Synthesis of Through-space Conjugated Polymers Containing the Pseudo-*ortho*-linked [2.2]Paracyclophane Moiety

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Summary

New through-space conjugated polymers comprising the pseudo-*ortho*-linked [2.2]paracyclophane moiety were synthesized by the Sonogashira coupling reaction. All the synthesized polymers were soluble in common organic solvents and could form thin films. The UV-vis absorption spectra of the synthesized polymers revealed an extension of the conjugation length owing to the through-space interactions. The polymers exhibited a blue-light emission in both solution and film states.

Introduction

[2.2]Paracyclophane has a compelling molecular structure consisting of two co-facial benzene rings in close proximity (ca. 2.8–3.1 Å) fixed by two ethylene chains [1]. The transannular electronic interaction between the co-facial benzene rings of [2.2]paracyclophane has attracted considerable attention [2], and a number of [2.2]paracyclophane derivatives have been prepared and characterized [3]. However, despite their potential application as a component of functional polymers, there have been a few studies on the incorporation of [2.2]paracyclophane and its derivatives into the conjugated polymer main chain [4]. Recently, we focused our attention on the synthesis of conjugated polymers comprising [2.2]paracyclophane as the repeating unit in their main chain [5–7]. This synthesis would give rise to a whole new class of conjugated polymers in which the conjugation length is extended via the through-space interaction of the benzene rings. In previous studies, pseudo-*para*-disubstituted [2.2]paracyclophane was used as the key monomer in the construction of a through-space conjugated framework [5–7].

The following are seven isomers of the disubstituted [2.2]paracyclophane: *ortho*-, *meta*-, *para*-, pseudo-*ortho*-, pseudo-*meta*-, pseudo-*para*-, and pseudo-*geminal*-disubstituted [2.2]paracyclophanes. Among these isomers, pseudo-*para*-dibromo[2.2]paracyclophane can be easily obtained from commercially available [2.2]paracyclophane [8]. Thermal isomerization of pseudo-*para*-dibromo[2.2]paracyclophane thus obtained conveniently affords pseudo-*ortho*-dibromo[2.2]paracyclophane [8,9]. Therefore, we decided to employ pseudo-*ortho*-linked [2.2]paracyclophane as a building block for through-space

conjugated polymers. In this report, we describe the synthesis of novel through-space conjugated polymers comprising pseudo-*ortho*-linked [2.2]paracyclophane in the main chain and compare the obtained polymer with the polymers possessing the pseudo-*para*-linked [2.2]paracyclophane units.

Experimental

General

^1H and ^{13}C NMR were recorded on a JEOL EX270 and 400 instrument at 270 and 400 MHz and 67.5 and 100 MHz, respectively. All samples were analyzed in $CDCl_3$, and chemical shift values were expressed relative to Me_4Si as an internal standard. UV-vis measurements were carried out on JASCO V-530 spectrophotometer at room temperature. Photoluminescence spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8020 and RI-8020 (TOSOH TSKgel G3000 column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Recyclable preparative high-performance liquid chromatography (HPLC) was performed for further purification of polymers on a Japan Analytical Industry Co. Ltd., Model 918R (JAIGEL-2.5H and 3H columns) using $CHCl_3$ as an eluent. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials

Et_2O, THF and NEt_3 were purified by passage through solvent purification columns under Ar pressure [10]. [2.2]Paracyclophane **1** was purchased from Sigma-Aldrich Co. *n*-BuLi (1.59 M in hexane) was purchased from Kanto Chemical Co., Inc. CH_2Cl_2, CCl_4, Br_2, Fe, triglyme, *t*-BuOK, and CuI were purchased from Wako Pure Chemicals Industries. $Pd(PPh_3)_4$ was purchased from Tokyo Chemical Industry Co., Ltd. Pseudo-*para*-dibromo[2.2]paracyclophane **2** [8], pseudo-*ortho*-dibromo[2.2]paracyclophane **3** [9], dibromomethyltriphenylphosphonium bromide [11], pseudo-*ortho*-diethynyl[2.2]paracyclophane **5** [9c], 2,5-dialkoxy-1,4-diiodobenzenes **6a-c** [12], and pseudo-*para*-diethynyl[2.2]paracyclophane **9** [6f] were synthesized according to the literature. Pseudo-*ortho*-diformyl[2.2]paracyclophane **4** was synthesized according to the literature with minor modification by using DMF as a reagent for formylation instead of formylpiperidine [9c], and the spectral data were matched with the literature's values [9c].

Polymerization

All of the solid reagents **5** (40 µmol), **6** (40 µmol), $Pd(PPh_3)_4$ (9.2 mg, 8 µmol), and CuI (1.5 mg, 8 µmol) were placed in a Schlenk tube equipped with a magnetic stirring bar and a three-way cock. This tube was then purged with Ar followed by introducing THF (1.2 mL) and Et_3N (1.2 mL). The reaction was carried out at 75°C for 48 h. After the reaction, ammonium salt was filtered off with celite and washed with THF. The combined organic solution was concentrated and washed with aqueous NH_3 solution (28%) to remove the inorganic species. The organic layer was dried over Na_2SO_4. The condensed organic layer was reprecipitated from EtOH, and

further reprecipitation from CHCl$_3$/EtOH was carried out at least three times to obtain the corresponding polymer as a yellow solid. Further purification by HPLC was carried out for polymers **7b** and **7c**.

7a. Yield: 58%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.79 (s, 6H), 1.20 (m, 16H), 1.45 (s, 4H), 1.82 (m, 4H), 2.85 (br, 2H), 3.04 (br, 2H), 3.30 (br, 2H), 3.79 (br, 2H), 3.91 (br, 4H), 6.53 (br, 4H), 7.00 (m, 2H), 7.20 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.1, 22.6, 26.3, 29.3, 29.6 (overlapping signals), 31.9, 33.6, 34.4, 69.4, 89.9, 95.0, 114.0, 116.1, 125.2, 132.9, 133.4, 134.1, 139.7, 142.2, 153.5.

7b. Yield: 23%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.85 (s, 6H), 1.22 (m, 32H), 1.44 (s, 4H), 1.83 (m, 4H), 2.86 (br, 2H), 3.04 (br, 2H), 3.30 (br, 2H), 3.79 (br, 2H), 3.91 (br, 4H), 6.54 (br, 4H), 6.99 (m, 2H), 7.21 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.1, 22.7, 26.4, 29.2, 29.4, 29.7 (overlapping signals), 31.9, 33.7, 34.4, 69.4, 90.0, 94.9, 114.0, 116.2, 125.3, 132.9, 133.4, 134.2, 139.7, 142.3, 153.5.

7c. Yield: 18%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.87 (s, 6H), 1.25 (m, 48H), 1.44 (s, 4H), 1.83 (m, 4H), 2.86 (br, 2H), 3.04 (br, 2H), 3.30 (br, 2H), 3.80 (br, 2H), 3.90 (br, 4H), 6.54 (br, 4H), 6.99 (m, 2H), 7.21 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.1, 22.7, 26.4, 29.4, 29.7, 29.8 (overlapping signals), 32.0, 33.7, 34.4, 69.4, 90.0, 95.0, 114.1, 116.1, 125.3, 133.0, 133.4, 134.2, 139.7, 142.3, 153.6.

Model compound 8

Ethynylxylene (0.32 g, 2.5 mmol), **6c** (0.70 g, 1.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (71 mg, 0.10 mmol), and CuI (18 mg, 0.090 mmol) were placed in a Schlenk tube equipped with a magnetic stirring bar and a three-way cock. This tube was then purged with Ar followed by introducing THF (5.0 mL) and Et$_3$N (2.0 mL). The reaction was carried out at 50°C overnight. After the reaction, ammonium salt was filtered off. The filtrate was dried and washed with MeOH. The residue was subjected to SiO$_2$ column (hexane/CH$_2$Cl$_2$, v/v = 4/1 as an eluent) to afford **8** as a pale yellow solid (0.57 g, 0.81 mmol, 81%).

Rf = 0.33 (SiO$_2$, hexane/CH$_2$Cl$_2$, v/v = 4/1). ^{1}H NMR (270 MHz, CDCl$_3$): δ 0.88 (t, J = 7.6 Hz, 6H), 1.25-1.36 (m, 32H), 1.51 (m, 4H), 1.84 (m, J = 6.4 Hz, 4H), 2.31 (s, 3H), 2.51 (s, 3H), 4.02 (t, J = 6.4 Hz, 4H), 7.00 (s, 2H), 7.04 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.33 (s, 2H). ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 14.1, 20.2, 20.7, 22.7, 26.1, 29.3, 29.5, 29.6 (overlapping signals), 31.9, 69.5, 89.6, 94.1, 114.0, 116.5, 129.1, 129.3, 132.3, 134.9, 137.2, 153.5. Anal. Calcd. for C$_{50}$H$_{70}$O$_2$: C, 85.41; H, 10.04. Found: C, 85.32; H, 10.15.
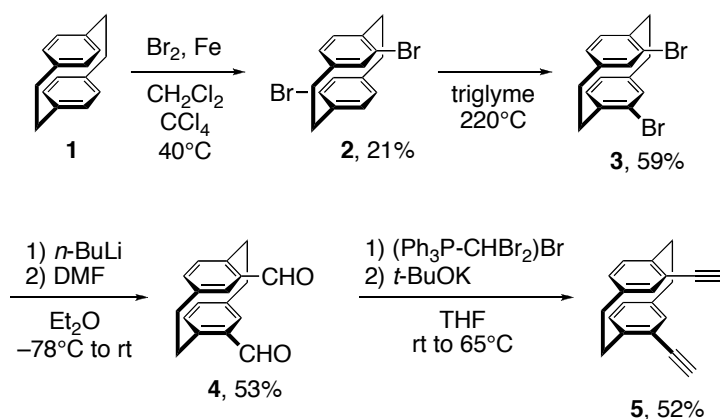
Polymer 10

Pseudo-*para*-diethynyl[2.2]paracyclophane **9** (10.3 mg, 40 μmol), **6b** (33.5 mg, 48 μmol), Pd(PPh$_3$)$_4$ (9.2 mg, 8 μmol), and CuI (1.5 mg, 8 μmol) were placed in a Schlenk tube equipped with a magnetic stirring bar and a three-way cock. This tube was then purged with Ar followed by introducing THF (1.2 mL) and Et$_3$N (1.2 mL). The reaction was carried out at 75°C for 48 h. After the reaction, ammonium salt was filtered off with celite and washed with THF. The combined organic solution was concentrated and washed with aqueous NH$_3$ solution (28%) to remove the inorganic species. The organic layer was dried over Na$_2$SO$_4$. The condensed organic layer was reprecipitated from EtOH, and further reprecipitation from

CHCl$_3$/EtOH was carried out to obtain the corresponding polymer **10** as a yellow solid (18.4 mg, 26.4 μmol, 66%).
^{1}H NMR (270 MHz, CDCl$_3$): δ 0.89 (br, 6H), 1.25-1.59 (br, 36H), 1.96 (br, 4H), 2.94-3.05 (m, 4H), 3.36 (m, 2H), 3.82 (m, 2H), 4.14 (br, 4H), 6.43-6.55 (m, 4H), 7.06-7.16 (m, 4H). ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 14.1, 22.7, 26.3, 29.7 (overlapping signals), 31.9, 34.1, 34.2, 69.6, 89.6, 95.2, 114.0, 116.3, 125.0, 130.3, 133.3, 137.2, 139.6, 142.2, 153.6.

Results and Discussion

Scheme 1 outlines the synthetic procedure for the key monomer, pseudo-*ortho*-diethynyl[2.2]paracyclophane **5**. Iron-catalyzed bromination of [2.2]paracyclophane **1** and successive recrystallization afforded only pseudo-*para*-dibromo[2.2]paracyclophane **2** in 21% yield [8]. Pseudo-*ortho*-dibromo[2.2]paracyclophane **3** was obtained in 59% yield by the thermal isomerization of **2** at 220°C in triglyme [9]. Pseudo-*ortho*-diformyl[2.2]paracyclophane **4** was synthesized by treating **3** with *n*-BuLi and DMF in succession. Diformyl compound **4** was converted to pseudo-*ortho*-diethynyl[2.2]paracyclophane **5**, by a method previously reported by Hopf and coworkers [9c]. Comonomers **6a–c** were synthesized according to the literature's procedure [12].

Scheme 1.   Synthesis of monomer **5**
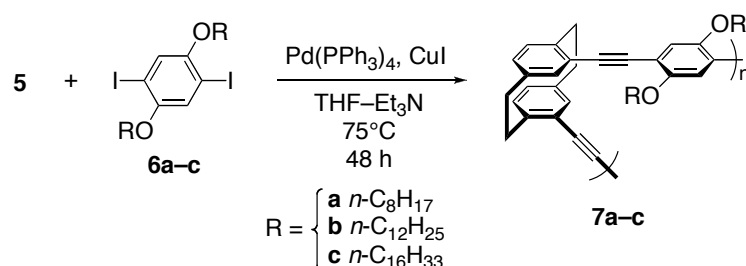
Scheme 2.   Synthesis of polymers **7a–c**

Polymerization was carried out via the Sonogashira coupling reaction, as shown in Scheme 2, and the results are summarized in Table 1. Treatment of monomers **5** and **6a–c** with a catalytic amount of Pd(PPh$_3$)$_4$/CuI in THF–Et$_3$N yielded the corresponding polymers **7a–c** in 58%, 23%, and 18% yields, respectively. Repeated purification of the crude polymers **7a–c** by reprecipitation from a CHCl$_3$/EtOH solution resulted in moderate yields. Further purification by HPLC was carried out for polymers **7b** and **7c**. The molecular weights of the polymers were measured by GPC (CHCl$_3$: eluent) and estimated by using polystyrene standards (Table 1). The obtained polymers were dissolved in common organic solvents such as CHCl$_3$, CH$_2$Cl$_2$, THF, and toluene. Thin films of these polymers were readily obtained by casting and spin-coating from one of the above mentioned solvents.

Table 1. Results of polymerization

Run	Polymer	Yield[a] %	M_n[b]	M_w[b]	M_w/M_n[b]
1	**7a**	58	2000	3100	1.6
2	**7b**	23	3800	4900	1.3
3	**7c**	18	6400	8800	1.4

[a] Isolated yield after reprecipitation at least three times.
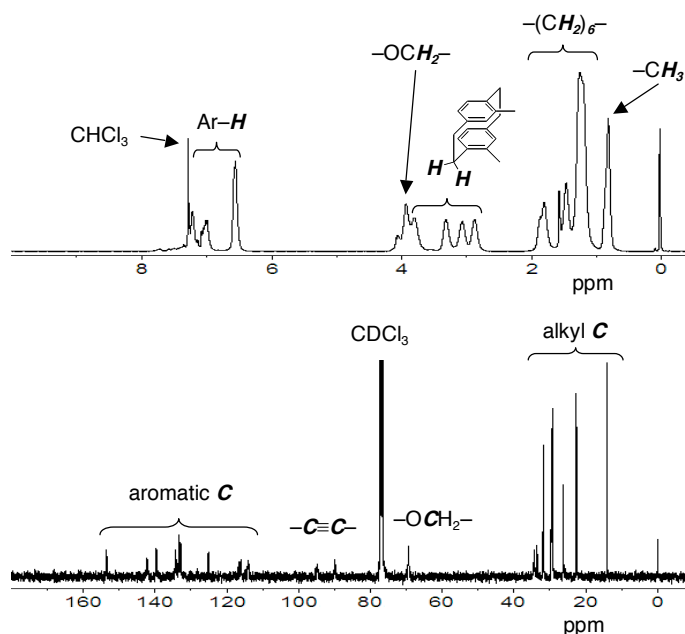[b] GPC (CHCl$_3$), polystyrene standards.

Figure 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of polymer **7a** in CDCl$_3$.

The structures of polymers **7a–c** were confirmed by ^{1}H and ^{13}C NMR spectra. Figure 1 shows the ^{1}H and ^{13}C NMR spectra of polymer **7a** in CDCl$_3$ (400 MHz and

100 MHz, respectively).   In the ^{1}H NMR spectrum of **7a** (Figure 1A), the signal due to the acetylene proton of monomer **5** at 3.28 ppm completely disappeared, indicating the presence of dialkoxyphenyl moieties at the ends of the polymer chain.   Signals at 0.8 ppm, 1.1–1.9 ppm, and 3.9 ppm were assignable to the –Me, –$(CH_2)_6$–, and –OCH_2– groups of the alkoxy side chains, respectively.   The peaks of the bridged methylene protons belonging to the [2.2]paracyclophane units were observed at 2.8–3.8 ppm as four broad signals.   Signals due to the aromatic protons in the [2.2]paracyclophane moieties appeared at 6.5 and 7.0 ppm, and aromatic protons in the alkoxybenzene units were observed at 7.2 ppm.   In the ^{13}C NMR spectrum, typical signals of the carbon-carbon triple bond were observed at 90 and 95 ppm, as shown in Figure 1B.

The optical characteristics of the polymers **7a–c** were studied with the spectrophotometer and luminescence spectrometer; and compared with those of model compound **8** and through-space conjugated polymer **10** consisting of pseudo-*para*-linked [2.2]paracyclophane.   Polymer **10** was synthesized in 66% yield (M_n = 6100) as shown in Scheme 3.   The optical behaviors of polymers **7a–c** were identical irrespective of the length of their alkyl side chains.   A summary of the optical properties is listed in Table 2.   Figures 2 and 3 show the absorption and emission spectra of **7b**, **8**, and **10** in dilute $CHCl_3$.   As shown in Figure 2, polymer **10**, which possesses the pseudo-*para*-linked [2.2]paracyclophane moiety, had the highest absorption maximum at 386 nm.   This was red-shifted relative to polymer **7b** and compound **8**.   However, the absorption spectra of polymers **7b** and **10** exhibited no perceptible difference, while the spectrum of **7b** exhibited a red-shift relative to that of **8**.   These observations are a direct consequence of the introduction of pseudo-*ortho*-linked [2.2]paracyclophane units into the polymer backbone, which resulted in the through-space conjugation in polymer **7b**.

8
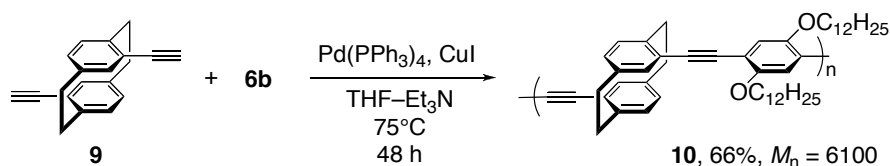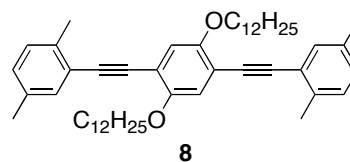
Scheme 3.   Synthesis of polymer **10** containing pseudo-*para*-linked [2.2]paracyclophane

As can be seen from Figure 3, the fluorescence emission spectra of polymers **7b** and **10** were almost similar, and an intense blue emission could be observed for both these polymers.   The fluorescence quantum efficiencies of polymers **7b** and **10** were found to be 0.86 and 0.82 (Runs 1 and 3, in Table 2), respectively, which were estimated from the quantum efficiency of the standard compound 9-anthracenecarboxylic acid. The fluorescence emission spectra of **7b** and **10** were also red-shifted relative to the spectrum of model compound **8**.

Table 2.   Optical properties of **7b**, **8**, and **10**

Run	Compound	Absorption[a] / nm	Emission[b] / nm	Quantum efficiency[c]
1	polymer **7b**	319, 377	411, 434	0.86
2	**8**	320, 369	398, 417	0.86
3	polymer **10**	319, 386	414, 438	0.82

[a] In CHCl$_3$, 1.0×10^{-5} M.
[b] In CHCl$_3$, 1.0×10^{-7} M.
[c] Relative efficiency calculated by using 9-anthracenecarboxylic acid as a standard.

On the other hand, the emission spectra of polymers **7b** and **10** exhibited a clear vibrational structure, similar to the emission spectrum of **8** despite their π-stacked structures (Figure 3).   This result indicates that polymers **7b** and **10** emit blue light in their monomer state rather than in the phane state.   In other words, the emission observed in the case of polymers **7b** and **10** is not from the excimer but from the localized monomer unit [2e–g].   The emission spectrum of thin film of polymer **7b** was broad and red-shifted by approximately 40 nm (λ_{max} = 471 nm) relative to that of **7b** in solution owing to the intermolecular π-π interactions (Figure 3).
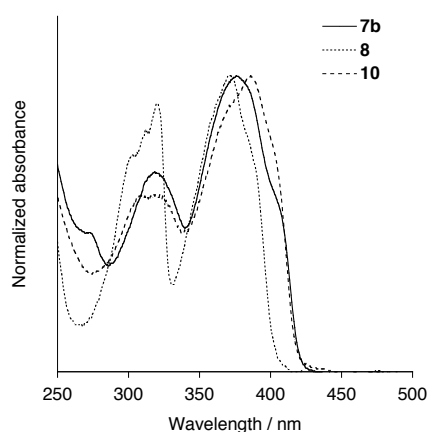

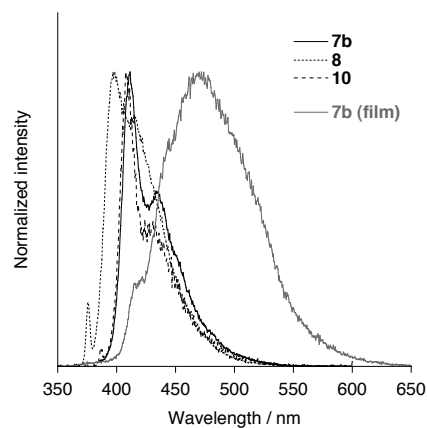Figure 2.   UV-vis absorption spectra of **7b**, **8**, and **10** in CHCl$_3$ (1.0×10^{-5} M).

Figure 3.   Fluorescence emission spectra of **7b** in CHCl$_3$ (1.0×10^{-7} M) and film, **8** in CHCl$_3$ (1.0×10^{-7} M), and **10** in CHCl$_3$ (1.0×10^{-7} M) excited at each absorption maximum.

Conclusion

Through-space conjugated polymers consisting of pseudo-*ortho*-linked [2.2]paracyclophane were synthesized by the Sonogashira coupling reaction.   The polymers exhibited an extension in the conjugation length via the through-space interaction of the [2.2]paracyclophane unit.   An intense blue emission with a fluorescence quantum efficiency of 0.86 was observed from the localized monomer state of the polymer, irrespective of the π-stacked structure in the polymer chain.   The optical profiles of these polymers were similar to those of the pseudo-*para*

analogs; pseudo-*ortho*-disubstituted [2.2]paracyclophane can be used to synthesize foldamers and hold attraction of planar chirality. Our future research will be focused on synthesizing optically active through-space conjugated polymers with planar-chiral pseudo-*ortho*-linked [2.2]paracyclophane and investigating the higher-ordered structures of foldamers.

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