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Notes

[2.2]Paracyclophane-Layered Polymers End-Capped with Fluorescence Quenchers

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Introduction

The design and synthesis of new conjugated polymers have attracted interest since the discovery of conductive polyacetylenes.[1] In order to tune the optical and/or electrical properties of these polymers, various aromatic compounds have been incorporated into a polymer chain and various conjugated backbone structures such as poly(*p*-phenylene−ethynylene),[2] poly(*p*-phenylenevinylene),[3] and poly(*p*-phenylene)[4] have been manipulated.[5] Almost all of the conjugated polymers prepared to date consist of a through-bond conjugation system comprising sp or sp^2 carbons. Although conjugated polymers have been attracting considerable attention, only a few studies have been conducted on through-space conjugated polymers that consist of π-stacked aromatic systems. The introduction of a $\pi-\pi$ stacking structure in the conjugated polymer backbone would allow effective hole, electron, and energy transfer in a polymer chain and in an aggregate of polymers. Considering this possibility, Nakano and co-workers have synthesized poly(dibenzofulvene)s with a π-stacked conformation[6] that exhibited a higher hole drift mobility than the through-bond conjugated poly(phenylenevinylene).[6b]

Recently, we have focused on the synthesis of through-space conjugated polymers by taking advantage of the π-stacked structure of [2.2]paracyclophane.[7–9] We have found that these [2.2]paracyclophane-containing polymers showed an extension of the conjugation length due to both the through-space conjugation of two-layered aromatic rings of [2.2]paracyclophane and through-bond conjugation. On the basis of this finding, we have designed and synthesized π-stacked polymers by using a xanthene compound as a scaffold and [2.2]paracyclophane as a layered aromatic ring.[9j,k] Polymers have been successfully prepared and characterized, and no information has been obtained on their effective $\pi-\pi$ stacking. However, the [2.2]paracyclophane-layered polymer end-capped by anthracene exhibited fluorescence resonance energy transfer (FRET) from the layered cyclophanes to the end-capping anthracenes due to the good overlap between the emission of the layered [2.2]paracyclophanes and the absorption of the anthracene moiety.[9k] In this Note, we report the synthesis and properties of [2.2]paracyclophane-layered polymers in which fluorescence quenchers exist at the ends of the polymer chain; these are responsible for photoexcited energy transfer from the layered [2.2]paracyclophane to the terminal units. These polymers give rise to a new class of molecular wires comprising π-stacked aromatic rings.[6,10]

Results and Discussion

[2.2]Paracyclophane-layered polymers **P3** and **P4** were synthesized by the polymerization of diethynyl[2.2]paracyclophane **1**, diiodo-9,9-dimethylxanthene **2**, and terminal alkynes **3** or **4** in the presence of a catalytic amount of Pd(PPh$_3$)$_4$/CuI,[11] as shown in Scheme 1. The polymerization results are listed in Table 1. Nitrobenzene was used for the end-capping aromatic groups of polymer **P3**. Polymers **P4** end-capped with [2.2]paracyclophanes were prepared as reference polymers.[9k] Their number-average molecular weight (M_n) was controlled by the molar ratio of the monomers (x:y:z). For example, the M_n value of polymer **P4a** (x:y:z = 9:10:2) possessing [2.2]paracyclophane termini was found to be 4100 by using ^{1}H NMR integral ratio (entry 4). This result indicates that an average of eight [2.2]paracyclophanes were linearly arranged in the polymer main chain. The M_n value of **P4a** obtained by gel permeation chromatography (GPC, polystyrene standards) was 2060. This value was lower than that obtained by ^{1}H NMR (M_n = 4100) because of the folded structure of the polymer chain. These polymers possessed good thermal stability, and polymers **P3a** and**P4a** exhibited 10% weight loss temperatures at 459 and 477 °C, respectively, by the thermogravimetric analysis (TGA) under N$_2$.[12]

The optical properties of the polymers were examined. Parts A and B of Figure 1show the UV−vis absorption spectra of

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

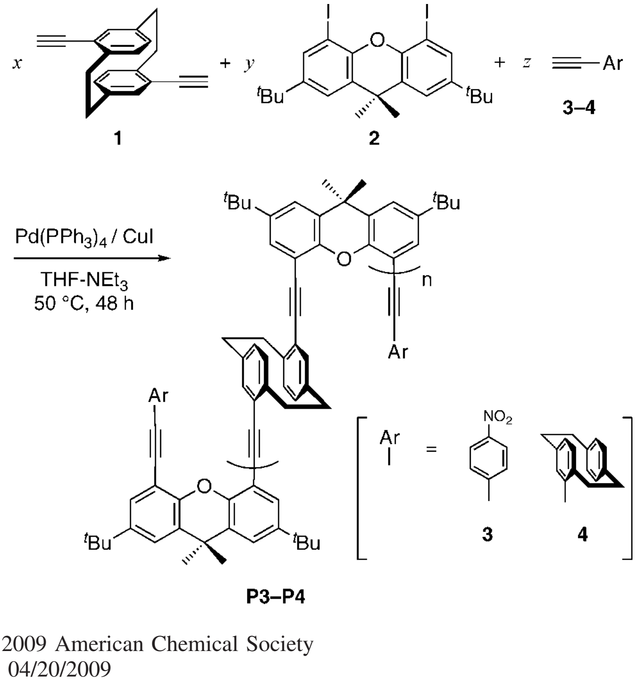

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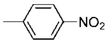
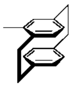
Table 1. Results of Polymerization

Entry	Polymer	–Ar	Mol. ratio *x*	*y*	*z*	Yield %	Calcd. M_n	Found M_n[a]	PDI[b]	n[c]
1	**P3a**		9	10	2	76	5786	5750	1.4	8.9
2	**P3b**		4	5	2	59	2912	3000	1.5	4.2
3	**P3c**		2	3	2	56	1762	1700	1.6	1.9
4	**P4a**		9	10	2	79	5956	4100	1.3	5.8
5	**P4b**		4	5	2	65	3082	3100	1.3	4.0
6	**P4c**		2	3	2	50	1933	2100	1.2	2.3

[a] Estimated by ^{1}H NMR integral ratio between bridged ethylene protons of the cyclophane unit and aromatic protons of the end-capping group. [b] M_w/M_n estimated by GPC (CHCl$_3$), polystyrene standards. [c] The number of the repeating unit estimated by ^{1}H NMR.

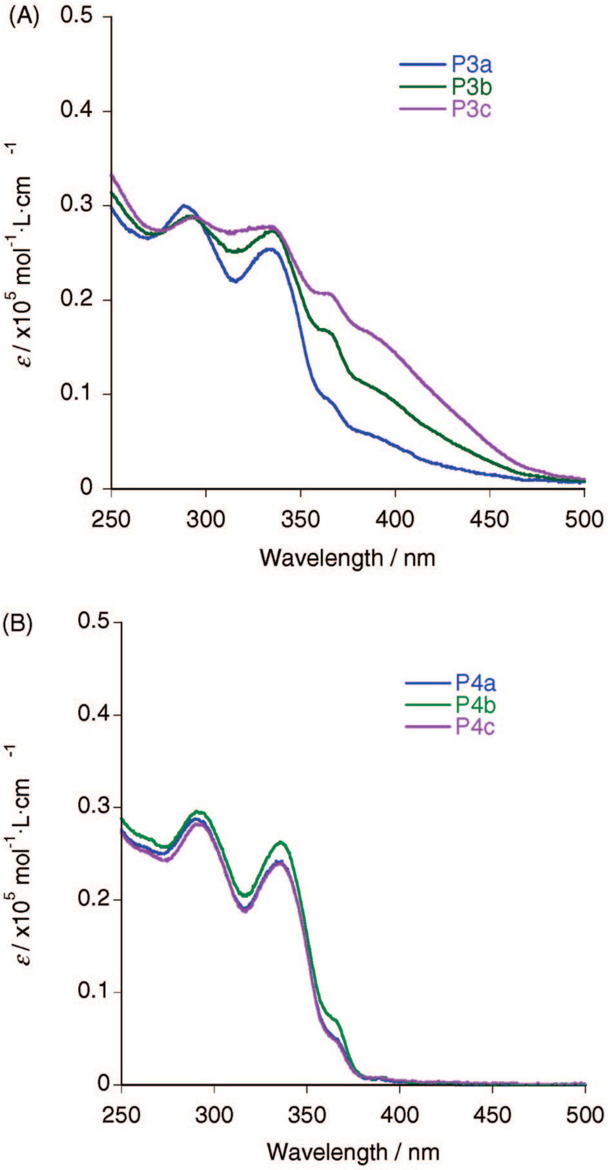


Figure 1. (A) UV–vis absorption spectra of **P3a–c** in CHCl$_3$ (1.0 × 10^{-5} M/repeating unit) and (B) UV–vis absorption spectra of **P4a–c** in CHCl$_3$ (1.0 × 10^{-5} M/repeating unit).

P3a–c and **P4a–c** in CHCl$_3$ (1.0 × 10^{-5} M), respectively. The absorption spectra of **P4a–c** exhibited $\pi-\pi^*$ absorption peaks of [2.2]paracyclophanes at around 290 and 330 nm, as shown in Figure 1B, while those of **P3a–c** exhibited broad absorption peaks at long wavelengths derived from the terminal nitrobenzene moieties, in addition to $\pi-\pi^*$ absorption peaks, as shown in Figure 1A. The relative concentration of the end-capping nitrobenzene unit increased as M_n decreased because the concentration (in CHCl$_3$, 1.0 × 10^{-5} M) was calculated using the number of [2.2]paracyclophane units. Therefore, in polymers **P3a–c**, the broad absorption peaks increased, while there was no change in the absorbance of [2.2]paracyclophane, regardless of M_n, as shown in Figure 1A. Moreover, the absorption spectra of **P4a–c** were independent of M_n, as shown in Figure 1B. It has been reported that the through-space conjugation length is saturated in the vicinity of approximately five face-to-face aromatic rings.[6b,10d] Thus, even polymer **P4c** with M_n = 2100 (nine benzene rings) and PDI = 1.2 had sufficiently extended through-space conjugations in the ground state.

The fluorescence emission spectra of **P3a–c** and **P4a** in dilute CHCl$_3$ solution (1.0 × 10^{-5} M) are shown in Figure 2. This concentration (1.0 × 10^{-5} M) was sufficiently low so that intermolecular interactions could be ignored (Figure S13 for **P3a** and Figure S16 for **P4a**). All the polymers were excited at 333 nm, and **P3a** and **P4a** exhibited almost identical fluorescence spectra with peak maxima at around 410 nm, which were assigned to the emission from the layered [2.2]paracyclophane units. The peak intensity of **P3a** was significantly lower than that of **P4a**,[13] and emissions were highly quenched in polymers **P3b** and **P3c**.[14] Fluorescence lifetime of **P3a–c** depended of the chain length, and the longer chain length exhibited the shorter lifetime, while that of **P4a–c** was almost independent of the chain length, as shown in Figure S26 and Table S1 in the Supporting Information. No emission peak from compound **5** consisting of [2.2]paracyclophane and two nitrobenzenes was detected, as expected from the Stern–Volmer plots (vide infra). The end-capping groups in **P3a–c** effectively quenched the photoluminescence from the layered [2.2]paracyclophanes via through-space interaction. The solvent polarity dependence of the fluorescence emission was examined in the case of **P3a** and **P4a**. It was observed that solvent effects were insignificant in dilute cyclohexane, CHCl$_3$, THF, CH$_2$Cl$_2$, and DMF,[15] indicating that energy transfer from the layered cyclophanes to the end-capping nitrobenzene moieties occurred dominantly. Considering

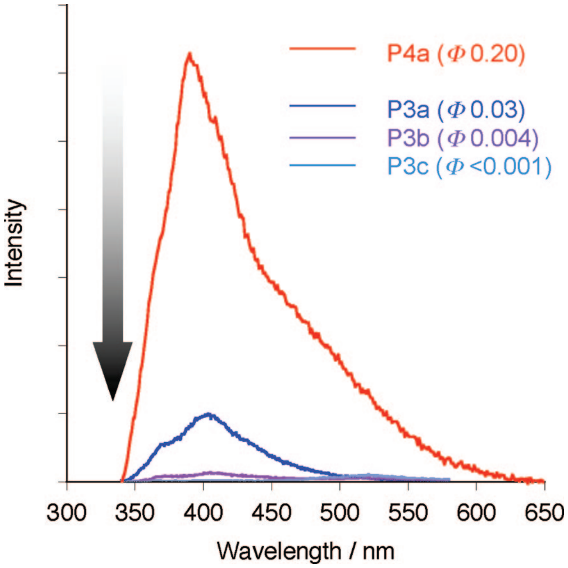
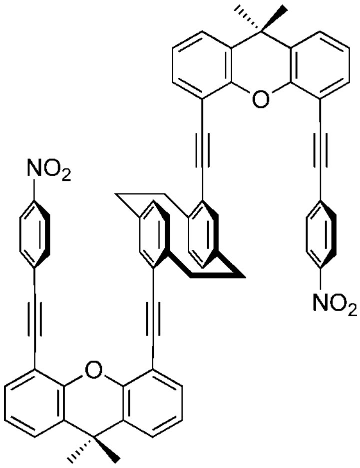


Figure 2. Fluorescence emission spectra of **P3a**−**c** and **P4a** in $CHCl_3$ (1.0×10^{-5} M/repeating unit) excited at 333 nm. Absolute fluorescence quantum efficiencies (Φ) are included.

the energy band gap of the layered [2.2]paracyclophane and the end-capping group, the energy transfer occurs from the layered [2.2]paracyclophanes to the terminal 4-nitrophenylethynylbenzene moiety rather than the nitrobenzene unit itself.[16] As shown in Figure 1A, the UV−vis absorption spectrum of polymers **P3a**−**c** exhibits a broad absorption band at around 375 nm derived from the terminal 4-nitrophenylethynylbenzene moiety.



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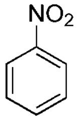

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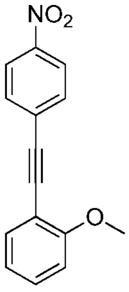

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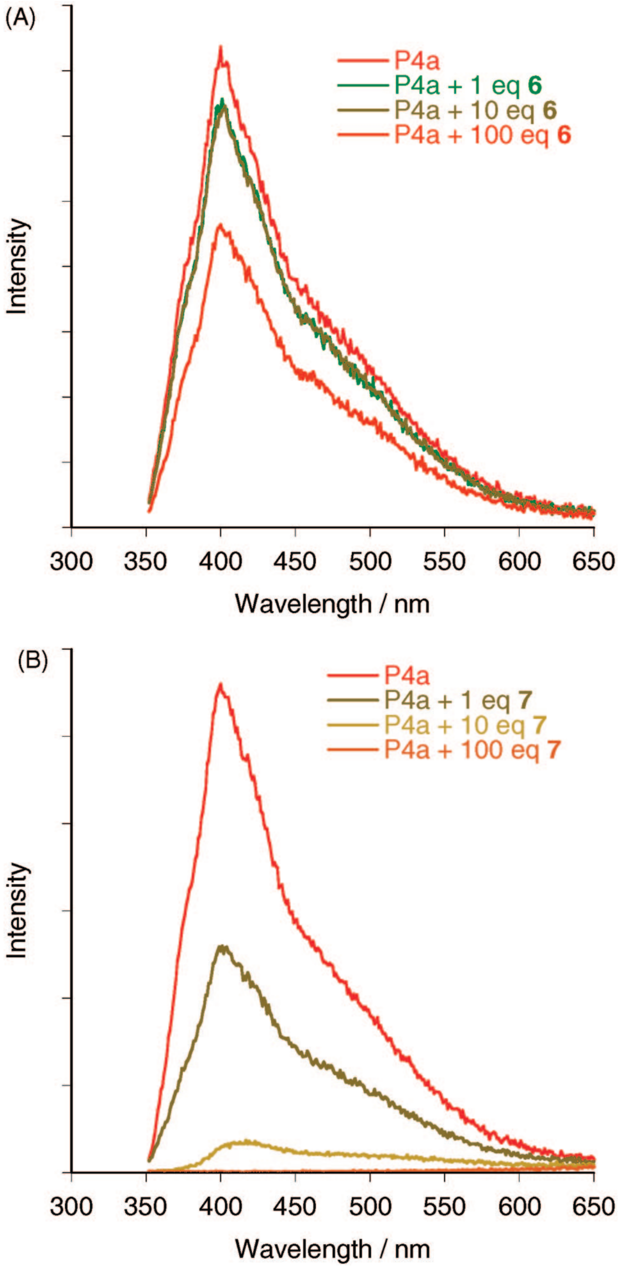

Figure 3. (A) Fluorescence emission spectra of **P4a** (1.0×10^{-5} M/repeating unit in $CHCl_3$) with 1, 10, and 100 equiv of nitrobenzenes (**6**) and (B) fluorescence emission spectra of **P4a** (1.0×10^{-5} M/repeating unit in $CHCl_3$) with 1, 10, and 100 equiv (1.0×10^{-5}, 1.0×10^{-4}, and 1.0×10^{-3} M in $CHCl_3$) of 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**) excited at 333 nm.

The emission spectra of **P4a** possessing [2.2]paracyclophane termini with additional nitrobenzene (**6**) or 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**) are shown in Figure 3A,B. Depending on the [2.2]paracyclophane unit, 1, 10, and 100 equiv of quenchers were added to the solution of **P4a**. In spite of the addition of 100 equiv of **6**, only 35% of the emission of **P4a** was quenched, whereas ~86% of the emission of **P3a** was quenched by only two end-capping nitrobenzenes.[13] In the case of the addition of **7** (Figure 3B), effective quenching was observed due to the overlap between the emission of the layered [2.2]paracyclophane moieties and the absorbance of **7**. In both cases, the two end-capping nitrobenzene moieties in polymer **P4a** effectively quenched the emission from the layered [2.2]paracyclophanes because there is no diffusion of the quenchers. The Stern−Volmer plots of **P3a**−**c** and **P4a** with additional quenchers are shown in Figure 4. The Stern−Volmer coefficient (K_{sv}) of **P3a**−**c** was 5.4×10^6, which was ap-

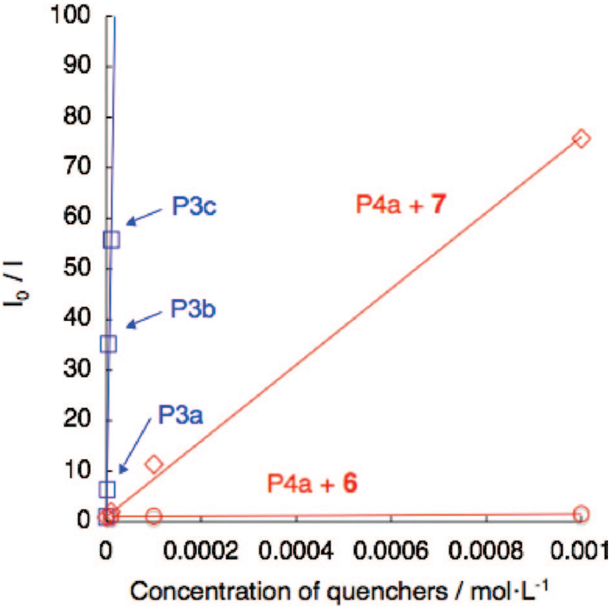

Figure 4. Stern−Volmer plots of **P3a**−**c** (1.0×10^{-5} M/repeating unit in $CHCl_3$) and **P4a** (1.0×10^{-5} M/repeating unit in $CHCl_3$) with nitrobenzene **6** and 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**).

proximately 1.0×10^4 times and 7.5×10 times larger than that of **P4a** containing additional quenchers **6** ($K_{sv} = 5.4 \times 10^2$) and **7** ($K_{sv} = 7.5 \times 10^4$), respectively. A significant polymer concentration effect was observed by the incorporation of nitrobenzene moieties into the polymer chain ends. This effect is regarded as a type of signal amplification effect of conjugated polymers.[17] Thus, effective energy transfer occurs in the [2.2]paracyclophane-layered polymer from the layered cyclophanes to nitrobenzene moieties.

In summary, [2.2]paracyclophane-layered polymers end-capped with fluorescence quenchers were synthesized by using the xanthene skeleton as a scaffold. Fluorescence emission from the layered [2.2]paracyclophane was quenched more effectively by the end-capping fluorescence-quencher units than by an excess amount of quenchers. By using our approach, various aromatic rings other than [2.2]paracyclophane can be used to form π-stacked structures. The new class of polymers containing layers of aromatic rings can be used to produce single molecular wires consisting of $\pi-\pi$ stacking and to fabricate optoelectronic devices. Energy (and/or an electron) is transferred to both terminals. The design and synthesis of π-stacked oligomers and polymers, which allow unidirectional flow of energy or electrons, are currently in progress.

Experimental Section

General Method. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 instrument at 400 and 100 MHz, respectively. The chemical shift values were expressed relative to Me_4Si as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. 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. Gel permeation chromatography (GPC) was carried out on a TOSOH 8020 (TSKgel G3000HXL column) instrument using $CHCl_3$ as an eluent after calibration with standard polystyrene samples. UV−vis absorption spectra were obtained on a Shimadzu UV3600 spectrophotometer. Photoluminescence spectra were obtained on a Perkin-Elmer LS50B luminescence spectrometer and a Horiba FluoroMax-4 luminescence spectrometer. Elemental analyses were performed with an Elementar Analysensysteme varioMICRO V1.5.8 system using the CHN mode or performed at the Microanalytical Center of Kyoto University.

Materials. THF, Et_2O, and Et_3N were purchased and purified by passage through purification column under Ar pressure.[18] $Pd(PPh_3)_4$ and CuI were obtained commercially and used without further purification. Pseudo-*p*-diethynyl[2.2]paracyclophane (**1**) was prepared from commercially available [2.2]paracyclophane as described in the literature.[9g] 1-Ethynyl-4-nitrobenene (**3**)[19] and 14-ethynyl[2.2]paracyclophane (**4**)[20] were prepared as described in the literature. 1-Methoxy-2-*p*-nitrophenylethynylbenzene (**7**) was prepared by the modified procedure as described in the literature.[21] All reactions were performed under an Ar atmosphere.

Polymerization. A typical procedure is as follows. Pseudo-*p*-diethynyl[2.2]paracyclophane (**1**) (23.1 mg, 0.090 mmol), 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (**2**) (57.4 mg, 0.100 mmol), 4-ethynyl[2.2]paracyclophane (**4**) (4.6 mg, 0.020 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol), and CuI (1.9 mg, 0.010 mmol) were placed in a 10 mL Pyrex tube equipped with a magnetic stirrer and a reflux condenser. The equipment was purged with Ar, followed by adding THF (4.0 mL) and Et_3N (2.0 mL). The reaction was carried out at 50 °C for 48 h. After cooling, the reaction mixture was diluted with $CHCl_3$ and washed with NH_3 aqueous solution, water, and brine. The organic layer was dried over Na_2SO_4, and then it was concentrated and reprecipitated from a large amount of methanol. The obtained polymer contained low molecular weight residues; it was purified by HPLC by using $CHCl_3$ as an eluent. The polymer was dried in vacuo to afford **P4a** as a yellow solid (47.1 mg, 79%).

Polymer 3. Yield: 76% for **P3a**, 59% for **P3b**, and 56% for **P3c**. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.20−1.49 (br, -*t*-Bu), 1.59−1.78 (br, $-CH_3$), 2.26−3.81 (br m, bridged ethylene protons of the cyclophane unit), 6.04−7.11 (br, aromatic protons of the cyclophane unit), 7.23−7.87 (br m, aromatic protons of the xanthene unit and the nitrobenzene group), 8.15−8.30 (br, 3,5-protons of 1-ethynyl-4-nitrobenzene group).

Polymer 4. Yield: 79% for **P4a**, 65% for **P4b**, and 50% for **P4c**. ^1H NMR (CD_2Cl_2, 400 MHz): δ 1.13−1.42 (br, -*t*-Bu), 1.49−1.71 (br, $-CH_3$), 2.30−3.79 (br m, bridged ethylene protons of the cyclophane unit), 6.05−7.03 (br, aromatic protons of the cyclophane unit), 7.12−7.80 (br m, aromatic protons of the xanthene unit).

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Supporting Information Available: Synthetic details and analytical data, ^1H and ^{13}C NMR spectra, absorption and fluorescence spectra, emission quenching studies, fluorescence decay studies, and thermal analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) TGA curves of polymers **P3a** and **P4a** are shown in Figure S27in the Supporting Information. Differential scanning calorimetry (DSC) analysis of **P4a** as a representative sample was also carried out, and no clear glass transition temperature (T_g) was observed from −20 to 200 °C, as shown in Figure S28.

(13) The number of repeating [2.2]paracyclophane units in **P3a** and **P4a** was approximately 9 and 6, respectively (Table 1). Namely, polymer **P4a** has ∼8 [2.2]paracyclophane units including two end-capping [2.2]paracyclophanes, and thus, both fluorescence peak intensities are comparable.

(14) Absolute fluorescence quantum efficiencies of polymers **P3a**−**c** and **P4a**−**c** are listed in Table S1in the Supporting Information.

(15) These spectra are shown in Figure S25in the Supporting Information.

(16) The UV−vis absorption spectrum of 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**) is shown in Figure S19.

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