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Synthesis and Properties of [2.2]Paracyclophane-Layered Polymers

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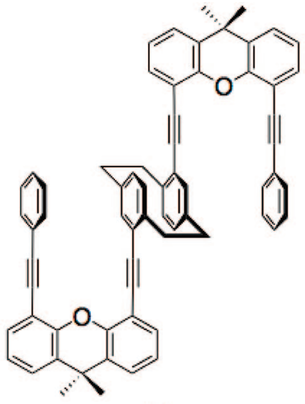
The field of conjugated polymers has shown dramatic growth over the past three decades[1] from the initial discovery and development of conductive polyacetylenes.[2] Numerous conjugated polymers have been synthesized and applied in optical, electronic, and sensing devices. The syntheses of new conjugated polymers have been intensively pursued;[1] however, there exist only a few reports on polymers which consist of aromatic rings via the through-space interaction of $\pi-\pi$ stacking. Utilizing $\pi-\pi$ stacking in the polymer main chain would allow effective hole, electron, and energy transfer in molecular wires as well as in optoelectronic devices. With this in mind, Nakano and co-workers fabricated π-stacked polymers by the polymerization of dibenzofulvene derivatives.[3] The obtained π-stacked poly(dibenzofulvene) exhibited a higher hole drift mobility than the through-bond conjugated poly(phenylenevinylene).[3b] Recently, Würthner and co-workers reported a perylene−bisimide oligomer comprising face-to-face orange, violet, and green perylene bisimide chromophores based on the calix[4]arene scaffold.[4] They attained the construction of efficient energy transfer system. Very recently, Jenekhe and co-workers synthesized the first examples of π-stacked side-chain conjugated polymers containing conjugated oligoquinolines in the side chain, which exhibited photoluminescence from the excimer state of side-chain groups in dilute solutions.[5] In addition, enhancement in electroluminescence efficiencies was also attained. We have focused on through-space conjugated polymers containing a cyclophane unit in the main chain.[6] Within this area, we described a new strategy to construct a π-stacked structure by using a xanthene compound as a scaffold and [2.2]paracyclophane as a layered aromatic ring.[6i,7] Herein, we report the synthesis and properties of [2.2]paracyclophane-layered polymers possessing fused aromatic rings at the ends of the polymer chain. Photoexcited energy transfer from the layered [2.2]paracyclophane to the terminal units was also observed. These polymers have a potential application in a new class of molecular wires consisting of $\pi-\pi$ stacking.[8]

The synthetic scheme for [2.2]paracyclophane-layered polymers **P3−6** and the polymerization results are shown in Table 1. Diethynyl[2.2]paracyclophane (**1**), diiodo-9,9-dimethylxanthene (**2**), and terminal alkynes **3−6** were polymerized by using a Pd(PPh$_3$)$_4$/CuI catalytic system.[9] The number-average molecular weight (M_n) of the target polymers was controlled by the molar ratio of the monomers (x:y:z). For example, M_n of polymer **P5a** (x:y:z = 9:10:2) possessing anthracene as an end-capping group was found to be 7.5 kDa by ^{1}H NMR. This result indicates that an average of 12 [2.2]paracyclophanes are linearly arranged in the polymer main chain. The M_n value obtained from gel permeation chromatography (GPC, polystyrene standards) was lower than that obtained from ^{1}H NMR because of the folded structure of the polymer chain.



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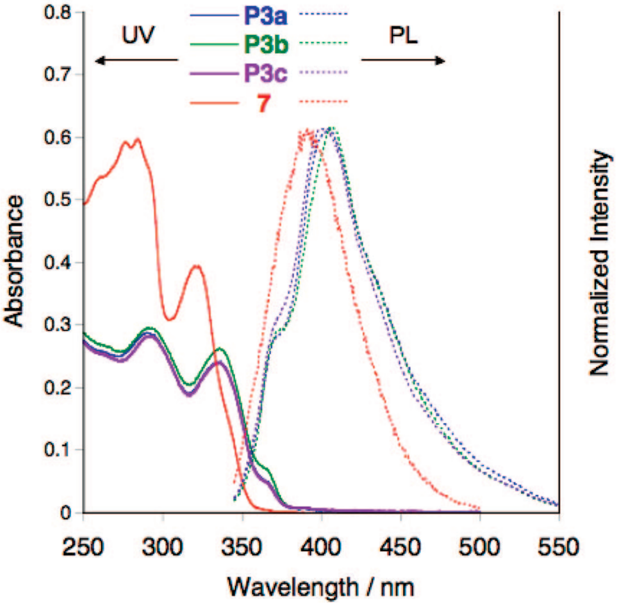

Figure 1. UV−vis absorption spectra of **P3a−c** and **7** (1.0×10^{-5} M) and normalized fluorescence emission spectra of **P3a−c** (5.0×10^{-7} M) and **7** (1.0×10^{-6} M) in CHCl$_3$.

The UV−vis absorption spectra (in CHCl$_3$, 1.0×10^{-5} M) of polymers **P3a−c** and compound **7** are shown in Figure 1. The absorption spectra of polymers **P3a−c** exhibited $\pi-\pi^*$ absorption peaks at around 290 and 330 nm and an edge at around 375 nm; these peaks appeared at longer wavelengths than the peaks of compound **7**. However, the patterns of the absorption spectra of **P3a−c** were independent of the number of layered [2.2]paracyclophanes. It has been reported that the wavelengths of the absorption peak and edge are saturated in the range of approximately five face-to-face aromatic rings;[3b,10,11] therefore, it is thought that even polymer **P3c** (M_n = 2.1 kDa, nine benzene rings) has sufficiently extended through-space interactions in the ground state. The absorbance of **7** was higher than those of **P3a−c** because concentrations of **P3a−c** were based on the [2.2]paracyclophane unit in disregard of the terminal unit. The fluorescence emission spectra of **P3a−c** and **7** in dilute CHCl$_3$ solutions (5.0×10^{-7} M)[12]

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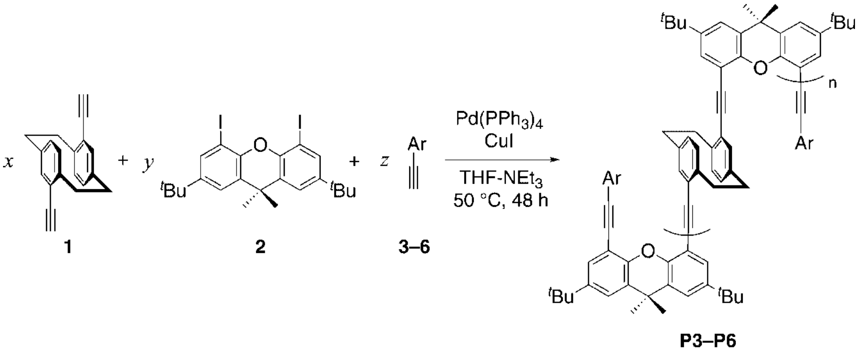
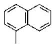
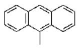
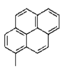
Table 1. Synthesis of [2.2]Paracyclophane-Layered Polymers



Polymer	Ar	Molar ratio			Yield (%)	Calcd. M_n (kDa)	Found$_{GPC}$[a]		Found$_{NMR}$[b]
		x	*y*	*z*			M_n (kDa)	M_w/M_n	M_n (kDa)
P3a		9	10	2	79	5.96	2.1	1.34	4.10
P3b		4	5	2	65	3.08	1.9	1.26	3.10
P3c		2	3	2	50	1.93	1.7	1.18	2.10
P4a		9	10	2	81	5.80	1.7	1.64	7.80
P4b		4	5	2	78	2.92	1.3	1.58	3.80
P4c		2	3	2	70	1.77	1.1	1.47	2.50
P5a		9	10	2	70	5.90	1.8	1.74	7.50
P5b		4	5	2	50	3.02	1.6	1.55	4.20
P5c		2	3	2	65	1.87	1.3	1.43	2.60
P6a		9	10	2	78	5.95	1.8	1.30	4.03
P6b		4	5	2	82	3.07	1.3	1.28	2.90
P6c		2	3	2	57	1.92	1.1	1.32	2.44

[a] Estimated by GPC ($CHCl_3$), polystyrene standards. [b] Estimated by ^1H NMR integral ratio between bridged ethylene protons of the cyclophane unit and aromatic protons of the end-capping group.

are also shown in Figure 1 as dotted lines. These spectra exhibited almost identical behaviors; i.e., emission from the layered [2.2]paracyclophane was observed.

The absorption spectra of polymers **P5a**−**c**, however, exhibited a strong absorption peak at around 270 nm and a broad absorption peak at around 400 nm in addition to the $\pi-\pi^*$ absorption band of [2.2]paracyclophane, as shown in Figure 2A. By comparison with the absorption spectrum of 9-ethynylanthracene (Figure S15), it could be seen that these absorption peaks at around 270 and 400 nm resulted from absorption by the end-capping anthracene units. The concentration of the anthracene units was calculated on the basis of that of the [2.2]paracyclophane unit; therefore, the relative concentration and absorption of the end-capping anthracene unit were found to increase as M_n decreased.

Figure 2B shows the fluorescence emission spectra of **P5a**−**c** in dilute $CHCl_3$ solutions (1.0×10^{-7} M) excited at 334 nm. At this excitation wavelength, only the layered [2.2]paracyclophane is effectively excited, while the end-capping anthracene unit is not. As shown in Figure 2B, an emission peak with the vibrational structure was observed for polymers **P5b** and **P5c**, and an emission peak at around 400 nm and a peak with a vibrational structure were observed for **P5a**. By comparison with the fluorescence spectrum of 9-ethynylanthracene (Figure S15), which has a vibrational structure similar to those of polymers **P3a**−**c** (Figure 1), in polymer **P5a**, we found that the emission peak at around 400 nm due to the layered [2.2]paracyclophane units remained, and a strong emission corresponding to the anthracene units appeared. In addition, polymers **P5b** and **P5c** with shorter chain lengths exhibited emission almost exclusively from the end-capping anthracene units.

Figure 3A shows the fluorescence emission spectra of polymers **P3a** (M_n = 4.1 kDa) and **P5b** (M_n = 4.2 kDa) in diluted $CHCl_3$ solutions (1.0×10^{-7} M) excited at 334 nm. The emission intensities of both the spectra are expected to be comparable because of their similar M_n values, i.e., similar concentrations of layered cyclophane in the polymer chains. The emission from the layered cyclophane units in polymer **P5b** decreased, and emission from the end-capping anthracene units was observed. This concentration (1.0×10^{-7} M) was sufficiently dilute to avoid intermolecular interactions according to the concentration effect of the photoluminescence spectra (Figures S18 and S24). We confirmed that the emission from cyclophanes had decreased and that emission from anthracene had increased from the time-resolved fluorescence spectra of polymer **P5a**, as shown in Figure 3B.[13] The efficiency of energy transfer from the layered cyclophanes to the anthracene units in **P5a** was estimated to be 57%, according to the fluorescence quantum yields of the layered cyclophanes. In polymers **P5a**−**c**, good overlap was observed between the emission peak of the layered-cyclophanes (~400 nm) and the absorption peak of 9-ethynylanthracene (at around 400 nm), which caused fluo-

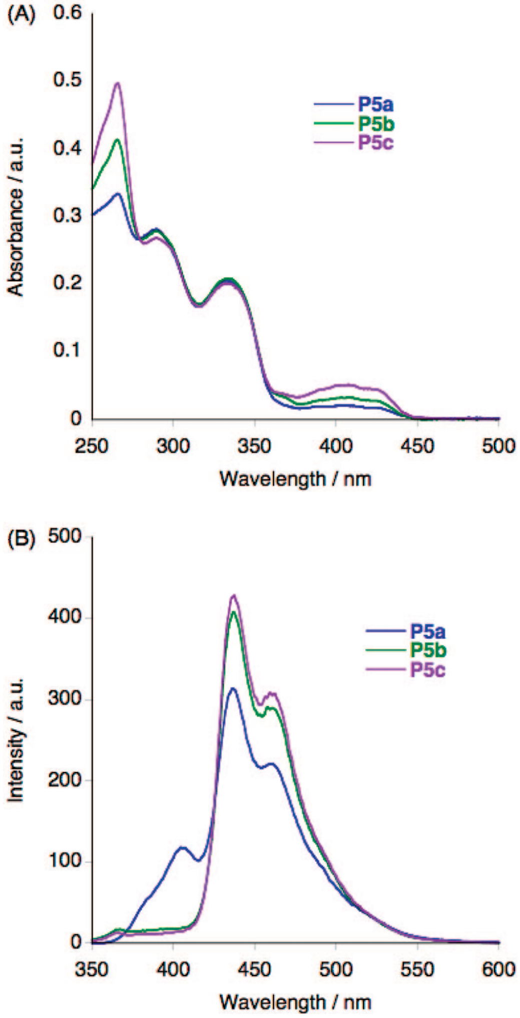


Figure 2. (A) Absorption spectra of **P5a−c** in CHCl$_3$ (1.0×10^{-5} M). (B) Fluorescence spectra of **P5a−c** excited at 334 nm in CHCl$_3$ (1.0×10^{-7} M).

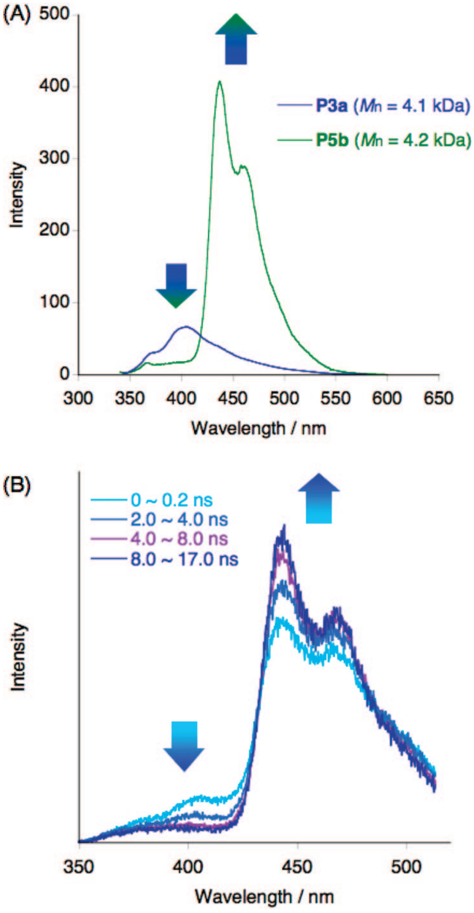


Figure 3. (A) Fluorescence spectra of **P3a** (M_n = 4.1 kDa) and **P5b** (M_n = 4.2 kDa) excited at 334 nm in CHCl$_3$ (1.0×10^{-7} M). (B) Time-resolved fluorescence spectra of **P5a** excited at 337 nm (N$_2$ laser) in CHCl$_3$.

rescence resonance energy transfer (FRET)[14] from the cyclophanes to the end-capping anthracenes.

On the other hand, it is not likely that FRET occurs in polymers **P4a−c** possessing the end-capping naphthalene units. As can be seen in Figure S15, the absorption edge of 1-ethynylnapthalene was observed at 330 nm, which was shorter wavelength than the emission from the layered cyclophanes (Figure 1). Therefore, both emissions from the end-capping naphthalene and the layered cyclophanes in polymers **P4a−c** were observed by excitation at 290 nm in CHCl$_3$ (1.0×10^{-7} M), as shown in Figure S20. In the case of polymers **P6a−c** possessing pyrene termini, absorption peaks of ethynylpyrene units were observed at 360 and 390 nm (Figure S27). Emission spectra of **6a−c** exhibited vibrational structures derived from the end-capping pyrene units as shown in Figure S28. An overlap between emission from [2.2]paracyclophanes and absorption of 1-ethynylpyrene moieties was relatively poor, and thus, polymers **6a−c** emitted from the end-capping pyrene units by FRET as well as from the layered cyclophane units.

In summary, this paper reports the procedures for the synthesis of [2.2]paracyclophane-layered polymers possessing fused aromatic rings as the end-capping groups. Polymers with anthracene at the chain ends exhibited FRET from the layered [2.2]paracyclophanes to the end-capping anthracene. This synthetic strategy enables the synthesis of various aromatic ring-layered polymers. Experiments are currently underway to construct a class of aromatic ring-layered polymers that allow energy or electrons to pass only in one direction.

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Supporting Information Available: Synthetic details, ^{1}H and ^{13}C NMR spectra (Figures S1−14), and absorption and fluorescence spectra (Figures S15−29). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) This concentration is sufficiently diluted because the emission spectrum of **P3a** was independent of concentrations below 1.0×10^{-5} M, as shown in Figure S18.

(13) Fluorescence decay curves and parameters of **P5a** are shown in Figure S26 and Table S1, respectively.

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