

# Construction of benzene ring-layered polymers

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**Abstract**—A simple and novel approach for synthesizing the benzene ring-layered polymers using [2.2]paracyclophane and xanthene skeletons was demonstrated. Palladium-catalyzed polymerization of pseudo-*p*-diethynyl[2.2]paracyclophane **1**, 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**, and ethynylferrocene **3** gave the corresponding polymers **4a–c**, which composed of 7–30 face-to-face benzene rings by changing the feed ratio of **1–3**.

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In the field of organic compounds, the presence of cyclophane compounds, particularly those that consist of intramolecular face-to-face  $\pi$ -conjugated systems, has been acknowledged.<sup>1</sup> Among these, [*n.n*]paracyclophanes (*n* = 2 or 3) have the  $\pi$ -electron-cloud-overlapped structure, and such phanes are central to the study of cyclophane chemistry. A number of [*n.n*]paracyclophane derivatives have been prepared, and their unique structural and electronic properties resulting from characteristic interactions between the two co-facial  $\pi$ -electron systems have been investigated in detail.<sup>1,2</sup> On the other hand, few studies have been conducted on cyclophane-containing conjugated polymers;<sup>3–6</sup> further, the structures and properties of these polymers are limited because of their poor solubility in common organic solvents.<sup>3–5</sup> Recently, we reported the novel preparation and the physical properties of well-defined conjugated polymers<sup>7</sup> having cyclophane derivatives as key units, and the obtained polymers showed an extension of  $\pi$ -delocalization via the through-space and exhibited intense photo- and electroluminescence.

Since charge transfer through the organic material is achieved effectively via intermolecular  $\pi$ – $\pi$  interaction between the conjugated systems, the incorporation of the compound with  $\pi$ -stacked benzene rings into the polymer backbone is expected to result in highly efficient charge hopping as well as energy transfer. Furthermore,

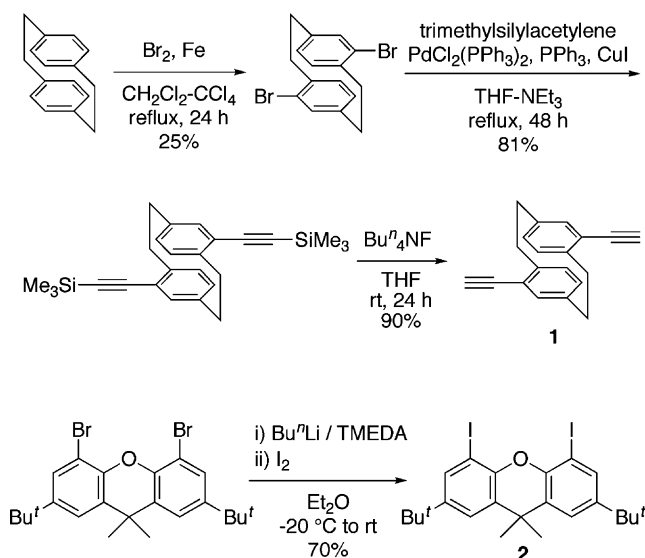
recently there has been considerable interest in the construction of a molecular wire using rigid-rod  $\pi$ -conjugated oligomers in order to realize one of the most sophisticated molecular devices.<sup>8,9</sup> From the above mentioned, therefore, it is desirable that the molecular wire is constructed by using the  $\pi$ -electron cloud via the through-space conjugation rather than the  $sp$  or  $sp^2$  bond via the through-bond conjugation.<sup>10</sup>

In this letter, we report a simple and novel process for the formation of the benzene ring-layered polymer, which consists of aligned benzene rings that face each other, by a palladium-catalyzed coupling reaction of pseudo-*p*-diethynyl[2.2]paracyclophane **1**<sup>7f</sup> with 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**.<sup>11</sup> Rotary motion of two aromatic rings attached to 1,8-position of naphthalene, biphenylene, xanthene, and so on, is restricted due to steric hindrance, and two aromatic rings having bulky units adopt a face-to-face structure. Rosenblum and co-workers reported the synthesis of the polymer having aligned metallocenes on the 1,8-position of the naphthalene skeleton by another approach, and investigated chemical, electrical, magnetic, and optical properties.<sup>12</sup> In this report, we focused on a novel construction of the molecular wires that are composed of layered benzene rings. The synthesis, characterization, and stereochemistry are discussed in detail.

The monomers pseudo-*p*-diethynyl[2.2]paracyclophane **1**<sup>7f</sup> and 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**<sup>11</sup> were prepared as shown in Scheme 1. Polymerization of **1**, **2** and ethynylferrocene **3** proceeded smoothly in the presence of catalytic amounts of Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI in THF–NEt<sub>3</sub> for 48 h at 50 °C

**Keywords:** [2.2]Paracyclophane; Benzene ring-layered polymer;  $\pi$ – $\pi$  Stacking; Through space; Molecular wire.

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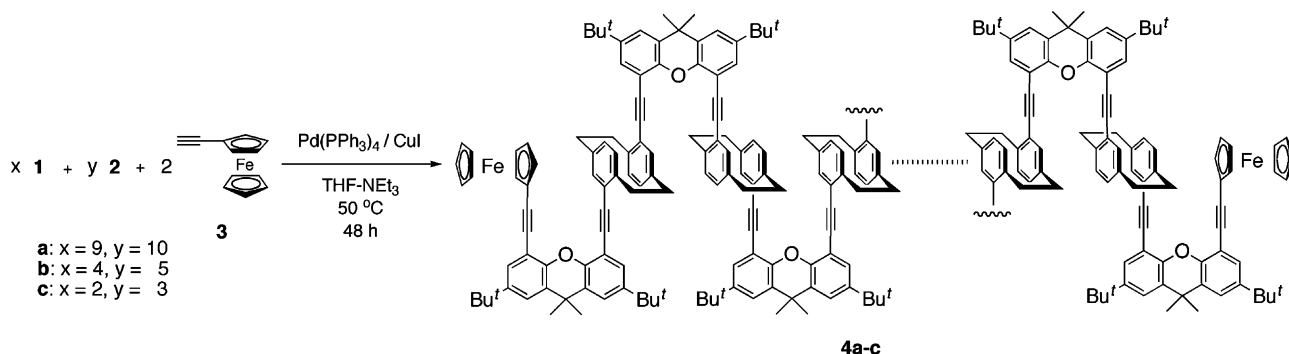
Scheme 1.

under  $\text{N}_2$  atmosphere,<sup>13</sup> as shown in Scheme 2. Ethynylferrocene was added for end-capping the polymer termini. After the reaction, solution was concentrated and poured into a large amount of  $\text{MeOH}$  to obtain the corresponding polymers **4a–c** in good yields (89–96%); the results of this reaction are summarized in Table 1. The molecular weight was estimated by the  $^1\text{H}$  NMR integral ratio between the protons of the terminal ferrocene group and those of the *t*-Bu group of the xanthene skeleton (Fig. 1(a)), and the results are also listed in Table 1. For example, the number-average molecular weight ( $M_n$ ) of polymer **4a** obtained from

run 1 was  $M_n = 9000$ , indicating that the number of cyclophane units incorporated into the polymer backbone is 15, that is,  $N = 32$  benzene rings including two terminal cyclopentadienyl units of ferrocene are aligned.

The  $^1\text{H}$  NMR spectra of (a) the benzene column **4a**, (b) the monomer **1**, and (c) the PPE-type [2.2]cyclophane-containing polymer prepared by us<sup>7a</sup> are shown in Figure 1. All signals in Figure 1a agree with the structure of the polymer **4a**. The number-average molecular weight ( $M_n$ ) and the number-average of layered benzene rings ( $N$ ), including two terminal cyclopentadienyl units of ferrocene were also calculated by assuming the  $^1\text{H}$  NMR integral ratio (*t*-Bu protons vs ferrocene protons) as  $M_n = 9000$  (calculated molecular weight = 5912) and  $N = 32$  (Fig. 1a). In Figure 1a–c, the signals observed at 2.5–4.0 ppm were assigned to the bridged methylene protons of the [2.2]paracyclophane unit as shown in the square. The bridged methylene protons of polymer **4a** displayed highly broad and upfield-shifted signals (Fig. 1a), while those of the PPE-type polymer (Fig. 1c) were observed in the same region as those of monomer **1** (Fig. 1b). This result implies that the bridged methylenes of polymer **4a** are affected by the ring current of the benzene ring of the subsequent [2.2]paracyclophane unit.<sup>15</sup>

Contrary to our expectation, the UV–vis spectra of polymers **4a–c** were almost identical and exhibited absorption maxima at approximately 330 nm and higher energy absorptions at approximately 290 nm (Fig. 2), regardless of the number of layered benzene rings. On the other hand, it was reported that the absorption spectra of multi-layered cyclophanes exhibited bathochromic and hyperchromic effects as the number of the



Scheme 2.

Table 1. Synthesis of benzene ring-layered polymers **4a–c**

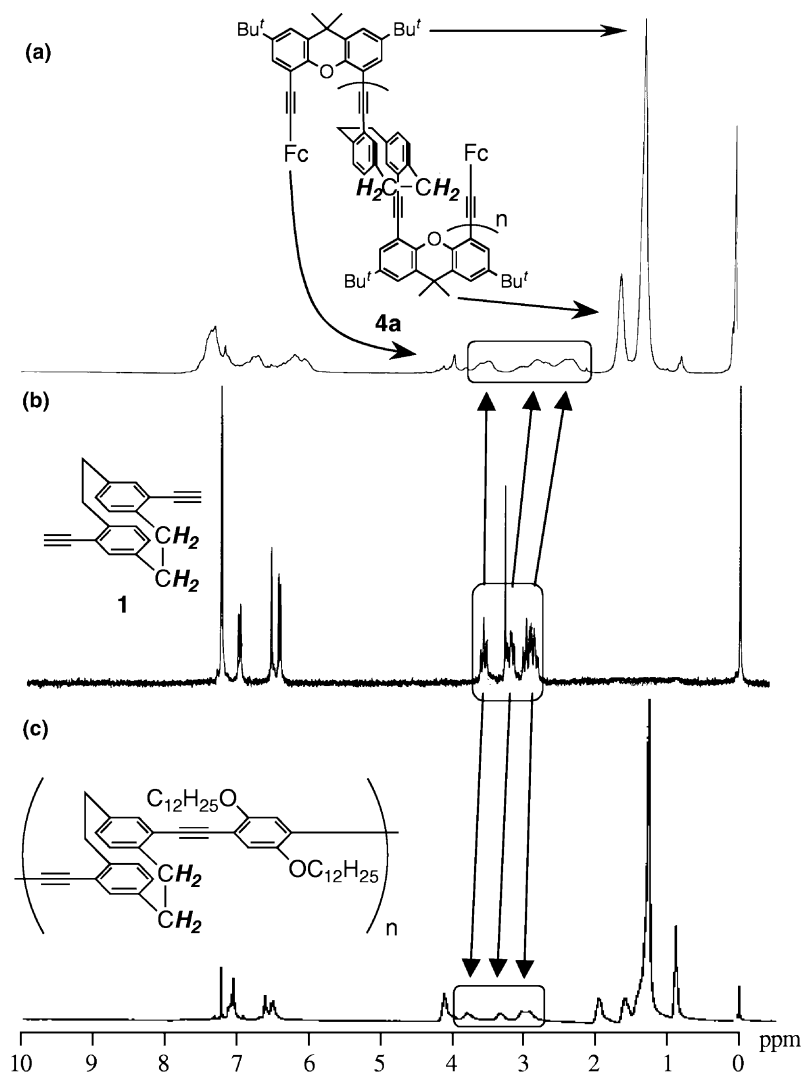
Polymer	Molar ratio <sup>a</sup>			Yield <sup>b</sup> (%)	Calcd.		Found <sup>d</sup>	
	1	2	3		$M_n$	$N^c$	$M_n$	$N^c$
<b>4a</b>	9	10	2	96	5912	20	9000	32
<b>4b</b>	4	5	2	96	3038	10	4900	16
<b>4c</b>	2	3	2	89	1888	6	2750	9

<sup>a</sup> 0.10 mmol of the monomer **2** was used.

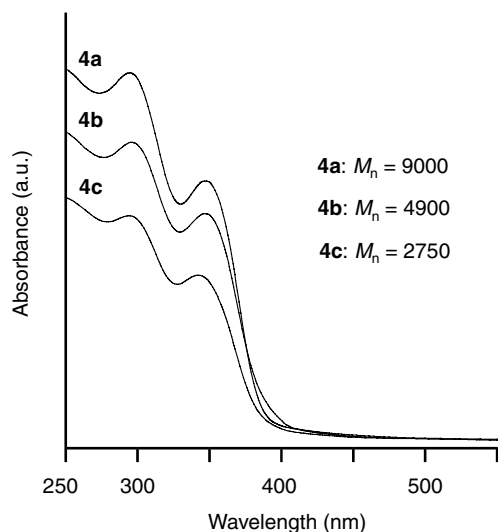
<sup>b</sup> Isolated yield after reprecipitation.

<sup>c</sup> The number of the layered benzene ring including two terminal cyclopentadienyl units of ferrocene.

<sup>d</sup> Estimated by the  $^1\text{H}$  NMR integral ratio.



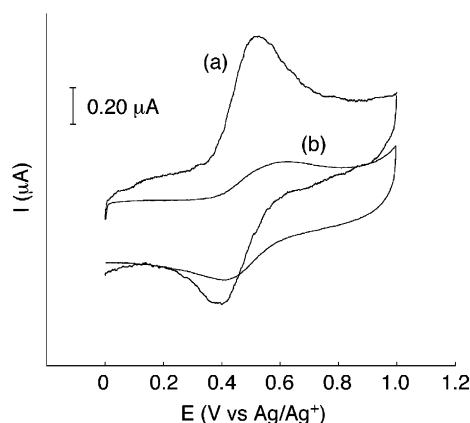
**Figure 1.**  $^1\text{H}$  NMR spectra of (a) polymer **4a**, (b) monomer **1**, and (c) PPE-type [2.2]paracyclophane-containing polymer in  $\text{CDCl}_3$  (270 MHz). The peaks in the square are the signals of the bridged methylene protons of [2.2]paracyclophane units.



**Figure 2.** UV-vis absorption spectra of the polymers **4a–c** in  $\text{CHCl}_3$ .

layered benzene rings increased.<sup>16,17</sup> Similar spectra were obtained from the fluorescence emission spectra of **4a–c**, while multi-layered cyclophanes exhibited bathochromic shifts similar to the behaviors of the UV spectra.<sup>16,17</sup> This observation suggests that effective  $\pi$ – $\pi$  stacking between cyclophane units in the solution is not achieved by the rotary motion (not a rotation due to steric hindrance) of each cyclophane.

The cyclic voltammetric analysis supports this finding. A broad oxidation peak derived from the oxidation of ferrocene units was obtained in the solution at approximately 0.52 V (Fig. 3a). Two terminal ferrocenes were oxidized simultaneously in the solution, because the information regarding the oxidation of one terminal ferrocene was not communicated to the other ferrocene. Cyclic voltammogram of the polymer thin film, which was shown to be amorphous by the powder X-ray analysis, exhibited the same result, as shown in Figure 3b. Polymer **4a** did not adopt the mixed valence state,  $[\text{Fc}^+\cdots\text{Fc}]^+$ , and two ferrocenes oxidized simultaneously



**Figure 3.** Cyclic voltammogram of (a) the polymer solution in  $\text{CH}_2\text{Cl}_2$  containing 0.10 M  $\text{Bu}_4\text{NPF}_6$  and (b) the polymer film coated on the ITO plate electrode in  $\text{CH}_3\text{CN}$  containing 0.10 M  $\text{Et}_4\text{NBF}_4$  (vs  $\text{Ag}/\text{Ag}^+$ ) at a scan rate of 100 mV/s.

in both the solution and the film. The distance between two benzene rings attached to 1,8-position of the xanthene skeleton is estimated to be approximately 4.5 Å. Therefore, it is considered that these benzene ring-layered polymers **4a–c** possess a wavy structure rather than a rigid column. In order to achieve communication between two terminal units of the benzene ring-layered polymer, a shorter distance between the neighboring cyclophane is required.

In summary, we demonstrated a simple and novel approach for synthesizing benzene ring-layered polymers using [2.2]paracyclophane and xanthene skeletons. This strategy offers a feasible methodology for the construction of the molecular wire via the through-space conjugation of aromatic rings, which is capable of realizing the effective transmission of information via the through-space interaction. Further studies on the synthesis of benzene ring-layered polymers using biphenylene or naphthalene instead of xanthene as a cyclophane scaffold are currently in progress.

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- 2,7-Di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.31 (s,  $-\text{Bu}^t$ , 18H), 1.61 (s,  $-\text{Me}$ , 6H), 7.34 (s, aromatic protons, 2H), 7.70 (s, aromatic protons, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  31.4, 32.0, 34.5, 35.7, 84.2, 122.7, 130.5, 134.7, 147.9, 148.1. Anal. Calcd for  $\text{C}_{23}\text{H}_{28}\text{I}_2\text{O}$ : C, 48.10; H, 4.91. Found: C, 48.07; H, 4.95.
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- A typical procedure<sup>14</sup> is as follows. A 50-mL Pyrex flask was charged with **1** (23 mg, 0.090 mmol), **2** (57 mg, 0.10 mmol), **3** (4.2 mg, 0.020 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (12 mg, 0.010 mmol),  $\text{CuI}$  (2.0 mg, 0.010 mmol),  $\text{NEt}_3$  (2.0 mL), THF (4.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at 50 °C for 48 h with stirring. The resulting solution was concentrated and poured into a large amount of MeOH to give the crude polymer as a brown powder. This powder was dissolved in  $\text{CHCl}_3$ , and the resulting solution was poured into a large amount of MeOH to precipitate the polymer. The resulting polymer **4a** was filtered, washed with MeOH, and dried in vacuo to give **4a** as a brown powder. Polymers **4a–c**. Yield: 89–96%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  1.35

- (s,  $-Bu^t$ ,  $18(n+1)H$ ), 1.67 (s,  $-Me$ ,  $6(n+1)H$ ), 2.1–3.1 (br, bridge methylene protons of cyclophane units,  $6nH$ ), 3.3–3.7 (br, bridge methylene protons of cyclophane units,  $2nH$ ), 3.9–4.2 (br, protons of ferrocene units,  $18H$ ), 5.9–6.3 (br, aromatic protons of cyclophane units,  $4nH$ ), 6.5–6.9 (br, aromatic protons of cyclophane units,  $2nH$ ), 7.0–7.5 (br m, aromatic protons of xanthene units,  $4(n+1)H$ ); **4a**  $n = 14.7$ , **4b**  $n = 7.2$ , and **4c**  $n = 3.5$ .
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