# Communications to the Editor

## Synthesis of Novel $\pi$ -Conjugated Polymers Having [2.2]Paracyclophane Skeleton in the Main Chain. Extension of $\pi$ -Conjugated Length via the Through-Space

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Introduction. [2.2]Paracyclophane, in which two benzene rings are close to each other and facing, is attracted to the structure, reactivity, and physical properties.<sup>1</sup> A number of paracyclophane derivatives have been prepared, and their physical properties, especially optical and electronic properties due to the characteristic interactions between the two co-facial  $\pi$ -electron systems, have been investigated.<sup>2</sup> In addition, several polymers having paracyclophane in the main chain (in the course of developing new processes for cross-linking resins)<sup>3</sup> or in the side chain<sup>4</sup> and oligothiophene-substituted polymers with a [2.2]paracyclophane core<sup>5</sup> have been studied so far. In 1986, Mizogami and Yoshimura reported that the first synthesis of polymetacyclophane by polycondensation reaction of an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane, which exhibited a conductivity of  $0.25 \text{ S cm}^{-1}$  by doping with H<sub>2</sub>SO<sub>4</sub> vapor.<sup>6</sup> However, no  $\pi$ -conjugated polymers using the longitudinal  $\pi - \pi$  interaction of paracyclophane as a repeating unit have yet been reported. On the other hand, the synthesis of novel  $\pi$ -conjugated polymers has received extensive attention due to their unique optical, electrochemical, and nonlinear optical properties.<sup>7</sup> [2.2]Paracyclophane seems to be a promising candidate for the aryl unit of  $\pi$ -conjugated polymers, e.g., poly(phenylene-ethynylene) and poly(phenylenevinylene). Here, we report on the first preparation and physical properties of novel  $\pi$ -conjugated polymers based on poly(p-phenylene-ethynylene) derivatives<sup>8</sup> via the through-space having a [2.2]paracyclophane skeleton in the main chain.

**Results and Discussion.** We initially examined palladium-catalyzed polymerization of pseudo-*p*-dibromo-[2.2]paracyclophane (1) with dialkoxy-substituted diethynylbenzenes (2a-c). 1 was prepared by ironcatalyzed dibromination of [2.2]paracyclophane and recrystallization.<sup>9</sup> Compounds 2a-c were synthesized by treating the corresponding 2,5-diiodo-1,4-bis(alkoxy)benzenes<sup>10a</sup> with trimethysilylacetylene in the presence of a catalytic amount of palladium complex and following desilylation.<sup>10b</sup>

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R = a n-Octyl; b n-Dodecyl; c n-Hexadecyl

The procedure for the synthesis of the [2.2]paracyclophane-containing polymer (3) was as follows (Scheme 1).<sup>11,12</sup> Treatment of **1** with **2** in the presence of a catalytic amount of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (5 mol<sup>-</sup>% to an acetylene unit), PPh<sub>3</sub>, and CuI in 1:1 THF:HNPr<sup>i</sup><sub>2</sub> at refluxed temperature for 48 h under a nitrogen atmosphere gave the dark-orange fluorescent solution. After filtration of the precipitated ammonium salt, the darkorange filtrate was concentrated and poured into a large amount of MeOH to obtain the corresponding polymers (3a-c) in 70–98% yields as an orange powder. The polymers obtained were soluble in common solvents such as THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and toluene and only partly soluble in DMF and acetone. These polymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra. The molecular weight measurements were performed by gel permeation chromatography (GPC) in THF eluent using a calibration curve of polystyrene standards (Table 1). For example, the polymer **3b** ( $\mathbf{R} = n$ -dodecyl) had a number-average molecular weight  $(M_{\rm n})$  of 8000, which corresponds to a degree of polymerization of 11.5, with  $M_{\rm w}/M_{\rm p}$  of 1.8. On the other hand, the reaction of 1 with diethynylbenzene (R = H) and dimethoxydiethynylben-



Table 1. Syntheses and Optical Properties of Polymers 5a <sup>-</sup> c <sup>a</sup>								
polymer	R	yield <sup>b</sup> (%)	$M_{ m w}{}^c$	$M_{ m n}{}^c$	$M_{\rm w}/M_{\rm n}^{c}$	UV $\lambda_{\max}^{d}$ (nm)	$\epsilon^d$	PL $\lambda_{\max}^{d,e}$ (nm)
3a	<i>n</i> -C <sub>8</sub> H <sub>17</sub> ( <b>2a</b> )	73	5300	3100	1.7	370	5500	501
3b	<i>n</i> -C <sub>12</sub> H <sub>25</sub> ( <b>2b</b> )	98	14000	8000	1.8	384	11500	517
3c	$n-C_{16}H_{33}$ (2c)	70	8600	5900	1.5	380	10900	505

Table 1 Symphones and Ontical Properties of Polymous 20, of

<sup>*a*</sup> A mixture of **1** (0.30 mmol), **2** (0.30 mmol),  $PdCl_2(PPh_3)_2$  (0.030 mmol),  $PPh_3$  (0.060 mol), CuI (0.040 mmol), THF (2.0 mL), and HNPr<sup>*i*</sup><sub>2</sub> (2.0 mL) in a 50 mL Pyrex flask was refluxed for 48 h under nitrogen atmosphere. <sup>*b*</sup> Isolated yields after reprecipitation into MeOH. <sup>*c*</sup> GPC (THF), polystyrene standards. <sup>*d*</sup> Absorption and emission spectra were recorded in dilute CHCl<sub>3</sub> solutions at room temperature. <sup>*e*</sup> Excited at 380 nm (2.0 × 10<sup>-4</sup> M).



**Figure 1.** (A) Absorption spectra of polymer **3b** and model compounds **4a** and **4b** in CHCl<sub>3</sub>. (B) Dependence on concentration of fluorescence spectra of polymer **3b** in CHCl<sub>3</sub> solution (excitation wavelength at 380 nm).

zene (R = Me) gave a low molecular weight oligomer due to their poor solubility.

The optical properties of polymers  $3\mathbf{a}-\mathbf{c}$  obtained above were examined, and the results are summarized in Table 1. The UV-vis spectra of  $3\mathbf{a}-\mathbf{c}$  in a dilute chloroform solution at room temperature exhibited absorption maxima near 310 and 380 nm. The UV-vis spectrum of **3b** was compared with those of two model compounds (**4a** and **4b**),<sup>13</sup> as shown in Figure 1A. The spectra showed a red shift of 15 nm for the absorption of **3b** ( $\lambda_{max} = 384$  nm) relative to **4a** ( $\lambda_{max} = 369$  nm) and 47 nm relative to **4b** having a paracyclophane core  $(\lambda_{\text{max}} = 337 \text{ nm})$ . This result indicates the extension of  $\pi$ -delocalization length via the through-space based on two facing benzene rings of [2.2]paracyclophane. The absorption spectrum of the polymer **3b** film was slightly red-shifted against the solution with  $\lambda_{max}$  values of about 390 nm. In the fluorescence emission spectrum of the solution of 3a-c in chloroform (2.0  $\times$   $10^{-4}$  M) at room temperature on excitation at 380 nm, the emission peaks of 3a-c were observed near 510 nm in a visible green region. In the case of polymer **3b**, the dependence on concentration was also measured (Figure 1B). The spectra of highly diluted solution (5.0  $\times$  10<sup>-7</sup> M) displayed an emission peak at 460 and 412 nm and a shoulder at 510 nm. This shoulder became an intense peak and was red-shifted about 7 nm, as the concentration was increased from 5.0  $\times$  10<sup>-7</sup> to 2.0  $\times$  10<sup>-4</sup> M. These findings suggested that the emission peak at 517 nm in concentrated solution would be the result of intermolecular excimer formation.<sup>14</sup> In addition, 3b showed a quantum yield of 0.30 in CHCl<sub>3</sub> solution by using 9-anthracenecarboxylic acid in CH<sub>2</sub>Cl<sub>2</sub> as a standard ( $\Phi = 0.442$ ).<sup>15</sup> In the measurement of fluorescence quantum yields, the absorbance of each sample was below 0.05 at the excitation wavelength (380 nm). On the other hand, the formation of excimer in the solid film resulted in a decrease in luminescence yield, and the weak emission  $\lambda_{max}$  of **3b** was observed at 523 nm.

In conclusion, we have synthesized novel  $\pi$ -conjugated polymers having [2.2]paracyclophane in the main chain. The extension of  $\pi$ -conjugation via the through-space was observed according to the UV-vis absorption spectral data in comparison with those of the model compounds. Further studies on the electronic and thermal properties of **3** and on the synthesis of novel  $\pi$ -conjugated polymers via the through-space using  $\pi$ - $\pi$ interaction are now underway.

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- (12) A typical procedure is as follows. A mixture of 1 (110 mg, 0.30 mmol), **2b** (148 mg, 0.30 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (210 mg, 0.030 mmol), PPh<sub>3</sub> (157 mg, 0.060 mmol), CuI (76 mg, 0.040 mol), HNPr<sup>4</sup><sub>2</sub> (2.0 mL), and THF (2.0 mL) was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under nitrogen atmosphere. The reaction was carried out under reflux (bath temperature 85 °C) for 48 h with stirring. After the reaction mixture was cooled, ammonium salt was filtered off and washed with THF. The filtrate was concentrated and poured into MeOH (50 mL) to precipitate the polymer. The resulting polymer (3b) was filtered, washed with MeOH, and dried in vacuo to give 208 mg (0.030 mmol, 98%) as an orange powder. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  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), 5.36 (m, 2H), 5.62 (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<sub>3</sub>):  $\delta$  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.
- (13) The model compounds 4a and 4b were prepared according

to the typical Heck–Sonogashira reaction condition.<sup>11</sup> **4a**: A pale yellow solid:  $R_f = 0.33$  (SiO<sub>2</sub>, eluent, hexane/CH<sub>2</sub>-Cl<sub>2</sub> = 4/1). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (t, J = 7.6Hz, 6H), 1.25–1.36 (m, 32H), 1.51 (m, 4H), 1.84 (m, J=6.4 Hz, 4(1), 2.31 (s, 3(1), 2.51 (s, 3(1), 4.02 (t, J = 6.4 Hz, 4(1), 7.00 (s, 2(1), 7.04 (d, J = 8.0 Hz, 2(1), 7.22 (d, J = 8.0 Hz, 2(1), 7.33 (s, 2(1), 1<sup>3</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>50</sub>H<sub>70</sub>O<sub>2</sub>: C, 85.41; H, 10.04. Found: C, 85.32; H, 10.15. **4b**: A white solid:  $R_f = 0.37$  (SiO<sub>2</sub>, eluent, hexane/CHCl<sub>3</sub> = 3/1). <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  0.87 (t, J = 6.7 Hz, 6H), 0.88 (t, J = 6.7 Hz, 6H), 1.25–1.46 (m, 72 H), 1.78 (m, J = 7.1 Hz, 4H), 1.90 (m, J = 6.7 Hz, 4H), 2.88 (m, 2H), 3.00 (m, 2H), 3.31 (m, 2H), 3.77 (m, 2H), 3.94 (t, J = 6.7 Hz, 4H), 4.05 (t, J = 6.7 Hz, 4H), 6.49 (d, J = 7.8 Hz, 2H), 6.58 (s, 2H), 6.85 (m, 4H), 7.08 (m, 4H). <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>): δ 14.1, 22.7, 26.1, 26.2, 29.3, 29.4, 29.5, 29.6, 29.7 (overlapping signals), 31.2, 33.8, 34.1, 68.8, 69.4, 89.4, 93.6, 113.2, 113.9, 116.0, 118.7, 125.1, 130.4, 133.1, 137.2, 139.5, 142.1, 152.7, 154.1. Anal. Calcd for C<sub>80</sub>H<sub>120</sub>O<sub>4</sub>: C, 83.86; H, 10.56. Found: C, 83.64; H, 10.80.

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