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Novel Conjugated Polymers Containing [2.2]Paracyclophane and Carbazole Units with Efficient Photoluminescence

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Summary

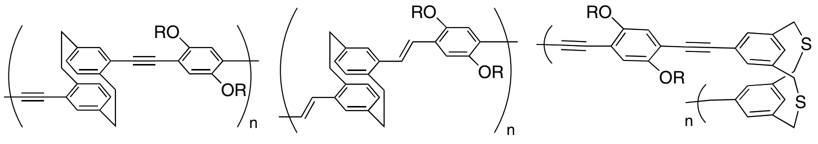
Novel through-space conjugated polymers based on PPE having [2.2]paracyclophane and *N*-alkylcarbazole units in the main chain were synthesized by Sonogashira-coupling reaction. All polymers were quite soluble in a variety of organic solvents. Transparent and uniform thin films of the polymers were obtained easily by casting or spin-coating from toluene solution. These polymers possessed good thermal stability. The polymers exhibited strong blue photoluminescence in solution and bluish-green photoluminescence in the solid state.

Introduction

In recent years, a great deal of interest has arisen in the synthesis of novel conjugated polymers [1], because of their unique properties including electrical conductivity [2], electroluminescence [3], liquid crystallinity [4], third-order nonlinear optical property [5], and chemical sensing [6]. The most prominent example of this class of polymers is poly(*p*-phenylenevinylene) (PPV). Since the first report on PPV in 1990 [7], PPV have led to polymer-based light-emitting diodes (LEDs) for displays and other purposes. In addition, poly(*p*-phenylene-ethynylene) (PPE) [8] is a promising candidate for the development of the molecular wire and PPE is used as an active component in polymer-based electronic and photonic devices. One of current research interests in conjugated polymers including PPVs and PPEs focuses on tuning their spectral and electrical properties. For this purpose, a number of aromatic compounds have been incorporated into the conjugated polymer backbone, and the physical properties of these compounds have been investigated in detail. Therefore, [2.2]paracyclophane, which has characteristic interactions between the face-to-face π-electron systems, seems to be a promising candidate for the aryl unit of the π-conjugated polymers.

To date, many cyclophane compounds have been prepared, and their reactivity and physical properties derived from their longitudinal π-π interactions have been investigated in detail [11-14]. Recently, we reported first preparation and the physical properties of the novel π-conjugated polymers (Chart 1) [13] using cyclophane derivatives as the key monomer unit. We found that the obtained polymers showed an extension of π-delocalization via the through-space interaction, and also exhibited an intense luminescence in solution.

Chart 1



1ref.13a **2**ref.13c **3**ref.13e

On the other hand, chemical and physical properties of the carbazole-containing polymers are subjects of current interest in view of their great potential for use in advanced materials such as hole-transporting materials and emitting materials [15]. In addition, carbazole derivatives have a rigid biphenyl unit, and their physical properties and solubility can easily be improved by substitution at the *N*-position. These derivatives are important building block in constructing the emitting polymers due to their high efficiency and good thermal as well as air stability. Here, we report the synthesis and properties of novel through-space conjugated polymers based on PPE having [2.2]paracyclophane and *N*-alkylcarbazole units in the main chain by Sonogashira-coupling reaction.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 or a JEOL EX400 spectrometer. All 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. Cyclic voltammetry was carried out using a BAS CV-50W voltammetric analyzer with a 0.10 M CH_3CN solution containing Et_4NBF_4 as an electrolyte, a platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode at a scan rate of 300 mV/s. Purification of the obtained polymers was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 ^{o}C/min). Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials

THF was distilled from sodium benzophenone ketyl. NEt_3 was distilled from KOH. Phenylacetylene **7** was purified by simple distillation. $PdCl_2(PPh_3)_2$, CuI, and PPh_3

were obtained commercially, and used without further purification. 4,16-Diethynyl[2.2]paracyclophane **4** [13g] and 3,6-diiodo-*N*-alkyl-carbazoles **5a-c** [15b,d] were prepared as described in the literature. All reactions were performed under an argon atmosphere using standard Schlenk techniques.

*Synthesis of the model compound **8***

The compounds **5a** (53 mg, 0.10 mmol), **7** (31 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.040 mmol), PPh_3 (21 mg, 0.080 mmol), and CuI (7.6 mg, 0.040 mmol) were dissolved in 14 mL of THF-NEt_3 (v/v = 5:2). The solution was stirred at reflux temperature for 12 h under an argon 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) as an eluent to give the model compound **8** (23 mg, 0.048 mmol, 48%) as a pale yellow solid.

^{1}H NMR (270 MHz, $CDCl_3$); δ 0.86 (t, J = 6.8 Hz, 3H), 1.25 (m, 10H), 1.85 (m, 2H), 4.27 (t, J = 7.0 Hz, 2H), 7.35 (m, 8H), 7.58 (d, J = 7.8 Hz, 4H), 7.65 (d, J = 8.0 Hz, 2H), 8.27 (s, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$); δ 14.0, 22.6, 27.2, 28.9, 29.1, 29.7, 31.7, 43.3, 87.6, 90.4, 108.8, 113.6, 122.2, 123.6, 123.9, 127.6, 128.0, 129.4, 131.2, 140.1. IR (KBr) 2280 cm^{-1}. Anal. calcd for $C_{36}H_{33}N$: C 90.15, H 6.93, N 2.92; found: C 90.04, H 6.99, N 2.97.

Polymerization

A typical procedure is as follows [16]. A mixture of **4** (51 mg, 0.20 mmol), **5a** (106 mg, 0.20 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.040 mmol), PPh_3 (21 mg, 0.080 mmol), CuI (7.6 mg, 0.040 mol), NEt_3 (4.0 mL), and THF (10 mL) was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The reaction was carried out at reflux temperature for 72 h with stirring. After the reaction mixture was cooled, precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated and poured into MeOH to precipitate the polymer **6a**. This polymer **6a** was filtered, washed with MeOH, and dried in vacuo. This crude polymer **6a** was dissolved in toluene and washed three times with aqueous NH_3 to remove the inorganic species. The organic layer was dried over $MgSO_4$. After filtration of $MgSO_4$, the solvent was evaporated and dried in vacuo. The resulting yellow residue was dissolved in $CHCl_3$ and was purified by a recycling preparative HPLC using $CHCl_3$ as an eluent. Finally, the solvent was concentrated and poured into a large amount of MeOH to give the yellow precipitates. This precipitates was washed with MeOH several times. After the product was dried under reduced pressure, a bright yellow polymer **6a** was obtained (58 mg, 0.11 mmol, 54%).

6a. Yield: 54%. ^{1}H NMR (400 MHz, $CDCl_3$); δ 0.87 (brs, 3H), 1.28 (m, 8H), 1.63 (brs, 2H), 1.91 (brs, 2H), 3.05 (m, 4H), 3.33 (m, 2H), 3.83 (m, 2H), 4.35 (brs, 2H), 6.61 (m, 4H), 7.13 (m, 2H), 7.47 (m, 2H), 7.75 (m, 2H), 8.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 14.1, 22.6, 27.2, 28.9, 29.1, 29.3, 31.8, 34.0, 34.3, 43.4, 88.2, 93.9, 110.0, 114.4, 122.6, 123.9, 125.2, 130.0, 133.3, 137.1, 138.1, 140.8, 141.9, 143.6. IR (film) 2200 cm^{-1}.

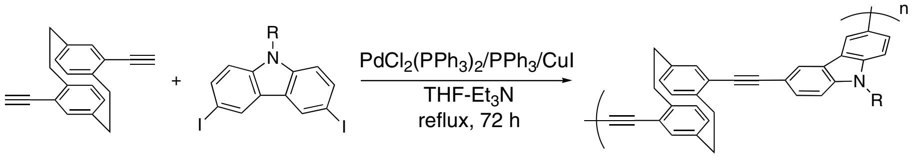
6b. Yield: 30%. ^{1}H NMR (400 MHz, CDCl$_3$); δ 0.93 (m, 6H), 1.52 (m, 10H), 3.31 (m, 8H), 4.22 (s, 1H), 6.61 (m, 2H), 6.68 (s, 2H), 7.14 (m, 2H), 7.75 (m, 2H), 8.41 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$); δ 109.4, 114.5, 122.5, 124.0, 128.4, 129.6, 130.0, 133.2, 137.1, 139.5, 140.8, 141.9. IR (film) 2200 cm^{-1}.

6c. Yield: 78%. ^{1}H NMR (400 MHz, CDCl$_3$); δ 0.88 (m, 3H), 1.25 (m, 18H), 1.90 (m, 2H), 3.30 (m, 8H), 4.34 (s, 2H), 6.58 (m, 2H), 6.67 (m, 2H), 7.12 (m, 2H), 7.45 (m, 2H), 7.73 (m, 2H), 8.40 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$); δ 14.2, 22.7, 27.3, 29.0, 29.3, 29.4, 29.5, 29.6, 31.9, 34.1, 34.3, 43.5, 88.3, 93.9, 109.1, 114.5, 122.5, 123.9, 128.5, 129.6, 130.0, 133.2, 137.1, 139.4, 140.3, 141.9. IR (film) 2200 cm^{-1}.

Results and Discussion

As shown in Scheme 1, monomers **4** and **5a-c** were easily polymerized to the corresponding polymers **6a-c** using the PdCl$_2$(PPh$_3$)$_2$/PPh$_3$/CuI catalyst system in THF-Et$_3$N at reflux temperature for 72 h according to the standard Sonogashira coupling method [16]. After the reaction was completed, inorganic by-products were filtered off and the filtrate was reprecipitated into a large amount of MeOH to obtain the crude polymers **6a-c**. The polymers **6a-c** were dissolved in CHCl$_3$ and washed three times with aqueous NH$_3$ to remove the remaining inorganic species. Finally, purification using the recycling preparative HPLC was carried out to remove the low molecular weight compounds, including phosphines, to give the corresponding polymers **6a-c** in moderate yields of 30-78% as a yellow powder. The results are summarized in Table 1. The polymers **6a-c** had good solubility in common organic solvents such as THF, CHCl$_3$, CH$_2$Cl$_2$, and toluene. On the other hand, the polymerization of **4** with 3,6-diiodo-9*H*-carbazole (R = H) or 3,6-diiodo-*N*-ethylcarbazole (R = Et) gave a low molecular weight oligomer due to their poor solubility. The polymers could be processed into transparent and uniform thin films

Scheme 1



4

5a R = *n*-octyl
5b R = 2-ethylhexyl
5c R = *n*-dodecyl

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6b R = 2-ethylhexyl
6c R = *n*-dodecyl

Table 1. Synthesis of the Polymers **6a-c**^{a}.

polymer	R (monomer)	yield^b / %	$M_w{}^c$	$M_n{}^c$	$M_w/M_n{}^c$
6a	*n*-octyl (**5a**)	54	8500	4400	1.9
6b	2-ethylhexyl (**5b**)	30	6800	3700	1.8
6c	*n*-dodecyl (**5c**)	78	10100	4100	2.5

^{a} Polymerization was carried out at reflux temperature for 72 h under Ar. ^{b} Isolated yields. ^{c} GPC (CHCl$_3$), polystyrene standards.

by casting or spin-coating from toluene solution, and were found to be air stable in solution and in the solid state.

The molecular weight measurements were performed by gel permeation chromatography (GPC) in eluent $CHCl_3$ using the calibration curve of polystyrene standards, as listed in Table 1. For example, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distribution (M_w/M_n) of the polymer **6a** obtained by run 1 were $M_n = 4400$, $M_w = 8500$, and $M_w/M_n = 1.9$, which resulted in estimation of the number-average degree of polymerization as 8.

These polymers were characterized by their ^{1}H, ^{13}C NMR, and FT-IR spectra. In the ^{1}H NMR spectrum of **6a** in $CDCl_3$ (Figure 1), the signals of the *N*-alkyl chains dominated in the region of 0.80-2.2 ppm and 4.35 ppm, and the bridged methylenes of the paracyclophane unit appeared at 2.8-3.8 ppm. The signals of the aromatic protons were between 6.5 and 8.4 ppm. In the ^{13}C NMR spectrum of the polymer **6a**, typical signals for acetylenic carbons were dominant in the region of 88-94 ppm. The acetylenic moieties were also characterized by IR spectrum, weak stretching vibration mode of a carbon-carbon triple bond was observed at 2200 cm^{-1}.

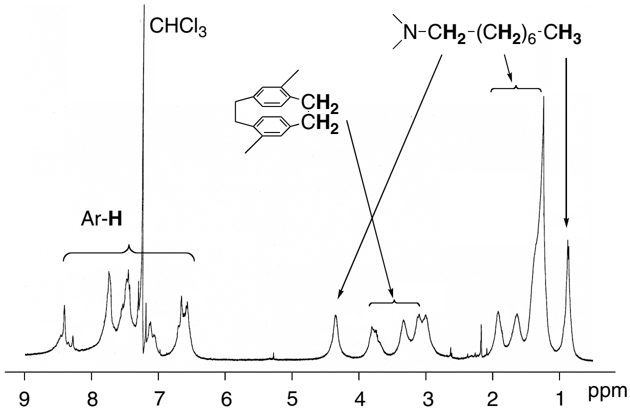


Figure 1. ^{1}H NMR spectrum of the polymer (**6a**) in $CDCl_3$.

Thermal stability of the polymer **6a** was evaluated by thermogravimetric analysis (TGA) under N_2, and the result is shown in Figure 2. This polymer possessed good thermal stability with a 10% weight loss temperature at 418 °C, at a heating rate of 10 °C/min. This TGA result reveals enough thermal stability of the titled polymer to be applied to light emitting materials.

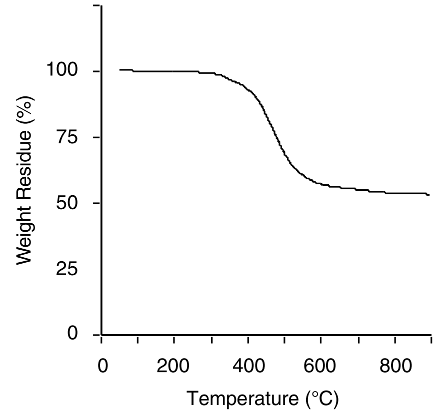


Figure 2. Thermogravimetric analysis (TGA) of **6a** under nitrogen (10 °C/min).

The optical properties of the polymers **6a-c** are summarized in Table 2. The absorption spectrum of **6a** as a representative polymer in solution is shown in Figure 3A. The polymer **6a** shows a strong absorption peak at 353 nm in $CHCl_3$ at room temperature (run 1), which is the π-π* transition band of the PPE polymer backbone. In addition, the absorption spectrum of the thin film of **6a** showed a broad

Table 2. Optical Properties of the Polymers **6a**-**c**.

	UV $\lambda_{max}{}^{a}$/ nm		PL $\lambda_{max}{}^{a,b}$ / nm		
polymer	solution	film	solution	film	$\Phi_{PL}{}^{c}$
6a	353	364	413	450	0.64
6b	353	364	413	450	0.58
6c	353	365	413	450	0.62

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [b] Excited at absorption maxima. [c] PL efficiencies in $CHCl_3$ determined relative to 9-anthracenecarboxylic acid in CH_2Cl_2.

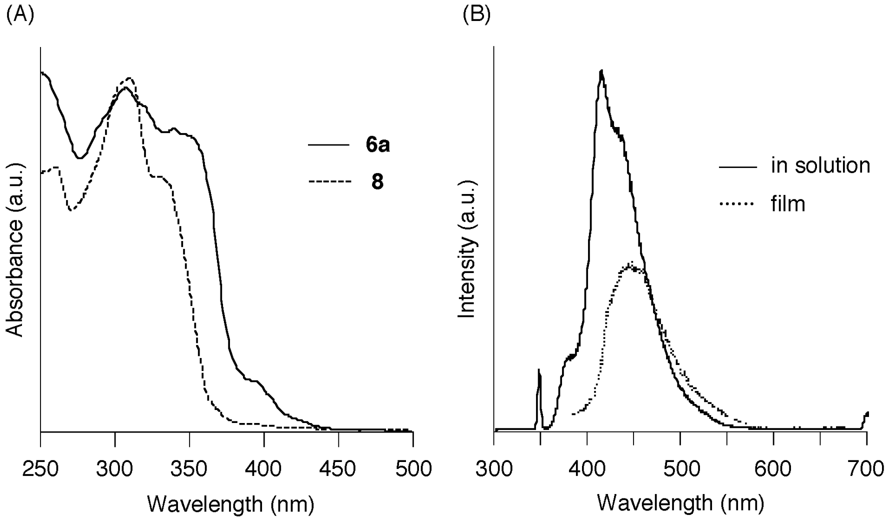
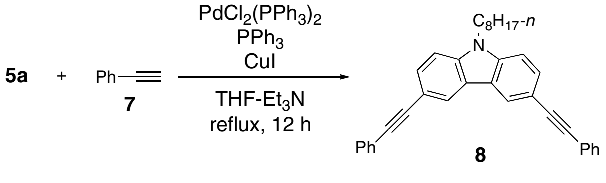


Figure 3. (A) Absorption spectra of the polymer **6a** and the model compound **8** in $CHCl_3$ solution. (B) Photoluminescence spectra of the polymer **6a** in solution and in the film state.

Scheme 2



peak maximum at 364 nm. On the other hand, the spectrum of the model compound **8** (Figure 3A), which was prepared as illustrated in Scheme 2, exhibited a blue-shift for the absorption maximum as well as for the absorption edge in comparison with those of **6a**. This result indicates the extension of the π-delocalization length of the polymer **6a** via the through-space interaction of the two face-to-face benzene rings.

In the fluorescence emission spectra of the polymers **6a-c** in dilute $CHCl_3$ solution at room temperature on excitation at absorption maxima, the emission peaks were observed around 415 nm in the visible blue region (Table 2, Figure 3B). The polymer solutions exhibited high quantum efficiency; for example, **6a** had an efficiency of 0.64 in $CHCl_3$ solution at room temperature, as demonstrated by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi = 0.442$) [17]. In the solid thin film of **6a**, the emission peak maximum at 450 nm in the visible bluish-green region was red-shifted approximately 40 nm from that in solution (Table 2, Figure 3B). The shapes and peaks of the absorption spectra and emission spectra of **6a-c** were independent on the nature of the alkyl side chains both in solution and in the solid state.

The cyclic voltammetry of the polymer film coated on ITO glass electrode in CH_3CN solution of 0.10 M Et_4NBF_4 was performed in a three-electrode cell using a Pt counter electrode and a Ag/AgCl reference electrode. As shown in cyclic voltammogram (Figure 4), the oxidation process gave the onset peak around 1.1 V *vs.* Ag/Ag^+ irreversibly. Further studies on electrochemical behaviors and evaluation of mobility of the hole through the cyclophane-carbazole-containing polymer are currently underway.

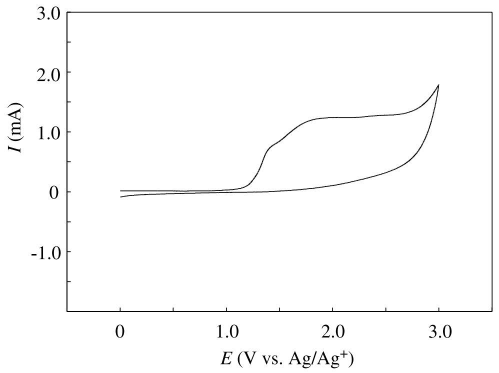


Figure 4. Cyclic voltammogram of the polymer film coated on the ITO plate electrode in CH_3CN containing 0.10 M Et_4NBF_4 as a supporting electrolyte (*vs.* Ag/Ag^+) at a scan rate of 300 mV/s.

Conclusion

Novel π-conjugated polymers with [2.2]paracyclophane and *N*-alkylcarbazole units appended to the PPE backbone were prepared by the Sonogashira coupling reaction. These polymers were soluble in common organic solvents, and transparent and uniform thin films of the polymers were obtained easily by casting or spin-coating from a toluene solution. These polymers possessed good thermal stability. The polymers exhibited strong blue photoluminescence in solution and bluish-green photoluminescence in the solid state. Further studies on the preparation of the cyclophane-containing polymers and their application as the hole-transporting materials as well as the conductive materials are now in progress.

Acknowledgements.

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17. The absorbance of each sample was below 0.05 at the excitation wavelength at 350 nm, in the measurement of the fluorescence quantum yield. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{\mathrm{unk}} = \Phi_{\mathrm{std}}[A_{\mathrm{std}}F_{\mathrm{unk}}/A_{\mathrm{unk}}F_{\mathrm{std}}][n_{\mathrm{D,unk}}/n_{\mathrm{D,std}}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_{D} is the refractive index [CH_2Cl_2 ($n_{\mathrm{D}} = 1.424$) and $CHCl_3$ ($n_{\mathrm{D}} = 1.446$) were used].