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ORIGINAL PAPER

Synthesis of through-space conjugated polymers containing the pseudo-*ortho*-linked [2.2]paracyclophane moiety

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Abstract 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.

Keywords Pseudo-*ortho*-[2.2]paracyclophane · Conjugated polymer · Through-space interaction

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 [2–8], and a number of [2.2]paracyclophane derivatives have been prepared and characterized [9–11]. 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 [12–15]. Recently, we focused our attention on the synthesis of conjugated polymers comprising

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[2.2]paracyclophane as the repeating unit in their main chain [16–30]. 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 [16–30].

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 [31]. Thermal isomerization of pseudo-*para*-dibromo[2.2]paracyclophane thus obtained conveniently affords pseudo-*ortho*-dibromo[2.2]paracyclophane [31–34]. 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

^{1}H 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 [35]. [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** [31], pseudo-*ortho*-dibromo[2.2]paracyclophane **3** [32–34], dibromomethyltriphenylphosphonium bromide [36], pseudo-*ortho*-diethynyl[2.2]paracyclophane **5** [34], 2,5-dialkoxy-1,4-diiodobenzenes **6a–c** [37], and pseudo-*para*-diethynyl[2.2]paracyclophane **9** [23] 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 [34], and the spectral data were matched with the literature's values [34].

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_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_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_2Cl_2, $v/v = 4/1$ as an eluent) to afford **8** as a pale yellow solid (0.57 g, 0.81 mmol, 81%).

$R_f = 0.33$ (SiO_2, hexane/CH_2Cl_2, $v/v = 4/1$). ^1H 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**

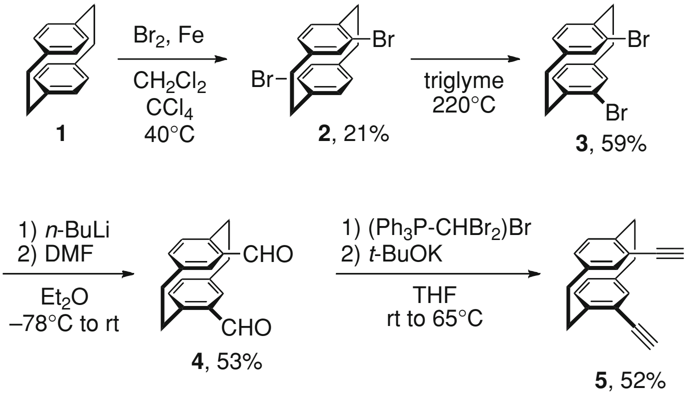
Pseudo-*para*-diethynyl[2.2]paracyclophane **9** (10.3 mg, 40 µmol), **6b** (33.5 mg, 48 µmol), $Pd(PPh_3)_4$ (9.2 mg, 8 µmol), and CuI (1.5 mg, 8 µmol) were placed in a Schlenk tube equipped with a magnetic stirring bar and a three-way cock. This tube was then purged with Ar followed by introducing 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_2SO_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%).

^1H 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.

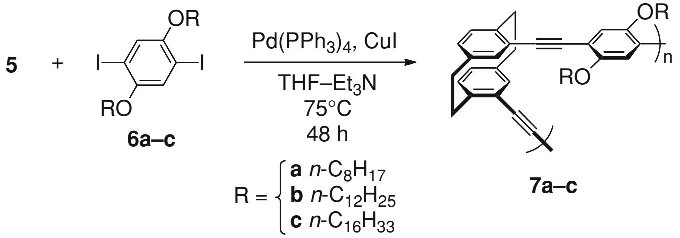
Results and discussion

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 [31]. Pseudo-*ortho*-dibromo[2.2]paracyclophane **3** was obtained in 59% yield by the thermal isomerization of **2** at 220 °C in triglyme [32–34]. 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 co-workers [34]. Comonomers **6a–c** were synthesized according to the literature's procedure [37].

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



Scheme 1 Synthesis of monomer **5**



Scheme 2 Synthesis of polymers **7a–c**

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_2Cl_2, THF, and toluene. Thin films of these polymers were readily obtained by casting and spin-coating from one of the above mentioned solvents.

The structures of polymers **7a–c** were confirmed by ^1H and ^{13}C NMR spectra. Figure 1 shows the ^1H and ^{13}C NMR spectra of polymer **7a** in $CDCl_3$ (400 and 100 MHz, respectively). In the ^1H NMR spectrum of **7a** (Fig. 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, 1.1–1.9, 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 Fig. 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

Table 1 Results of polymerization

Run	Polymer	Yield[a] %	M_n^b	M_w^b	M_w/M_n^b
1	**7a**	58	2,000	3,100	1.6
2	**7b**	23	3,800	4,900	1.3
3	**7c**	18	6,400	8,800	1.4

[a] Isolated yield after reprecipitation at least three times

[b] GPC ($CHCl_3$), polystyrene standards

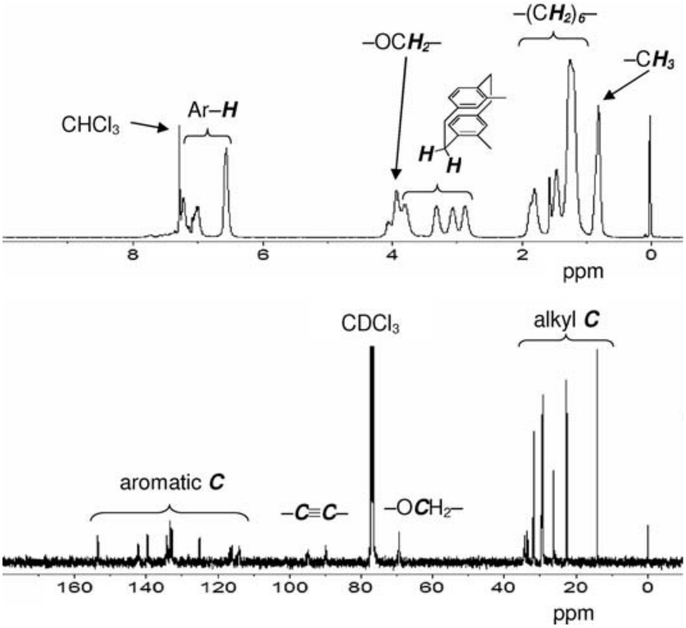
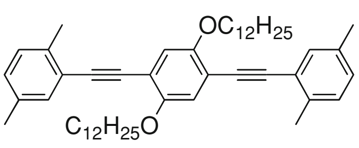


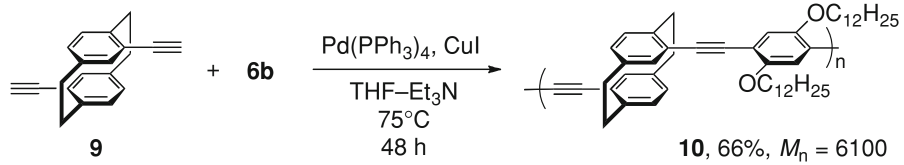
Fig. 1 ^{1}H NMR and ^{13}C NMR spectra of polymer **7a** in $CDCl_3$

pseudo-*para*-linked [2.2]paracyclophane. Polymer **10** was synthesized in 66% yield ($M_n = 6{,}100$) 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 Fig. 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**.

As can be seen from Fig. 3, the fluorescence emission spectra of polymers **7b** and **10** were almost similar, and an intense blue emission could be observed for both



8



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

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

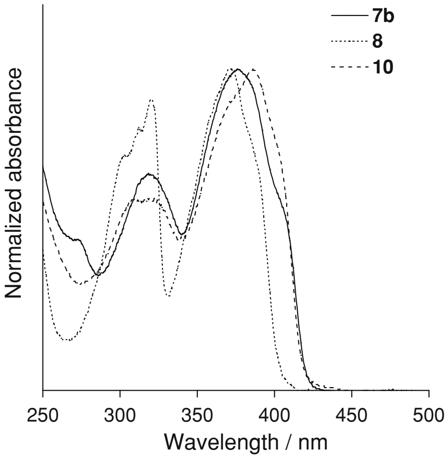
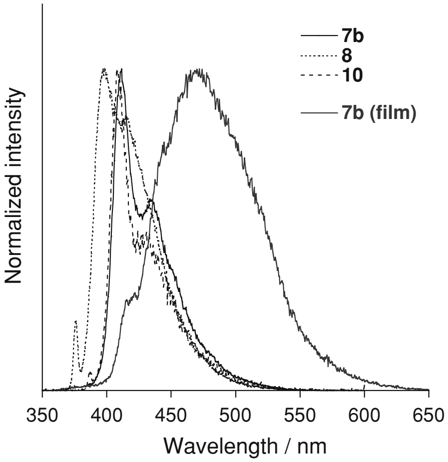


Fig. 2 UV–vis absorption spectra of **7b**, **8**, and **10** in $CHCl_3$ (1.0×10^{-5} M)

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-

Fig. 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



anthracenecarboxylic acid. The fluorescence emission spectra of **7b** and **10** were also red-shifted relative to the spectrum of model compound **8**.

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 (Fig. 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 [6–8]. The emission spectrum of thin film of polymer **7b** was broad and red-shifted by approximately 40 nm ($\lambda_{max} = 471$ nm) relative to that of **7b** in solution owing to the intermolecular π–π interactions (Fig. 3).

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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