

Supporting Information

[2.2]Paracyclophane-layered Polymers End-capped with Fluorescence Quenchers

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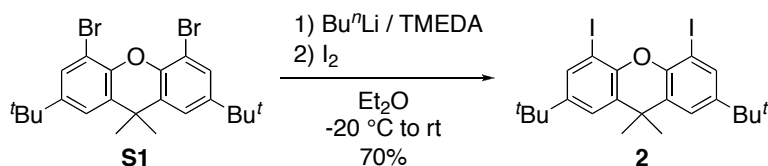
General

^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 F₂₅₄ 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. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). Differential scanning calorimetry (DSC) thermograms were recorded on a Seiko DSC200 instrument (10 °C/min). Fluorescence lifetime measurement was performed on a Hamamatsu Photonics C4780 picosecond fluorescence lifetime measurement system with an integrated streak scope (Hamamatsu Photonics C4334) and a N_2 pulse laser (337 nm) as an excitation light source. 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.¹ $\text{Pd}(\text{PPh}_3)_4$ 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.² 4,5-Dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**S1**) was obtained commercially and used without further purification. 1-Ethynyl-4-nitrobenzene (**3**),³ and 4-ethynyl[2.2]paracyclophane (**4**),⁴ were prepared as described in the literature. 1-Methoxy-2-*p*-nitrophenylethynylbenzene (**7**) was prepared by the modified procedure as described in the literature.⁵ All reactions were performed under Ar atmosphere.

Synthetic Procedures

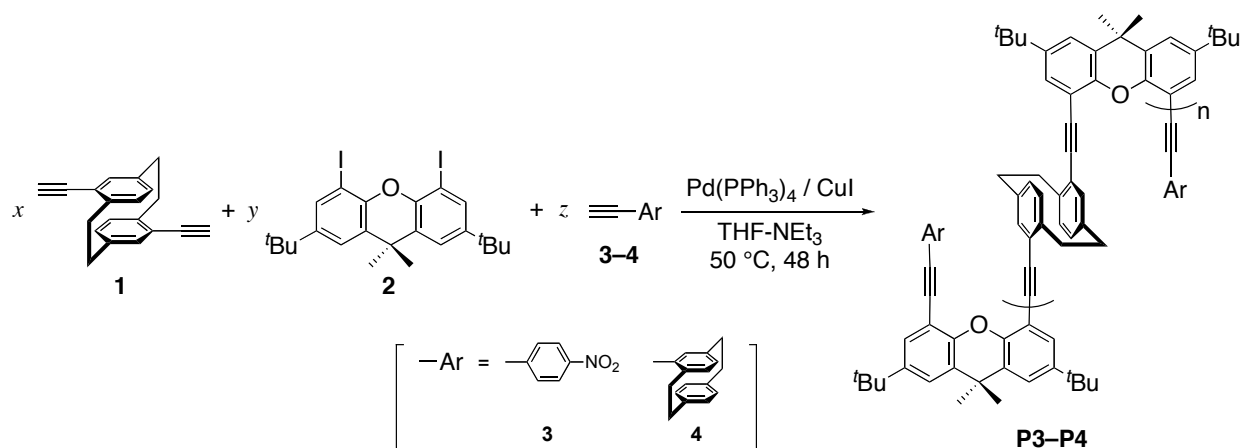
2,7-Di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (**2**).



To cooled solution ($-5\text{ }^{\circ}\text{C}$) of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**S1**) (2.4 g, 5.0 mmol) in Et_2O (200 mL) was added Bu^nLi (4.5 mL of 2.6 M hexane solution, 12 mmol)/TMEDA (2.0 mL) from a dropping funnel dropwise under Ar. After 20 min, a solution of iodine (2.8 g, 11 mmol) in Et_2O (30 mL) was added dropwise over a period of 1 h at $-20\text{ }^{\circ}\text{C}$. This solution was stirred for 30 min at $0\text{ }^{\circ}\text{C}$ and for 2 h at room temperature. The reaction was quenched by the addition of saturated aqueous Na_2SO_3 (150 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O several times. The combined organic layers were dried over MgSO_4 . The solvent was removed on a evaporator to give the pale yellow solid residue, which was recrystallized from hot hexane to obtained pure **2** (2.0 g, 3.6 mmol, 70%) as white crystals.

Mp $148.1\text{--}158.1\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): δ 7.47 (d, $J = 2.2\text{ Hz}$, 2H), 7.33 (d, $J = 2.2\text{ Hz}$, 2H), 1.62 (s, -Me, 6H), 1.32 (s, 18H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.2, 131.1, 128.5, 121.5, 110.4, 77.2, 35.7, 34.5, 32.0, 31.4. 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.

Polymerization.

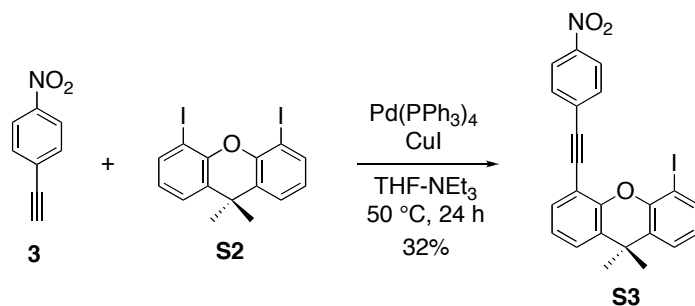


A typical procedure is as follows. Pseudo-*p*-diethynyl[2.2]paracyclophane (**1**) (23.1 mg, 0.090 mmol), 2,7-di-*t*-butyl-4,5-diiodo-9,9-dimethylxanthene (**2**) (57.4 mg, 0.100 mmol), 4-ethynyl[2.2]paracyclophane (**4**) (4.6 mg, 0.020 mmol), Pd(PPh₃)₄ (11.6 mg, 0.010 mmol), and CuI (1.9 mg, 0.010 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 Et₃N (2.0 mL). The reaction was carried out at 50 °C for 48 h. After cooling, the reaction mixture was diluted with CHCl₃, and washed with NH₃ aqueous solution, water and brine. The organic layer was dried over Na₂SO₄. 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 CHCl₃ 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 (CDCl₃, 400 MHz): δ 8.15-8.30 (br, 3,5-protons of 1-ethynyl-4-nitrobenzene group), 7.23-7.87 (br m, aromatic protons of the xanthene unit and the nitrobenzene group), 6.04-7.11 (br, aromatic protons of the cyclophane unit), 2.26-3.81 (br m, bridged ethylene protons of the cyclophane unit), 1.59-1.78 (br, -CH₃), 1.20-1.49 (br, -*t*-Bu).

Polymer 4. Yield: 79% for **P4a**, 65% for **P4b**, and 50% for **P4c**. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.12-7.80 (br m, aromatic protons of the xanthene unit), 6.05-7.03 (br, aromatic protons of the cyclophane unit), 2.30-3.79 (br m, bridged ethylene protons of the cyclophane unit), 1.49-1.71 (br, -CH₃), 1.13-1.42 (br, -*t*-Bu).

4-*p*-Nitrophenylethynyl-5-iodo-9,9-dimethylxanthene (**S3**).

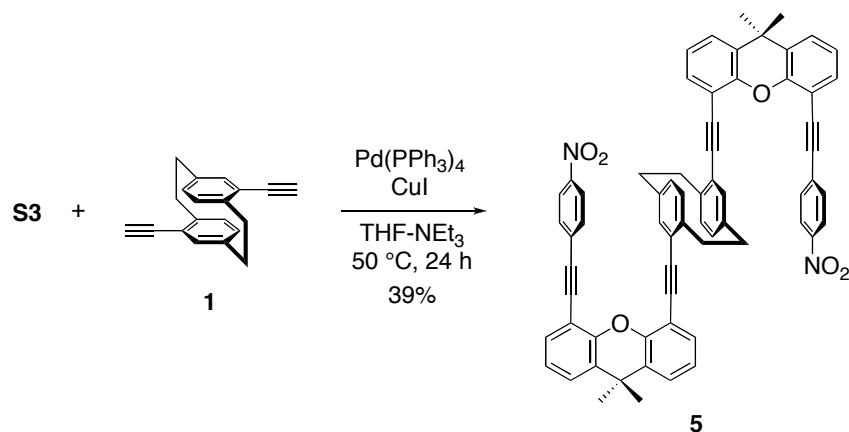


4-Nitrophenylacetylene (**3**) (59 mg, 0.40 mmol), 4,5-diiodo-9,9-dimethylxanthene (**S2**)⁶ (186 mg, 0.40 mmol), Pd(PPh₃)₄ (23 mg, 0.02 mmol), and CuI (4 mg, 0.02 mmol) were placed in a 50 mL Pyrex flask equipped with a magnetic stirrer and a reflux condenser. The equipment was

purged with Ar, followed by adding THF (8.0 mL) and Et₃N (8.0 mL). The reaction was carried out at 50 °C for 24 h. After cooling, the reaction mixture was diluted with Et₂O and washed with NH₃ aqueous solution, water and brine. The organic layer was dried over Na₂SO₄. And then, it was concentrated in vacuo to afford the crude product. Then, it was purified by silica gel column chromatography (hexane/CHCl₃ v/v = 2/1 as an eluent) to afford **S3** as a colorless liquid (55 mg, 0.13 mmol, 32%).

R_f = 0.29 (hexane/CHCl₃, v/v = 2/1). ¹H NMR (CDCl₃, 400 MHz): δ 8.23 (2H, d, J = 9.0 Hz), 7.81 (2H, d, J = 9.0 Hz), 7.72 (1H, d, J = 7.8 Hz), 7.47 (1H, d, J = 7.8 Hz), 7.46 (1H, d, J = 7.8 Hz), 7.41 (1H, d, J = 7.8 Hz), 7.13 (1H, t, J = 7.8 Hz), 6.88 (1H, t, J = 7.8 Hz), 1.63 (6H, s). ¹³C NMR (CDCl₃, 100 MHz): δ 151.4, 149.2, 146.9, 137.6, 132.5, 131.5, 131.2, 130.7, 130.6, 127.1, 126.2, 125.2, 123.6, 123.4, 111.0, 92.4, 90.8, 84.8, 34.8, 32.0. HRMS (FAB): m/z calcd for C₂₃H₁₆NO₂ (M^+): 481.0175. Found: 481.0160. Anal. calcd for C₂₃H₁₆NO₂: C 57.40; H 3.35; N 2.91. Found: C 57.55; H 3.49; N 2.92.

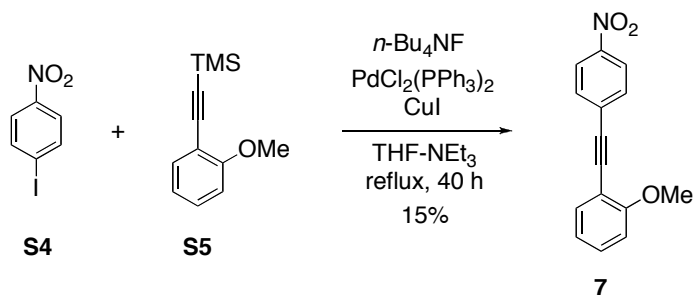
Pseudo-*p*-bis(4-(*p*-nitrophenyl)ethynyl-9,9-dimethylxanthen-5-yl)[2.2]paracyclophane (5**).**



The compound **S3** (48 mg, 0.10 mmol), **1** (13 mg, 0.052 mmol), Pd(PPh₃)₄ (6.0 mg, 0.0052 mmol), and CuI (1.0 mg, 0.0052 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 Et₃N (2.0 mL). The reaction was carried out at 50 °C for 24 h. After cooling, the reaction mixture was diluted with CHCl₃, and washed with NH₃ aqueous solution, water and brine. The organic layer was dried over Na₂SO₄. And then, it was concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/CHCl₃, v/v = 2/1 as an eluent) to afford **5** as a colorless solid (38 mg, 0.040 mmol, 39%).

$R_f = 0.50$ (hexane/ CHCl_3 , v/v = 1/1). Mp 262.8 °C (dec.). ^1H NMR (CDCl_3 , 400 MHz): δ 7.64-7.60 (6H, m), 7.47 (4H, d, $J = 7.8$ Hz; two overlapping doublet peaks), 7.42 (2H, d, $J = 7.8$ Hz), 7.31-7.27 (4H, m), 7.22 (2H, t, $J = 7.8$ Hz), 7.11 (2H, t, $J = 7.8$ Hz), 6.94 (2H, d, $J = 7.9$ Hz), 6.35 (2H, s), 6.28 (2H, d, $J = 7.9$ Hz), 3.67-3.61 (2H, m), 3.12-3.05 (2H, m), 2.79-2.72 (2H, m), 2.68-2.61 (2H, m), 1.70 (6H, s), 1.68 (6H, s). ^{13}C NMR (CDCl_3 , 100 MHz): δ 150.8, 149.8, 146.5, 142.3, 139.3, 137.4, 133.0, 132.2, 132.1, 131.7, 130.5, 130.2, 130.1, 129.8, 127.3, 126.3, 124.6, 123.5, 123.1, 112.3, 110.9, 94.0, 92.2, 90.3, 88.6, 34.3, 34.1, 33.7, 32.6, 32.2. HRMS (FAB): m/z calcd for $\text{C}_{66}\text{H}_{46}\text{N}_2\text{O}_6$ (M^+): 962.3356. Found: 962.3363. Anal. calcd for $\text{C}_{66}\text{H}_{46}\text{N}_2\text{O}_6$: C 82.31; H 4.81; N 2.91. Found: C 82.00; H 4.98; N 2.93.

1-Methoxy-2-*p*-nitrophenylethynylbenzene (7).



4-Iodonitrobenzene (**S4**) (0.80 g, 3.2 mmol), 1-methoxy-2-trimethylsilylethynylbenzene (**S5**)⁷ (0.33 g, 1.6 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (28 mg, 0.040 mmol), and CuI (7.6 mg, 0.040 mmol) were placed in a 50 mL Pyrex tube equipped with a magnetic stirrer and a reflux condenser. The equipment was purged with Ar, followed by adding THF (3.0 mL) and Et_3N (1.5 mL). $n\text{-Bu}_4\text{NF}$ (1.6 mmol, 1 M THF solution) was added by a syringe, and the reaction mixture was refluxed for 40 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 in vacuo. The crude product was purified by silica gel column chromatography (hexane/ CHCl_3 , v/v = 1/1 as an eluent) to give a yellow solid. And then, it was purified by recrystallization from hexane and CHCl_3 to afford **7** as a yellow solid (62 mg, 0.24 mmol, 15%).

Although it is reported that compound **7** was a yellow oil,⁵ it was obtained as a yellow solid. ^1H and ^{13}C NMR spectra were almost matched with the literature's values.⁵

$R_f = 0.20$ (hexane/ CHCl_3 , v/v = 1/1). Mp 61.8–63.7 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 8.21 (2H, d, $J = 8.6$ Hz), 7.68 (2H, d, $J = 8.6$ Hz), 7.51 (1H, d, $J = 7.3$ Hz), 7.38 (1H, t, $J = 7.3$ Hz),

6.98 (1H, d, $J = 7.3$ Hz), 6.93 (1H, d, $J = 7.3$ Hz), 3.94 (3H, s). ^{13}C NMR (CDCl_3 , 100 MHz): δ 160.2, 146.8, 133.8, 132.3, 130.9, 130.6, 123.6, 120.6, 111.3, 110.7, 91.5, 91.4, 55.8. HRMS (FAB): m/z calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_3$ (M^+): 253.0739. Found: 253.0742. Anal. calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_3$: C 71.14; H 4.38; N 5.53. Found: C 70.96; H 4.53; N 5.48.

^1H and ^{13}C NMR spectra of **2**, **P3a**, **P4a**, **S3**, **5** and **7** are shown in Figures S1–12.

NMR Spectra

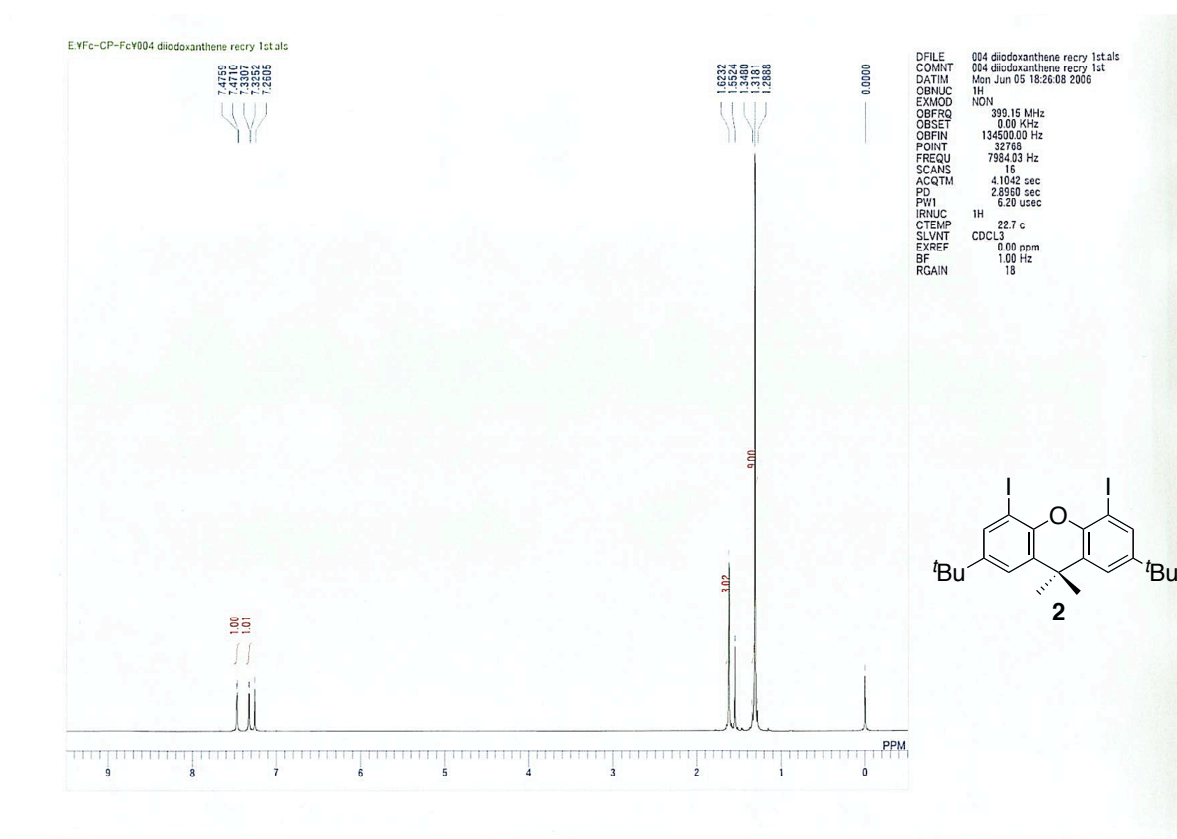


Figure S1. ¹H NMR spectrum of **2**, 400 MHz, CDCl₃.

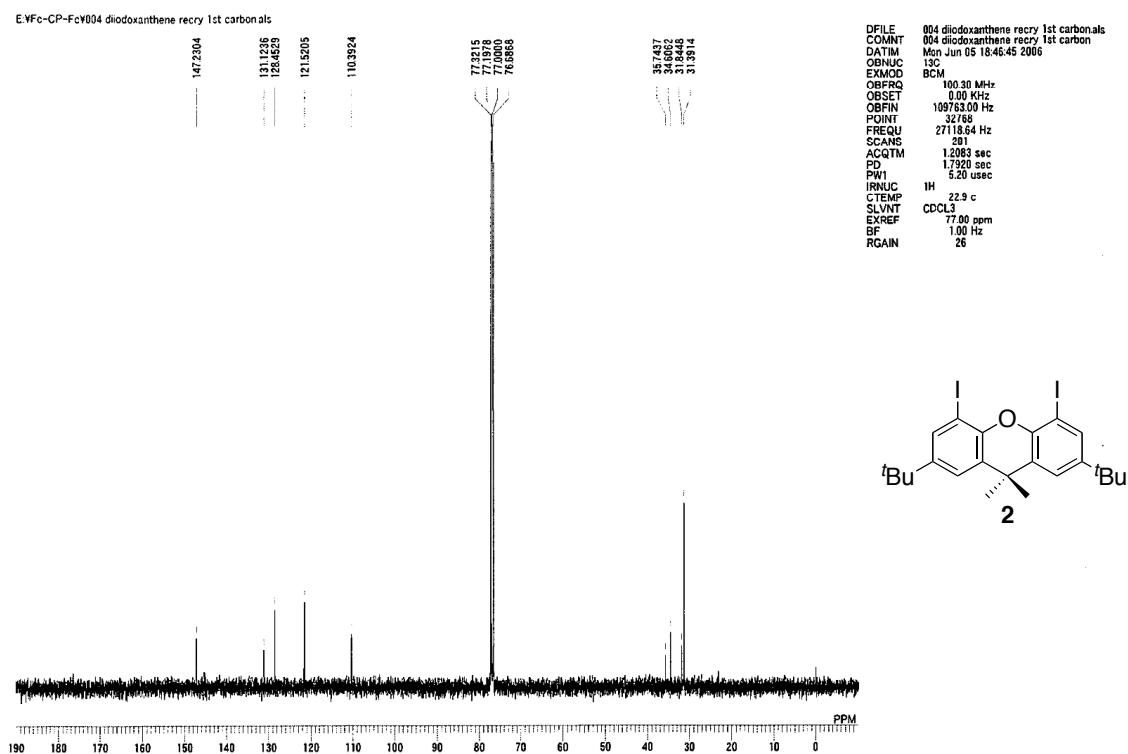
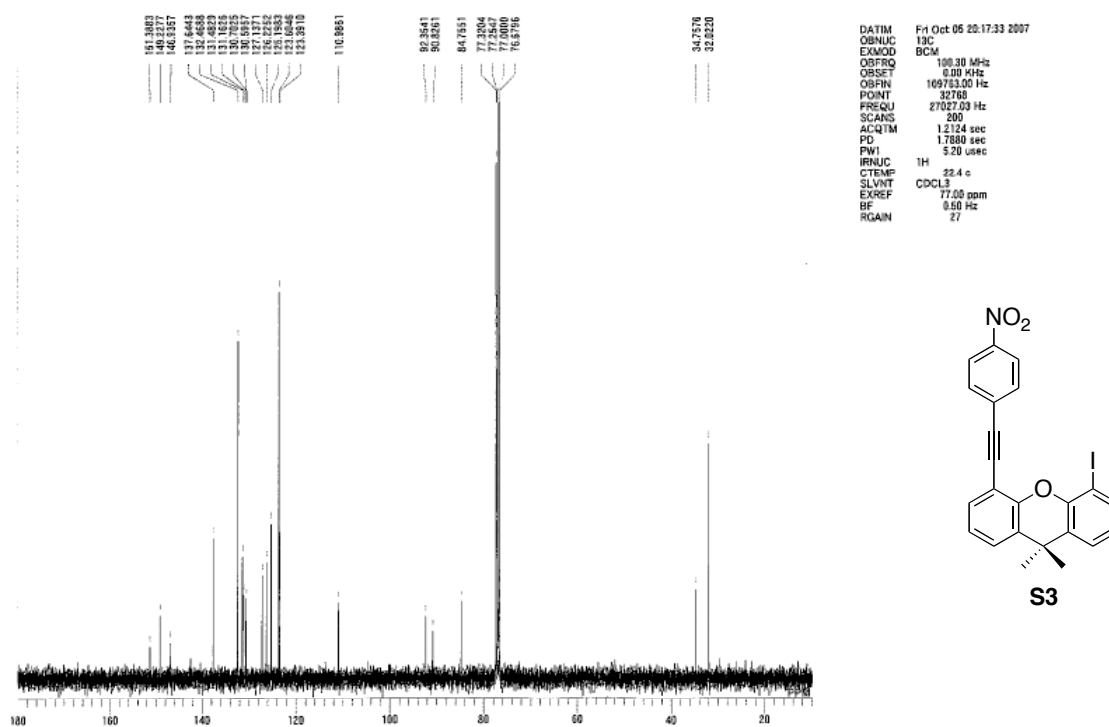
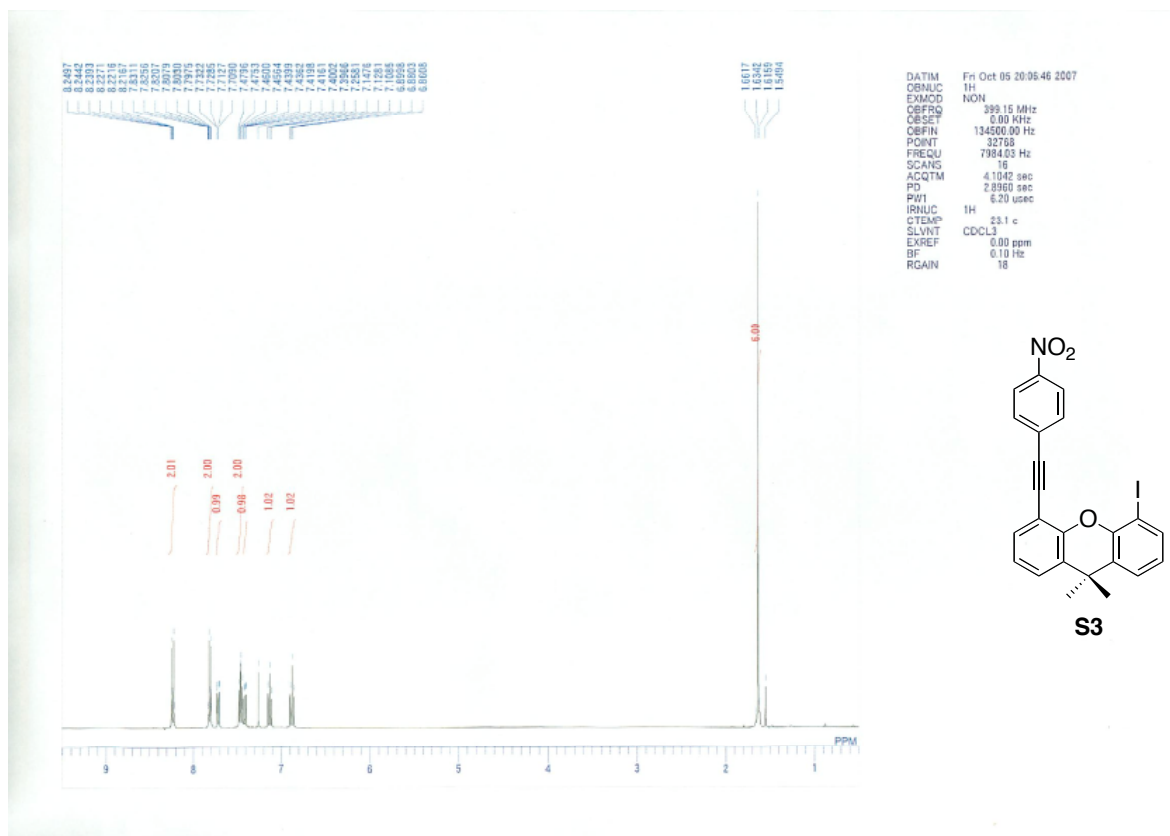


Figure S2. ¹³C NMR spectrum of **2**, 100 MHz, CDCl₃.



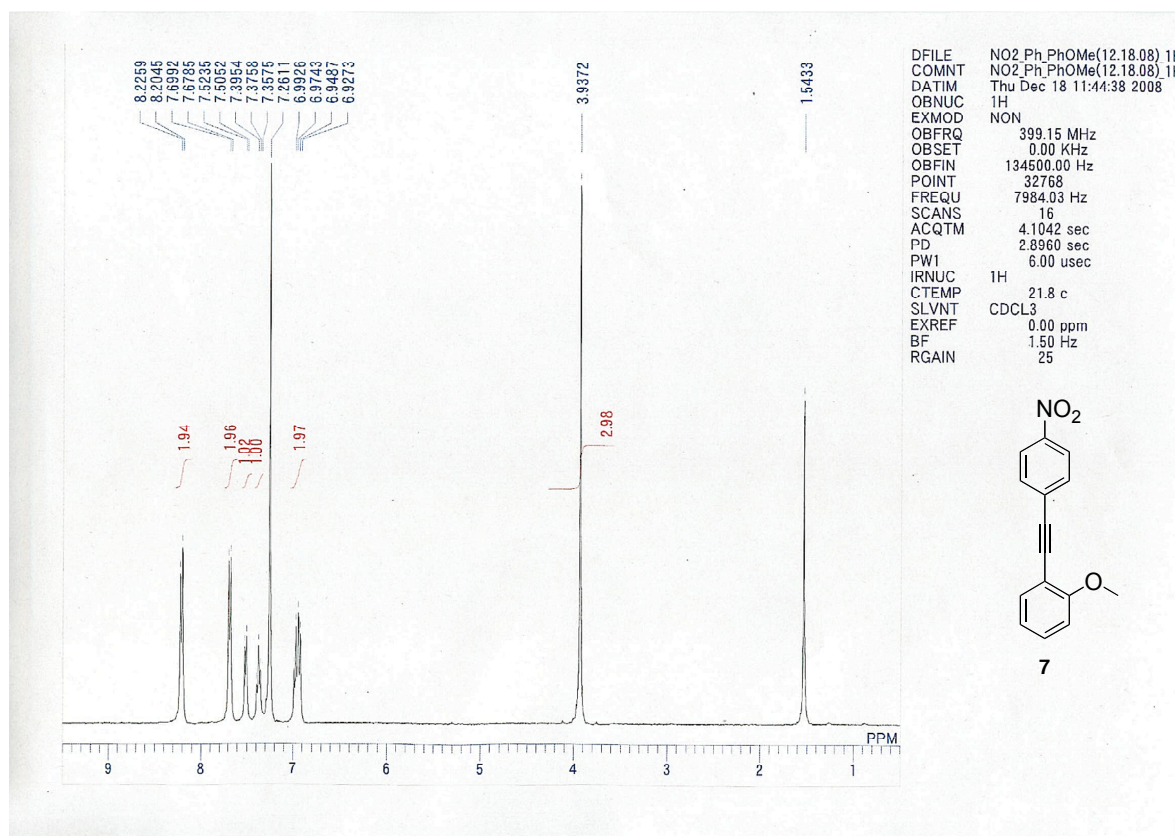


Figure S1. ^1H NMR spectrum of **7**, 400 MHz, CDCl_3 .

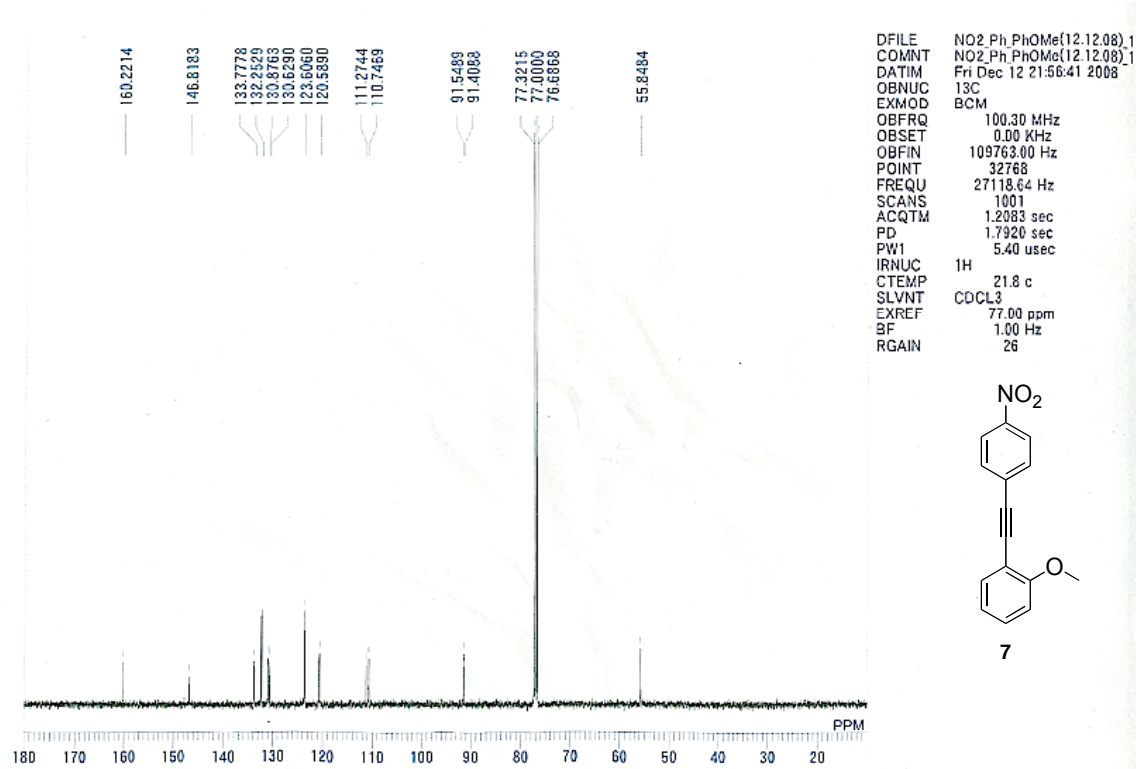


Figure S2. ^{13}C NMR spectrum of **7**, 100 MHz, CDCl_3 .

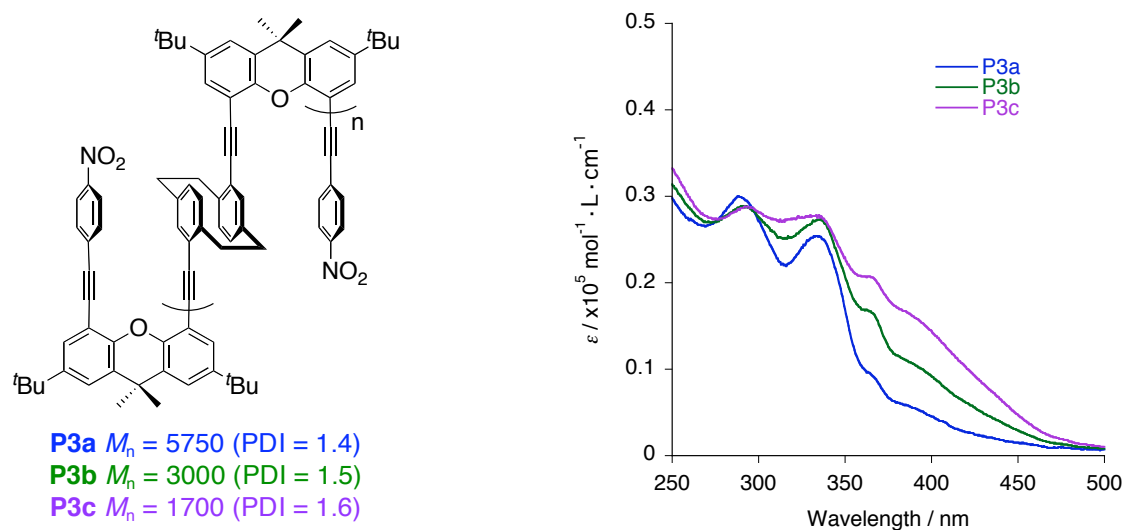


Figure S13. UV-vis absorption spectra of polymers **P3a-c** in CHCl₃ (1.0×10^{-5} M).

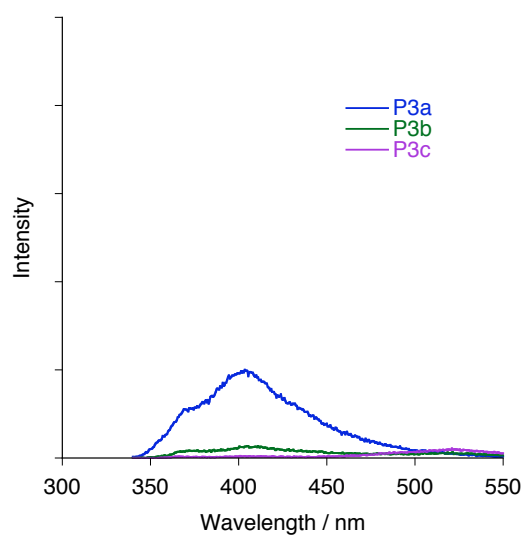


Figure S14. Emission spectra of polymers **P3a-c** excited at 333 nm in CHCl₃ (1.0×10^{-5} M).

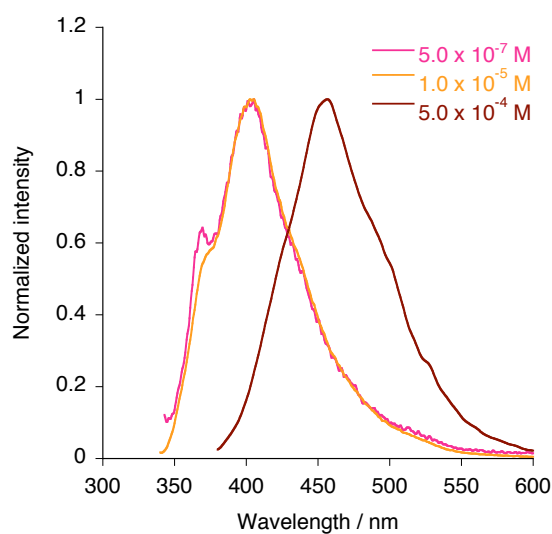


Figure S15. Concentration effect on fluorescence emission of polymer **P3a** in CHCl₃.

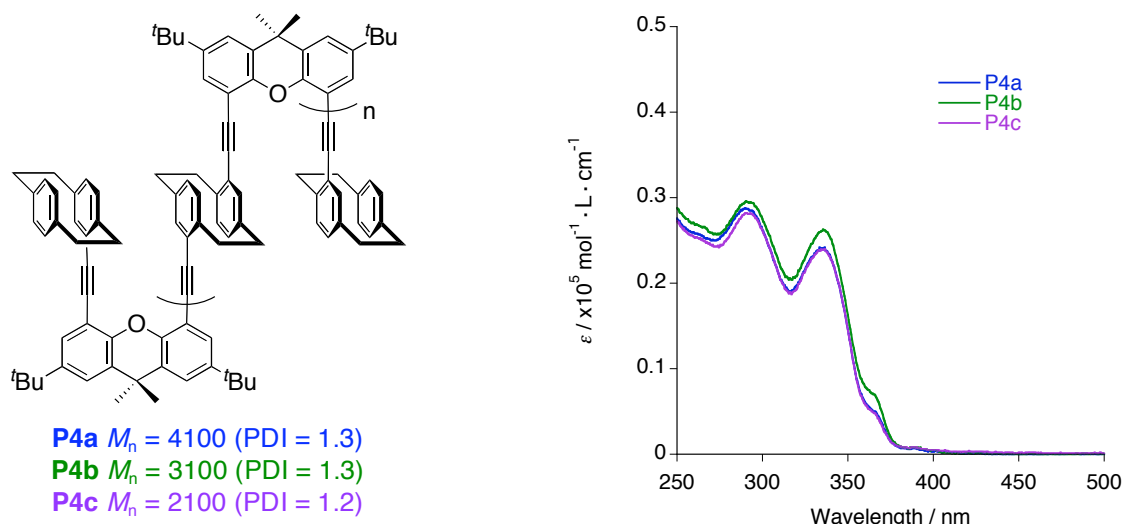


Figure S16. UV-vis absorption spectra of polymers **P4a-c** in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$).

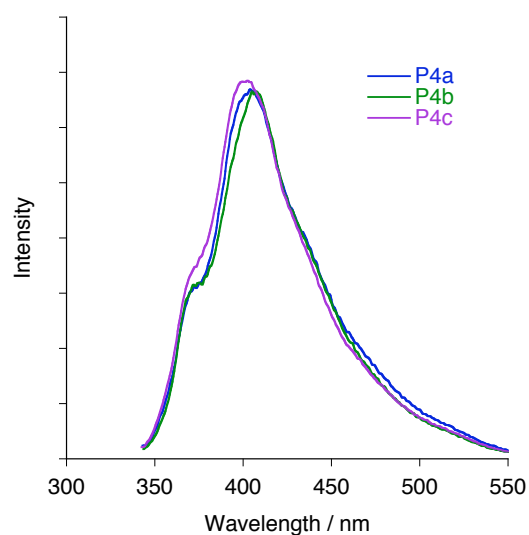


Figure S17. Emission spectra of polymers **P4a-c** excited at 333 nm in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$).

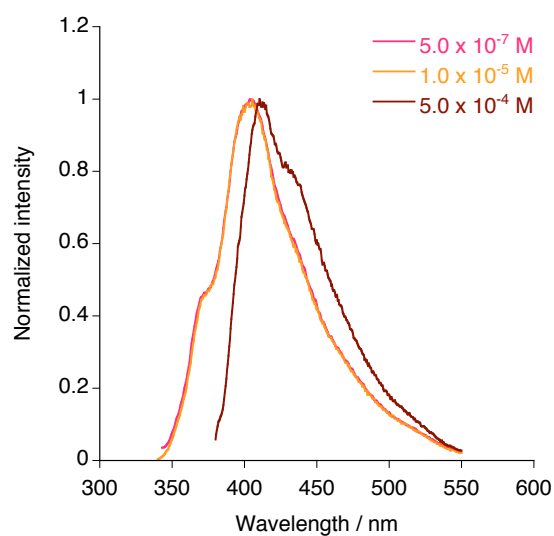


Figure S18. Concentration effect on fluorescence emission of polymer **P4a** in CHCl_3 .

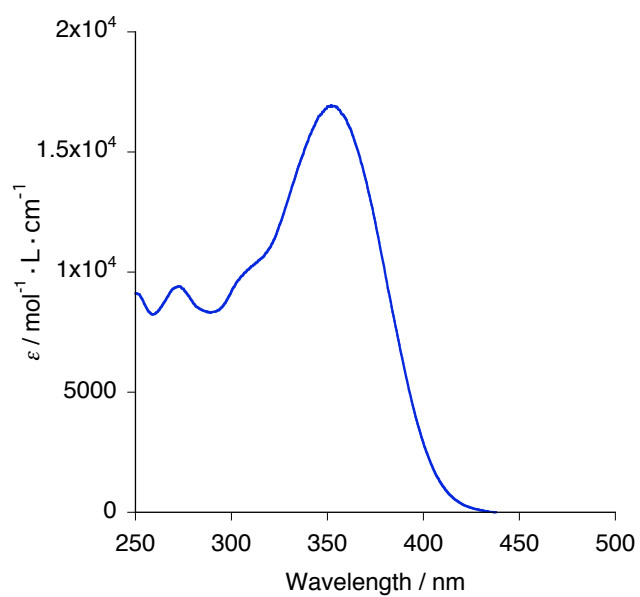


Figure S19. UV-vis absorption spectrum of 1-methoxy-2-[(4-nitrophenyl)ethynyl]benzene **7** in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$).

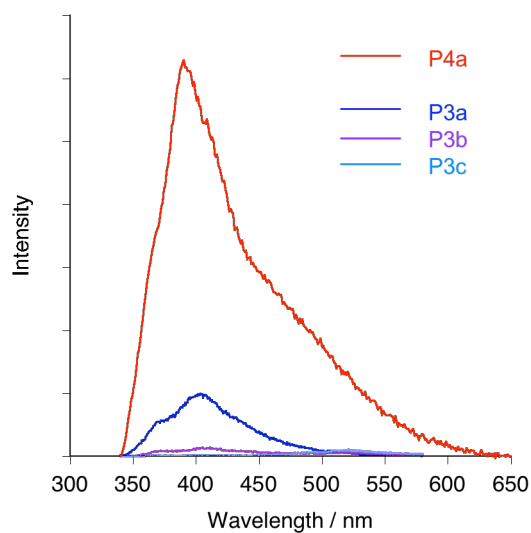


Figure S20. Fluorescence emission spectra of **P3a–c** and **P4a** in CHCl_3 (1.0×10^{-5} M) excited at 333 nm.

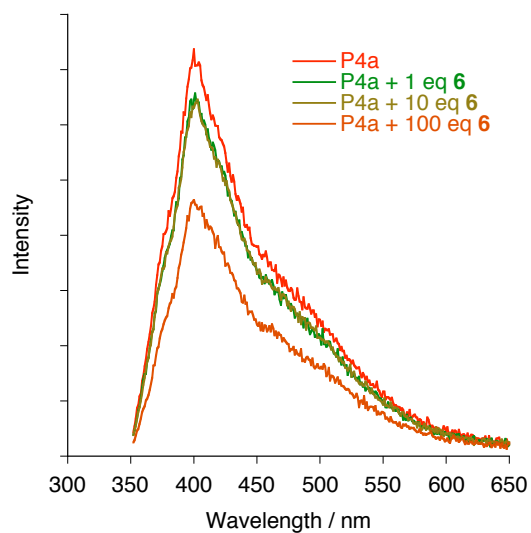


Figure S21. Fluorescence emission spectra of **P4a** in CHCl_3 (1.0×10^{-5} M) with 1, 10, and 100 equivalents of nitrobenzene **6** excited at 333 nm.

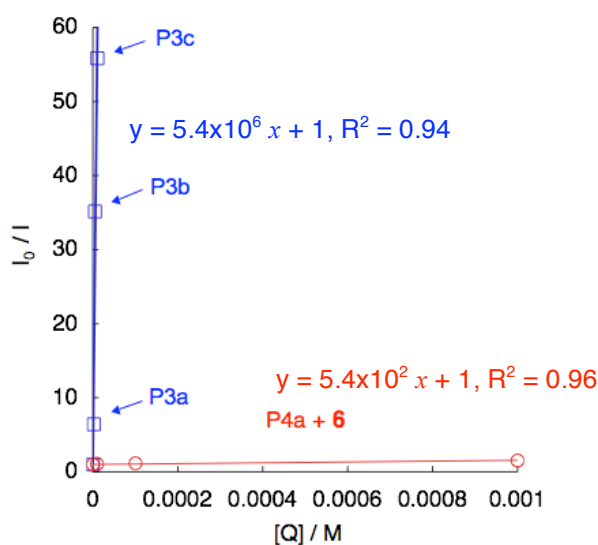


Figure S22. Stern-Volmer plots of **P3a–c** (1.0×10^{-5} M/repeating unit) and **P4a** (1.0×10^{-5} M/repeating unit) with nitrobenzene **6** in CHCl_3 .

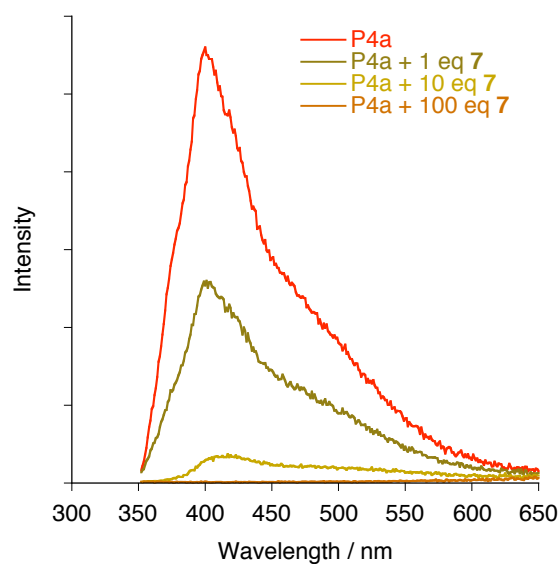


Figure S23. Fluorescence emission spectra of **P4a** in CHCl_3 (1.0×10^{-5} M) with 1, 10, and 100 equivalents of 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**) excited at 333 nm.

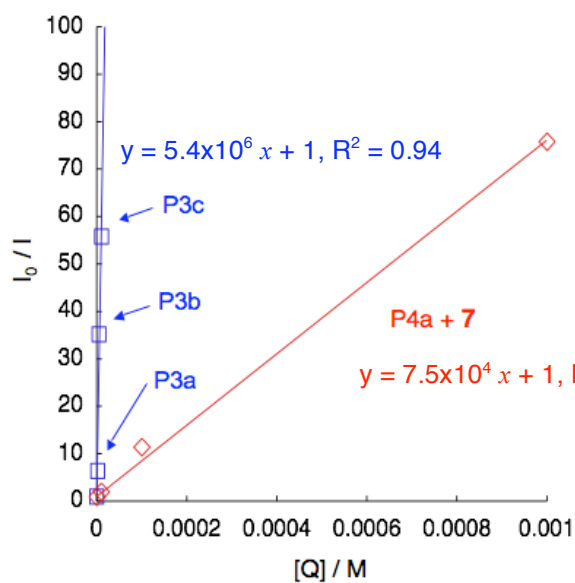


Figure S24. Stern-Volmer plots of **P3a-c** (1.0×10^{-5} M/repeating unit) and **P4a** (1.0×10^{-5} M/repeating unit) with 1-methoxy-2-*p*-nitrophenylethynylbenzene (**7**) in CHCl_3 .

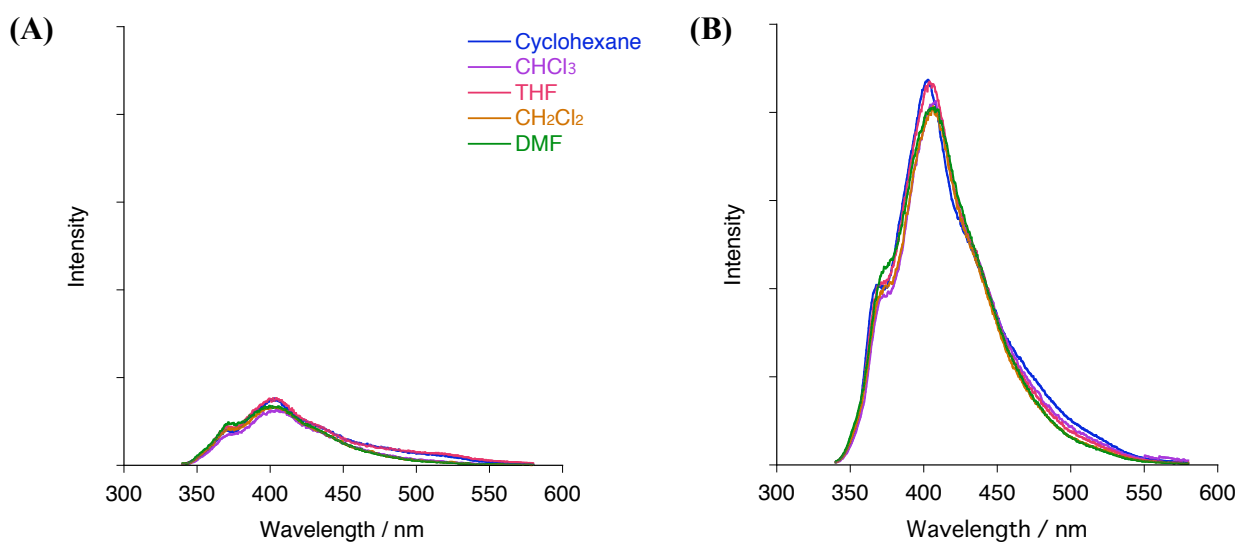


Figure S25. Solvent effect on photoluminescence spectra of (A) **P3a** and (B) **P4a** excited at 333 nm.

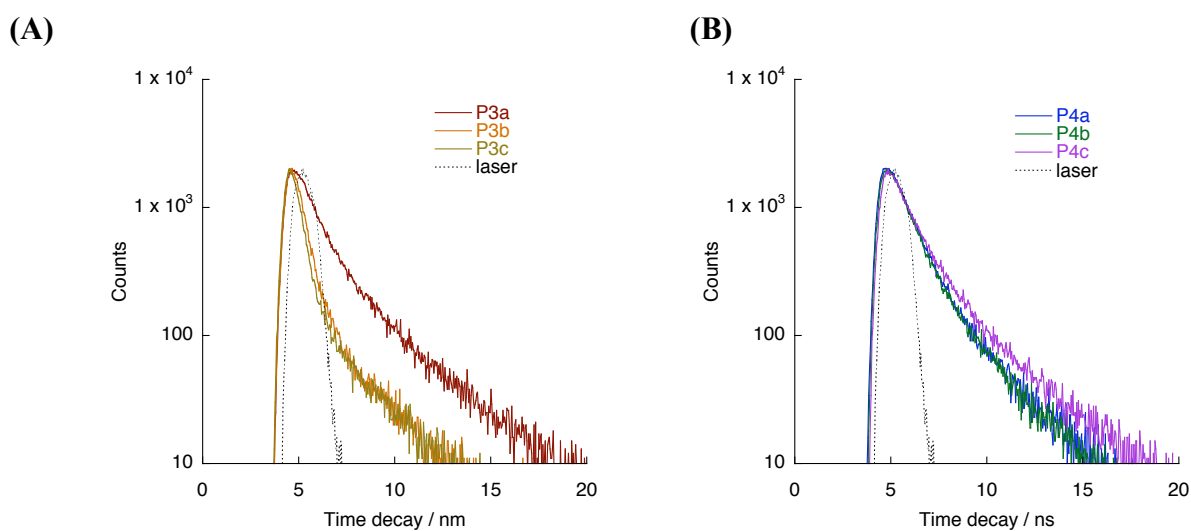


Figure S26. Fluorescence decay curves of (A) **P3a-c** and (B) **P4a-c** in CHCl₃ excited at 337 nm (N₂ laser).

Table S1. Summary of the optical data of **P3a-c** and **P4a-c**.

Polymer	Φ^a	τ_1 / ns	τ_2 / ns	α_1	α_2	χ^2
P3a	0.03	0.90	3.2	0.191	0.007	1.02
P3b	0.004	0.50	2.8	0.169	0.007	1.32
P3c	< 0.001	0.40	2.8	0.100	0.022	1.17
P4a	0.20	1.1	3.4	0.107	0.011	1.06
P4b	0.18	1.0	3.1	0.105	0.013	0.83
P4c	0.20	1.1	3.5	0.093	0.017	1.05

^a Absolute fluorescence quantum efficiency in CHCl₃ excited at 333 nm.

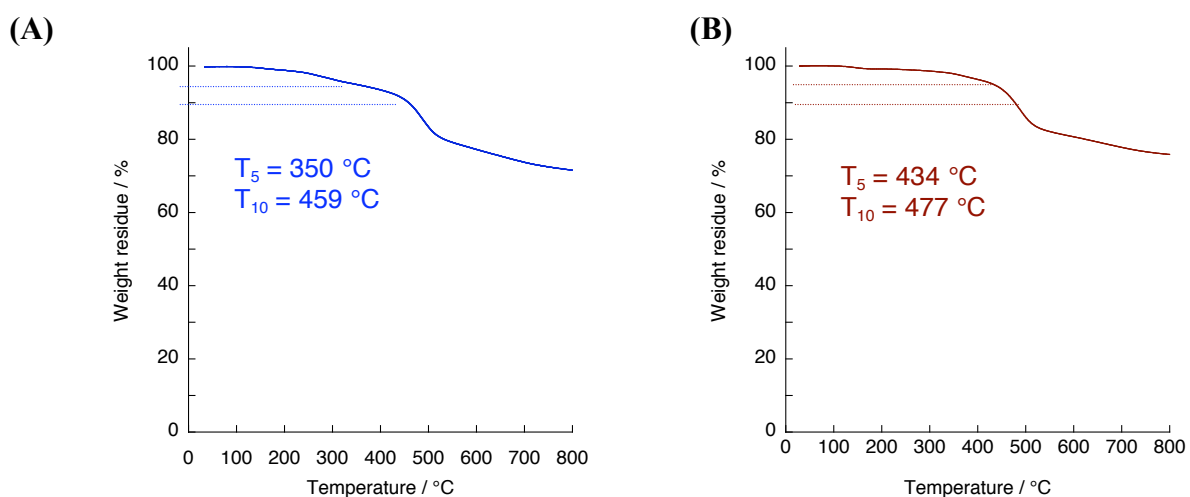


Figure S27. TGA curves of (A) **P3a** and (B) **P4a** under N_2 ($10\text{ }^\circ\text{C/min}$).

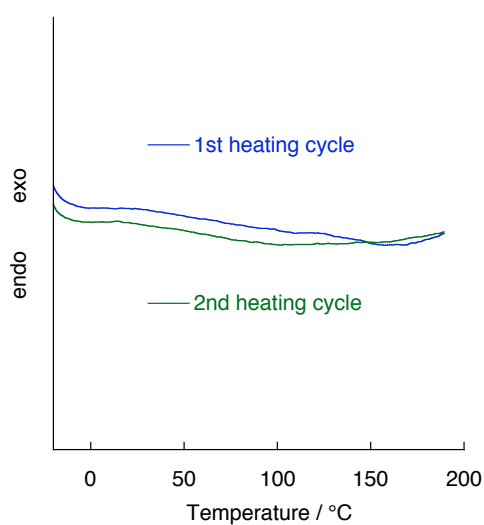


Figure S28. DSC analysis of **P4a** ($10\text{ }^\circ\text{C/min}$).

References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- (2) Morisaki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 9319–9324.
- (3) Kosynkin, D. V.; Tour, J. M.; *Org. Lett.* **2001**, *3*, 993–995.
- (4) Bondarenko, L.; Dix, I.; Hinrichs, H.; Hopf, H. *Synthesis* **2004**, *16*, 2751–2759.
- (5) Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 10292–10296.
- (6) McWilliams, K.; Kelly, J. W. *J. Org. Chem.* **1996**, *61*, 7408–7414.
- (7) Jankova, S.; Dracinsky, M.; Cisarova, I.; Katora, M. *Eur. J. Org. Chem.* **2008**, 47–51.