Articles

Synthesis and Properties of Novel Through-Space π-Conjugated Polymers Based on Poly(*p*-phenylenevinylene)s Having a [2.2]Paracyclophane Skeleton in the Main Chain

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ABSTRACT: Palladium-catalyzed polymerization of pseudo-*p*-divinyl[2.2]paracyclophane (**2**) and 2,5-dialkoxy-1,4-diiodobenzenes (**3a** and **3b**) was carried out to give the corresponding polymers (**4a** and **4b**) having [2.2]paracyclophane as a repeating unit. The structures of the polymers were supported by ^{1}H and ^{13}C NMR spectra. The polymers obtained were soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and DMF. Polymer **4a** showed an extension of π-delocalization via the through-space with $\pi-\pi$ stacking according to the UV−vis absorption spectra in comparison with those of the model compounds **9** and **10**. In the fluorescence emission spectrum of **4a** in chloroform solution, an intense emission peak was observed at 462 nm ($\Phi_F = 0.92$) in the visible green region. In the solid state, the absorption spectrum of **4a** was very similar to that in solution, while in the emission spectrum of **4a** the peak maximum at 507 nm was red-shifted about 45 nm from that in solution. This result indicates that the aggregation or the excimer formation of the polymer would occur in the film 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 intriguing properties such as electrical conductivity,[2] electroluminescence,[3] liquid crystallinity,[4] third-order nonlinear optical properties,[5] and chemical sensing.[6] The most prominent example concerns poly(*p*-phenylenevinylene)s, PPVs, which have led to polymer-based light-emitting diodes (LEDs) for displays and other purposes since the first report on PPVs in 1990.[7] Current research interests on π-conjugated polymers focus on tuning their spectral and electrical properties. The extended strategy toward the appropriate design of π-conjugated polymers involves variation of the phenylene building block, i.e., replacement of phenylene units by other heterocyclic arenes, fused carbocyclic arenes, or substituted carbocyclic arenes. Therefore, [2.2]paracyclophane, in which two benzene rings are close to each other and facing, seems to be a promising candidate for the aryl unit of PPVs.

On the other hand, a number of paracyclophane derivatives have been prepared so far, and their physical properties have been investigated, especially optical and electronic properties, due to their characteristic interactions between the two co-facial π-electron systems.[8,9] In addition, several nonconjugated polymers, each having a paracyclophane skeleton in the main chain (in the course of developing new processes for cross-linking resins)[10] or in the side chain,[11] have been synthesized. Recently, oligothiophene-substituted polymers having [2.2]paracyclophane in the main chain were reported as π-conjugated polymers.[12] However, [2.2]paracyclophane was not used as a repeating unit but as the core of the polymer backbone. In 1985, Mizogami and co-workers reported the first synthesis of polymetacyclophane by a polycondensation reaction of 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.[13] However, π-conjugated polymers using the longitudinal $\pi-\pi$ interaction of paracyclophane as a repeating unit are strictly limited.[14,15] Recently, we reported the first synthesis and physical properties of [2.2]paracyclophane-containing π-conjugated polymers (**1**) based on the poly(*p*-phenylene-ethynylene) derivatives using the longitudinal $\pi-\pi$ interaction of paracyclophane.[14a] In this paper, we present the synthesis and physical properties of novel PPVs having a [2.2]paracyclophane skeleton in the main chain as a repeating unit. The obtained polymer showed an extension of π-delocalization via the through-space with $\pi-\pi$ stacking according to the UV−vis absorption spectra in comparison with those of the model compound.

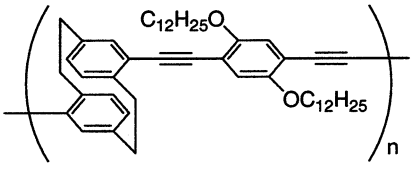

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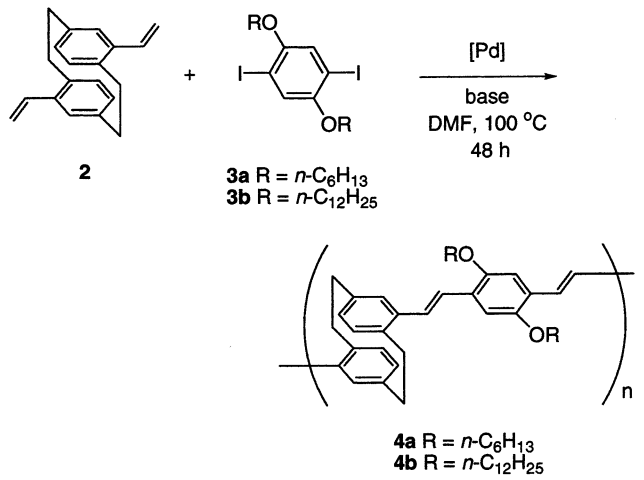
Table 1. Effect of the Catalyst on the Synthesis of Polymers 4a and 4b[a]

run	R	catalyst	additive	base	yield(%)[b]	M_w[c]	M_n[c]	M_w/M_n
1	n-C_6H_{13} (**3a**)	$Pd_2(dba)_3$	PCy_3	NEt_3	59	3200	2100	1.5
2		$Pd_2(dba)_3$	Bu^n_4NI	K_2CO_3	31	7200	4300	1.7
3		$Pd_2(dba)_3$	Bu^n_4NI	KF	12	2200	1900	1.1
4		$Pd(OAc)_2$	Bu^n_4NI	K_2CO_3	70	4400	3200	1.4
5		$PdCl_2(PPh_3)_2$	Bu^n_4NI	K_2CO_3	69	8300	4200	2.0
6		$PdCl_2(PPh_3)_2$	Bu^n_4NI	$NaHCO_3$	43	2300	1700	1.4
7		$Pd(PPh_3)_4$	Bu^n_4NCl	K_2CO_3	27	1700	1400	1.2
8	n-$C_{12}H_{25}$ (**3b**)	$Pd(OAc)_2$	$P(p\text{-Tol})_3$	NEt_3	51	2700	2000	1.3
9		$Pd(PPh_3)_4$	$P(o\text{-Tol})_3$	NEt_3	22	2000	1500	1.4
10		$PdCl_2(PPh_3)_2$	Bu^n_4NI	K_2CO_3	96	7400	2800	2.6

[a] Polymerizations were carried out in DMF in a 50 mL Pyrex flask at 100 °C for 48 h under nitrogen atmosphere. [b] Isolated yields after reprecipitation into MeOH. [c] GPC ($CHCl_3$), polystyrene standards.

Scheme 1



Results and Discussion

We initially examined the polymerization reaction condition of pseudo-*p*-divinyl[2.2]paracyclophane (**2**) with 2,5-dialkoxy-1,4-diiodobenzenes (**3a,b**) in the presence of several palladium complexes (Scheme 1). The results are summarized in Table 1.

The reaction of **2** with **3a,b** in the presence of a catalytic amount of palladium complex and base in DMF at 100 °C for 48 h under a nitrogen atmosphere gave dark fluorescence solutions. After the reaction was completed, inorganic byproducts were filtered off and the filtrate was reprecipitated into a large amount of MeOH to obtain the corresponding titled polymers (**4a,b**) in good yields as a yellowish-green powder. An appropriate catalyst system was critically important for the success of the polymerization. The typical Heck coupling condition[16] (run 1) was not so effective for this reaction. On the other hand, Jeffery reported that the Heck-type reactions proceed readily under solid−liquid-phase transfer conditions using a $Pd(OAc)_2$ complex, Bu^n_4NCl as the phase transfer agent, and K_2CO_3 as the base.[17] Among the catalysts examined, the modified phase transfer condition, i.e., the $PdCl_2(PPh_3)_2/Bu^n_4NI/K_2CO_3$ system, showed the highest catalytic activity (run 5).

The polymers obtained were soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and DMF. These polymers were characterized by ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of **4a** in $CDCl_3$ (Figure 1a), the peak corresponding to vinyl protons at 5.5−6.5 ppm of **2** almost disappeared, while olefinic protons of **4a** appeared at 7.2 ppm and overlapped with aromatic protons. In the ^{13}C NMR spectrum of polymer **4a** (Figure 1b), the signals of the alkyl side chains and bridged methylenes of the paracyclophane unit were dominating in the region of 15−35 ppm, and the methylene groups adjacent to oxygen were shifted downfield to 70 ppm. The signals of the aromatic and olefinic carbons were between 110 and 150 ppm. Polymers **4a** and **4b** were very stable under air, both in solution and in the solid state. The thermal stability of polymer **4a** was investigated by thermogravimetric analysis (TGA) and the results are shown in Figure 2. **4a** sustained a 10% weight loss at temperature of 400 °C both under air and nitrogen, respectively, at a heating rate of 10 °C/min, and weight loss was completed at 500 °C under nitrogen. Under air, the decomposition of polymer **4a** involved two steps. The first step started from 410 °C, which may be assigned to thermal decomposition of alkyl side chain of the polymer, and the second one, which started from 570 °C and was completed at 630 °C, is attributed to the decomposition of the polymer backbone.

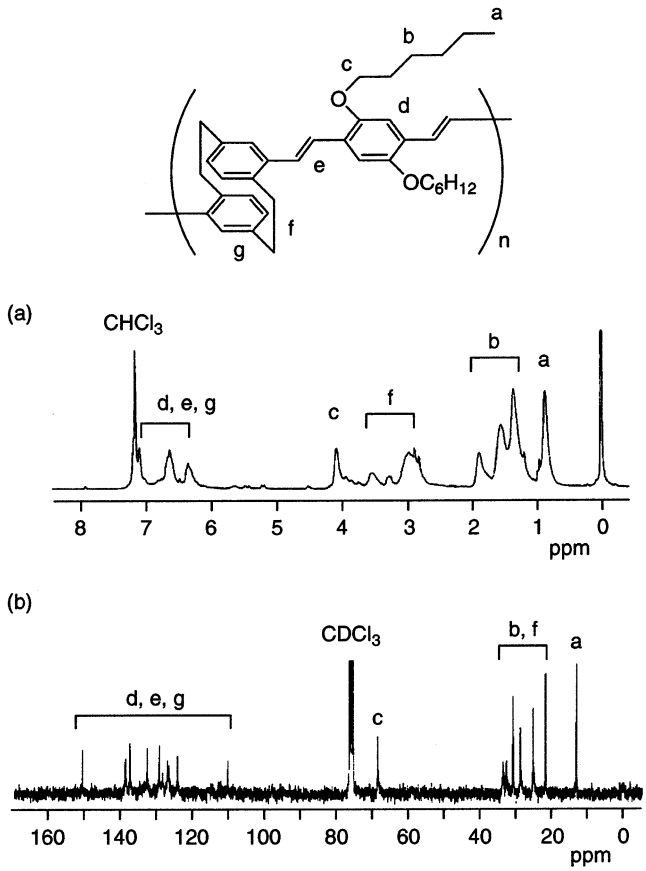


Figure 1. ^1H NMR (a) and ^{13}C NMR (b) spectra of **4a** in $CDCl_3$.

Table 2. Optical Properties of Model Compound 9 and Polymers 4a−c

		UV λ_{max}[a], nm		PL λ_{max}[a,b], nm	
run	compound	in solution (log ϵ)	film	in solution (Φ_F[c])	film
1	model (**9**)	325 (4.19), 383 (4.38)		446	
2	**4a**	336 (3.11), 398 (4.62)	330 sh, 397	462 (0.92)	507
3	**4b**	340 sh, 397 (4.32)	335, 396	462 (0.92)	505
4	**4c**	362 (4.53), 423 sh	422 br	487 (0.52)	525

[a] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [b] The sample solutions were excited at 380, 400, 400, and 360 nm for **9**, **4a**, **4b**, and **4c**, respectively. Films **9** and **4a—c** were excited at 400 nm. [c] The quantum yield (Φ_F) was calculated in $CHCl_3$ at room temperature by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard.

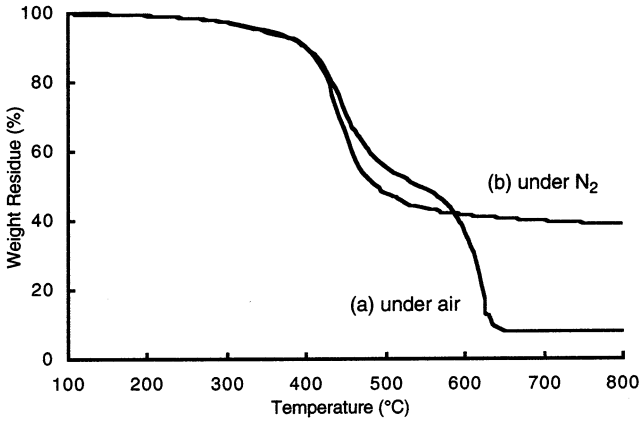
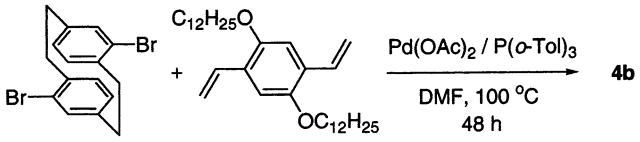


Figure 2. TGA traces (10 °C/min) of **4a** under air (a) and under nitrogen (b).

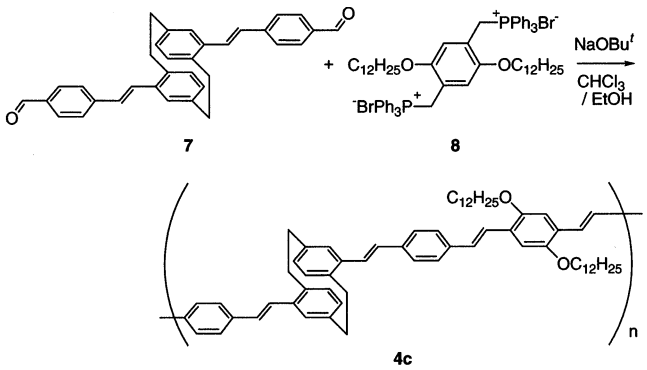
Scheme 2



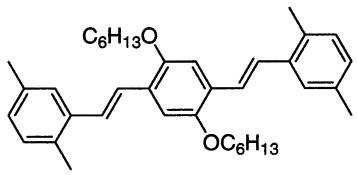
5 **6**

The molecular weight measurements were performed by gel permeation chromatography (GPC) in $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). 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 (**4a**) obtained by run 5 were $M_n = 4200$, $M_w = 8300$, and $M_w/M_n = 2.0$, which resulted in the estimation of the number-average degree of polymerization as 8. In the case of the polymer (**4b**) having a longer alkyl chain, however, M_n was 2800, smaller than that of polymer **4a**, which corresponds to the number-average degree of polymerization of 4.5. This would result from the incompatibility between a polar DMF solvent and a nonpolar long alkyl chain of both the monomer and the polymer. As another synthetic route to polymer **4b**, the reaction of pseudo-*p*-dibromo[2.2]paracyclophane (**5**) with didodecyloxydivinylbenzene (**6**) was tried. Treatment of **5** and **6** in the catalytic amount of $Pd(OAc)_2$ / $P(o\text{-Tol})_3/NEt_3$ in DMF at 100 °C for 48 h gave the corresponding polymer (**4b**) in only 5% yield and low molecular weight ($M_n = 1200$, Scheme 2). **5** is relatively inert against the oxidative addition to palladium complex due to the lower reactivity of aryl bromide relative to aryl iodide and to the steric hindrance and the electron-rich feature of a paracyclophane moiety. Furthermore, we synthesized the other poly(*p*-phenylenevinylene) derivatives (**4c**) having [2.2]paracyclophane in the main chain by a Wittig reaction from **7** and **8**, with 48% yield, $M_w = 13\,500$, and $M_n = 3900$ (Scheme 3).

Scheme 3



We investigated the optical properties of the polymers obtained. The results are listed in Table 2. Figure 3 shows the UV−vis absorption spectra in the chloroform solution of polymer **4a** and model compound **9** prepared from dihexyloxydivinylbenzene and bromoxylene via Heck coupling reaction. Two broad absorption bands of **4a** were observed at 336 nm (log $\epsilon = 3.11$) and 398 nm (log $\epsilon = 4.62$), while model compound **9** had a spectrum similar to that of **4a**, containing two absorption maxima at 325 and 383 nm, respectively. The 398 nm band was red-shifted about 15 nm compared with that of **9**. In



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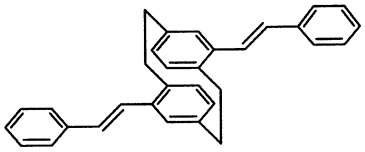
addition, a stilbenoid dimer (**10**), which was prepared by Bazan and co-workers, showed absorption maximum



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at 307 in hexane.[9a] These findings indicate the extension of π-delocalization length via the through-space based on the two facing benzene rings of the [2.2]paracyclophane moiety. The absorption spectra of **4a—c** in $CHCl_3$ solution are shown in Figure 4. For polymers **4a** and **4b**, the shapes and peaks of the absorption spectra are almost the same and are independent of the length of the alkoxy side chain. The spectrum of polymer **4c** also displayed two peaks, a broad peak at 362 nm and a shoulder peak at 423 nm.

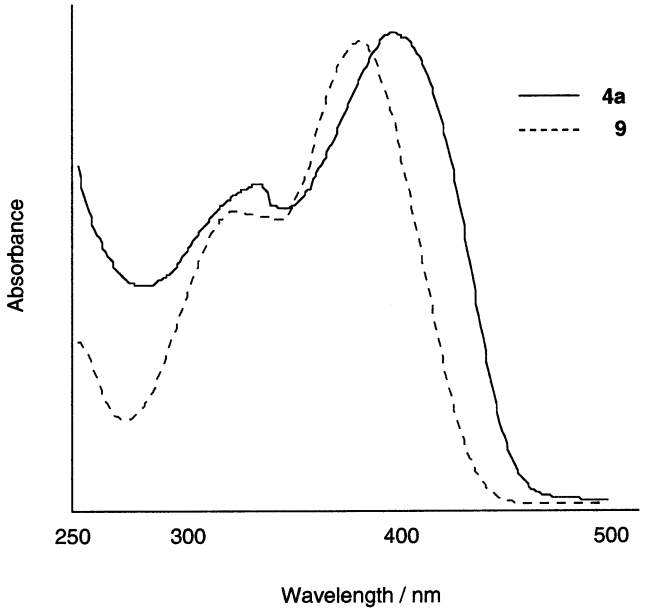

Figure 3. Absorption spectra of polymer **4a** and model compound **9** in $CHCl_3$ solution.

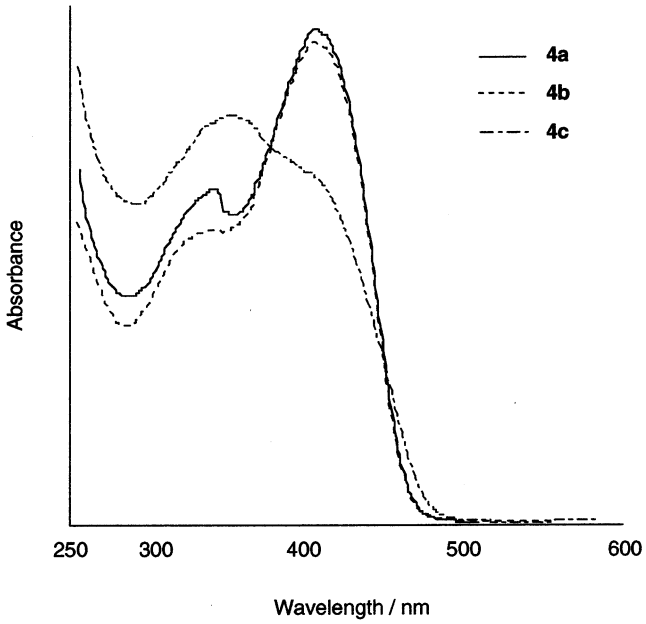

Figure 4. Absorption spectra of **4a—c** in $CHCl_3$ solution.

The fluorescence spectra of the dilute chloroform solutions of **4a—c** at room temperature are shown in Figure 5. The highly intense emission λ_{max} values of **4a** and **4b** were observed in the visible green region with an excitation wavelength at 400 nm. Furthermore, Figure 5 shows the excitation spectrum of **4a**, and almost the same peaks as in the UV−vis spectrum were observed. These findings indicate that two absorption peak maxima in UV−vis spectrum correspond to the same absorbing species, and the typical emission of phenylenevinylene units of the polymer backbone is observed. The quantum yield (Φ_F) for 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. Both **4a** and **4b** showed a strong emission at 462 nm, and the quantum efficiency of each was 0.92 using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi_F = 0.442$) on excitation at 380

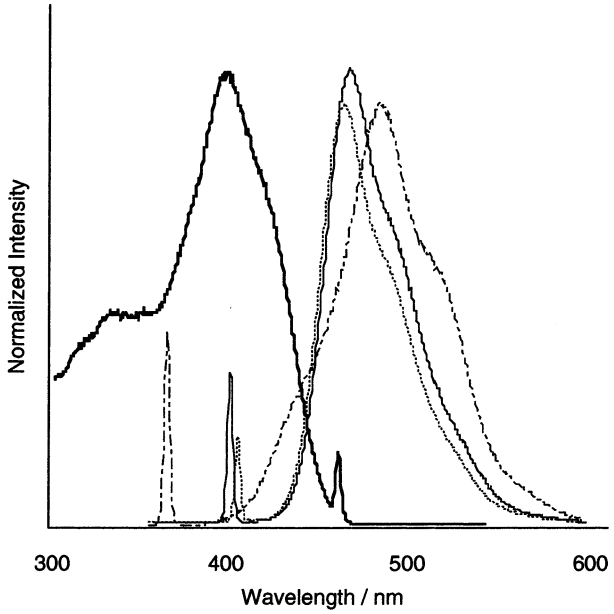

Figure 5. Emission spectra of **4a** (−), **4b** (···), and **4c** (-·-·-) and excitation spectrum of **4a** (—) in $CHCl_3$ solution.

nm. The quantum yield (Φ_{unk}) of an unknown sample was calculated by the following equation:

$$\Phi_{unk} = \Phi_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{D,std}]^2$$

Here A_{std} and A_{unk} are the absorbance of the standard and unknown samples, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_D is the refractive index [CH_2Cl_2 (n_D = 1.424) and $CHCl_3$ (n_D = 1.446) were used].

The UV−vis absorption spectra of the polymer films were also recorded. The absorption spectra of **4a** and **4b** in the solid state were very similar to those in solution, while in the spectrum of **4c** a broad peak was observed at around 422 nm. The solid-state emission spectra of **4a—c** are shown in Figure 6. In those spectra, the peak maxima at 507, 505, and 525 nm were each red-shifted about 45 nm from those in solution (Table 2 and Figure 4). This result indicates that the aggregation or the excimer formation[14a] of the polymer would occur in the film state.

Conclusions

Novel through-space π-conjugated polymers (**4a—c**) have been synthesized by a modified Heck coupling reaction and a Wittig reaction. The polymers have a [2.2]paracyclophane skeleton as a repeating unit in the main chain and are soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$, toluene, and DMF. The UV−vis absorption peak of polymer **4a** in $CHCl_3$ solution appears at a longer wavelength compared with those of the corresponding model compounds **9** and **10** due to the longitudinal $\pi-\pi$ interaction of paracyclophane moiety. In $CHCl_3$ solution, both **4a** and **4b** show a strong emission at 462 nm in a visible green region. The absorption spectra of **4a—c** in the solid-state resemble those in solution, while the emission spectra of polymer films show a red-shift of about 45 nm from the solution to the film states. These results suggest that the emission would be the result of aggregation or excimer formation. The through-space π-conjugated polymers

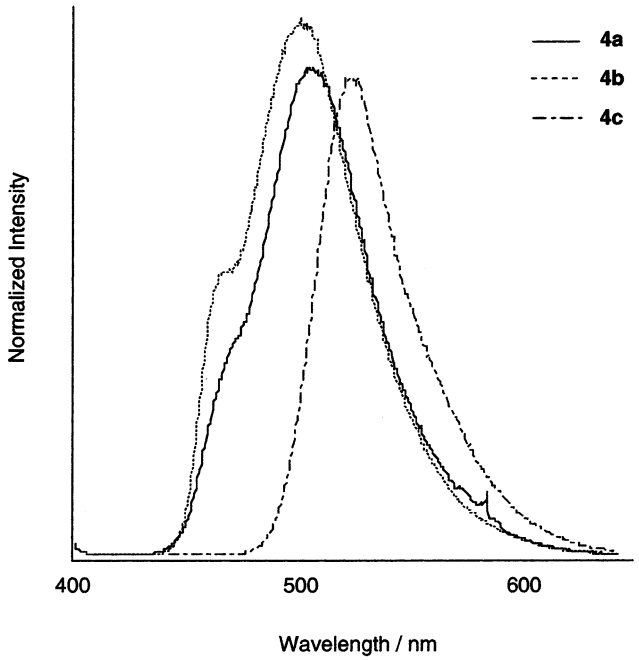

Figure 6. Solid-state emission spectra of **4a—c**.

having paracyclophane moieties may find useful applications for photonic and electronic applications.

Experimental Section

General Data. ^{1}H 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. 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 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. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 silica gel. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Materials. *N*,*N*-Dimethylformamide (DMF) was distilled from calcium hydride. NEt_3 was distilled from KOH. $CHCl_3$ was distilled from calcium chloride. K_2CO_3, $NaHCO_3$, KF, $NaOBu^t$, Bu^n_4NI, Bu^n_4NCl, tri-*o*-tolylphosphine (P(*o*-Tol)$_3$), tri-*p*-tolylphosphine (P(*p*-Tol)$_3$), tricyclohexylphosphine (PCy_3), Pd(OAc)$_2$, $Pd_2(dba)_3$, $PdCl_2(PPh_3)_2$, and 2-bromo-*p*-xylene were obtained commercially and were used without further purification. $Pd(PPh_3)_4$ was prepared as described in the literature.[18] Pseudo-*p*-divinyl[2.2]paracyclophane (**2**) was prepared as described in the literature with minor modification.[9a] 2,5-Dialkoxy-1,4-diiodobenzenes (**3a** and **3b**),[19] pseudo-*p*-dibromo[2.2]paracyclophane (**5**),[20] 1,4-didodecyloxy-2,5-divinylbenzene (**6**),[21] and pseudo-*p*-(4-carboxaldehyde-styryl)[2.2]paracyclophane (**7**)[9a] were prepared as described in the literature. Didodecyloxybis[(triphenylphosphonio)methyl]benzene dibromide (**8**) was prepared from 2,5-bis(bromomethyl)-1,4-didodecyloxybenzene as described in the literature.[22]

Pseudo-*p*-divinyl[2.2]paracyclophane (2). A mixture of pseudo-*p*-dibromo[2.2]paracyclophane (**5**) (599 mg, 1.6 mmol), Pd(OAc)$_2$ (18 mg, 0.080 mmol), P(*p*-Tol)$_3$ (124 mg, 0.41 mmol), NEt_3 (1.5 mL), and DMF (8.0 mL) was placed in 100 mL stainless steel autoclave under a flow of nitrogen. Ethylene was then pressured to 8 atm at room temperature, and the mixture was magnetically stirred at 100 °C for 24 h. After cooling, the reaction mixture was diluted with Et_2O and precipitated ammonium salts were removed by filtration. The filtrate was subjected to column chromatography on SiO_2 with CH_2Cl_2/hexane (1/2) as an eluent to give the product (**2**) (284 mg, 1.1 mmol, 67%) as a white solid. ^{1}H and ^{13}C NMR data of **2** match the literature values.[9a]

1,4-Bis(2,5-dimethylstyryl)-2,5-dihexyloxybenzene (9). The model compound (**9**) was prepared from 2-bromo-*p*-xylene and 1,4-dihexyloxy-2,5-divinylbenzene. A mixture of 2-bromo-*p*-xylene (0.31 mL, 2.3 mmol), 1,4-dihexyloxy-2,5-divinylbenzene (309 mg, 0.94 mmol), Pd(OAc)$_2$ (4.2 mg, 0.020 mmol), P(*o*-Tol)$_3$ (43.7 mg, 0.14 mmol), NEt_3 (3.0 mL), and DMF (5.0 mL) was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar under a flow of nitrogen. The reaction was carried out at 120 °C for 60 h with stirring. After cooling, the reaction mixture was diluted with $CHCl_3$ and washed with H_2O, and the organic layer was dried over $MgSO_4$. The solvent was evaporated, and the crude product was subjected to column chromatography on SiO_2 with CH_2Cl_2/hexane (3/5) as an eluent to give the product (**9**) (41 mg, 0.080 mmol, 8%) as a bright yellow solid. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.91 (t, J = 5.7 Hz, 6H), 1.36 (m, 12H), 1.86 (m, 4H), 2.36 (s, 6H), 2.40 (s, 6H), 4.05 (t, J = 6.2 Hz, 4H), 7.01 (s, 2H), 7.08 (d, J = 8.9 Hz, 4H), 7.34 (d, J = 8.9 Hz, 4H), 7.44 (s, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 14.5, 20.0, 21.5, 23.1, 26.5, 30.0, 32.1, 70.1, 111.9, 125.4, 126.5, 127.5, 127.6, 128.6, 130.7, 133.2, 135.9, 137.3, 151.7. Anal. Calcd for $C_{38}H_{50}O_2$: C 84.71; H 9.35. Found: C 83.91; H 9.39.

Polymerization of 2 with 3. A typical procedure is as follows. A 50 mL Pyrex flask was charged with **2** (35 mg, 0.13 mmol), **3a** (70 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (4.6 mg, 7.0×10^{-3} mmol), Bu^n_4NI (109 mg, 0.30 mmol), K_2CO_3 (43 mg, 0.31 mmol), DMF (3.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at 100 °C for 48 with stirring. The resulting solution was diluted with $CHCl_3$ and washed with H_2O. The organic layer was dried over Na_2SO_4. After filtration of Na_2SO_4, the solvent was concentrated and reprecipitated into a large amount of MeOH. The obtained precipitate was washed with MeOH several times. After the product was dried under reduced pressure, a yellowish green polymer was obtained.

4a. Yield: 50 mg, 69%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.85 (br, 6H), 1.35 (br, 8H), 1.55 (m, 4H), 1.87 (m, 4H), 2.90 (m, 6H), 3.53 (m, 2H), 4.10 (br; 4H), 6.38 (m, 2H), 6.65 (m, 2H), 7.10 (br, 2H), 7.18−7.25 (br, 4H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 14.1, 22.7, 26.1, 29.7, 31.7, 33.5, 34.5, 69.6, 111.1, 125.1, 127.8, 129.2, 130.3, 133.4, 138.2, 139.4, 151.3.

4b. Yield: 157 mg, 96%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.89 (br, 6H), 1.26 (br, 32H), 1.64 (br, 4H), 1.96 (br, 4H), 2.75−3.17 (br, 6H), 3.62 (br, 2H), 4.16 (br, 4H), 6.46 (br, 2H), 6.76 (br, 4H), 7.19 (br, 2H), 7.27 (br, 4H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 13.1, 18.8, 21.7, 23.3, 25.4, 28.4, 29.2, 30.9, 32.6, 33.5, 68.6, 110.2, 124.1, 126.4, 126.9, 127.1, 128.4, 129.1, 132.8, 137.1, 138.4, 150.3.

Polymerization of 7 with 8. A 50 mL Pyrex flask was charged with **7** (63 mg, 0.13 mmol), **8** (156 mg, 0.13 mmol), $NaOBu^t$ (39 mg, 0.41 mmol), $CHCl_3$ (4.0 mL), EtOH (2.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at room temperature for 48 h with stirring. The resulting solution was diluted with $CHCl_3$ and washed with H_2O. The organic layer was dried over Na_2SO_4. After filtration of Na_2SO_4, the solvent was concentrated and reprecipitated into a large amount of MeOH. The obtained precipitate was washed with MeOH several times. After the product was dried under reduced pressure, the orange polymer (**4c**) was obtained (57 mg, 0.062 mmol, 48%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.88 (br, 6H), 1.27 (br, 32H), 1.58 (br, 4H), 1.89 (br, 4H), 3.00 (br, 6H), 3.61 (br, 2H), 4.10 (br, 4H), 6.45 (m, 2H), 6.69 (m, 4H), 7.17 (br, 2H), 7.39 (m, 4H), 7.58 (br, 8H). ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 13.1, 21.7, 25.8, 28.4, 28.7, 30.9, 32.3, 33.6, 68.6, 109.6, 122.4, 125.9, 129.3, 132.7, 136.1, 137.8, 138.6, 150.2.

References and Notes

(1) Skothim, T. A., Elsenbaumer, R. L., Reynolds, J., Eds. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1997.
(2) Pomerantz, M. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998; p 277.
(3) For a recent review, see: Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.
(4) (a) Nehring, J.; Amstutz, H.; Holmes, P. A.; Nevin, A. *Appl. Phys. Lett.* **1987**, *51*, 1283. (b) Moll, A.; Siegfried, N.; Heitz, W. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 485. (c) Witteler, H.; Lieser, G.; Wegner, G.; Schulze, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 471.
(5) See, for example: (a) *Nonlinear Optical Effects in Organic Polymers*; Messier, J., Kajzar, F., Prasad, P. N., Ulrich, D. R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (b) *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Prasad, P. N., Williams, D. J., Eds.; Wiley: New York, 1990. (c) *Materials for Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (d) *Molecular Nonlinear Optics: Materials, Physics, and Devices*; Zyss, J., Ed.; Academic Press: Boston, MA 1994. (e) Bredas, J. L.; Adant, C.; Tackx, P.; Persoons, A. *Chem. Rev.* **1994**, *94*, 243.
(6) For a recent review, see: McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(7) Burrousghes, J. H.; Bradey, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. *Nature (London)* **1990**, *347*, 539.
(8) For recent reviews, see: (a) Vögtle, F. *Cyclophane Chemistry*; Wiley & Sons: New York, 1993. (b) Shultz, J.; Vögtle, F. *Top. Curr. Chem.* **1994**, *172*, 42.
(9) Bazan, Mukamel, and co-workers recently reported the unique photophysical properties of a series of stilbenoid dimers having a [2.2]paracyclophane core: (a) Bazan, G. C.; Oldham, W. J., Jr.; Lachicotte, R. J.; Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Am. Chem. Soc.* **1998**, *120*, 9188. (b) Wang, S.; Bazan, G. C.; Tretiak, S.; Mukamel, S. *J. Am. Chem. Soc.* **2000**, *122*, 1289. (c) Zyss, J.; Ledoux, I.; Volkov, S. Chernyak, V.; Mukamel, S.; Bartholomew, G. P.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 11956.
(10) (a) Meyers, R. A.; Hamersma, J. W.; Green, H. E. *J. Polym. Sci., Polym. Lett. Ed.* **1972**, *10*, 685. (b) Sivaramakrishnan, K. P.; Samyn, C.; Westerman, I. J.; Wong, D. T.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1083. (c) Chang, D. M.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2507. (d) Lin, S.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1151.
(11) (a) Furukawa, J.; Nishimura, J. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 85. (b) Longone, D. T.; Glatzhofer, D. T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1725. (c) Longone, D. T.; Glans, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 405. (d) Iwatsuki, S.; Itoh, T.; Kubo, M.; Okuno, H. *Polym. Bull. (Berlin)* **1994**, *32*, 27.
(12) Collard, D. M.; Lee, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41* (1), 241.
(13) Mizogami, S.; Yoshimura, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1736.
(14) (a) Morisaki, Y.; Chujo, Y. *Macromolecules* **2002**, *35*, 587. (b) Morisaki, Y.; Chujo, Y. *Chem. Lett.* **2002**, 194.
(15) Independently, Audebert et al. have reported synthesis of the π-conjugated polymers having thiophene and [2.2]paracyclophane as a repeating unit by electrochemical polymerization: Guyard, L.; Audebert, P. *Elecrochem. Commun.* **2001**, *3*, 164.
(16) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.
(17) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287.
(18) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(19) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52.
(20) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527.
(21) Peng, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 1785.
(22) Chen, Z.-K.; Meng, H.; Lai, Y.-H.: Huang, W. *Macromolecules* **1999**, *32*, 4351.

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