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Synthesis and optical properties of the [2.2]paracyclophane-containing π-conjugated polymer with a diacetylene unit

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Summary

Novel through-space π-conjugated polymer based on poly(*p*-phenylene-ethynylene)/poly(*p*-phenylenebutadiynylene) hybrids containing a [2.2]paracyclophane unit in the main chain was synthesized by copper-catalyzed alkyne coupling reaction. The structure of the polymer was supported by ^{1}H NMR and IR spectra. The obtained polymer was soluble in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$ and toluene. The number-average of molecular weight of the polymer was estimated to be 63000 by GPC. The polymer emitted a bluish green light in solution and in the solid state.

Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers [1], because of their unique properties such as electrical conductivity [2], electroluminescence [3], liquid crystallinity [4], third-order nonlinear optical properties [5], and chemical sensing [6]. During the last decade, ever since the first demonstration of a light-emitting diode (LED) based on poly(*p*-phenylenevinylene) (PPV) in 1990 [7], a number of π-conjugated polymers with efficient luminescence have been synthesized, and are being applied to photoluminescence (PL) and/or electroluminescence (EL) materials. Current research interest in conjugated polymers has focused on the tuning of their spectral and electrical properties. The extended strategy toward the appropriate design of π-conjugated polymers involves varying the arylene building block and the strategy to bind arylene units, i.e., binding directly (–Ar–Ar–), with a carbon-carbon double bond (–Ar–C□C–Ar–), with a triple bond (–Ar–C≡C–Ar–), and so on. While polyarylenes, poly(arylenevinylene)s, and poly(arylene-ethynylene)s have played increasingly important roles as organic semiconductors, a few attempts have been made to synthesize the polymers which have a diacetylene moiety (–Ar–C≡C–C≡C–Ar–) in the polymer backbone [8].

On the other hand, [2.2]paracyclophane is a very attractive molecule, because the two

benzene rings face close together. A number of [2.2]paracyclophane derivatives have been prepared to date, and their physical properties have been investigated in detail, due to their characteristic interactions between the two co-facial π-electron systems [9]. In addition, several non-conjugated polymers, which have a paracyclophane skeleton in the main chain [10] or in the side chain [11], have been synthesized. However, few π-conjugated polymers using the longitudinal π-π interactions of cyclophane as a repeating unit have been reported so far [12-13]. In 1985, Mizogami and Yoshimura reported the first synthesis of polymetacyclophane achieved by a polycondensation reaction using an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane, which exhibited a conductivity of 0.25 S cm^{-1} by doping with H_2SO_4 vapor [14]. Recently, we reported the synthesis and physical properties of the first well-defined [2.2]paracyclophane-containing π-conjugated polymers based on poly(*p*-phenylene-ethynylene)s (PPEs) and PPVs. In these studies, we demonstrated that the polymers obtained were capable of extended π-delocalization, via the through-space, with a π-π stacking of a [2.2]paracyclophane moiety [13a, 13c]. In the present study, we report the synthesis and optical properties of the [2.2]paracyclophane-containing π-conjugated polymer having a diacetylene unit, with the aim of controlling the optical properties.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 MHz, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using chloroform as an eluent after calibration with standard polystyrene.

Materials

THF was distilled from sodium benzophenone ketyl under nitrogen. Et_3N and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled from KOH. Chlorobenzene and $CHCl_3$ were distilled from $CaCl_2$. PPh_3, $PdCl_2(PPh_3)_2$, CuI, CuCl, [2.2]paracyclophane (**1**), trimethylsilylacetylene, Bu^n_4NF (1.0 M solution in THF) were obtained commercially, and used without further purification. 4,16-Dibromo[2.2]paracyclophane (**2**) [15] and 2,5-didodecyloxy-1,4-diiodobenzene (**5**) [16] were prepared as described in the literature. All new compounds are characterized below.

4,16-Bis[(trimethylsilyl)ethynyl][2.2]paracyclophane (3). 4,16-Dibromo[2.2]-paracyclophane (**2**) (3.5 g, 9.7 mmol), trimethylsilylacetylene (10 mL), $PdCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol), PPh_3 (0.52 g, 2.0 mmol), and CuI (0.20 g, 1.0 mmol) were

dissolved in 70 mL of THF/Et_3N (v/v = 5:2). The solution was stirred at 75 ^oC for 2 days under a nitrogen atmosphere. Precipitated ammonium salts were filtered off and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO_2 with hexane-$CHCl_3$ (v/v = 2:1, R_f = 0.15) as an eluent to give the compound (**3**) (2.7 g, 6.8 mmol, 81%) as a white powder. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.31 (s, 18H), 2.80 (m, 2H), 2.97 (m. 2H), 3.14 (m, 2H), 3.57 (m, 2H), 6.44 (d, J = 7.8 Hz, 2H), 6.49 (s, 2H), 7.98 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 0.13, 33.5, 34.0, 97.5, 105.8, 124.6, 130.1, 133.0, 137.4, 139.3, 142.6; Anal. Calcd for $C_{26}H_{32}Si_2$: C 77.93, H 8.05. Found: C 77.82, H 8.02.

4,16-Diethynyl[2.2]paracyclophane (4). To a solution of **3** (2.0 g, 5.0 mmol) in 50 mL of THF was added Bu^n_4NF (10 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 20 h under a nitrogen atmosphere. The solution was evaporated under vacuum and the residue was subjected to column chromatography on SiO_2 with hexane-$CHCl_3$ (v/v = 2:1, R_f = 0.55) as an eluent to give the compound (**4**) (1.1 g, 4.5 mmol, 90%) as a white powder. ^1H NMR ($CDCl_3$, 270 MHz): δ 2.92 (m, 4H), 3.19 (m, 2H), 3.27 (s, 2H), 3.59 (m, 2H), 6.44 (d, J = 7.0 Hz, 2H), 6.56 (s, 2H), 7.00 (d, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 33.7, 33.8, 80.2, 83.9, 123.5, 130.6, 133.2, 137.8, 139.5, 142.6; Anal. Calcd for $C_{20}H_{16}$: C 93.71, H 6.29. Found: C 93.45, H 6.26.

4-Iodo-2,5-didodecyloxy-1-[(trimethylsilyl)ethynyl]benzene (6). 2,5-Didodecyloxy-1,4-diiodobenzene (**5**) (1 g, 30 mmol), trimethylsilylacetylene (3.5 g, 35 mmol), $PdCl_2(PPh_3)_2$ (0.70 g, 1.0 mmol), and CuI (0.20 g, 1.0 mmol) were dissolved in 120 mL of THF/Et_3N (v/v = 7:5). The solution was stirred at room temperature for 24 h under a nitrogen atmosphere. Precipitated ammonium salts were filtered off and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO_2 with hexane-$CHCl_3$ (v/v = 9:1, R_f = 0.60) as an eluent to give the compound (**6**) (2.3 g, 3.5 mmol, 12%) as a pale yellow powder. The compound (**5**) (R_f = 0.95) and 2,5-diiodo-1,4-[bis(trimethylsilyl)ethynyl]benzene (R_f = 0.33) were removed by column chromatography. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.26 (s, 9H), 0.88 (t, J = 4.3 Hz, 6H), 1.26-1.31 (m, 32H), 1.51 (m. 4H), 1.79 (m, 4H), 3.93 (t, J = 4.0 Hz, 4H), 6.83 (s, 1H), 7.25 (s, 1H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 0.06, 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6 (overlapping signals), 31.9, 69.8, 70.1, 87.9, 99.4, 100.8, 113.4, 116.3, 123.9, 151.7, 154.9; Anal. Calcd for $C_{35}H_{61}IO_2Si$: C 62.85, H 9.19. Found: C 63.10, H 8.94.

Bis-4,16-[2,5-didodecyloxy-4-[(trimethylsilyl)ethynyl]phenyl]ethynyl][2.2]paracyclophane (7). The compound (**4**) (0.39 g, 1.5 mmol), **6** (2.0 g, 3.0 mmol), $PdCl_2(PPh_3)_2$ (0.070 g, 0.10 mmol), and CuI (0.020 g, 0.10 mmol) were dissolved in 8 mL of THF/Et_3N (v/v = 5:3). The solution was stirred at 50 ^oC for 24 h. Precipitated ammonium salts were filtered off and the filtrate was evaporated under vacuum. The residue was subjected to column chromatography on SiO_2 with hexane-$CHCl_3$ (v/v = 1:1, R_f = 0.67) as an eluent to give the compound (**7**) (2.0 g, 1.5 mmol, 99%) as a white powder. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.25 (s, 18H), 0.86 (t, J = 4.7 Hz, 6H), 0.87 (t, J = 4.7 Hz, 6H), 1.25-1.36 (m, 64H), 1.53 (m. 8H),1.81 (m, 4H), 1.91 (m, 4H), 2.89 (m, 2H), 3.00 (m, 2H), 3.30 (m, 2H), 3.76 (m, 2H), 4.03 (t, J = 4.3 Hz, 4H), 4.05 (t, J = 4.3 Hz, 4H), 6.49 (d, J = 5.4 Hz, 2H), 6.59 (s, 2H), 6.98 (s, 2H), 7.08 (d, J = 5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 0.00, 14.1, 22.7, 26.1, 26.2, 26.6, 29.1, 29.3, 29.4, 29.5, 29.6

(overlapping signals), 31.9, 32.2, 33.8, 34.1, 69.5, 69.6, 89.2, 95.2, 99.5, 101.3, 100.8, 113.4, 114.5, 116.5, 117.3, 124.8,130.6, 133.2, 137.1, 139.6, 142.2, 153.5, 154.1; Anal. Calcd for $C_{90}H_{136}O_4Si_2$: C 80.78, H 10.24. Found: C 80.00, H 10.11.

Bis-4,16-[2,5-didodecyloxy-4-[(ethynyl)phenyl]ethynyl][2.2]paracyclophane (8). To a solution of **7** (1.9 g, 1.4 mmol) in 20 mL of THF was added Bu^n_4NF (0.50 mL, 1.0 M solution in THF). The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The solution was evaporated under vacuum and the residue was subjected to column chromatography on SiO_2 with hexane-$CHCl_3$ (v/v = 2:1, R_f = 0.55) as an eluent to give the compound (**8**) (0.61 g, 0.51 mmol, 36%) as a yellow powder. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.87 (t, J = 4.6 Hz, 12H), 1.25 (m, 64H), 1.50 (m. 8H), 1.88 (m, 8H), 2.93 (m, 4H), 3.30 (m, 2H), 3.36 (s, 2H), 3.72 (m, 2H), 4.05 (m, 4H), 4.05 (t, J = 4.3 Hz, 4H), 6.51 (d, J = 7.5 Hz, 2H), 6.60 (s, 2H), 7.03 (s, 2H), 7.10 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 14.1, 22.7, 25.9, 26.2, 29.2, 29.3, 29.5, 29.6 (overlapping signals), 31.9, 33.8, 34.1, 69.3, 69.7, 80.1, 82.1, 89.1, 95.3, 112.3, 114.9, 117.0, 124.8, 130.6, 133.2, 137.2, 139.6, 142.2, 142.3, 153.4, 154.1; Anal. Calcd for $C_{84}H_{120}O_4$: C 84.51, H 10.13. Found: C 84.04, H 10.09.

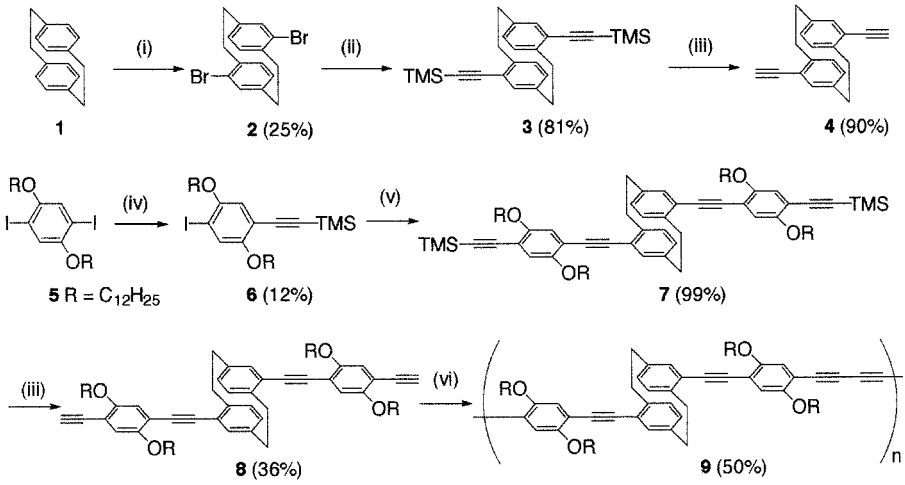
Polymerization

A typical procedure is as follows. A 50-mL Pyrex flask was charged with **8** (0.12 g, 0.10 mmol), CuCl (1.2 mg, 0.012mmol), TMEDA (1.6 mg, 0.012 mmol), chlorobenzene (1.0 mL), and a stirring bar under a flow of nitrogen. Stream of oxygen was bubbled through the reaction mixture for 5 h at room temperature, and the mixture was stirring for additional 67 h (total 3 days) under an oxygen atmosphere. The solution was evaporated. The residue was dissolved in $CHCl_3$ and poured into a large amount of MeOH to give the corresponding polymer (**9**) in 50% yield (60 mg, 0.050 mmol) as a light yellow powder. ^1H NMR ($CDCl_3$, 270 MHz): δ 0.82 (br, 12H), 1.26 (br, 72H),1.87 (br, 8H), 2.85-3.10 (m, 4H), 3.33 (br, 2H), 3.77 (br, 2H), 6.50 (br, 2H), 6.61 (s, 2H), 7.03 (s, 2H), 7.04 (br, 2H); IR (film): 2202 cm^{-1} (vw, –C≡C–), 2142 cm^{-1} (vw, –C≡C–C≡C–).

Results and Discussion

We synthesized the monomer (**8**), which has a dialkoxy substituted phenylene spacer, since the long alkoxy chain provides good solubility for the long and rigid π-conjugated polymer. The synthetic route is shown in Scheme 1. The synthesis of 4,16-diethynyl[2.2]paracyclophane (**4**) started from commercially available [2.2]paracyclophane (**1**). The iron-catalyzed electrophilic dibromination of **1** and recrystallization afforded only pseudo-*p*-dibromo[2.2]paracyclophane (**2**) in 25% isolated yield due to highly poor solubility [15]. The $PdCl_2(PPh_3)_2$/CuI-catalyzed cross-coupling [17] of **2** and trimethylsilylacetylene provided **3** (71%), which was then converted to the compound (**4**) by Bu^n_4NF-promoted desilylation in 90% yield. 4-Iodo-2,5-didodecyloxy-1-[(trimethylsilyl)ethynyl]benzene (**6**) was prepared by the treatment of **5** with trimethylsilylacetylene in the presence of the Pd/Cu catalyst. The reaction of **4** with **6** using a Sonogashira coupling reaction, and finally deprotection of the trimethylsilyl group, gave the desired monomer (**8**) in 36% yield.

The procedure for the synthesis of the polymer (**9**) was carried out as follows (Scheme 1). Treatment of the monomer (**8**) in the presence of a catalytic amount of CuCl and TMEDA for 3 days under an oxygen atmosphere gave the titled polymer (**9**) in 50% yield after purification. The polymer (**9**) was soluble in common organic solvents such as THF, CH_2Cl_2, $CHCl_3$, and toluene. The polymer (**9**) could be processed into a self-standing film, and was thermally stable in solution and in the solid state. The molecular weight measurements were performed by gel permeation chromatography (GPC) in a $CHCl_3$ eluent using a calibration curve of polystyrene standards, and the polymer (**9**) was shown to have the number-average molecular weight (M_n) of 63000, which corresponds to a degree of polymerization of about 52, with a M_w/M_n of 1.6.



Reagents: (i) Br_2, Fe, CH_2Cl_2/CCl_4. (ii) TMS-C≡CH, $PdCl_2(PPh_3)_2$, PPh_3, CuI, THF-Et_3N. (iii) Bu^n_4F, THF. (iv) TMS-C≡CH, $PdCl_2(PPh_3)_2$, CuI, THF/Et_3N. (v) **4**, $PdCl_2(PPh_3)_2$, CuI, THF/Et_3N. (vi) CuCl, TMEDA, O_2, chlorobenzene.

Scheme 1. Monomer and polymer synthesis.

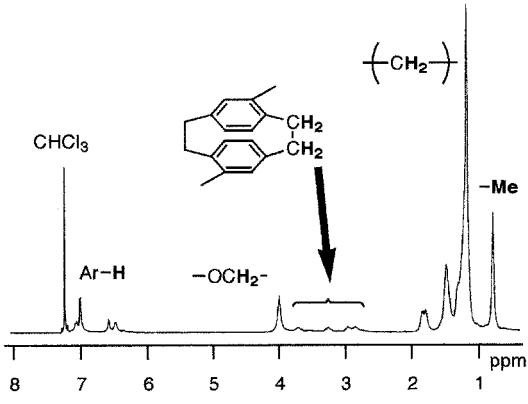


Figure 1. ^1H NMR spectrum of **9** in $CDCl_3$.

This polymer was characterized by the ^1H NMR and IR spectra. In the ^1H NMR spectrum of **9** in $CDCl_3$ (Figure 1), the peak corresponding to the terminal alkyne protons at 3.0 ppm of **8** disappeared. The signals of the alkoxy side chains were dominating in the region of 0.80-2.0 ppm, and the bridged methylenes of the paracyclophane unit appeared at 2.8-3.8 ppm. The methylene groups adjacent to the oxygen were shifted downfield to 4.1 ppm. The signals of the aromatic protons were between 6.5 and 7.0 ppm. The ^{13}C NMR spectrum of **9** was not clearly obtained, due to relatively low solubility. The IR spectrum of **9** in the film state exhibited a very weak absorption peak at 2202 cm^{-1} (–C≡C–) and 2142 cm^{-1} (–C≡C–C≡C–), respectively.

We investigated the optical properties of the polymer (**9**). The absorption and emission spectra of the polymer (**9**) are shown in Figure 2. The polymer (**9**) showed an absorption peak at 310 nm and 406 nm, respectively. Based on the absorption edge, the band gap energy of **9** was about 2.67 eV. The peak of the absorption spectrum of the polymer film was almost the same as in the solution. As shown in Figure 2, the polymer (**9**) exhibited strong blue fluorescence with a peak maximum at 442 nm in dilute $CHCl_3$ solution (1.0×10^{-5} M) at room temperature with an excitation wavelength at 405 nm. The quantum yield (Φ□) for the emission was measured at room temperature in a highly diluted chloroform solution, in which the UV-vis absorbance was between 0.05 and 0.01, and the quantum efficiency of the polymer (**9**) was 0.45 using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard (Φ□ = 0.442) on excitation at 380 nm. The solid state emission spectrum of **9** is also shown in Figure 2. In this spectrum, the peak maximum at 497 nm in the visible green region was red-shifted by 55 nm from that in the solution. In addition, we studied the effect of concentration of the titled polymer solution. As the concentration was increased, the intense peak at 442 nm became highly weak, and the new peak at around 500 nm appeared. These results indicate that the aggregation or the excimer formation of the polymer would occur in the film state [13a].

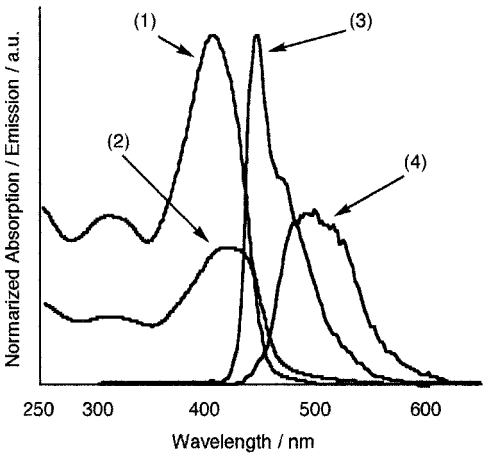


Figure 2. UV-vis spectra of **9** (1) in $CHCl_3$ and (2) in the film state, and fluorescence emission spectra of **9** (3) in $CHCl_3$ (1.0×10^{-5}) and (4) in the film state.

In conclusion, the copper-catalyzed oxidative polycondensation of the monomer (**8**) with a [2.2]paracyclophane core gave the corresponding π-conjugated copolymer (**9**) having a diacetylene unit in the main chain in 50% yield with a high molecular weight. The thermally stable polymer (**9**) exhibited good solubility in common organic solvents, and could be processed into a self-standing film. The photoluminescence spectra of the polymer showed a strong emission in solution and in the solid state. The polymer obtained is a promising candidate for blue light-emitting materials with extreme photoluminescence and electroluminescence.

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