectra-Physics INDI-HG Nd/YAG laser, operated with the pulse duration of 5-8 ns and 10 Hz). For 580 and 1020 nm pulsed photoinjection measurements, pulses were generated by the EKSPLA NT300 Nd/YAG laser, operated with the pulse duration of 3-5 ns and 10 Hz. The laser wavelength was tuned by the OPO to generate pulses with photon density of 3.0×10^{15} photons cm^{-2} and 5.2×10^{15} photons cm^{-2} for 580 and 1020 nm excitation pulse, respectively. The SWCNT or SWCNT/PDI sample was inserted to the X-band microwave cavity resonating with TE₁₀₂ mode at ca. ~9.1 GHz from a Gunn diode oscillator or from a signal generator Rhode & Schwarz SMF 100A. The incident power of microwave was typically set at 3 mW, and the power reflection from the cavity was amplified and recorded with a MDO3024 oscilloscope and converted directly into the electric conductivity transients.

In both instrumental set-ups, linear polarization dependence was measured by introducing a cube polarizer and a half-waveplate into the excitation beam path to control the linear polarization. CPL-TRMC experiments were carried out by introducing a quarter waveplate to the linear polarization-dependent measurements to generate a circularly polarized beam. For all polarization-dependent measurements, conductivity transients were recorded as three sets of 512 traces averaging for each polarization by alternating polarization for every

measurement and average values were taken. The schematic diagram of CPL-TRMC is shown in Figure 27.

Circular polarization resolved femtosecond transient absorption (fs-TA)

Circular polarization-resolved fs-TA spectroscopy was conducted using a Coherent Libra Ti:sapphire laser, operated with an output of 800 nm at 1 kHz. A TOPAS optical parametric amplifier (OPA) generated 1020 nm pulses with pulse duration of ~150 fs. The pulse train was adjusted at 500 Hz through an optical chopper. White-light continuous probe pulses with a range of 500–1500 nm were generated via self-phase modulation by pumping a 1 cm thick sapphire crystal with an 800 nm pulse. Circularly polarized pump pulses were generated by introduction of a quarter waveplate into the beam path. A Helios spectrometer (Ultrafast Systems) was used for collecting fs-TA spectra.^{156,160}

Results and discussions

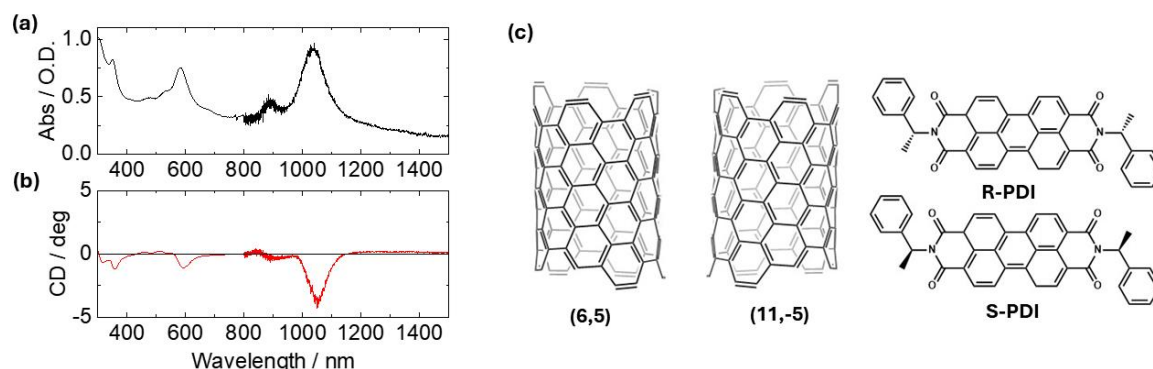


Figure 28. The steady-state (a) absorption and (b) circular dichroism (CD) spectra of *R*-PDI-(6,5) SWCNT film. 50 μ L of *R*-PDI 1 mg/mL tetrahydrofuran solution was drop-casted to pristine (6,5) film to produce *R*-PDI-(6,5) film. (c) structures of (6,5) and (11,-5) SWCNT and *R/S*-PDI.

Design of a photo-induced charge transfer system is the key for the measurements where the electrons are unidirectionally transferred under the electrochemical potentials with no external electric field, allowing pure spectroscopic assessment of chirality-induced spin selectivity.¹⁵⁹ To facilitate the charge transfer, the author chose perylenediimide (PDI) as the electron acceptor which is expected to form type-II heterojunction with (6,5) and (11,-5) SWCNTs ((6,5)- and (6,5)+ or left- and right-handed (6,5)).¹⁷³ the author also adopted chiral *R/S*-PDI to examine their interaction with handedness-sorted SWCNT films, with an exemplary heterojunction referred to as *R*-PDI-(6,5). The chirality of both the donor (SWCNT) and acceptor (PDI) allows the author to investigate how their structural and electronic interactions, and the resulting photoexcited interfacial charge transfer, depend on their chirality combination.

Figure 28a shows steady-state UV-vis-IR absorption for the *R*-PDI-(6,5) film. The allowed optical transitions from electric field parallel to the SWCNT axis: E_{ii} were observed at 1030, 580, 350 nm for E_{11} , E_{22} , and E_{33} , respectively. The former two peaks showed bathochromic shifts in relation to those observed in the isolated (6,5) SWCNT with E_{11} and E_{22} transitions at 975 and 567 nm.¹⁷⁴ These shifts could be attributed to the bundling of the carbon nanotubes in the film.¹⁷⁵ The circular dichroism (CD) spectra (Figure 28b) showed three negative peaks at similar peak positions to the absorption spectrum, where the maximum value reached ca. 4×10^3 mdeg. The difference in the absorption between left-handed circularly polarized light (LCPL)

and right-handed circularly polarized light (RCPL) of *R*-PDI-(6,5) film was calculated to be 12% at E_{11} transition, which is significantly higher than the 0.33% difference in the pristine (11,-5) film (Figure S16c). Only this specific *R*-PDI-(6,5) film shows strong enhancement in the CD peaks at E_{11} , E_{22} , and E_{33} transitions compared to the corresponding pristine SWCNT film, while other *R*-PDI or *S*-PDI deposited SWCNT films did not show such a strong CD enhancement (Figure S16d, S18c,d). The possibility of apparent CD effect, which is an extrinsic CD effect from sample morphology was examined in pristine (6,5) and (11,-5) film. (Figure S19)¹⁷⁶ Apparent CD effect was not observed, yielding identical CD spectra for front and back side of the pristine (6,5) and (11,-5) film. This lack of the apparent CD effect can be explained by randomness of the orientation of SWCNTs on the film and enhancement of the CD observed in *R*-PDI-(6,5) film is also expected to be not from apparent CD effect owing to the randomness of the SWCNT orientation in this film.

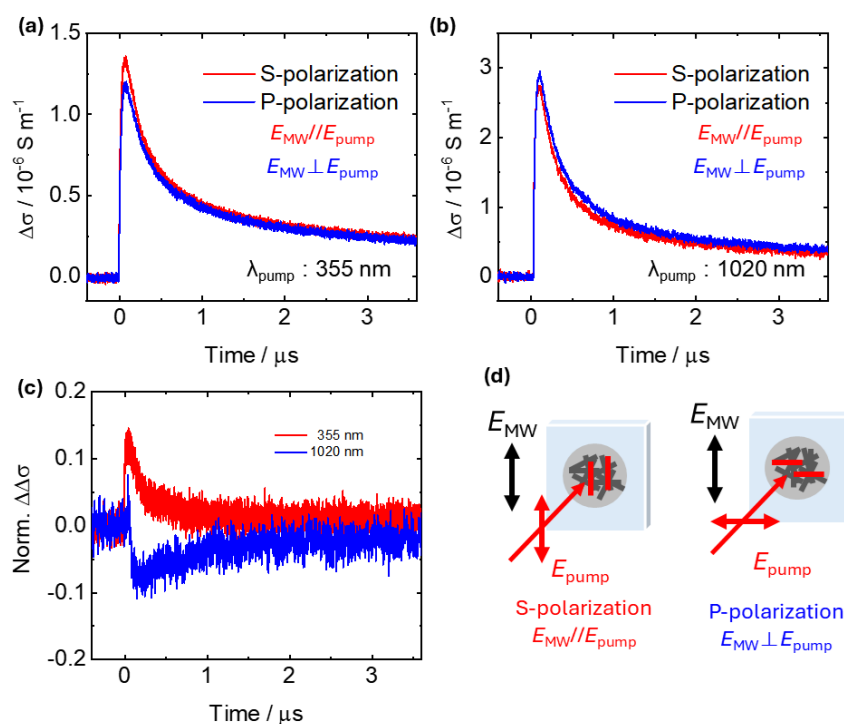


Figure 29. FP-TRMC traces of *R*-PDI-(6,5) SWCNT under (a) 355 (E_{33}) and (b) 1020 nm (E_{11}) excitation. (c) Differential conductivity transients normalized at the peak value. Linear polarization state of the excitation pulse was adjusted to S- (red) and P- (blue) polarization. The excitation pulse was tuned to $0.5 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ at 355 nm and $1 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ at 1020 nm, respectively. The relative orientation of the electric field for microwave (E_{MW}) and pump pulse (E_{pump}) is depicted in Figure 29d.

First, anisotropic photoconductivity in FP-TRMC was studied to clarify the charge carrier dynamics in the *R*-PDI-(6,5) film with linearly polarized excitation light sources and represented in Figure 29. Polarization of the excitation pulse was adjusted to be linear, and S- and P-polarizations of the pump pulse are defined as perpendicular and parallel polarization in relation to the optical table surface, respectively. The microwave electric field (E_{MW}) is perpendicular to the optical table surface, hence, S- and P- polarization of the pump is parallel and perpendicular to the E_{MW} , respectively (Figure 29d). Both excitation wavelengths clearly showed a prompt enhancement in photoconductivity due to photo-carrier injection within the pump pulse (3-5 ns), followed by a decay in the μ s range reflecting the recombination of the free charge carriers (Figure 29a, b). In the case of 355 nm excitation (E_{33} , Figure 29a), S-polarization pump resulted in slightly higher photoconductivity for the short time regime ($<1 \mu$ s) and converged into equivalent photoconductivity at the later regime, indicating the decay of conductivity anisotropy (Figure 29a, c). The conductivity anisotropy reversed upon E_{11} (1020 nm) excitation of *R*-PDI-(6,5) with reduced anisotropy signals relative to E_{33} pumping. It should be noted that the conductivity anisotropy lasted over 3 μ s regime (Figure 29b, c).

The conductivity anisotropy is impacted by the following relative alignments of E_{pump} , E_{MW} , and SWCNT axes: 1) The parallel alignment of SWCNT axes and E_{pump} enhances conductivity from selective excitation of SWCNT, 2) Photo-injected carriers confined in the SWCNT give the higher conductivity under the parallel alignment of E_{MW} and SWCNT axes. (Figure 29d) Since the SWCNT film is oriented randomly, the number of carbon nanotubes in the excited states can be presumed to be identical upon S- or P- polarization of light, cancelling the above factor 1) allowing the author to consider only the relative alignments of E_{pump} against E_{MW} .

If charge generation occurs predominantly within a nanotube (intra-tubular), the charge movement and associated microwave mobility of photo-generated charge carriers confined within SWCNTs will remain aligned with E_{pump} , yielding a microwave conductivity anisotropy signal corresponding to S-polarization ($E_{pump} // E_{MW}$ configuration). On the other hand, if inter-tubular charge separation and/or charge transfer to PDI dominate, conductivity anisotropy is expected to be lower than that of intra-tubular charge separation due to the randomization of the charged SWCNT axes. Exciton diffusion, prior to charge separation, and charge diffusion will also suppress the anisotropy by transferring excitons and charges onto

randomly oriented SWCNTs. In this manner, stronger S-polarization photoconductivity observed upon E_{33} excitation, compared to E_{11} excitation, can be interpreted as 1) a decrease in the exciton diffusion for E_{33} excitation, or 2) more efficient charge transfer to adjacent SWCNTs and/or PDI in the film for E_{11} excitation.

The photoconductivity anisotropies observed in Figure 29 imply that different CS pathways can be activated for different excitation wavelengths. From the ultrafast charge separation observed in fs-TA of SWCNT films (presented in a later section), The author expect the above 1) process (exciton diffusion prior to charge separation) is not the dominant mechanism impacting the observed polarization anisotropies. Thus, the decrease in linear polarization conductivity anisotropy observed at FP-TRMC measurement in R-PDI-(6,5) film can be interpreted as activation of the inter-tubular CS or CS to PDI upon E_{11} excitation. The difference between E_{33} and E_{11} excitation in this film can be interpreted by the exciton dissociation process in SWCNT depending on E : the intra-tubular CS process dominates via the higher energy (E_{33} and E_{22}) excited state, making contrast to both of inter-tubular CS and CS to PDI contributing to the photo-carrier generation via the lower (E_{11}) excited state. Existence of spontaneous dissociation process from the higher excited state is expected to be contributing to the excitation wavelength dependence in the carrier yield and the CS pathway change.¹⁷⁷⁻¹⁷⁸ This is also supported by the linear dependence of the observed conductivity upon fluence of pumping pulses (Figure S25), suggesting the nature of single photon process of CS in this fluence regime.

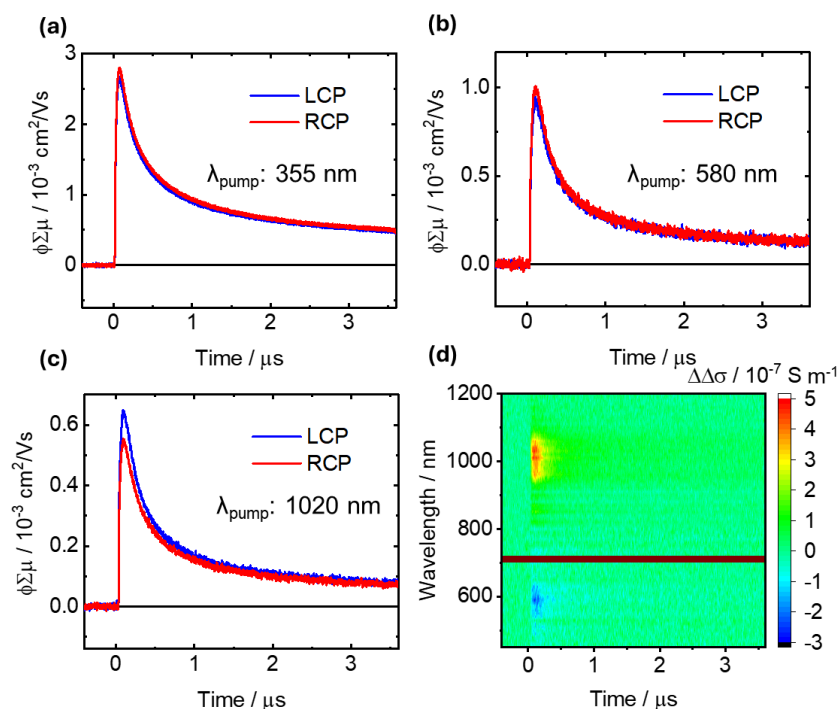


Figure 30. CPL-TRMC photoconductivity traces of the *R*-PDI-(6,5) film at (a) 355 nm: E_{33} (b) 580 nm: E_{22} (c) 1020 nm: E_{11} excitation. The excitation pulse was tuned to $0.5 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ at 355 nm and $1 \text{ mJ pulse}^{-1} \text{ cm}^{-2}$ at 580 and 1020 nm. Circular polarization state of the excitation pulse was adjusted to left-handed circular polarization (blue, LCP) and right-handed circular polarization (red, RCP). (d) Differential conductivity measured at the excitation wavelength range from 450 to 1200 nm.

In order to assess photo-generated electron spin-dependency upon CPL excitation of the *R*-PDI-(6,5) film, photoconductivity transients in the *R*-PDI-(6,5) film were observed by the newly developed CPL-TRMC measurement setup. The film was photo-excited at 355, 580, and 1020 nm which correspond to the E_{33} , E_{22} and E_{11} transitions of the (6,5)-SWCNT, where the PDI is transparent against 1020 nm, but presumed to have some overlapped absorption at 355 and 580 nm (Figure S17).

Upon E_{33} and E_{22} excitation, photoconductivity under RCPL excitation was higher than LCPL, and the difference in the LCPL and RCPL excitation at the peak was estimated to be 5% as represented by Figures 30a and 30b. This sign difference agrees with the difference in the relative absorption change of LCPL and RCPL estimated from CD ($\sim 5\%$). On the other hand, upon E_{11} excitation at 1020 nm (Figure 30c), remarkably higher photoconductivity of ca. 15% was observed with LCPL excitation, which showed striking contrast to the higher

absorption of RCPL suggested by CD. Decay analysis of the photoconductivity traces was also conducted by fitting with double exponential decay curves to evaluate the time constant as summarized in Table 1. Regardless of the excitation wavelength and polarization, calculated time constants were estimated to be almost identical among all traces, with τ_1 and τ_2 of approximately 0.20 and 1.2 μs , respectively, implying the recombination rates unchanged for different wavelengths and circular polarization (CP) states of pumping pulses.

Table 1. Decay fitting coefficients of CPL-TRMC traces

$\lambda_{\text{exc}} / \text{nm}$		$t_1^{\text{a}} / \mu\text{s}$	$t_2^{\text{a}} / \mu\text{s}$	y_0 (%)	A_1 (%)	A_2 (%)
355	LCP	0.20	1.22	13.0	56.4	30.6
	RCP	0.20	1.20	12.8	56.6	30.6
580	LCP	0.20	1.18	10.4	61.5	28.0
	RCP	0.20	1.21	10.2	62.0	27.8
1020	LCP	0.20	1.23	10.2	64.5	25.2
	RCP	0.22	1.34	11.5	61.3	27.2

^aPhotoconductivity traces were fitted with the function $\varphi(t) \sum \mu = A_1 e^{t/\tau_1} + A_2 e^{t/\tau_2} + y_0$

Unlike direct injection of the spin-polarized charges through ferromagnetic electrodes, the spin-dependent CS process mediates the spin polarization of charge carriers that are *photo-injected* into a system. The yield and spin polarization of the charges are the major factors for the CS processes, which can be determined by the rates of CS for up- ($k_{\text{CS}\uparrow}$) and down-spins ($k_{\text{CS}\downarrow}$), spin-flip (k_{flip}), and exciton relaxation to the ground state (k_{F} and k_{n}) as shown in Figure S24. The yield and spin-polarization of the photo-injected free charges thus depend strongly on the relative rate of competing processes. If the spin-flip process has a competitive rate with charge separation processes (i.e., $k_{\text{flip}} \sim k_{\text{CS}\uparrow}$ or $k_{\text{CS}\downarrow}$), the CS process with low rate constants can be impacted by the spin flipping, leading to the observable single CS. This also causes the final CS state to be condensed with the spin with the higher CS rate, and thus the spin polarization would not be identical to that in the primary excited states. This spin-flip process is widely observed in systems with chirality-induced spin selectivity (CISS); PES experiments

with DNA embedded on gold show spin polarization almost identical from RCPL and LCPL excitation.¹⁴⁸ The primary photophysical process will be discussed in the later fs-TA section.

Since charge separation in the PDI-SWCNT composites is expected to be faster than the excitation pulse duration, the author can only probe the impact of the pump-prepared spin polarization on CS by quantifying the total carrier yield and the recombination rate upon CPL excitation. The dependence of recombination rate, however, may not be significant because the spin polarization in the final CS states can be mitigated by spin-flipping at the primary excited states and by the spin relaxation after CS.

The values of end-of-pulse conductivity ($\phi\Sigma\mu_{\max}$) depend clearly on the CPL states of the excitation pulse in all three wavelengths (Figure 30a-c). The $\phi\Sigma\mu_{\max}$ values can be also impacted by 1) the number of the photons absorbed by the film with LCPL and RCPL excitation, and by 2) the spin-dependent CS processes via spin-selective excitation by LCPL and RCPL represented by $k_{CS\uparrow}$, $k_{CS\downarrow}$, k_F , k_n and/or k_{flip} . If this dependence solely comes from 1), photoconductivity traces should be proportional to the absorption of the LCPL and RCPL. This is well represented by the cases of excitations at E_{33} and E_{22} supporting scenario 1). On the other hand, reversed polarity observed in E_{11} excitation opens the possibility of 2). This is also suggestive of the values of $\phi\Sigma\mu_{\max}$ being more likely to convey the dependence of CS efficiency on the handedness of CPL excitation.

From the linear polarization experiment, the author deduced that in *R*-PDI-(6,5) film, inter-tubular or charge separation to the PDI is promoted upon E_{11} compared to E_{33} excitation. Thus, the difference in CPL dependency upon excitation wavelength change in *R*-PDI-(6,5) film can be explained by the switching of CS pathways from the higher (E_{33} and E_{22}) to lower (E_{11}) excited state, and this change in CS pathway is expected to be responsible for the spin-dependent CS processes observed in CPL-TRMC.

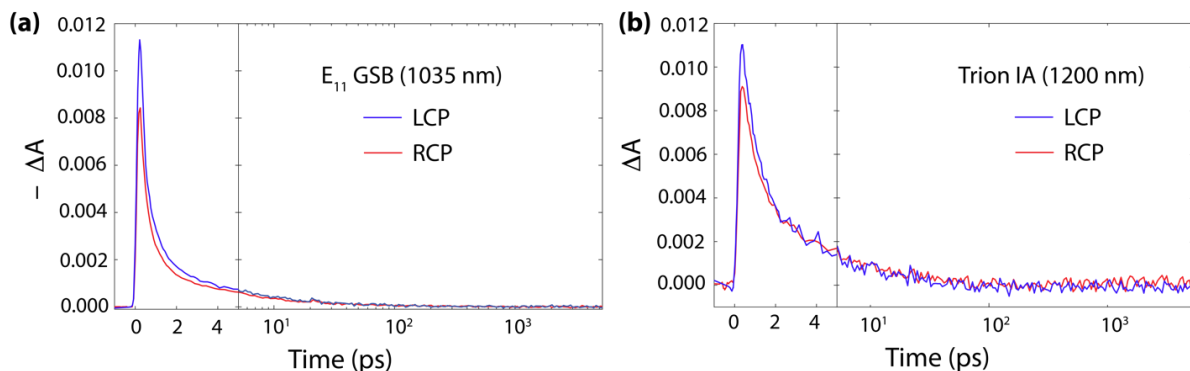


Figure 31. Dynamics from femtosecond transient absorption spectroscopy of the *R*-PDI-(6,5) film, pumped at 1000 nm to excite the (6,5) E_{11} with either a LCP (blue) or RCP pump (red) beam and probed with a linear probe beam. (a) Dynamics probed at 1035 nm to probe the E_{11} ground-state bleach (GSB). (b) Dynamics probed at 1200 nm to probe the trion induced absorbance (IA).

In order to elucidate the early photophysics of the *R*-PDI-(6,5) film, circular polarization resolved femtosecond transient absorption (fs-TA) measurements were conducted (Figure 31). In these measurements, pump and probe beams were circularly polarized and linearly polarized, respectively. Upon 1000 nm (E_{11}) excitation, the *R*-PDI-(6,5) film showed a sub-ps rise of SWCNT trion induced absorption (IA) at 1200 nm (Figure 31b), which can be attributed to the fast charge separation process in SWCNTs.¹⁷⁹⁻¹⁸⁰ Strong anisotropy to the circular polarization state of the pump beam was observed for both the E_{11} ground-state bleaching (GSB) peak (Figure 31a) and trion IA (Figure 31b). The TA anisotropy favors LCP excitation of the (6,5) E_{11} , which is in line with the CPL conductivity anisotropy observed in the CPL-TRMC measurements (Figure 30c). IA peaks from PDI anion around 700 nm are not pronounced significantly, indicating spin-dependent CS process is occurring solely in/between SWCNTs and PDI is not likely to be involved in the initial CS process.¹⁸¹

The impact of probe pulse polarization dependence was also examined, by controlling the polarization of the probe pulse to be the same as the pump pulse. (Figure S28) Upon 1020 nm excitation, quenching of the difference between the signal intensity in the CP excitation of the E_{22} GSB signal was observed upon this configuration, and this could be attributed to the cancellation between the difference in the absorbance and the evolution of the GSB signal upon CPL excitation, which strongly suggests that the origin of signal difference observed in

polarization-uncontrolled probe measurements were not simply originated anisotropy in the absorbance of CP light.

Apart from the initial assumption that charge separation occurs between PDI and SWCNT, fs-TA results suggest that initial charge separation takes place within SWCNTs. Involvement of PDI in photophysical process in *R*-PDI-(6,5) was further investigated by washing *R*-PDI-(6,5) samples by solvents. The removal of PDI from the surface of SWCNT was confirmed by Raman spectroscopy before/after the immersion processes into CHCl₃. The PDI showed specific vibrational peaks at 1297, 1377, and 1570 cm⁻¹ (Figure S20a). Although *R*-PDI-(6,5) film showed peaks of both *R*-PDI and pristine SWCNT, the peaks from PDI (especially 1377 cm⁻¹) totally disappeared after the washing process at the boiling point of CHCl₃ for 2 h, clearly suggesting the negligible residue of PDI in the washed film. CPL-TRMC results of the washed *R*-PDI-(6,5) film suggest that PDI does not contribute to the carrier dynamics measured by the 9 GHz probe, since *E*₁₁ CPL excitation of the washed film yielded almost identical photoconductivity traces to those of the film before washing (Figure S19a). The author also tried deposition of *S*-PDI which has opposite chirality to initially deposited *R*-PDI after washing, however, it did not induce any change in the photoconductivity traces (Figure S19b), still giving the inverted polarity in CPL-TRMC to the CD spectra. Addition of the *R*-PDI onto pristine (6,5) films with vapor deposition and drop-casting did not induce enhancement of CD of the *E*₁₁ peak, which indicates the enhancement of this peak shown in Figure 29b is likely to be coming from the SWCNT film itself (Figure S18). Thus, the author concludes that the spin-selectivity observed in CPL-TRMC upon *E*₁₁ excitation of *R*-PDI-(6,5) film is originating from the charge separation within a SWCNT or in between adjacent SWCNT, but not from CS between SWCNT and PDI.

CPL dependency in CPL-TRMC and CPL resolved fs-TA was only observed in *R*-PDI-(6,5) upon *E*₁₁ excitation, whereas pristine (11,-5) and *S*-PDI-(11,-5) did not show similar CPL dependence (Figure S7d-f). the author may attribute the lack of CPL dependence observed in pristine (11,-5) and *S*-PDI-(11,-5) to the difference in CS pathways, where the inter-tubular CS is not activated in these films upon *E*₁₁ excitation (Figure S21a-d). The linear polarization conductivity anisotropy in FP-TRMC in these films was estimated to be rather higher in 1020 nm (*E*₁₁) compared to 355 (*E*₃₃) excitations for both films, with the anisotropy of $\phi\Sigma\mu_{\max}$ estimated as 7.1% and 18.3% for the pristine (11,-5) and 13.1% and 22.2% for *S*-PDI-(11,-5) film upon *E*₃₃ and *E*₁₁ excitations, respectively. The inversion of the polarity with attenuation

was not observed for both of the pristine (11,-5) and *S*-PDI-(11,-5) films, indicating intra-tubular charge separation is predominant in these films upon E_{11} excitations. From these results, the author concludes that facilitation of inter-tubular charge separation is the key in spin-selective CS behavior observed in *R*-PDI-(6,5) films upon E_{11} excitation. Since this behavior holds for films where the *R*-PDI has been removed from the heterojunction, this spin-selective CS behavior appears to be an inherent property of the (6,5) SWCNT film.

Conclusions

In conclusion, the author established CPL-TRMC instrument and successfully probed the CP induced conductivity anisotropy of the *R*-PDI-(6,5) film. By using CPL-TRMC technique, the author could observe inverted conductivity anisotropy to the CD originating from spin-dependent CS in SWCNT in *R*-PDI-(6,5) film upon E_{11} excitation. The origin of the spin-dependent behavior observed in CPL-TRMC was explained by activation of inter-tubular CS in SWCNT upon E_{11} excitation in contrast to the dominant intra-tubular CS upon E_{33} and E_{22} excitation, revealed by the linear polarization conductivity anisotropy in FP-TRMC and the fs-TA. The CPL-TRMC developed in the present work is expected to serve as a powerful tool for the ultra-fast screening of chiral molecular condensates as potential chiral electronic and spintronic materials in the future.

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Chapter 3 Appendix

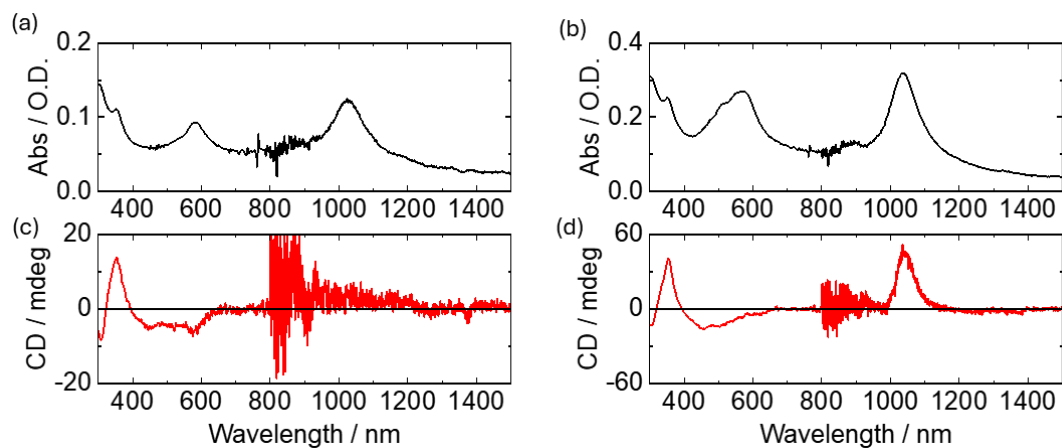


Figure S16. UV-Vis-NIR spectra of (a) pristine (11,-5) and (b) *S*-PDI-(11,-5) film and CD spectra of (c) pristine (11,-5) and (d) *S*-PDI-(11,-5) film. 50 μ L of *S*-PDI 1 mg/mL tetrahydrofuran solution was drop-casted to pristine (11,-5) film to produce *S*-PDI-(11,-5) film.

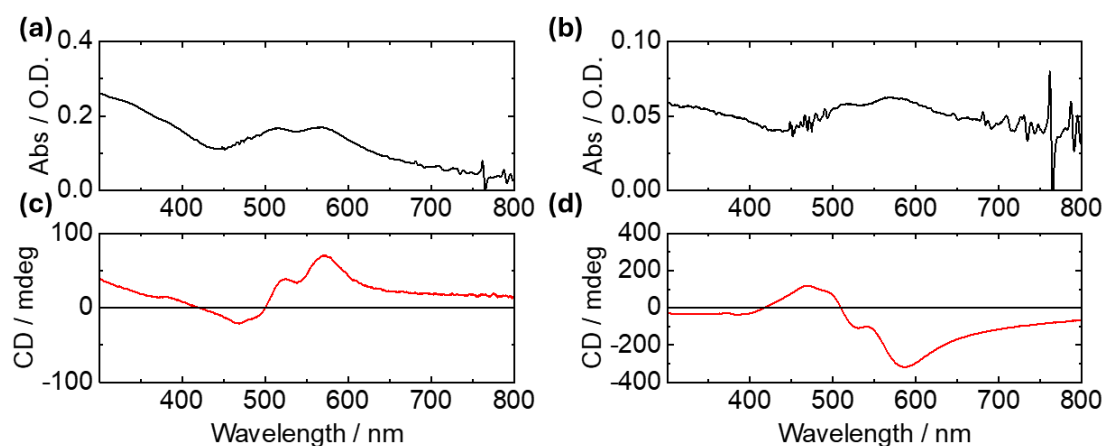


Figure S17. UV-Vis-NIR spectra of drop-casted (a) *S*-PDI and (b) *R*-PDI and CD spectrum of (c) *S*-PDI and (d) *R*-PDI. *R/S*-PDI films were made by drop casting 50 μ L of *R/S*-PDI to quartz plate.

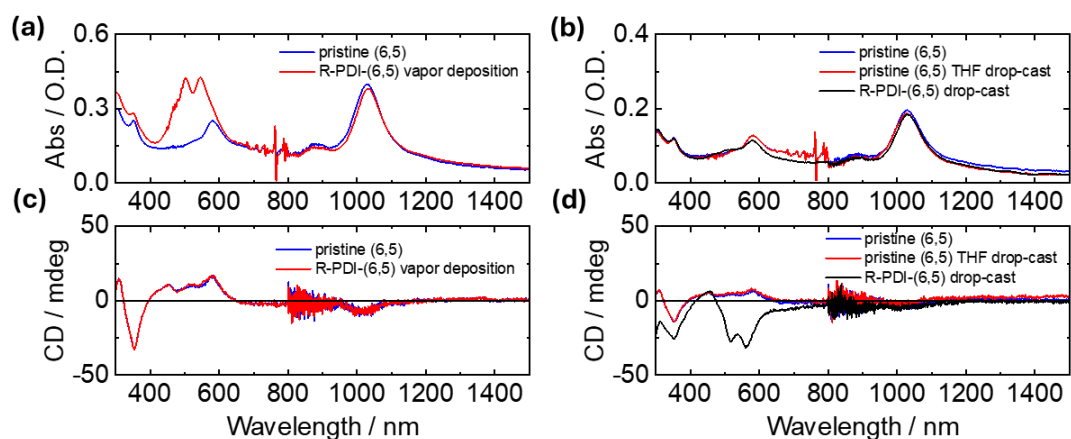


Figure S18. UV-Vis-NIR spectra of *R*-PDI-(6,5) film from another batch, fabricated by (a) vapor deposition and (b) drop-casting of *R*-PDI onto the pristine (6,5) film. CD spectrum of of *R*-PDI-(6,5) film fabricated by (c) vapor deposition and (d) drop-casting.

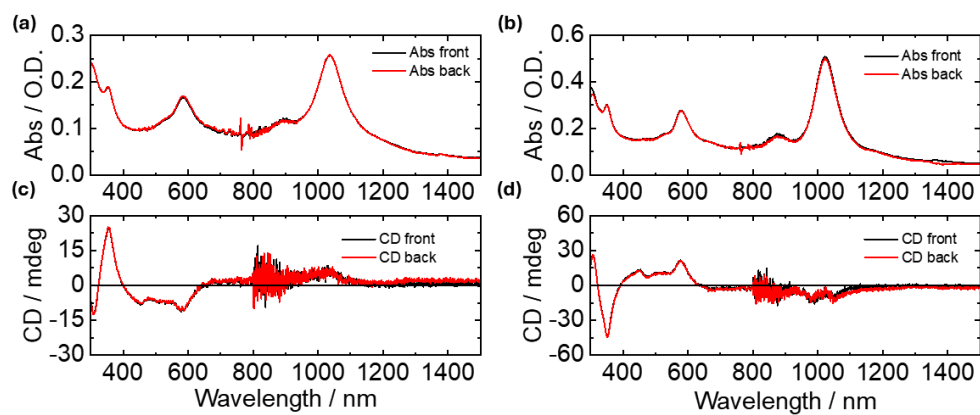


Figure S19. UV-Vis-NIR spectra of (a) pristine (11,-5) and (b) pristine (6,5) and CD spectra of (c) pristine (11,-5) and (d) pristine (6,5), measured from front and back side of the film.

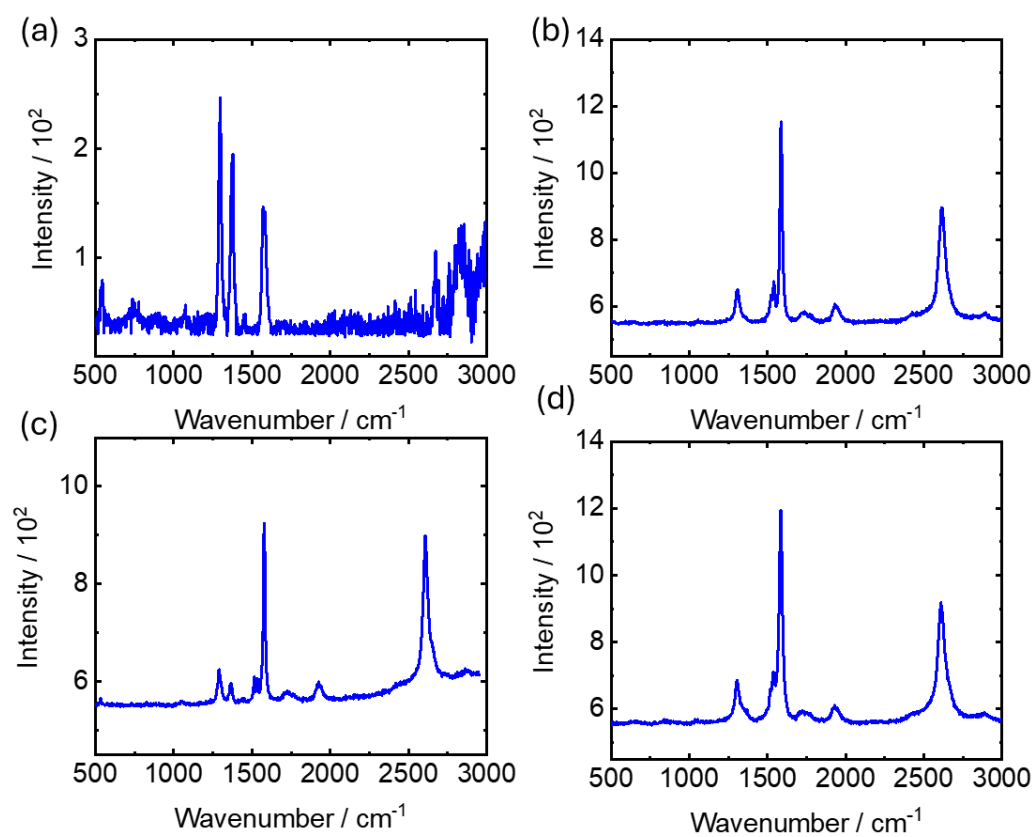


Figure S20. Raman scattering spectra of (a) *R*-PDI, (b) pristine (11,-5), (c) *R*-PDI-(6,5), and (d) *R*-PDI-(6,5) after washing by CHCl_3 for 2h at the boiling point, 334 K (61°C).

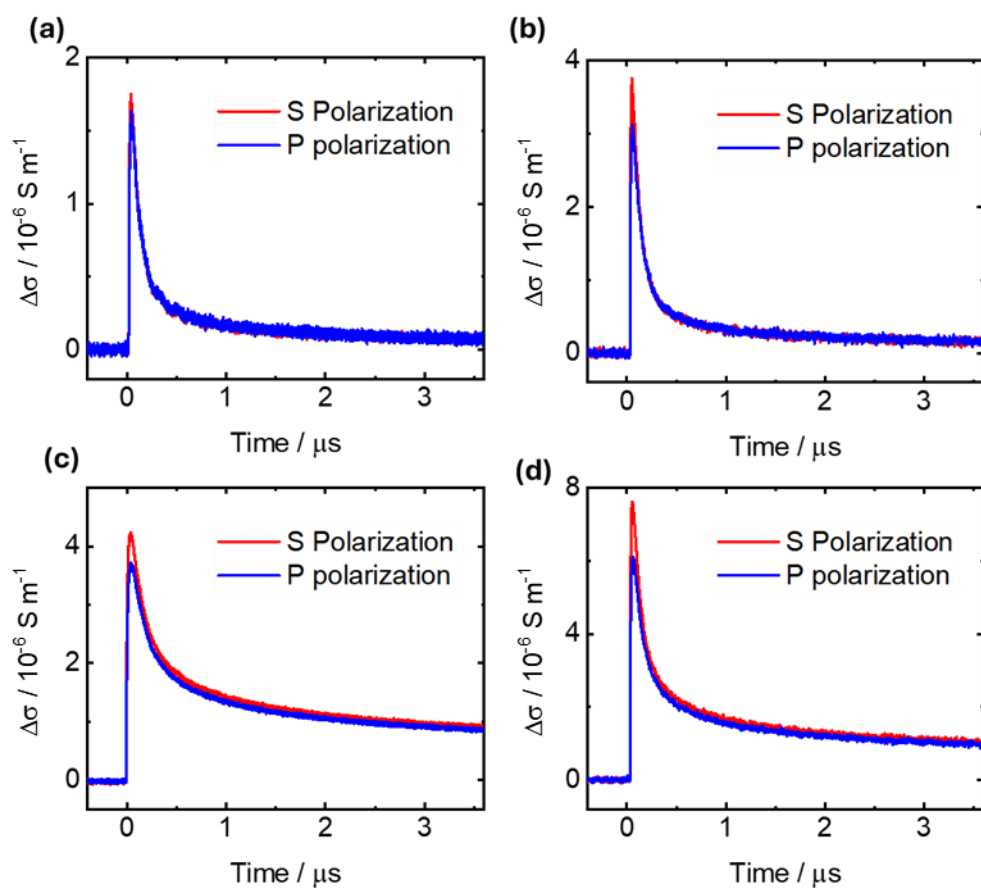


Figure S21. Linear polarization dependent FP-TRMC traces of (a) 355 nm (b) 1020 nm excitation of pristine (11,-5) film and (c) 355 nm (d) 1020 nm excitation of *S*-PDI-(11,-5) film. . Linear polarization state of the excitation pulse was adjusted to S- (red) and P- (blue) polarization. The excitation pulse was tuned to 0.5 mJ pulse⁻¹ cm⁻² at 355 nm and 1 mJ pulse⁻¹ cm⁻² at 1020 nm, respectively.

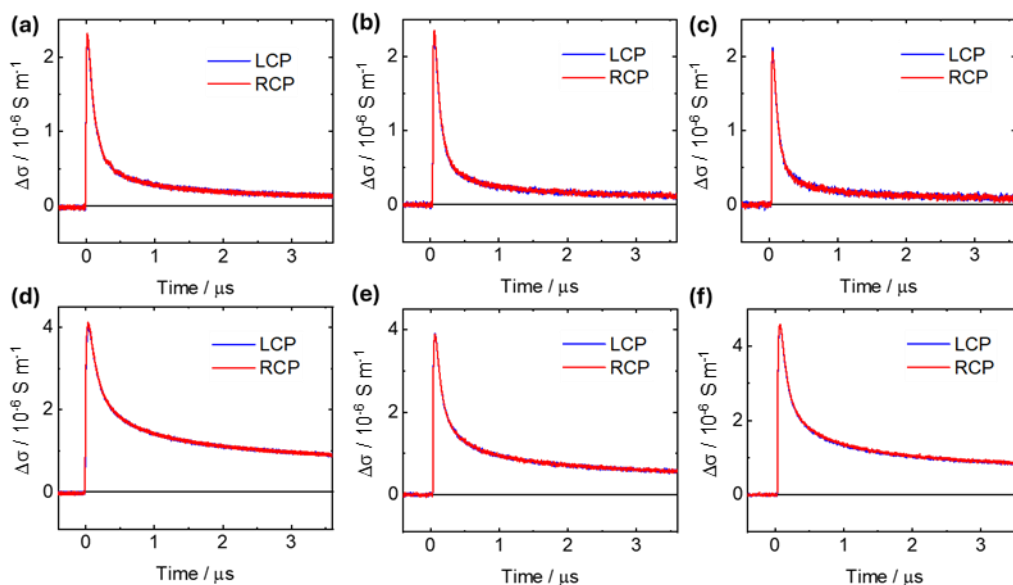


Figure S22. CPL-TRMC traces of (a) 355 nm (b) 580 nm (c) 1020 nm excitation of pristine (11,-5) film and (d) 355 nm (e) 580 nm (f) 1050 nm excitation of *S*-PDI-(11,-5) film. The excitation pulse was tuned to 0.5 mJ pulse⁻¹ cm⁻² at 355 nm and 1 mJ pulse⁻¹ cm⁻² at 580 and 1020 nm, respectively. Circular polarization state of the excitation pulse was adjusted LCP (blue) and RCP (red).

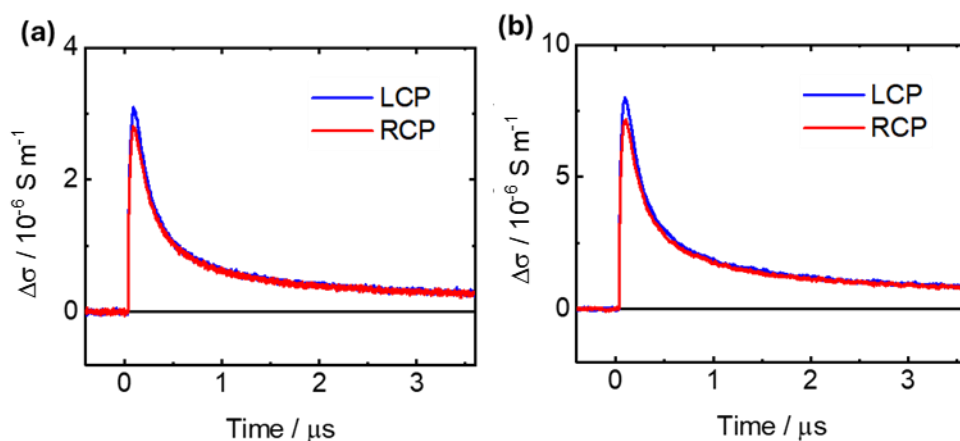


Figure S23. 1020 nm excitation of (a) washed and (b) *S*-PDI re-deposited (6,5) film. 50 μL of *S*-PDI 1 mg/mL tetrahydrofuran solution was drop-casted washed (6,5) film to produce *S*-PDI deposited film. The excitation pulse was tuned to 1 mJ pulse⁻¹ cm⁻². Circular polarization state of the excitation pulse was adjusted LCP (blue) and RCP (red).

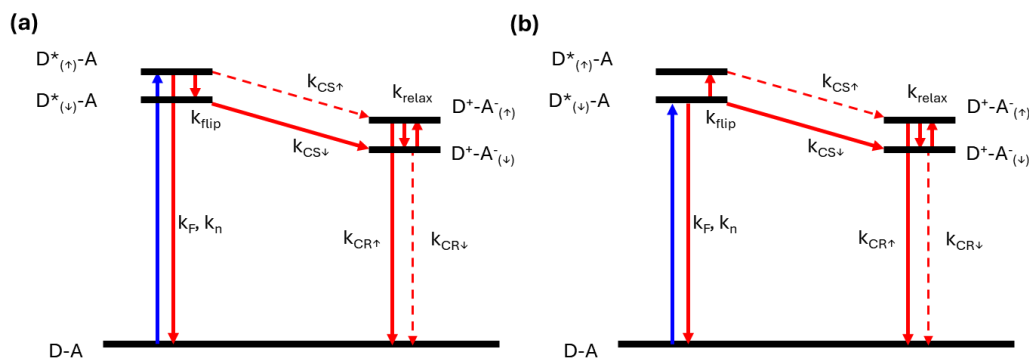


Figure S24. Schematics of photophysical process upon excitation of up-and down-spin of donor in chiral donor-acceptor composite. k_n , k_F , k_{flip} , $k_{\text{CS}\downarrow}$, $k_{\text{CS}\uparrow}$, k_{relax} , $k_{\text{CR}\downarrow}$ and $k_{\text{CR}\uparrow}$ stands for rate constant of nonradiative decay, radiative decay, spin flip, charge separation of up-spin, charge separation of down-spin, spin relaxation, charge recombination of up-spin and charge recombination of down-spin, respectively.

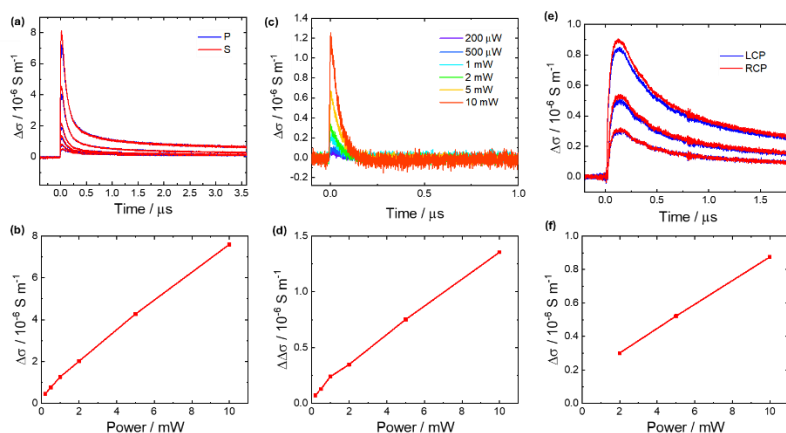


Figure S25. Fluence dependence in FP-TRMC with linear polarization of pristine (11,-5) film upon 355 nm excitation (a-d). (a) S - and P - polarization dependent FP-TRMC traces measured in 0.2, 0.5, 1, 2, 5, and 10 mW (b) power-conductance curve calculated from the average peak value of S - and P - polarization. (c) differential conductance traces measured in 0.2, 0.5, 1, 2, 5, and 10 mW. (d) power-differential conductance curve calculated from the peak value. Fluence dependence in CPL-TRMC of R-PDI-(6,5) film upon 355 nm excitation (e-f). (e) CPL-TRMC traces measured in 2, 5, and 10 mW. (f) Power-conductance curve calculated from the average peak value of LCP and RCP excitation.

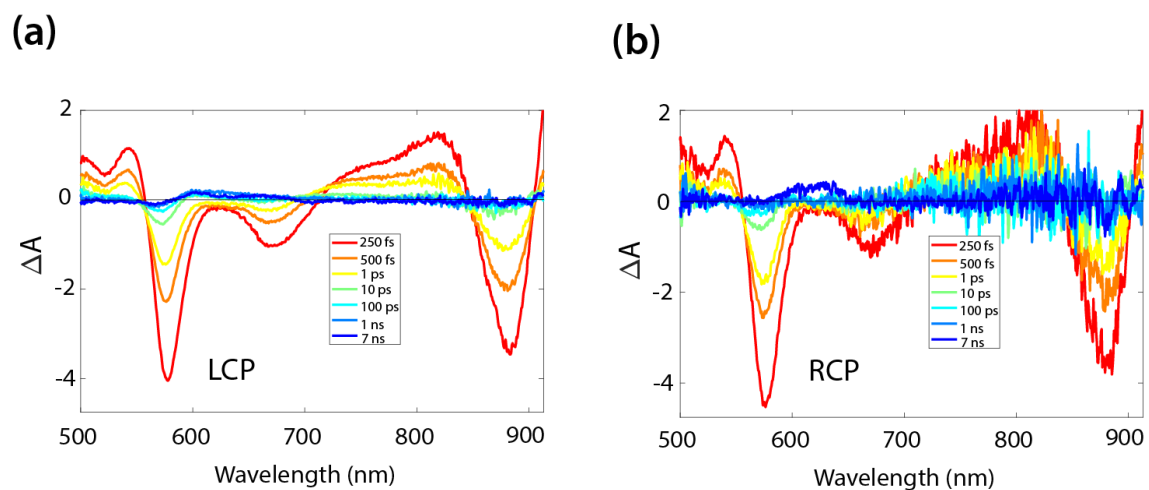


Figure S26. Femtosecond transient absorption spectra of the *R*-PDI-(6,5) film, pumped at 1000 nm to excited the E_{11} with either (a) LCP (b) RCP pump.

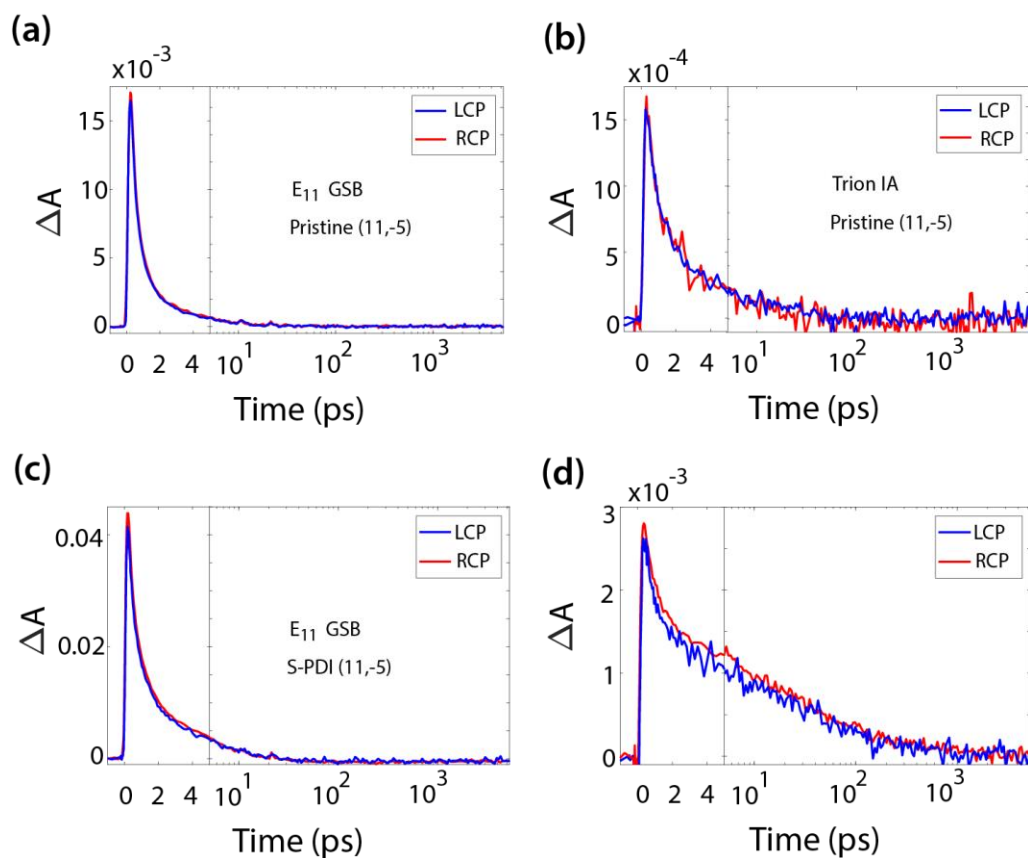


Figure S27. Dynamics from femtosecond transient absorption spectra of the pristine (11,-5) and S-PDI-(11,-5) films, pumped at 1000 nm to excite the (11,-5) E_{11} with either a LCP (blue) or RCP pump (red) beam and probed with a linear probe beam. Dynamics probed at (a) 1035 nm and (b) 1200 nm of pristine (11,-5) film and dynamics probed at (c) 1035 nm and (d) 1200 nm of S-PDI-(11,-5) film.

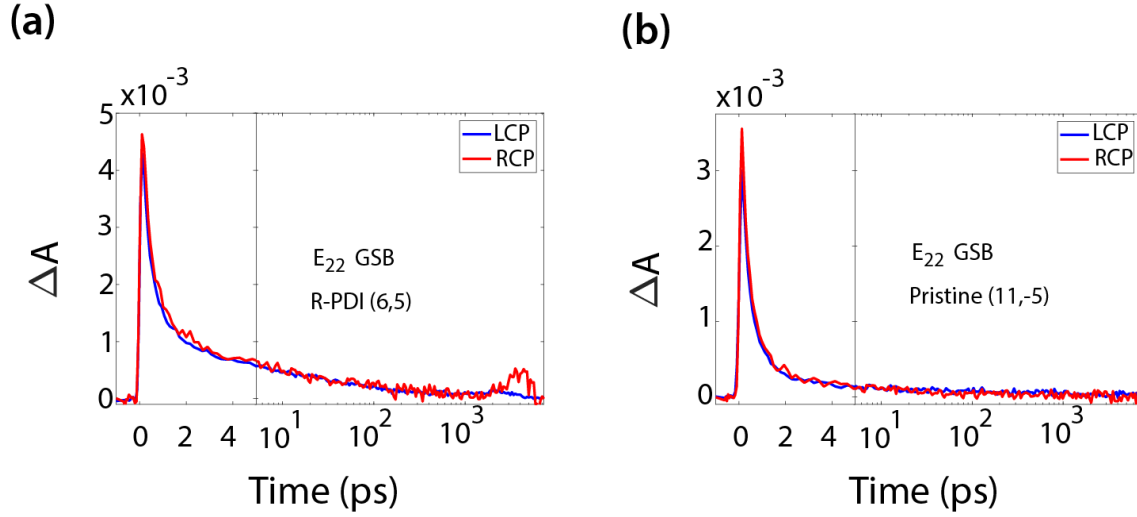


Figure S28. Dynamics from probe-polarization dependent femtosecond transient absorption spectroscopy of the *R*-PDI-(6,5) and pristine (11,-5) films, pumped at 1020 nm to excited the E_{11} with either a LCP (blue) or RCP pump (red) beam and probed with a circularly polarized probe beam with same polarization to the pump beam. Dynamics probed at 576 nm (a) *R*-PDI-(6,5) and (b) pristine (11,-5) film.

Table S1. Standard uncertainties of decay fitting coefficients of CPL-TRMC traces.

$\lambda_{\text{exc}} / \text{nm}$		$t_1^{\text{a}} / \text{ns} (\%)$	$t_2^{\text{a}} / \text{ns} (\%)$	$y_0 (\%)$	$A_1 (\%)$	$A_2 (\%)$
355	LCP	0.62 (0.31)	5.33 (0.44)	0.19	0.15	0.26
	RCP	1.77 (0.88)	4.79 (0.40)	0.18	0.14	0.25
580	LCP	2.17 (1.09)	17.3 (1.46)	0.69	0.54	0.98
	RCP	1.71 (0.85)	16.6 (1.37)	0.69	0.40	0.86
1020	LCP	1.63 (0.83)	18.3 (1.49)	0.70	0.39	0.88
	RCP	2.12 (0.98)	25.1 (1.88)	0.92	0.47	0.99

^aPhotoconductivity traces were fitted with the function $\varphi(t) \sum \mu = A_1 e^{t/\tau_1} + A_2 e^{t/\tau_2} + y_0$

Conclusion

In this thesis, the structure and the optoelectronic properties of the various π -conjugated materials in condensed phase were extensively studied with the combination of various steady and time-resolved spectroscopic techniques.

In chapter 1, crystalline particles of poly-3-hexylthiophene P3HT-CP was fabricated by new method and the morphological characteristics of the polymer particle was examined through electron microscopy and steady-state spectroscopic methods. The P3HT-CP particles were fabricated by solvent-vapor diffusion and separated by centrifugation. The electron diffraction pattern observed in TEM and the sharp edge observed in SEM indicates the long-range ordering through the conjugation and stacking direction, and analysis on the PXRD pattern yield crystallite size in interchain plain of 9.2 nm, which is comparable to the crystalline nanowires. Further analysis on the vibronic bands in absorption spectrum suggests approximately 50 interacting thiophene repeating units, which is close to the chain length of the P3HT used for crystalline particle fabrication.

In chapter 2, effect of protonation on the packing structure and the optoelectronic properties induced by protonation in solid state were studied with **TTF₂-Rub**, which is a core modified expanded porphyrin fused with two benzotetrathiafulvalene. Protonation induced change in packing structure was examined with X-ray crystallography and the significant packing structure change in the solid state was observed upon the protonation of **TTF₂-Rub**, featuring close π -stacking of TTF units which is not observed in the packing of neutral **TTF₂-Rub**. Formation of effective conducting pathway through stacked TTF units was confirmed by FP-TRMC, giving significantly increased conductivity of $\phi\Sigma\mu = 1.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in **H₂TTF₂-Rub²⁺** crystallites while neutral **TTF₂-Rub** crystallites are giving negligible conductivity.

In chapter 3, a new spectroscopic method CPL-TRMC for tracking circular-polarization dependent conductivity was developed and demonstrated on the composite of chiral PDI and handedness-sorted SWCNTs. Spin-dependent charge separation in *R*-PDI-(6,5) film was tracked with extensive analysis on the linear polarization and circular polarization dependence in the TRMC and TA measurement to elucidate the origin of the CPL dependence

observed in CPL-TRMC measurements. Spin-dependent charge separation in carbon nanotube activated by excitation of E_{11} band of the SWCNT which yields opposite trend to the CD was observed in CPL-TRMC while excitation of E_{33} and E_{22} band are not yielding spin-dependence. The difference in the charge separation pathway between excitation E_{33} and E_{11} band of SWCNT was elucidated through linear polarization dependence in FP-TRMC, that intra-tubular charge separation is preferred in E_{33} transition in contrast to E_{11} which prefers inter-tubular charge separation. The early photophysical processes were tracked with circular polarization resolved fs-TA and ultrafast charge separation in SWCNT was estimated be the source of the circular-polarization dependent CPL-TRMC trace observed upon E_{11} band excitation.

Throughout the thesis, the author demonstrated how the various spectroscopic methods can be employed and analyzed together in the research on π -conjugated materials in solid state to investigate their structural and electronic properties. Based on the knowledge on the spectroscopic methods, the author developed new spectroscopic method CPL-TRMC for the analysis of spin-dependent process in chiral materials in condensed phase and successfully demonstrated how this technique can be utilized in the research with conjunction to other spectroscopic methods.

List of Publication

Chapter 1

1. “Poly(3-hexylthiophene) Crystalline Cubes: A Facile Preparation of Polymer Particles Featuring Long-range Ordering”

Won-Young Cha, Jae-yeon Lee, Jinwoo Park, **Yun Hee Koo**, Juhyun Park, Shu Seki, Won-Suk Kim, and JaeHong Park, *Chemistry Letters* **2020**, 49 (12), 1494–1496.

Chapter 3

2. “Circularly Polarized Light-Induced Microwave Conductivity Measurement: Rapid Screening Technique of Electronic Conductivity in Chiral Molecular Materials”

Yun Hee Koo, Yusuke Tsutsui, Mikito Omoto, Yohei Yomogida, Kazuhiro Yanagi, Yuichiro K. Kato, M. Alejandra Hermosilla-Palacios, Jeffrey L. Blackburn, and Shu Seki, *The Journal of Physical Chemistry Letters* **2025**, 16, 13 3232–3239.

Supplementary Publication

3. “Synthesis and electron-transport properties of a stable antiaromatic Ni II norcorrole with the smallest meso-substituent”

Shusaku Ukai, **Yun Hee Koo**, Norihito Fukui, Shu Seki and Hiroshi Shinokubo, *Dalton Transactions* **2020**, 49 (41), 14383-14387.

4. “Dibenzodiazapyracylenes: Doubly N-Doped Cyclopenta-fused Polycyclic Molecules That Exhibit High Carrier Mobility”

Yuki Morimoto, **Yun Hee Koo**, Kazuya Otsubo, Hidetsugu Kitakado, Shu Seki, Atsuhiko Osuka and Takayuki Tanaka, *Angewandte Chemie* **2022** 134(14), e202200341.

5. “Truxenone Triimide: Two-Dimensional Molecular Arrangements of Triangular Molecules for Air Stable n-Type Semiconductors”
Sharvan Kumar, **Yun Hee Koo**, Tomohiro Higashino, Wakana Matsuda, Samrat Ghosh, Yusuke Tsutsui, Masayuki Suda, Hiroshi Imahori, Katsuaki Suzuki, Hironori Kaji and Shu Seki, *Advanced Electronic Materials* **2022**, 8(7), 2101390.
6. “Norcorroles as antiaromatic π -electronic systems that form dimension-controlled assemblies”
Soh Ishikawa, Kazuhisa Yamasumi, Shinya Sugiura, Shunsuke Sato, Go Watanabe, **Yun Hee Koo**, Shu Seki, Yuya Bando, Yohei Haketa, Hiroshi Shinokubo and Hiromitsu Maeda, *Chemical Science* **2024**, 15(20), 7603-7609.
7. “Photoconductivity Switching in Semiconducting Two-Dimensional Crystals via Molecular Tetris”
Kalipada Koner, Kaustav Das, Rajendra Prasad Paitandi, Rohan Mahapatra, Abhradeep Sarkar, Adhra Sury, **Yun Hee Koo**, Yingying Zhang, Thomas Heine, Agnieszka Kuc, Pramod P. Pillai, Shu Seki, Malla Reddy and Rahul Banerjee, *Journal of the American Chemical Society* **2025**, 147, 11, 9972–9980

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