

Electronic Supplementary Information for

Emissive Tetraphenylethylene (TPE) Derivatives in a Dissolved State Tightly Fastened by a Short Oligo(Ethylene Glycol) Chain

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Experimental section

Materials and general measurements.

Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. The reaction was carried out under nitrogen atmosphere. ^1H (500 MHz) and ^{13}C (126 MHz) NMR measurements were recorded on a Bruker Biospin AVANCE DRX500 instrument, using 0.05% tetramethylsilane (TMS) as an internal standard. UV-vis spectra were recorded on a JASCO V-570 spectrophotometer. Emission spectra and fluorescence quantum yield (Φ_F) were obtained with SHIMADZU RF5300PC spectrofluorometer. The absolute Φ_F was measured by a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and a 150W continuous-wave xenon light source. X-ray diffraction (XRD) patterns were obtained by using a Bruker D8Advance / D with Cu $K\alpha$ radiation source (40 kV, 40mA). Electrospray ionization mass spectroscopy (ESI-MS) was carried out at Global facility center, Hokkaido University. Chiral column chromatography was carried out on a SHIMAZU LC-9A system (DAICEL CHIRALPAK IF column) with a SHIMAZU RID-10A reflective index.

X-ray crystallography analysis.

Single crystal was mounted in the loop using paraffin oil. The data were collected on a Rigaku XtaLAB Synergy-S with graphite monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a PhotonJet-S microfocus generator operating at 50 kV and 1 mA. Diffraction data were collected and processed using the CrysAlisPro program. Structures were solved by direct methods using SHELXS.² Structural refinements were conducted by the full-matrix least-squares method using SHELXS.² Non-H atoms were refined anisotropically, and H atoms were refined using a riding model. All calculations were performed using the OLEX2³ software packages.

Fluorescence quantum yields.

Fluorescence quantum yields were measured in THF or cyclohexane from the following formula(1) with corresponding 9,10-diphenylanthracene as a standard¹. The quantum yields of PAHs in CH_3CN were determined with their quantum yields in cyclohexane or ethanol as standards.¹ All measurements were carried out in the same experimental settings: excitation wavelength, slit widths, photomultiplier voltage.

$$\Phi_x = \Phi_{std.} \times \frac{A_{std.}}{A_x} \times \frac{F_x}{F_{std.}} \times \frac{n_{std.}^2}{n_x^2} \quad \dots (1)$$

Φ : quantum yield

A : absorbance

F : integral area of emission spectrum

n : reflective index of solvent

Photoirradiation. Photoirradiation was carried out using USHIO Deep UV lamp UXM-500SX with band-pass filter (AGC Asahi Glass UV-D33S and HOYA HA50). TPE macrocycles were dissolved in CDCl₃ (3 mM), and the first isomer ratio was determined by integral ratio of ¹H NMR. Then the photoirradiation was carried out by the deep UV lamp with setting the quartz NMR tube at 15 cm position from the lamp. Then, the second isomer ratio was determined by integral ratio of ¹H NMR.

Synthesis and characterization⁴

Synthesis of bis(benzophenone) oligoethylene glycol ether. In a 200 mL two necked flask, A suspension of K₂CO₃ (1.67 g, 12.1 mmol), 4-hydroxybenzophenone (1.24 g, 2.99 mmol) and diethyleneglycol ditosylate (1.24 g, 2.99 mmol) in DMF (40 mL) was stirred at 80°C for 16 h. After filtration and distilling off DMF, the organic layer was separation and the aqueous layer was extracted with CH₂Cl₂. The organic layer was combined, dried over MgSO₄ and the solvent was removed under reduced pressure. After the purification of the crude product by flash chromatography on SiO₂ (n-hexane/ethyl acetate), **bz-p2** was obtained.

bz-p2 (0.551 g, 40%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.99 (4H, t, *J* = 4.7 Hz), 4.25 (4H, t, *J* = 4.8 Hz), 6.99 (4H, d, *J* = 8.9 Hz), 7.47 (4H, t, *J* = 7.6 Hz), 7.57 (2H, t, *J* = 7.4 Hz), 7.75 (4H, d, *J* = 6.9 Hz), 7.82 (4H, d, *J* = 8.9 Hz).

bz-p3 (1.27g, 83%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 3.78 (4H, s), 3.91 (4H, t, *J* = 4.8 Hz), 4.21 (4H, t, *J* = 4.8 Hz), 6.97 (4H, d, *J* = 8.8 Hz), 7.47 (4H, t, *J* = 7.6 Hz), 7.56 (2H, t, *J* = 7.4 Hz), 7.74 (4H, d, *J* = 7.1 Hz) , 7.81 (4H, d, *J* = 8.8 Hz).

bz-p4 (2.20 g, 60%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 3.70–3.76 (8H, m), 3.89 (4H, t, *J* = 4.8 Hz), 4.21 (4H, t, *J* = 4.8 Hz), 6.97 (4H, d, *J* = 8.9 Hz), 7.47 (4H, t, *J* = 7.6 Hz), 7.56 (2H, t, *J* = 7.5 Hz), 7.74 (4H, d, *J* = 8.5 Hz) , 7.81 (4H, d, *J* = 8.9 Hz).

bz-p5 (0.588 g, 83%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 3.67–3.70 (8H, m), 3.73–3.74 (4H, m) , 3.89 (4H, t, *J* = 4.8 Hz), 4.21 (4H, t, *J* = 4.8 Hz), 6.97 (4H, d, *J* = 8.9 Hz), 7.47 (4H, t, *J* = 7.6 Hz), 7.56 (2H, t, *J* = 7.6 Hz), 7.74 (4H, d, *J* = 5.0 Hz) , 7.81 (4H, d, *J* = 8.9 Hz).

bz-p6 (1.78 g, 83%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) 3.65–3.69 (12H, m), 3.73 (4H, t, *J* = 5.1) , 3.89 (4H, t, *J* = 4.8 Hz), 4.21 (4H, t, *J* = 4.8 Hz), 6.97 (4H, d, *J* = 8.9 Hz), 7.47 (4H, t, *J* = 7.6 Hz), 7.56 (2H, t, *J* = 7.4 Hz), 7.74 (4H, d, *J* = 7.0 Hz) , 7.81 (4H, d, *J* = 8.8 Hz).

bz-m2 (1.15 g, 82%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.96 (4H, t, *J* = 4.7 Hz), 4.21 (4H, t, *J* = 4.7 Hz), 7.14–7.17 (2H, m), 7.34–7.39 (6H, m), 7.48 (4H, t, *J* = 7.7 Hz), 7.59 (2H, t, *J* = 7.4 Hz), 7.79 (4H, d, *J* = 7.8 Hz).

bz-m3 (0.679 g, 53%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.75 (4H, s), 3.88 (4H, t, *J* = 4.9 Hz), 4.17 (4H, t, *J* = 4.7), 7.13–7.15 (2H, m), 7.33–7.37 (6H, m), 7.46 (4H, t, *J* = 7.9 Hz), 7.57 (2H, t, *J* = 7.5 Hz), 7.78 (4H, d, *J* = 8.5 Hz).

bz-m4 (1.29 g, 78%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.68–3.74 (8H, m), 3.87 (4H, t, *J* = 4.8 Hz), 4.17 (4H, t, *J* = 4.8), 7.13–7.16 (2H, m), 7.33–7.38 (6H, m), 7.47 (4H, t, *J* = 7.7 Hz), 7.58 (2H, t, *J* = 8.0 Hz), 7.79 (4H, d, *J* = 8.1 Hz).

bz-m5 (1.42 g, 83%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.66–3.73 (12H, m), 3.86 (4H, t, *J* = 4.7

Hz), 4.17 (4H, t, $J = 4.7$), 7.14–7.16 (2H, m), 7.33–7.38 (6H, m), 7.48 (4H, t, $J = 7.7$ Hz), 7.58 (2H, t, $J = 7.4$ Hz), 7.79 (4H, d, $J = 8.1$ Hz).

bz-m6 (1.28 g, 93%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) : 3.65–3.73 (16H, m), 3.87 (4H, t, $J = 4.7$ Hz), 4.17 (4H, t, $J = 4.8$), 7.15 (2H, d, $J = 7.7$ Hz), 7.35–7.38 (6H, m), 7.48 (4H, t, $J = 7.6$ Hz), 7.59 (2H, t, $J = 7.4$ Hz), 7.80 (4H, d, $J = 7.3$ Hz).

bz-o3 (1.09 g, 93%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) : 3.18 (4H, s), 3.42 (4H, t, $J = 5.1$ Hz), 4.00 (4H, d, $J = 5.0$ Hz), 6.96 (2H, d, $J = 8.3$ Hz), 7.06 (2H, t, $J = 7.2$ Hz), 7.37–7.42 (6H, m), 7.45 (2H, t, $J = 7.6$ Hz), 7.51 (2H, t, $J = 7.4$ Hz), 7.77 (4H, d, $J = 6.9$ Hz).

bz-o4 (1.15 g, 71%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) : 3.32–3.39 (8H, m), 3.47 (4H, t, $J = 5.0$ Hz), 4.03 (4H, t, $J = 5.0$ Hz), 6.97 (2H, d, $J = 8.4$ Hz), 7.06 (2H, t, $J = 7.5$ Hz), 7.39–7.46 (8H, m), 7.53 (2H, t, $J = 7.4$ Hz), 7.77 (4H, t, $J = 7.3$ Hz).

Synthesis of TPE macrocycles. In a 300 mL three necked flask, zinc powder (3.17 g, 48.5 mmol), THF (58 mL), pyridine 0.5 mL and 1M $\text{TiCl}_4/\text{CH}_2\text{Cl}_2$ solution were added and heated at 80°C. Then **bz-p2** (0.500 g, 1.07 mmol) in anhydrous THF (21 mL) was dropped into this slurry over for 6 h and the resulting mixture was stirred at 80°C for 16 h. After cooling to room temperature, the mixture was hydrolyzed by addition of aqueous K_2CO_3 solution (18 mL, 10 %) and distilled water (18 mL). After filtration and distilling off THF, the organic layer was separation and the aqueous layer was extracted with CH_2Cl_2 . The organic layer was combined, dried over MgSO_4 and the solvent was removed under reduced pressure. After the purification of the crude product by flash chromatography on SiO_2 (n-hexane/ethyl acetate), **p2** was obtained.

p2 (0.206 g, 44%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) : 3.61 (4H, t, $J = 4.4$ Hz), 4.25 (4H, t, $J = 4.5$ Hz), 6.63 (4H, d, $J = 8.7$ Hz), 6.74 (4H, d, $J = 8.6$ Hz), 7.14–7.18 (6H, m), 7.21–7.23 (4H, m). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 68.77, 71.85, 115.76, 126.72, 127.80, 130.86, 132.18, 138.12, 141.35, 142.10, 157.36. HRMS(ESI) Calcd. for $\text{C}_{30}\text{H}_{26}\text{O}_3$ $[\text{M}+\text{Na}]^+$: m/z 457.1780, Found: m/z 457.1768.

p3 (0.12 g, 11%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) 3.65 (4H, s), 3.72 (4H, t, $J = 4.6$ Hz), 4.24 (4H, t, $J = 4.5$ Hz), 6.70 (4H, t, $J = 8.8$ Hz), 6.85 (4H, d, $J = 8.8$ Hz), 7.09~7.12 (10H, m). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 68.46, 70.50, 71.47, 115.05, 126.43, 127.65, 131.25, 132.36, 137.34, 140.62, 142.94, 157.14. HRMS(ESI) Calcd. for $\text{C}_{32}\text{H}_{30}\text{O}_4$ $[\text{M}+\text{Na}]^+$: m/z 501.2042, Found: m/z 501.2028.

p4 (0.0140 g, 4%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) 3.61–3.65 (8H, m), 3.77 (4H, t, $J = 4.6$ Hz), 4.16 (4H, t, $J = 4.6$ Hz), 6.67 (4H, t, $J = 8.8$ Hz), 6.88 (4H, d, $J = 8.8$ Hz), 7.05–7.12 (10H, m). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 67.92, 69.66, 70.64, 71.20, 114.38, 126.33, 127.61, 131.31, 132.46, 137.05, 140.25, 143.45, 157.06. HRMS(ESI) Calcd. for $\text{C}_{34}\text{H}_{34}\text{O}_5$ $[\text{M}+\text{Na}]^+$: m/z 545.2304, Found: m/z 545.2286.

p5 (0.0895 g, 16%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) 3.67–3.68 (12H, m), 3.79 (4H, t, $J = 4.6$ Hz), 4.10 (4H, t, $J = 4.6$), 6.66 (4H, d, $J = 8.7$ Hz), 6.89 (4H, d, $J = 8.7$ Hz), 7.03–7.05 (4H, m), 7.08–7.10 (6H, m). ^{13}C NMR (126 MHz, CDCl_3) δ (ppm): 67.63, 69.47, 70.47, 70.65, 71.05, 113.99, 126.27, 127.58, 131.35, 132.48, 136.86, 140.07, 143.68, 157.06. HRMS(ESI) Calcd. for $\text{C}_{36}\text{H}_{38}\text{O}_6$ $[\text{M}+\text{Na}]^+$: m/z 589.2566, Found: m/z 589.2556.

p6 (0.341 g, 35%): ^1H NMR (500 MHz, CDCl_3) δ (ppm) 3.67–3.71 (16H, m), 3.82 (4H, t, $J = 4.7$ Hz), 4.08 (4H, t, $J = 4.7$ Hz), 6.67 (4H, d, $J = 8.8$ Hz), 6.91 (4H, d, $J = 8.8$ Hz), 7.01–7.03 (4H, m), 7.07–7.09 (6H, m).

¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.31, 69.65, 70.63, 70.68, 70.84, 70.98, 113.80, 126.20, 127.55, 131.38, 132.45, 136.65, 139.85, 143.94, 157.12. HRMS(ESI) Calcd. for C₃₈H₄₂O₇ [M+Na]⁺: *m/z* 633.2829, Found: *m/z* 633.2810.

m2 (0.177 g, 38%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.61 (4H, t, *J* = 4.6 Hz), 4.16 (4H, t, *J* = 4.6 Hz), 6.60 (2H, d, *J* = 7.6 Hz), 6.67 (2H, d, *J* = 8.2 Hz), 6.88 (2H, t, *J* = 2.0 Hz), 7.01 (2H, t, *J* = 16 Hz), 7.09–7.13 (10H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 68.89, 71.43, 116.16, 119.16, 123.89, 126.53, 127.68, 128.67, 131.01, 141.10, 142.63, 144.94, 158.76. HRMS(ESI) Calcd. for C₃₀H₂₆O₃ [M+Na]⁺: *m/z* 457.1780, Found: *m/z* 457.1769.

m3 (0.0470 g, 10%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.65–3.68 (8H, m), 3.94 (4H, t, *J* = 4.8 Hz), 6.60 (2H, d, *J* = 7.6 Hz), 6.71–6.72 (4H, m), 7.03–7.06 (6H, m), 7.09–7.10 (6H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.68, 69.41, 71.04, 114.11, 118.10, 123.83, 126.51, 127.65, 128.78, 131.18, 141.00, 143.03, 145.14, 158.06. HRMS(ESI) Calcd. for C₃₂H₃₀O₄ [M+Na]⁺: *m/z* 501.2042, Found: *m/z* 501.2031.

m4 (0.238 g, 43%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.67–3.68 (8H, m), 3.71 (4H, t, *J* = 4.7 Hz), 3.86 (4H, t, *J* = 4.7 Hz), 6.60 (2H, d, *J* = 7.7 Hz), 6.67–6.71 (4H, m), 7.02–7.10 (12H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.68, 69.27, 70.56, 70.95, 114.02, 117.12, 123.77, 126.49, 127.64, 128.82, 131.22, 140.99, 143.15, 145.13, 158.17. HRMS(ESI) Calcd. for C₃₄H₃₄O₅ [M+Na]⁺: *m/z* 545.2304, Found: *m/z* 545.2288.

m5 (0.201 g, 33%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.64–3.72 (16H, m), 3.84 (4H, t, *J* = 4.8 Hz), 6.61 (4H, d, *J* = 7.9 Hz), 6.69 (2H, d, *J* = 8.1 Hz), 7.02–7.10 (12H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.43, 69.40, 70.70, 70.72, 70.81, 114.02, 116.87, 123.90, 126.47, 127.63, 128.78, 131.24, 140.94, 143.25, 145.08, 158.11. HRMS(ESI) Calcd. for C₃₆H₃₈O₆ [M+Na]⁺: *m/z* 589.2566, Found: *m/z* 589.2550.

m6 (0.134 g, 21%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.61–3.69 (22H, m), 3.85 (4H, t, *J* = 4.8 Hz), 6.60–6.34 (4H, m), 6.69 (2H, d, *J* = 8.2 Hz), 7.01–7.11 (12H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.43, 69.43, 70.76, 70.81, 70.85, 113.97, 117.16, 123.93, 126.47, 127.62, 128.78, 131.24, 140.90, 143.28, 145.03, 158.07. HRMS(ESI) Calcd. for C₃₈H₄₂O₇ [M+Na]⁺: *m/z* 633.2829, Found: *m/z* 633.2818.

o3 (0.0755 g, 16%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.57 (2H, t, *J* = 8.8 Hz), 3.76–3.81 (8H, m), 3.92 (2H, t, *J* = 8.3 Hz), 6.70 (2H, d, *J* = 8.2 Hz), 6.74 (2H, t, *J* = 7.4 Hz), 6.97–7.12 (14H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 67.94, 70.21, 70.97, 111.17, 120.10, 125.83, 126.92, 128.00, 129.58, 132.03, 132.56, 138.93, 143.12, 157.27. HRMS(ESI) Calcd. for C₃₂H₃₀O₄ [M+Na]⁺: *m/z* 501.2042, Found: *m/z* 501.2027.

o4 (0.0866 g, 16%): *cis-o4* (0.0770 g, 14%) was obtained by silica gel column chromatography due to difference in retention time. In this system, *cis-o4* was eluted first and *cis-trans* mixture (*cis-o4* 0.0175 g, 3% *trans-o4* 0.0096, 2%) later eluted. *cis-o4*: ¹H NMR (500 MHz, CDCl₃) δ (ppm) : 3.29–3.33 (2H, m), 3.55–3.58 (2H, m), 3.66–3.77 (12H, m), 6.65–6.70 (4H, m), 6.98 (1H, d, *J* = 1.7 Hz), 7.00 (1H, d, *J* = 1.7 Hz), 7.03–7.08 (12H, m). ¹³C NMR (126 MHz, CDCl₃) δ (ppm): 68.58, 69.13, 70.54, 70.72, 112.45, 119.78, 125.82, 127.28, 127.97, 130.74, 132.61, 132.95, 137.84, 143.61, 156.53. HRMS(ESI) Calcd. for C₃₄H₃₄O₅ [M+Na]⁺: *m/z* 545.2304, Found: *m/z* 545.2287.

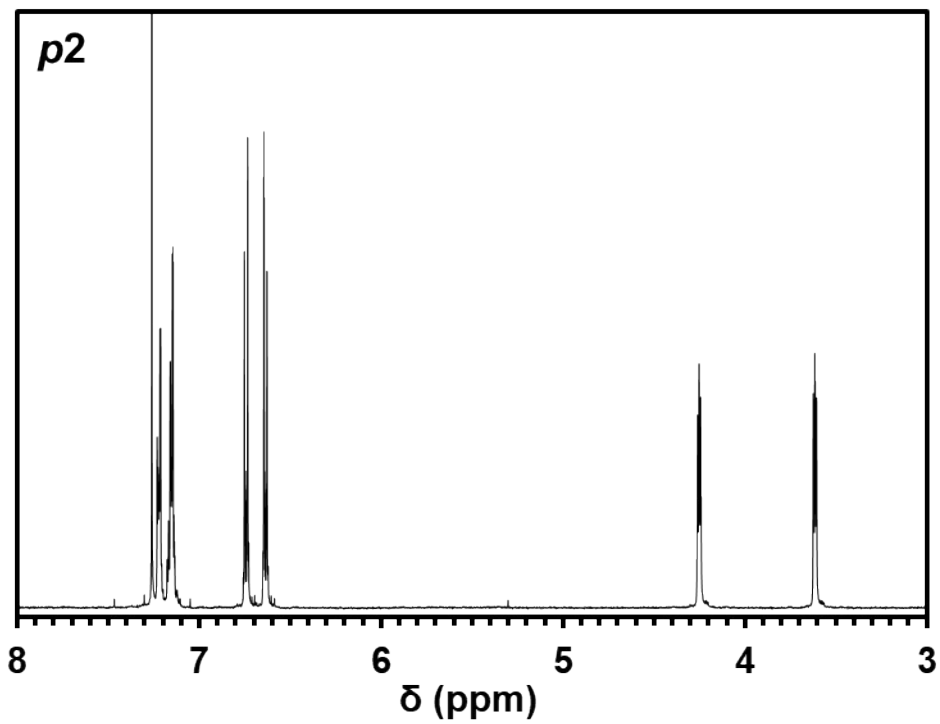


Fig. S1 ^1H NMR spectrum of *p2*.

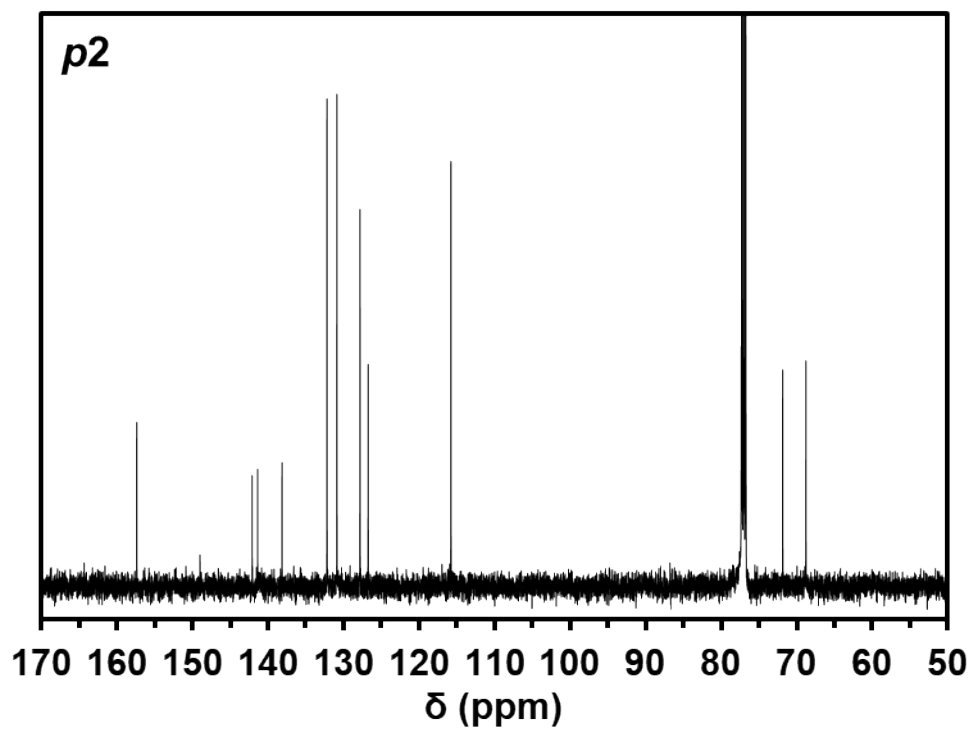


Fig. S2 ^{13}C NMR spectrum of *p2*.

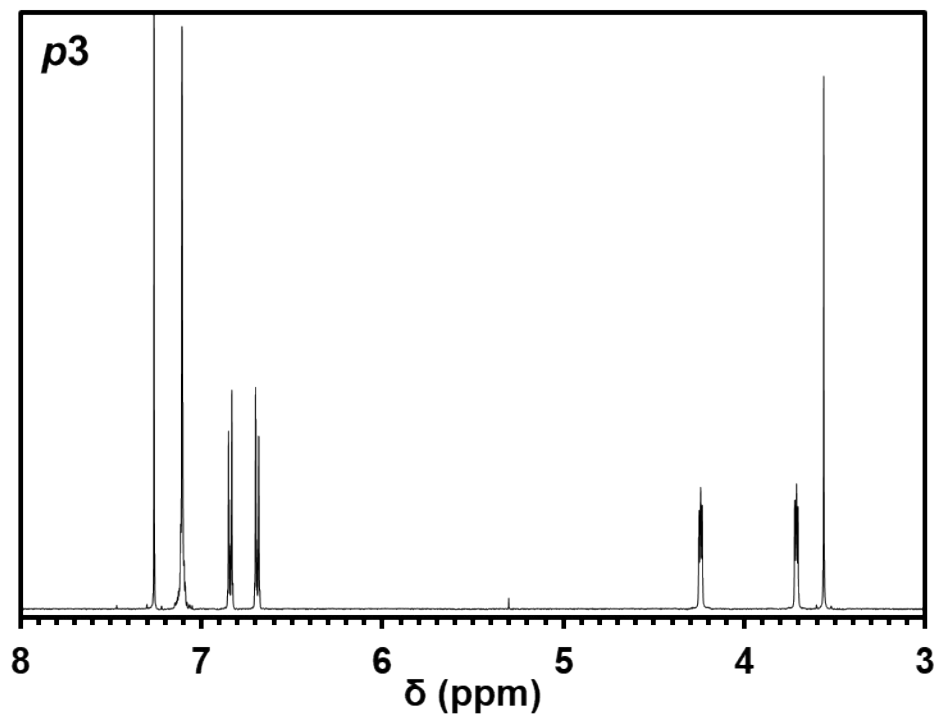


Fig. S3 ^1H NMR spectrum of *p3*.

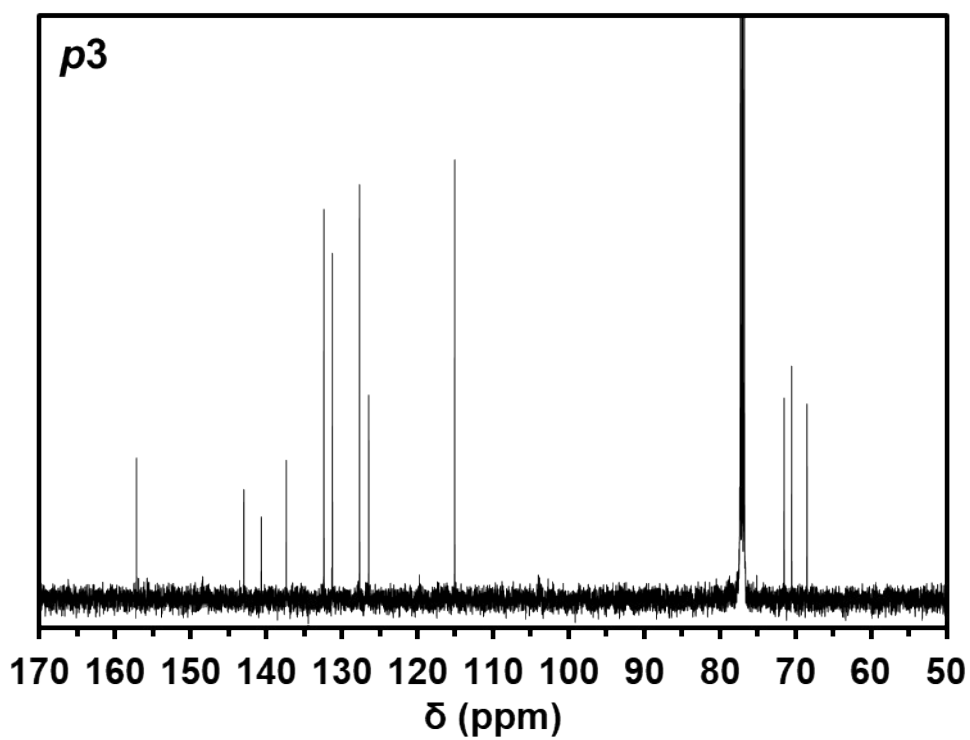


Fig. S4 ^{13}C NMR spectrum of *p3*

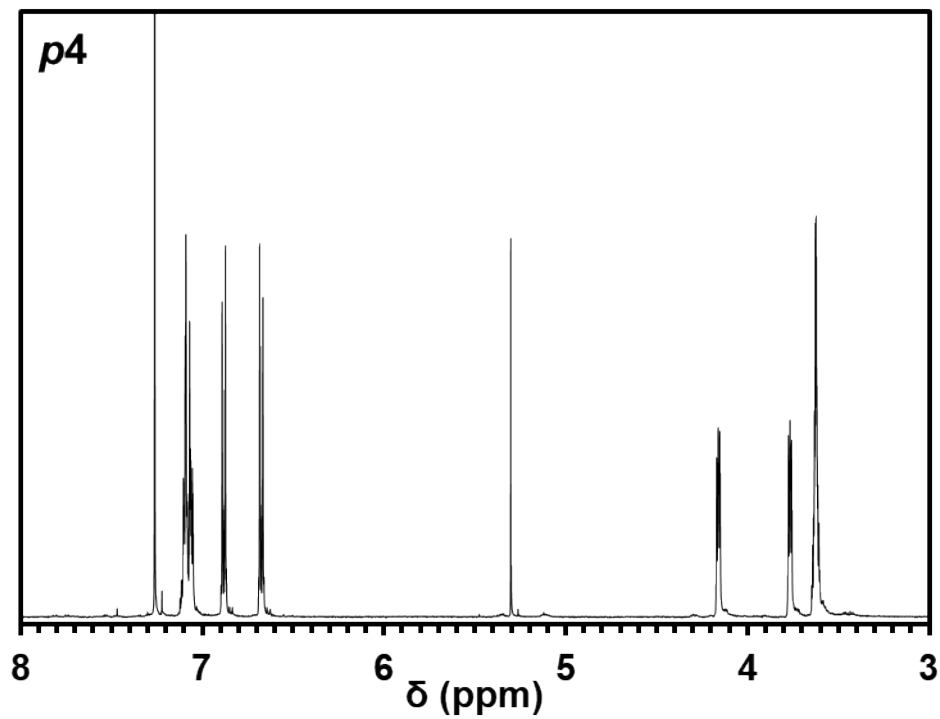


Fig. S5 ^1H NMR spectrum of *p4*.

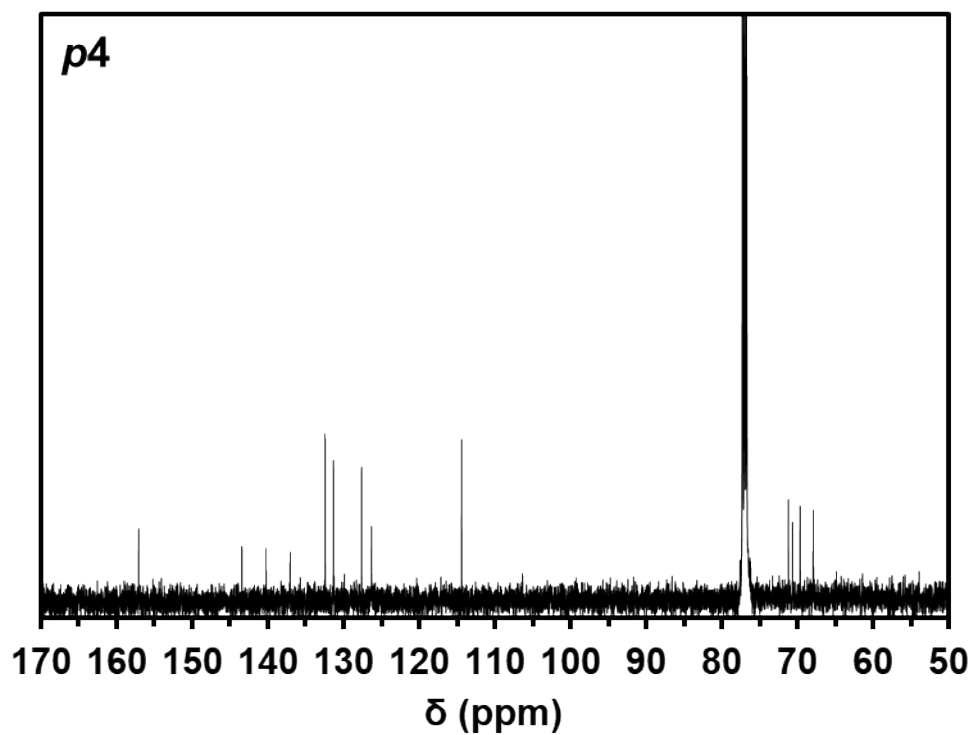


Fig. S6 ^{13}C NMR spectrum of *p4*.

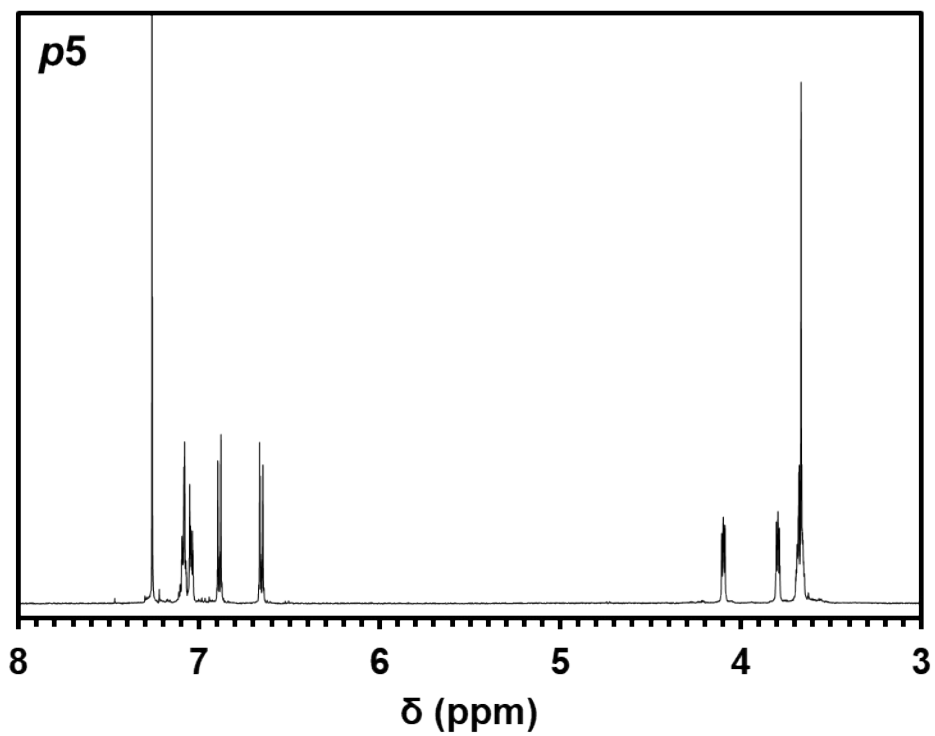


Fig. S7 ¹H NMR spectrum of *p5*.

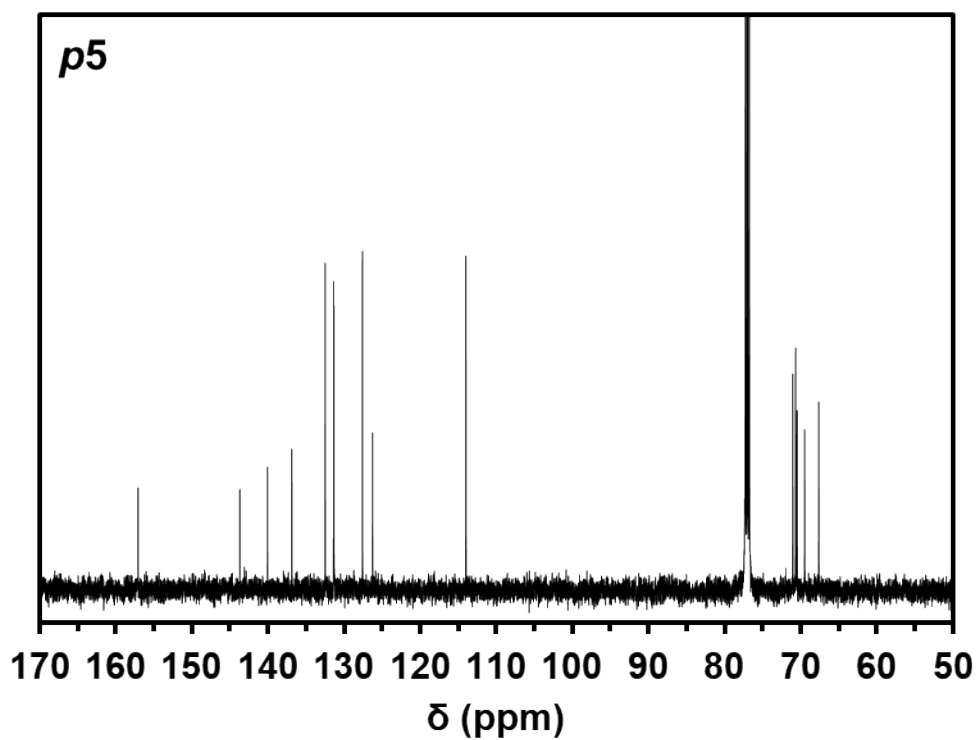


Fig. S8 ¹³C NMR spectrum of *p5*.

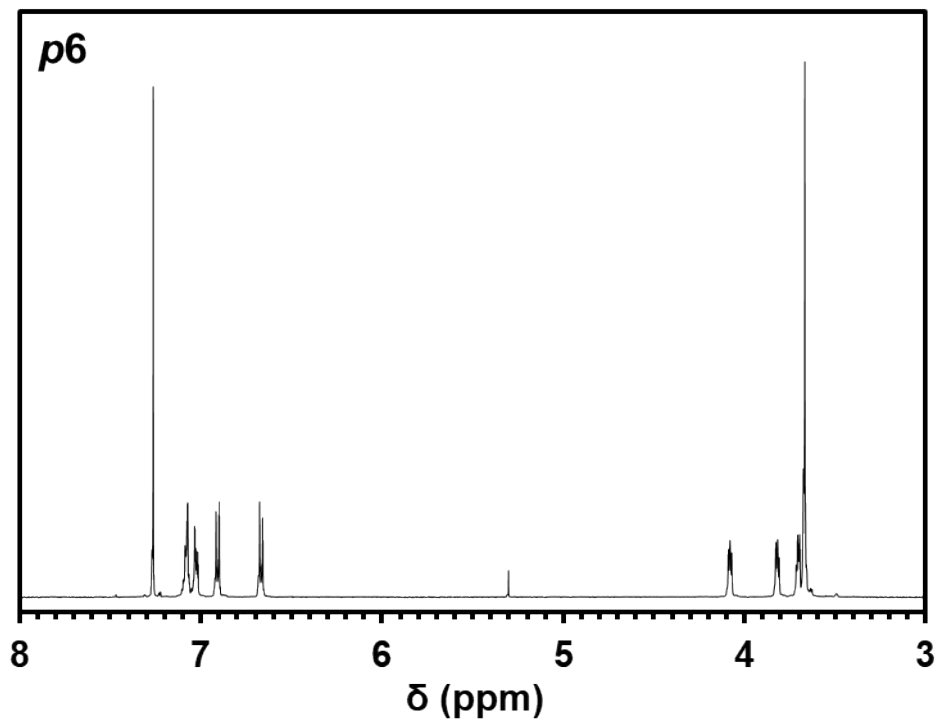


Fig. S9 ^1H NMR spectrum of *p6*.

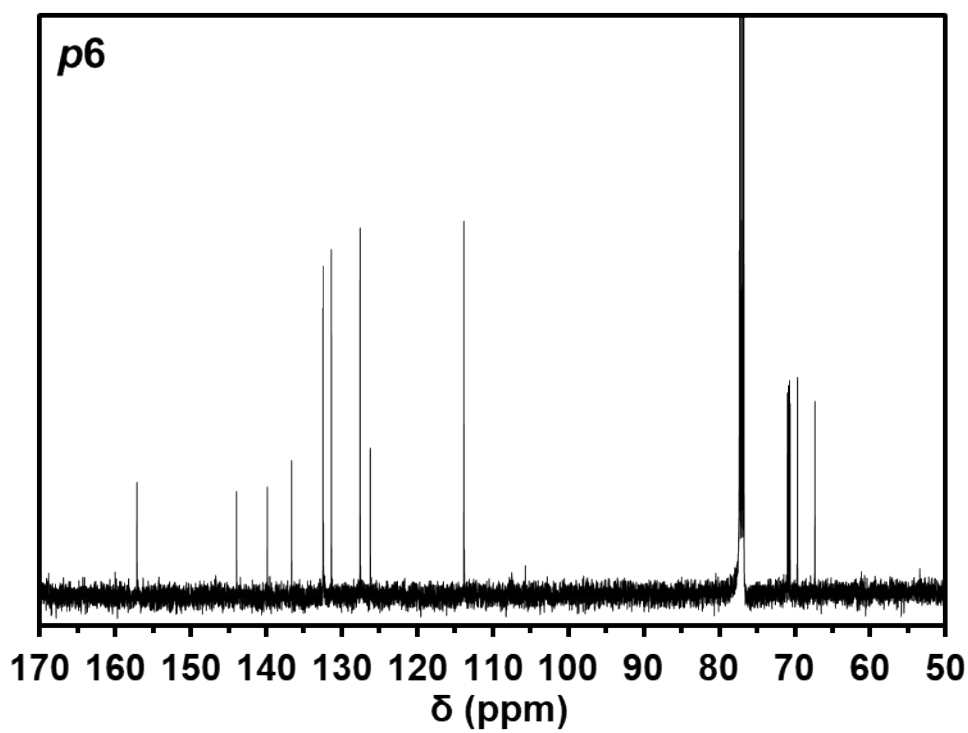


Fig. S10 ^{13}C NMR spectrum of *p6*.

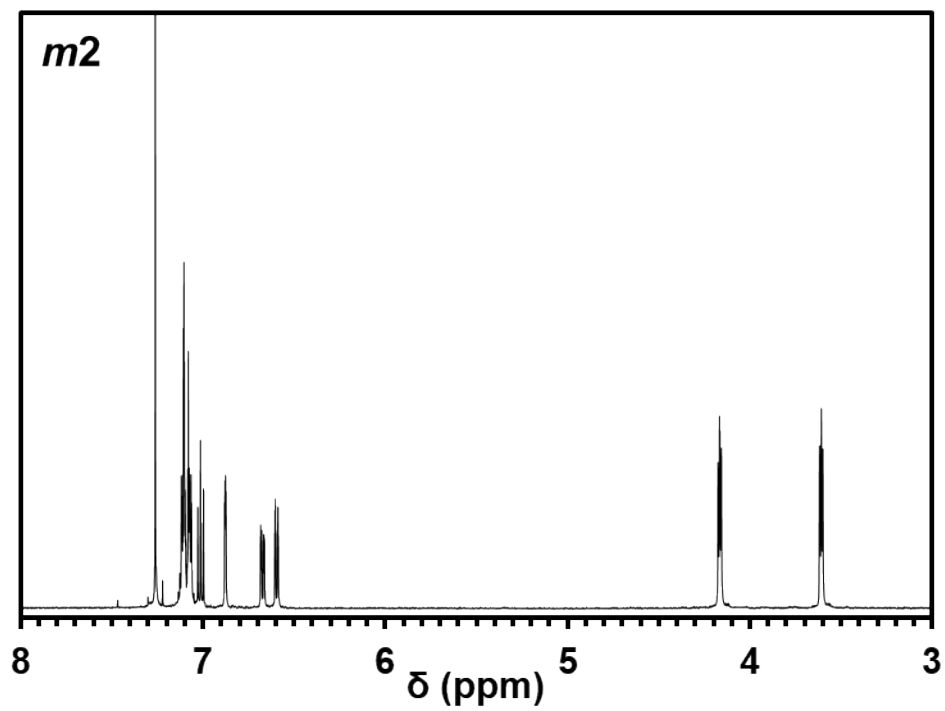


Fig. S11 ^1H NMR spectrum of *m2*.

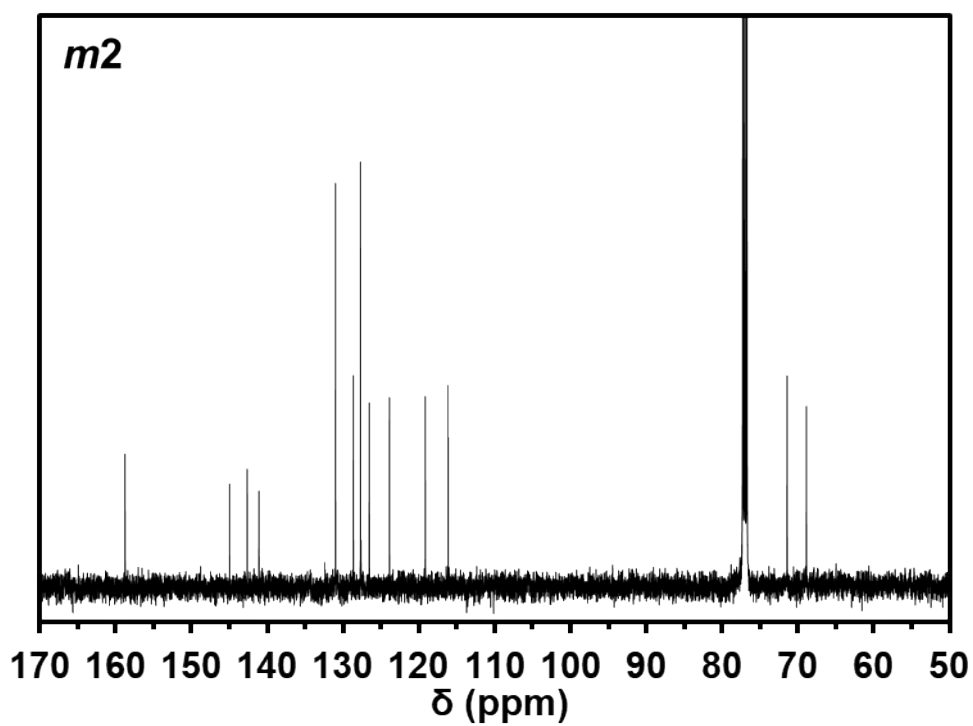


Fig. S12 ^{13}C NMR spectrum of *m2*.

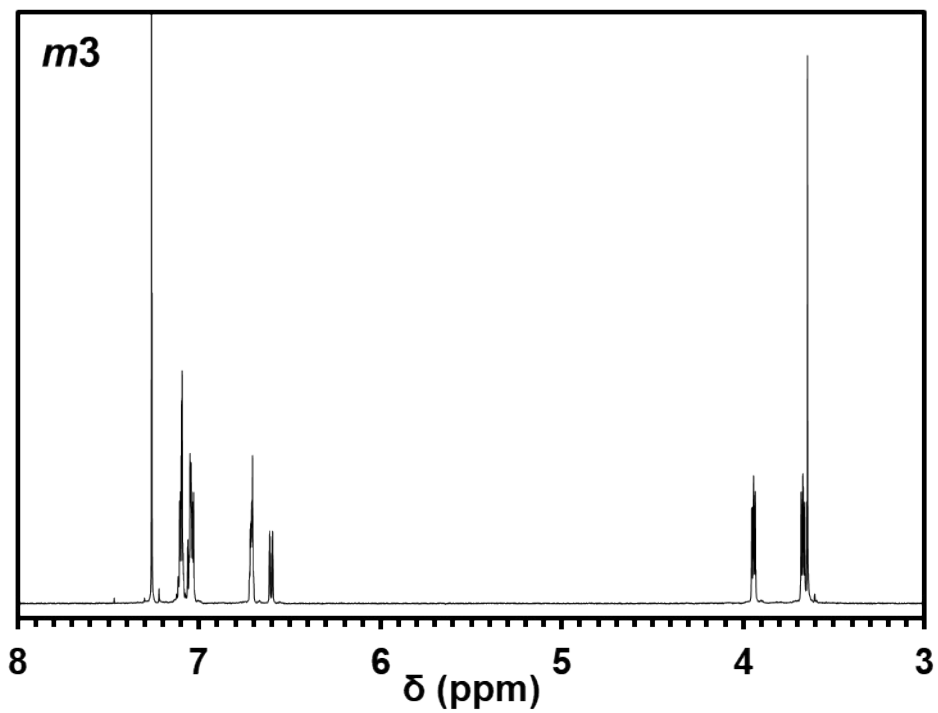


Fig. S13 ¹H NMR spectrum of *m3*.

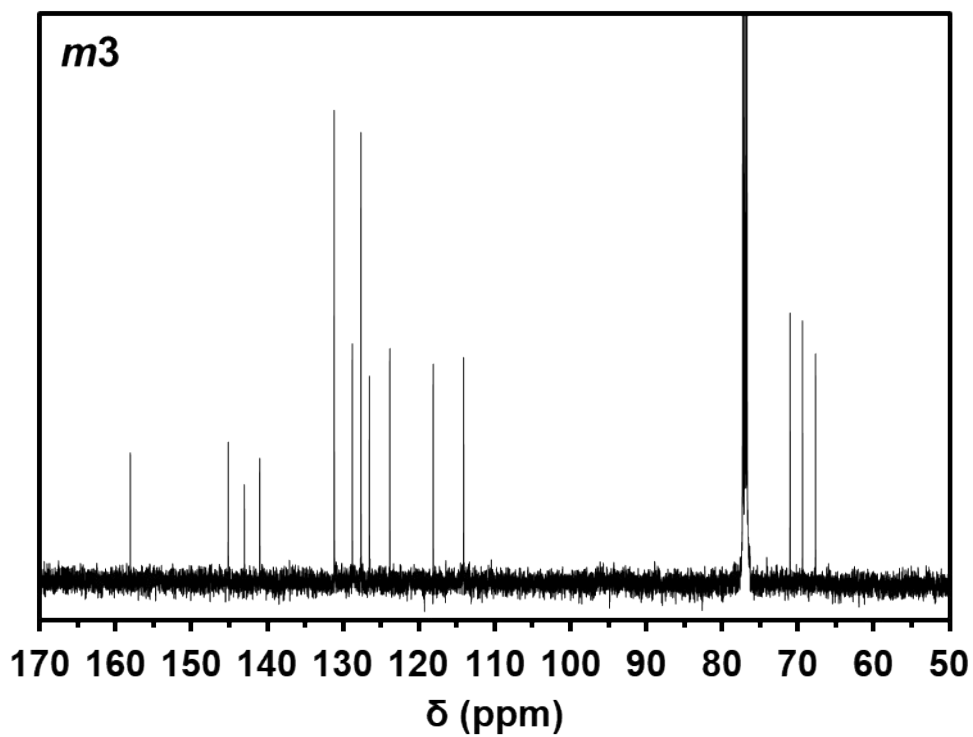


Fig. S14 ¹³C NMR spectrum of *m3*.

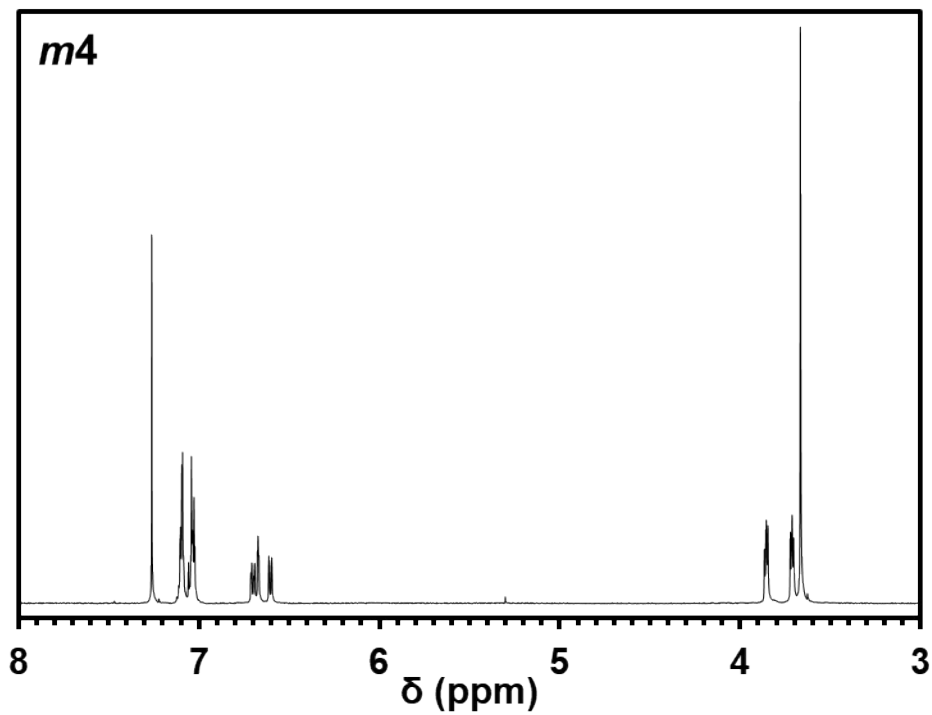


Fig. S15 ^1H NMR spectrum of *m4*.

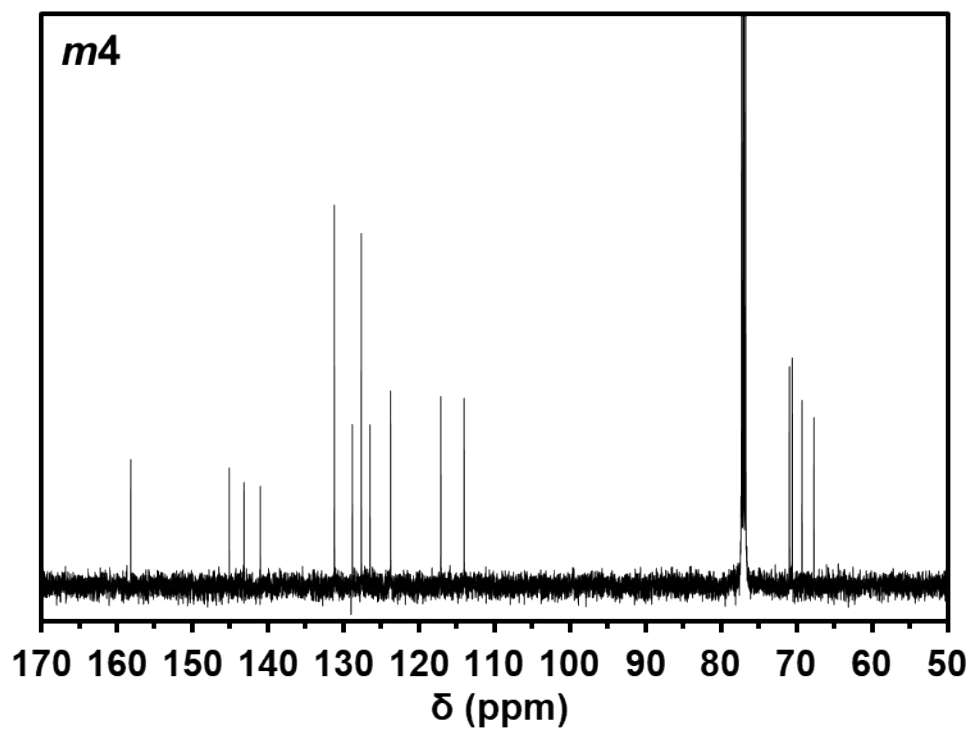


Fig. S16 ^{13}C NMR spectrum of *m4*.

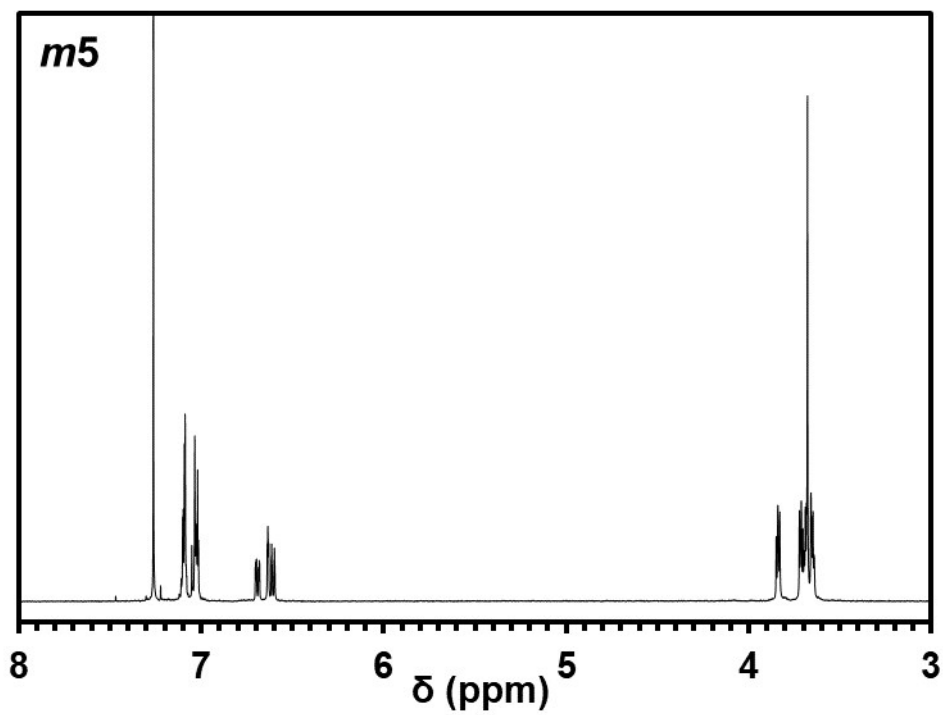


Fig. S17 ^1H NMR spectrum of *m5*.

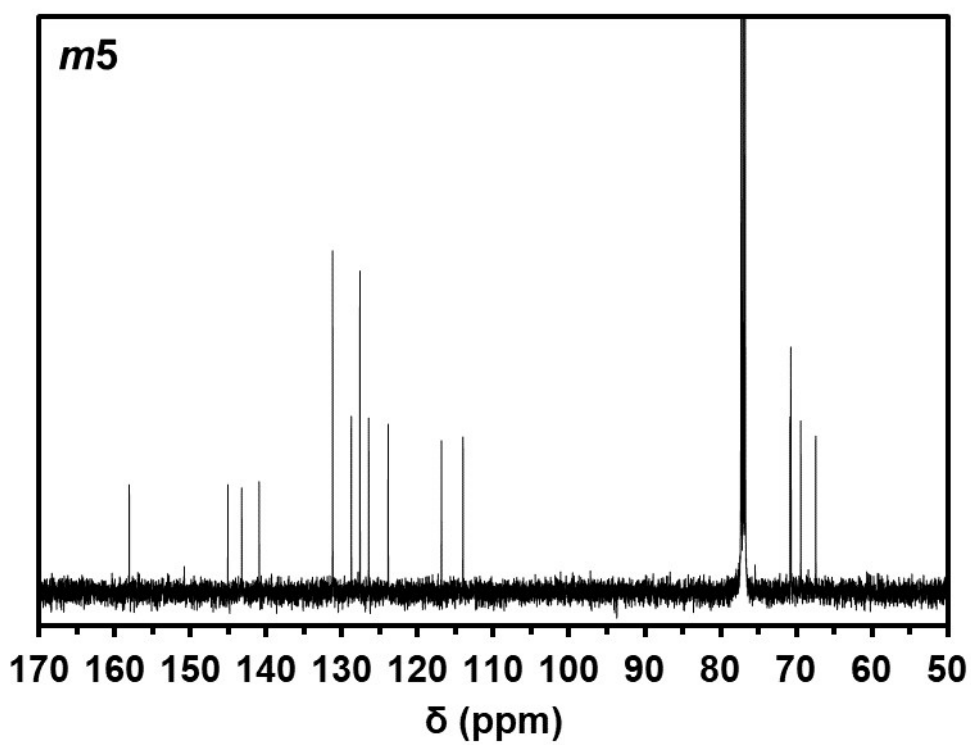


Fig. S18 ^{13}C NMR spectrum of *m5*.

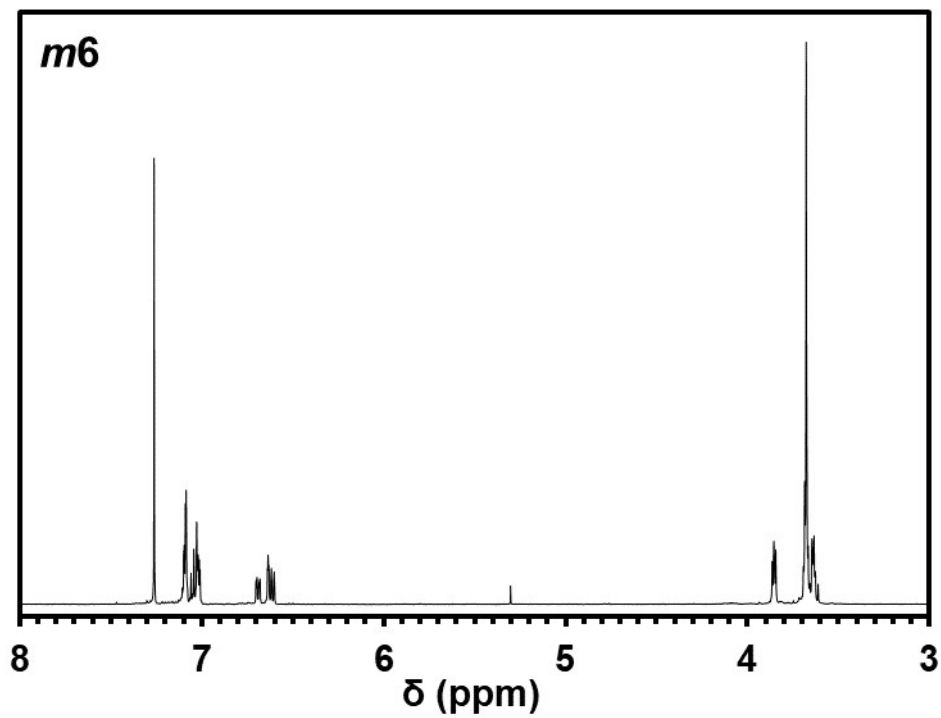


Fig. S19 ^1H NMR spectrum of *m6*.

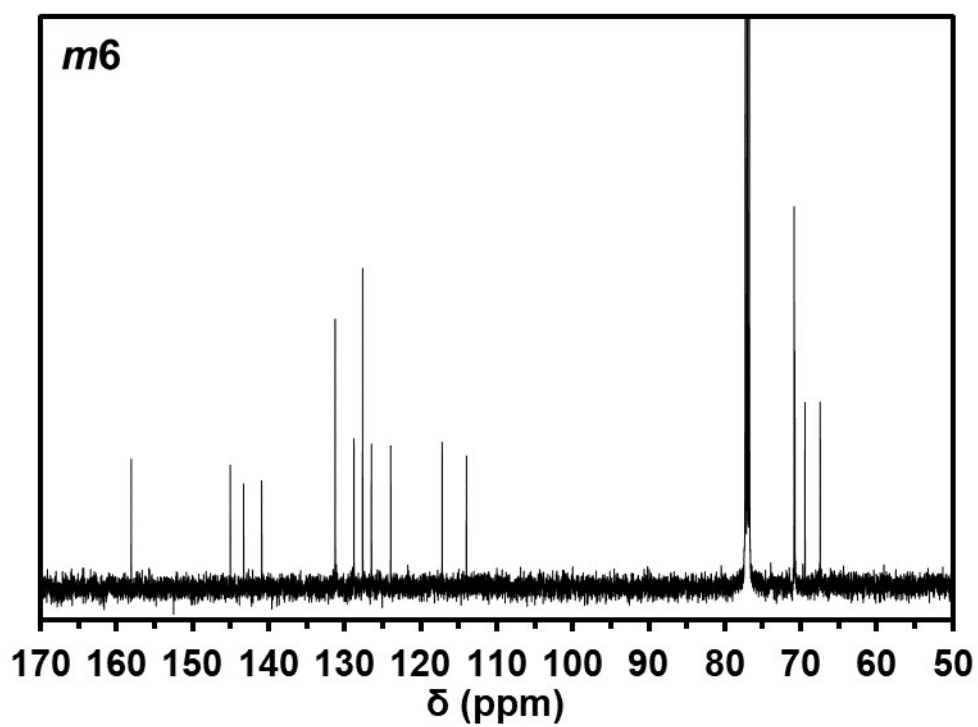


Fig. S20 ^{13}C NMR spectrum of *m6*.

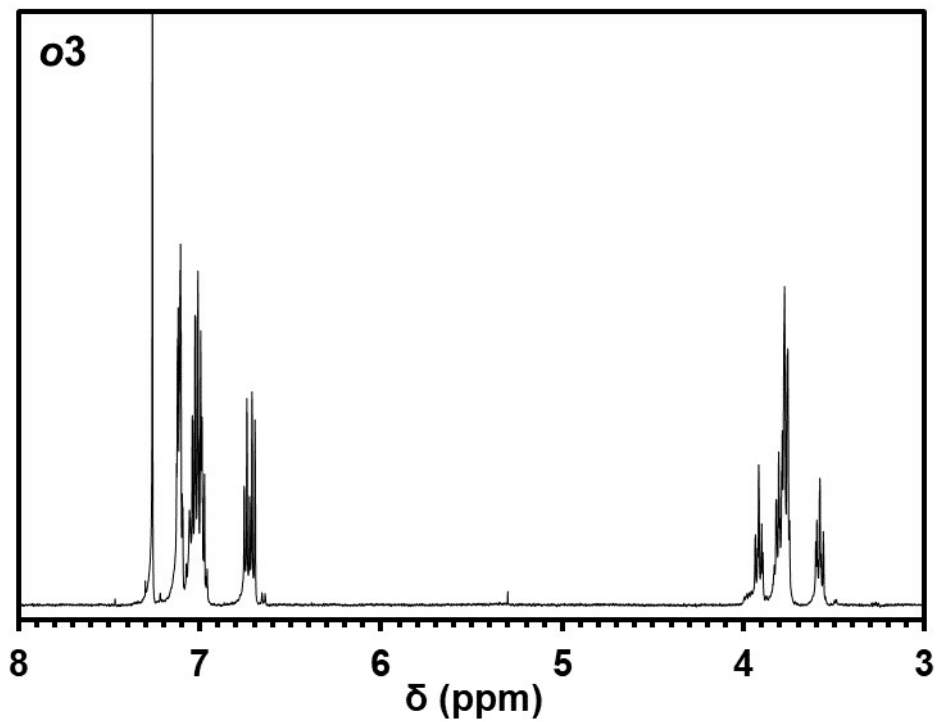


Fig. S21 ^1H NMR spectrum of *o3*.

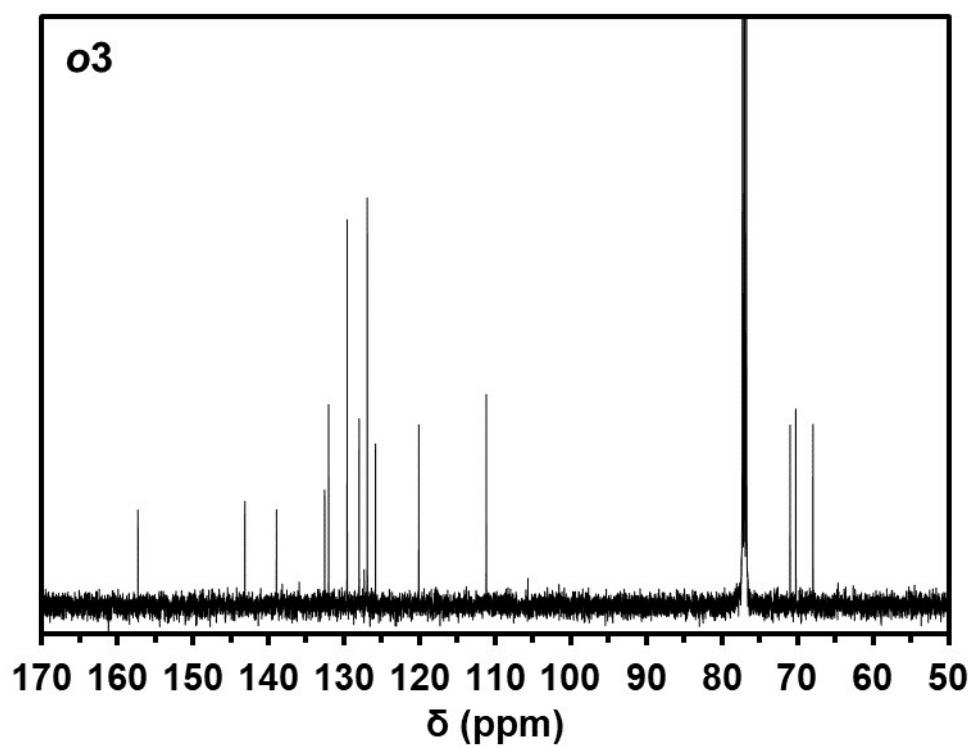


Fig. S22 ^{13}C NMR spectrum of *o3*.

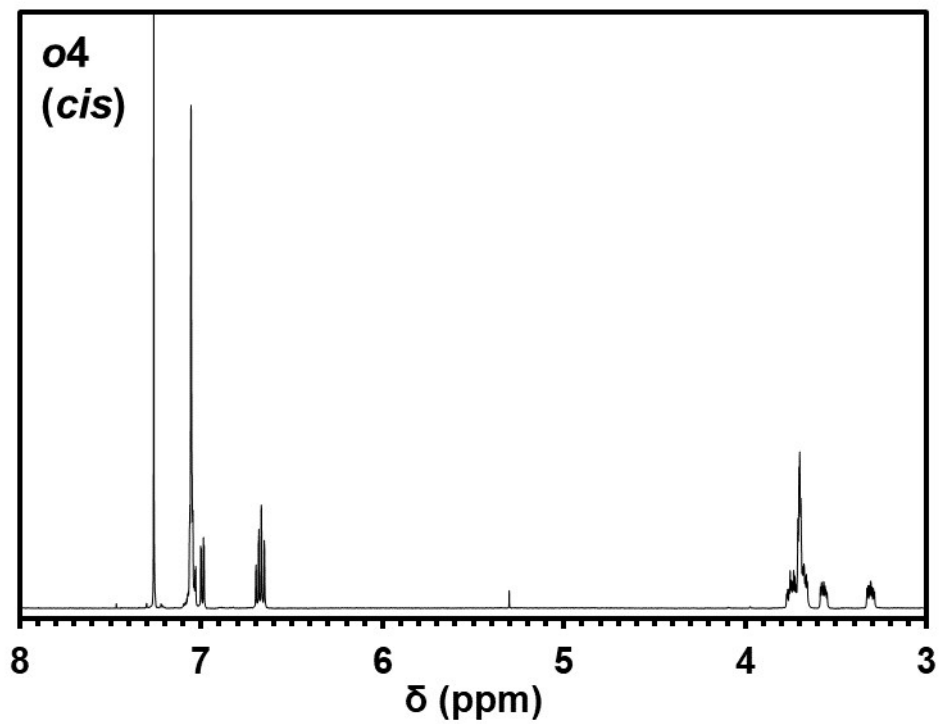


Fig. S23 ¹H NMR spectrum of *o4* (cis).

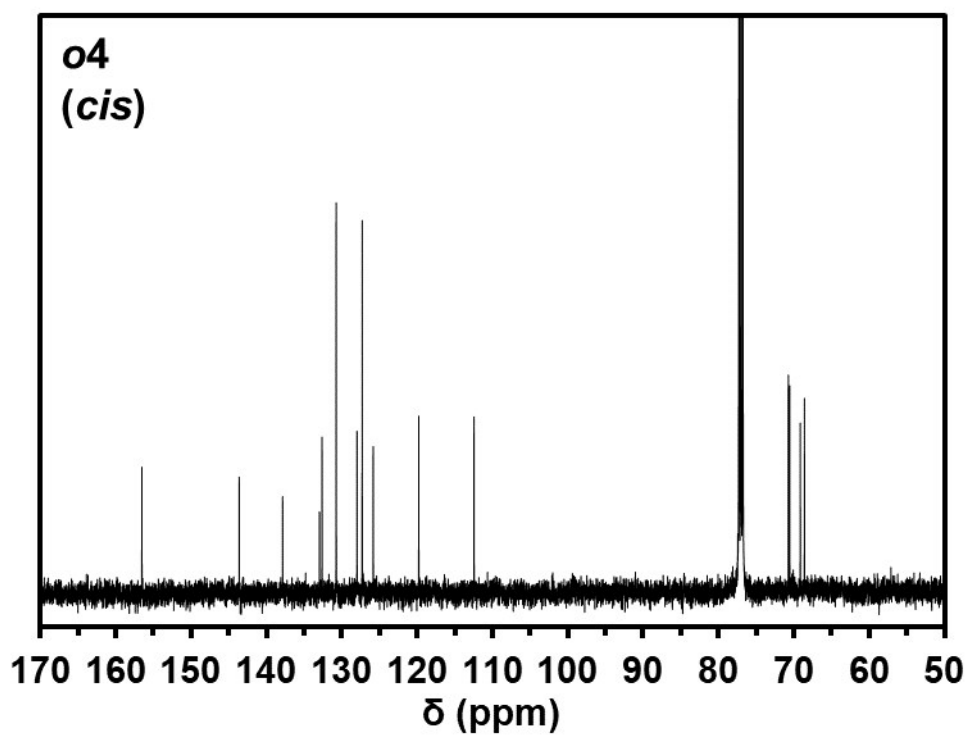


Fig. S24 ¹³C NMR spectrum of *o4* (cis).

Table S1. Summary of crystallographic data.

Identification code	<i>p3</i>	<i>m2</i>
Empirical formula	C ₃₂ H ₃₀ O ₄	C ₃₀ H ₂₆ O ₃
Formula weight	478.59	434.51
Temperature (K)	193(2)	193(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	13.9927(3)	13.49730(10)
b (Å)	13.9930(4)	8.90620(10)
c (Å)	14.3817(4)	19.1393(2)
α(°)	74.428(2)	90
β(°)	74.344(2)	90.6610(10)
γ(°)	71.519(2)	90
Volume (Å ³)	2519.52(11)	2300.58(4)
<i>Z</i>	2	4
Calculated density (g/cm ³)	1.262	1.254
Absorption coefficient (mm ⁻¹)	0.653	0.630
F(000)	1016	920
Reflections collected / unique	17346 / 9007 [<i>R</i> _{int} = 0.0160]	16678 / 4690 [<i>R</i> _{int} = 0.0233]
Completeness to theta = 77.40	84.0%	96.0%
Goodness-of-fit on <i>F</i> ²	1.016	1.052
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0744, <i>wR</i> ₂ = 0.2159	<i>R</i> ₁ = 0.0513, <i>wR</i> ₂ = 0.1331
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0790, <i>wR</i> ₂ = 0.2206	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.1354

Table S1 (continued). Summary of crystallographic data.

Identification code	<i>o3</i>	<i>o4 (cis)</i>
Empirical formula	C ₃₂ H ₃₀ O ₄ ·CH ₄ O	C ₃₄ H ₃₄ O ₅
Formula weight	510.63	522.61
Temperature (K)	193(2)	193(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a (Å)	10.8265(3)	9.6286(3)
b (Å)	11.5183(3)	10.0918(3)
c (Å)	12.4106(3)	15.5411(3)
α(°)	78.076(2)	78.560(2)
β(°)	66.748(2)	82.821(2)
γ(°)	85.843(2)	67.359 (3)
Volume (Å ³)	1391.18(6)	1364.09(6)
<i>Z</i>	2	2
Calculated density (g/cm ³)	1.219	1.272
Absorption coefficient (mm ⁻¹)	0.648	0.674
F(000)	544	556
Reflections collected / unique	18129 / 5646 [<i>R</i> _{int} = 0.0223]	14953 / 5492 [<i>R</i> _{int} = 0.0265]
Completeness to theta = 76.74	96.1%	96.2%
Goodness-of-fit on <i>F</i> ²	1.066	1.059
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0676, <i>wR</i> ₂ = 0.2012	<i>R</i> ₁ = 0.0519, <i>wR</i> ₂ = 0.1435
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0723, <i>wR</i> ₂ = 0.2062	<i>R</i> ₁ = 0.0544, <i>wR</i> ₂ = 0.1461

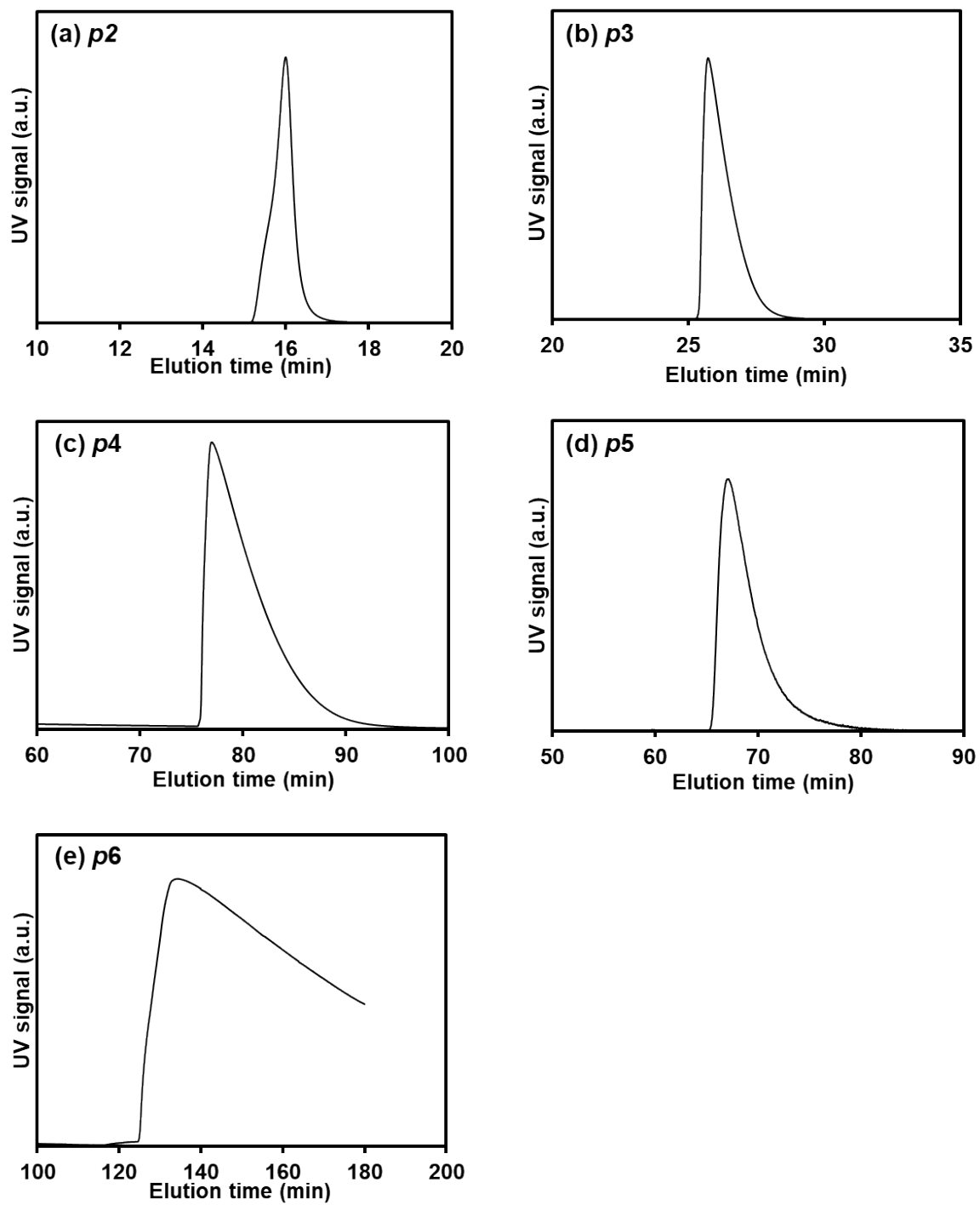


Fig. S25 Chiral column chromatograms of (a) *p2*, (b) *p3*, (c) *p4*, (d) *p5*, and (e) *p6*.

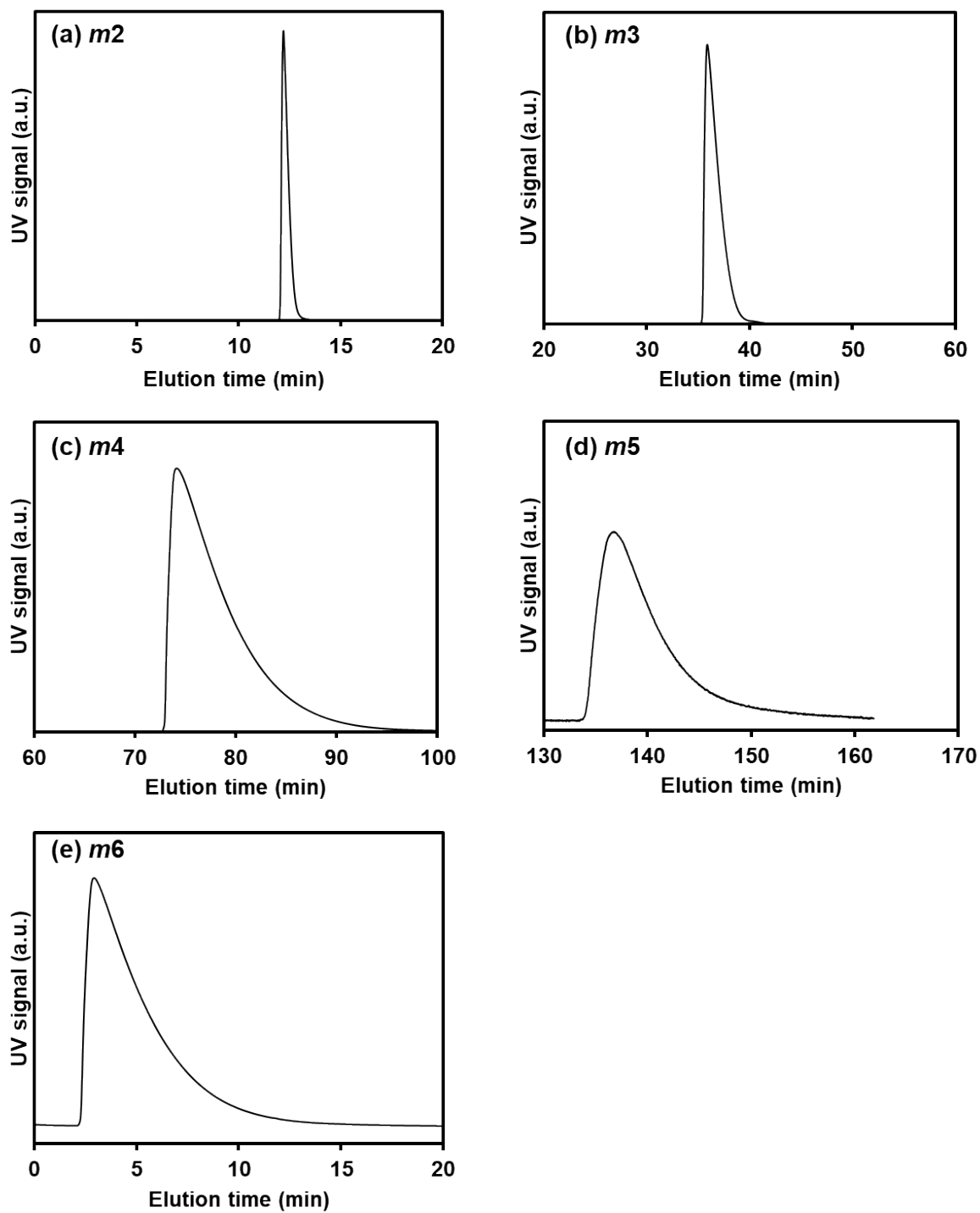


Fig. S26 Chiral column chromatograms of (a) *m2*, (b) *m3*, (c) *m4*, (d) *m5*, and (e) *m6*.

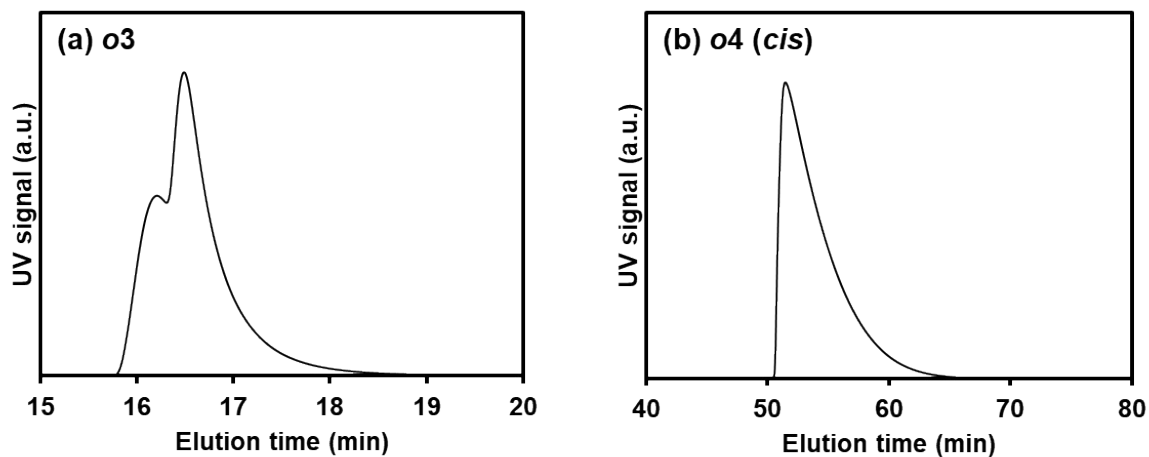


Fig. S27 Chiral column chromatograms of (a) **o3** and (b) **o4 (cis)**.

Table S2. Summary of fluorescence quantum yields of the aggregated state and absolute quantum yields of the solid state.

Molecule	$\Phi_{F,Aggregate}^a$	$\Phi_{F,Solid}^b$
p2	0.537	0.433
p3	0.190	0.385
p4	0.180	0.431
p5	0.176	0.955
p6	0.173	0.688
m2	0.0710	0.804
m3	0.0526	0.184
m4	0.0423	0.109
m5	0.0311	0.157
m6	0.0255	0.350
o3	0.197	0.329
o4 (cis)	0.228	0.121
o4 (mixture)	0.149	0.239

^a Fluorescence quantum yields of the aggregated state (THF/H₂O = 1/99, 10 μ M). The concentration is set at 10 μ M, and 9,10-diphenylanthracene was used as a standard.¹ ^b Absolute quantum yield estimated by an integral sphere.

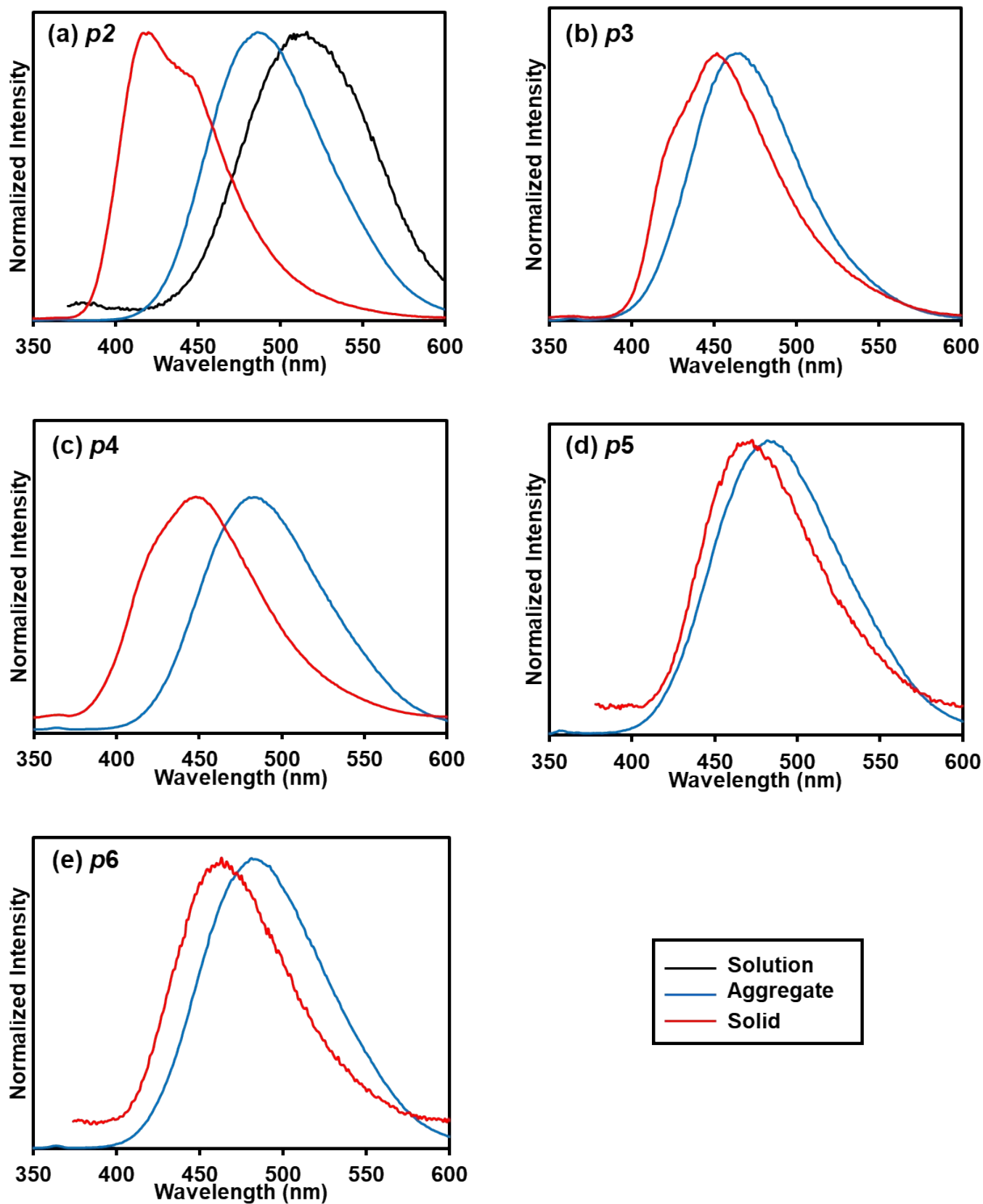


Fig. S28 Normalized emission spectra of (a) $p2$, (b) $p3$, (c) $p4$, (d) $p5$, and (e) $p6$ in solution (only for $p2$), aggregate (THF/H₂O = 1/99, 10 μ M), and solid.

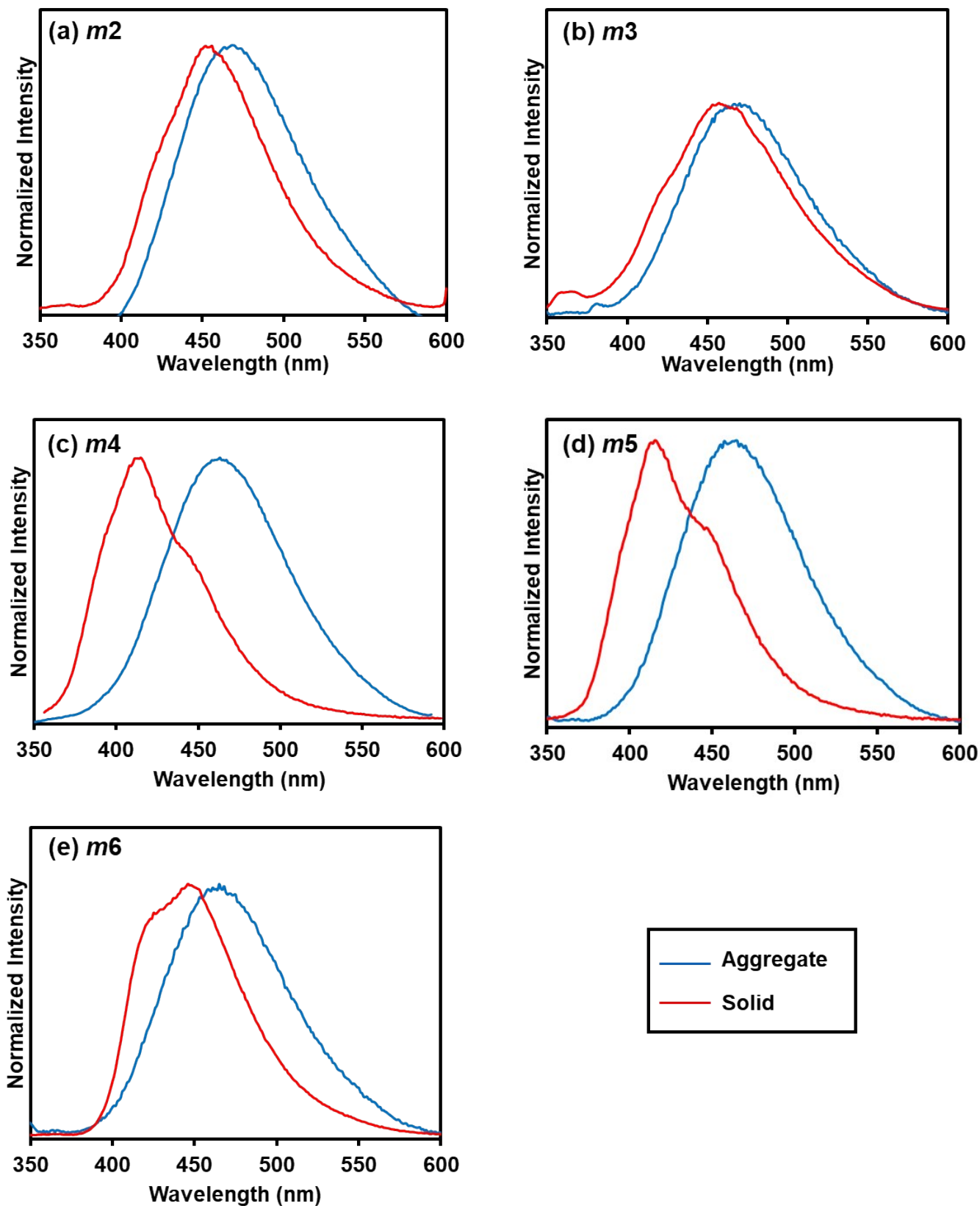


Fig. S29 Normalized emission spectra of (a) *m2*, (b) *m3*, (c) *m4*, (d) *m5*, and (e) *m6* in aggregate (THF/H₂O = 1/99, 10 μ M), and solid.

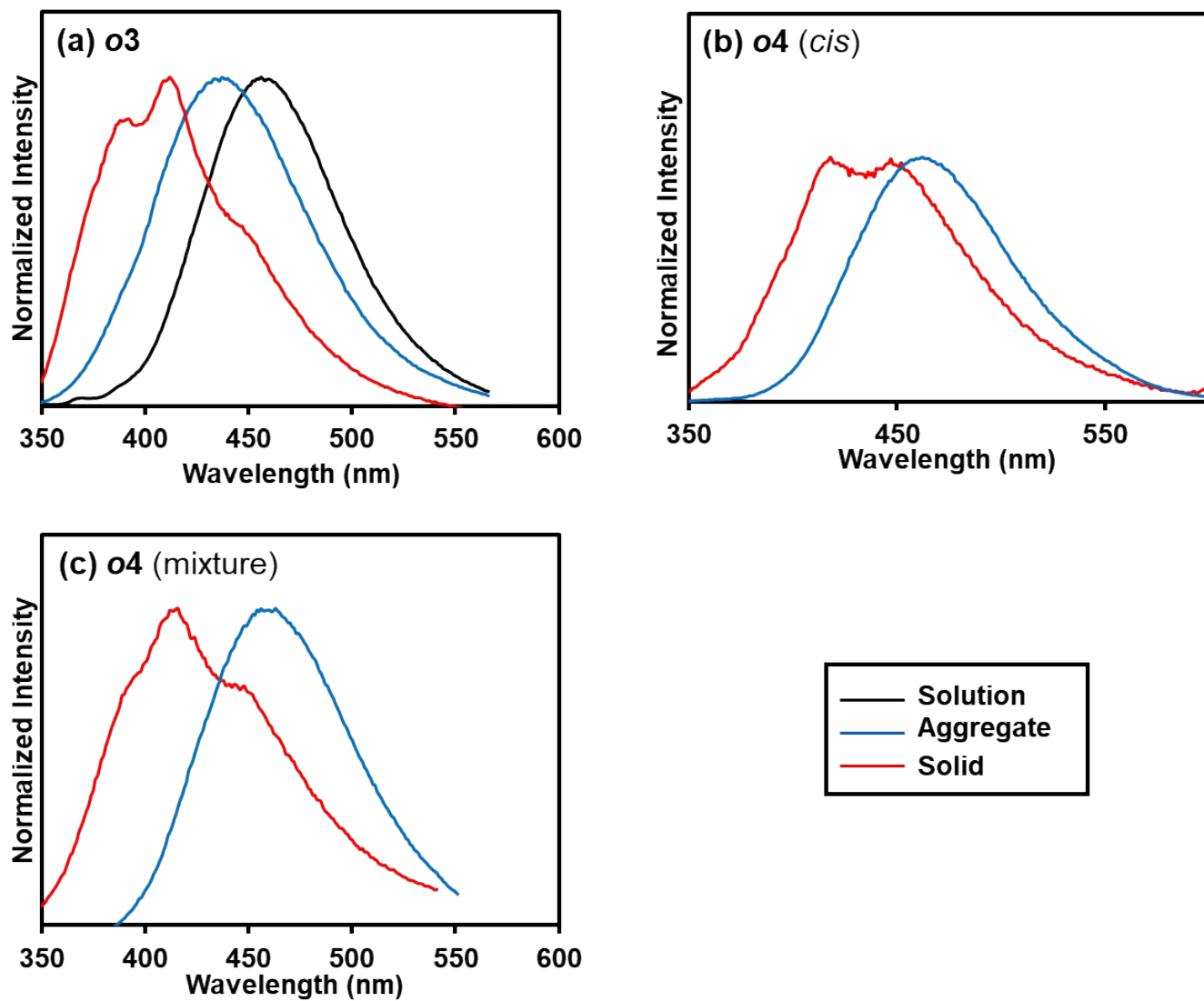


Fig. S30 Normalized emission spectra of (a) **o3**, (b) **o4 (cis)**, and (c) **o4 (mixture)**, in solution (only for **o3**), aggregate (THF/H₂O = 1/99, 10 μM), and solid.

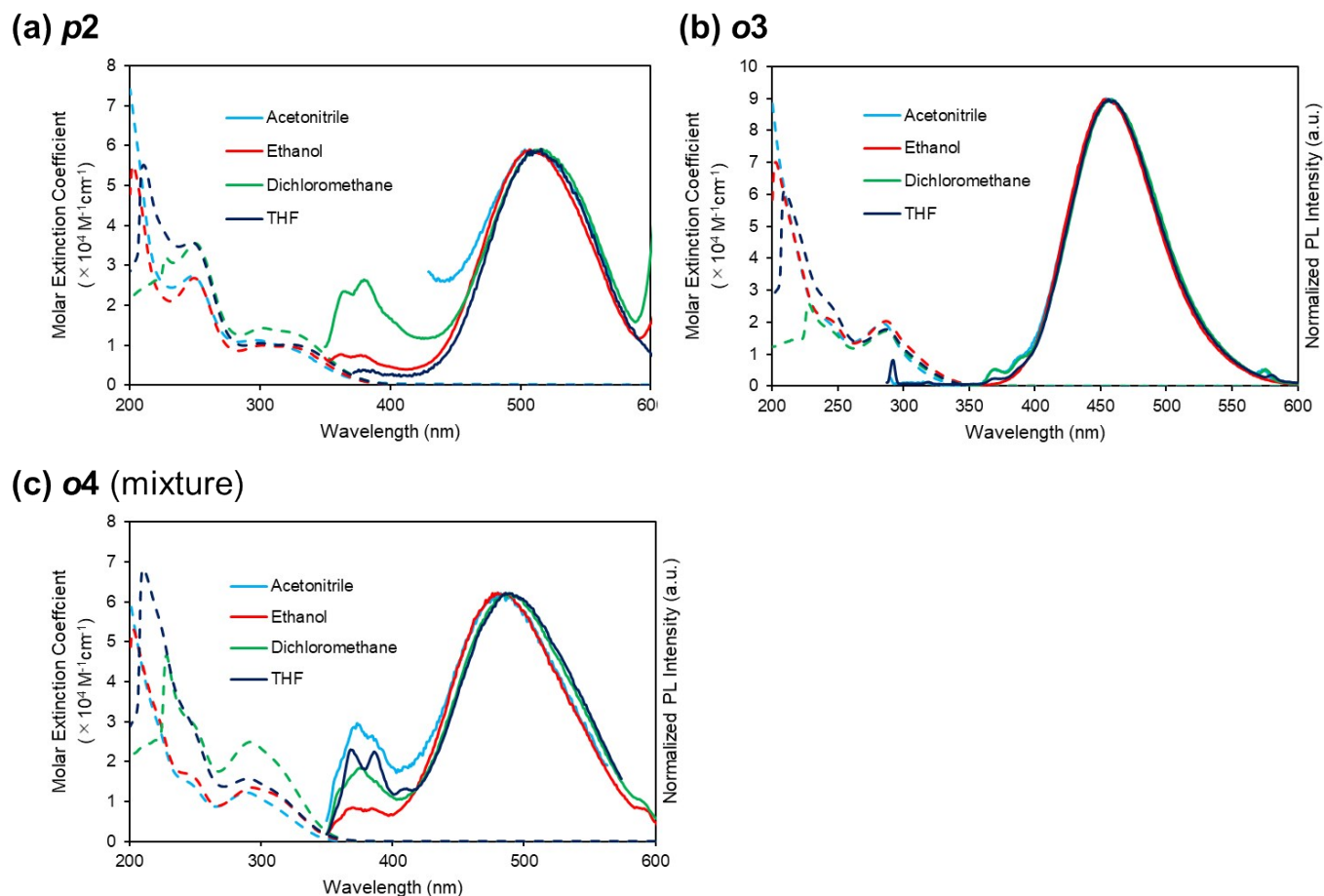


Fig. S31 The absorption (dashed line) and emission (solid line) spectra in various solvents such as ethanol, acetonitrile, dichloromethane, and THF of (a) *p2*, (b) *o3*, and (c) *o4* (mixture) (10 μ M).

Table S3. Summary of fluorescence quantum yields (Φ_F) of *p2*, *o3*, and *o4* (mixture) in solution^a

Molecule	Solvent	Φ_F
<i>p2</i>	Acetonitrile	1.9×10^{-4}
	Ethanol	1.3×10^{-3}
	Dichloromethane	4.3×10^{-4}
	THF	2.3×10^{-3}
<i>o3</i>	Acetonitrile	0.29
	Ethanol	0.26
	Dichloromethane	0.30
	THF	0.30
<i>o4</i> (mixture)	Acetonitrile	2.6×10^{-3}
	Ethanol	5.5×10^{-3}
	Dichloromethane	5.4×10^{-3}
	THF	1.6×10^{-2}

^a The concentration is set at 10 μ M, and 9,10-diphenylanthracene was used as a standard.¹

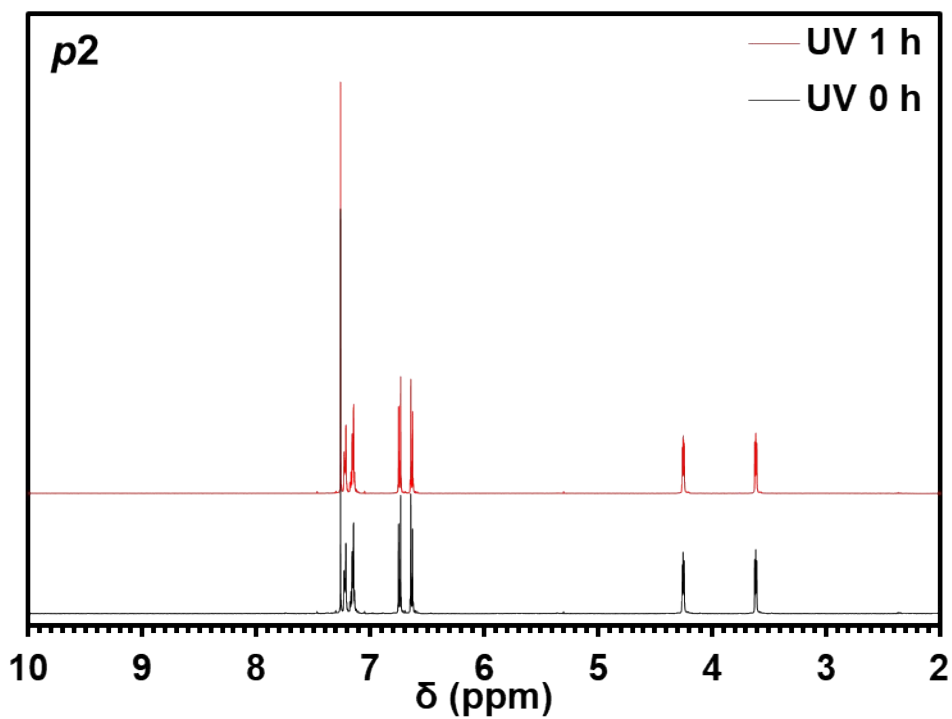


Fig. S32 ¹H NMR spectra of *p2* upon photoirradiation.

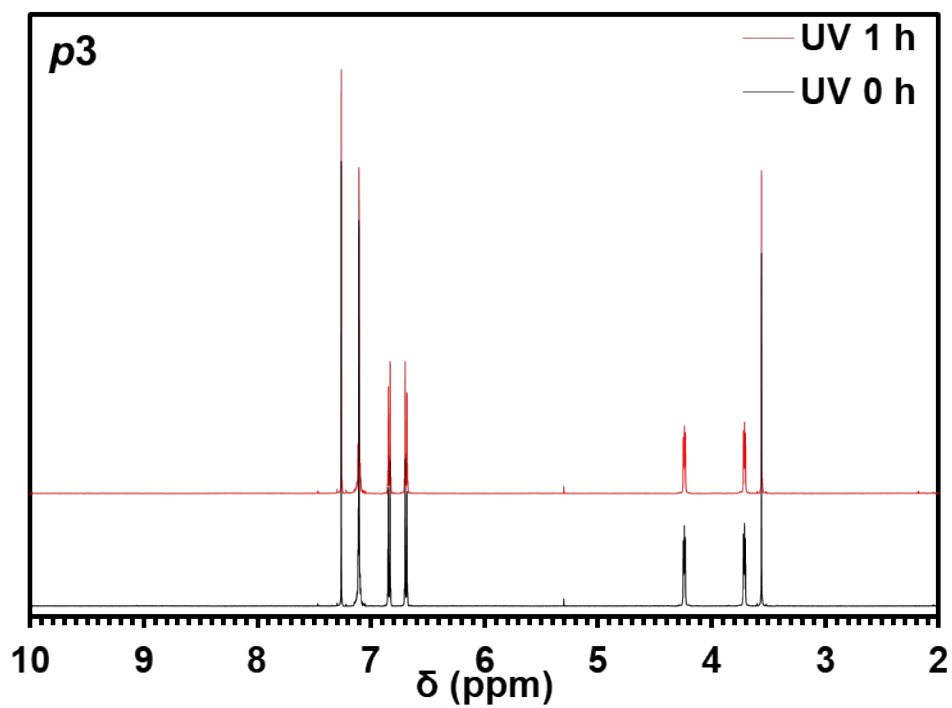


Fig. S33 ¹H NMR spectra of *p3* upon photoirradiation.

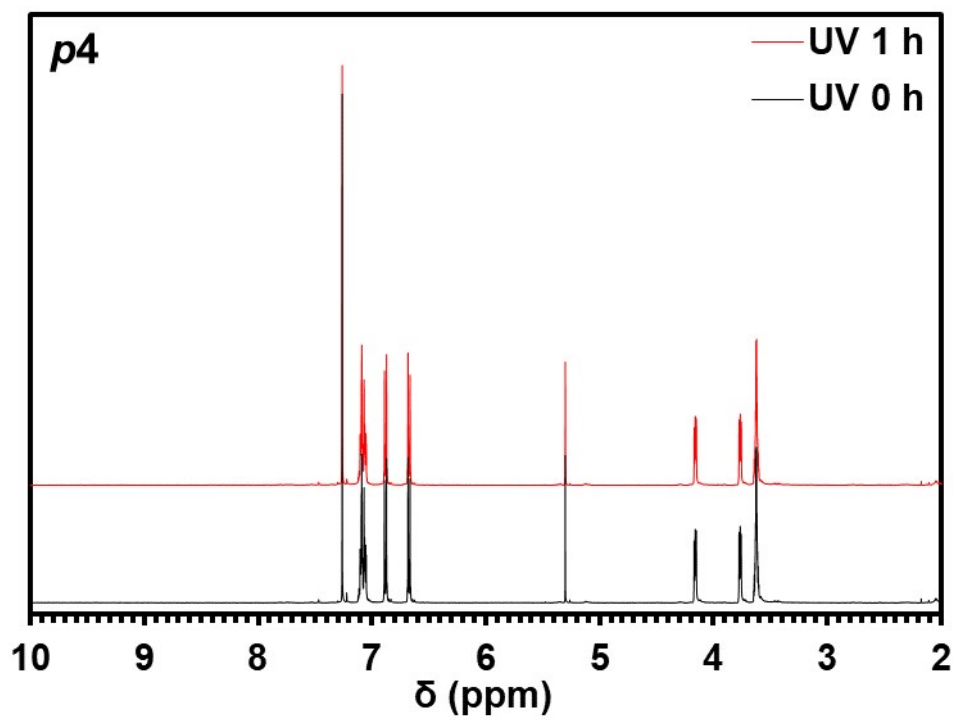


Fig. S34 ¹H NMR spectra of *p4* upon photoirradiation.

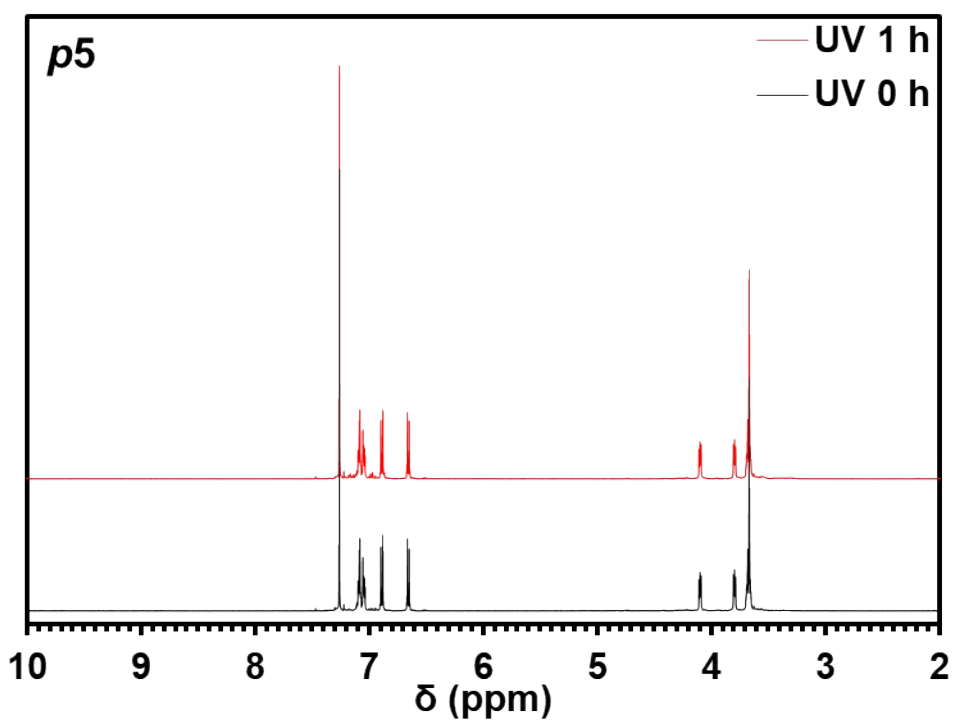


Fig. S35 ¹H NMR spectra of *p5* upon photoirradiation.

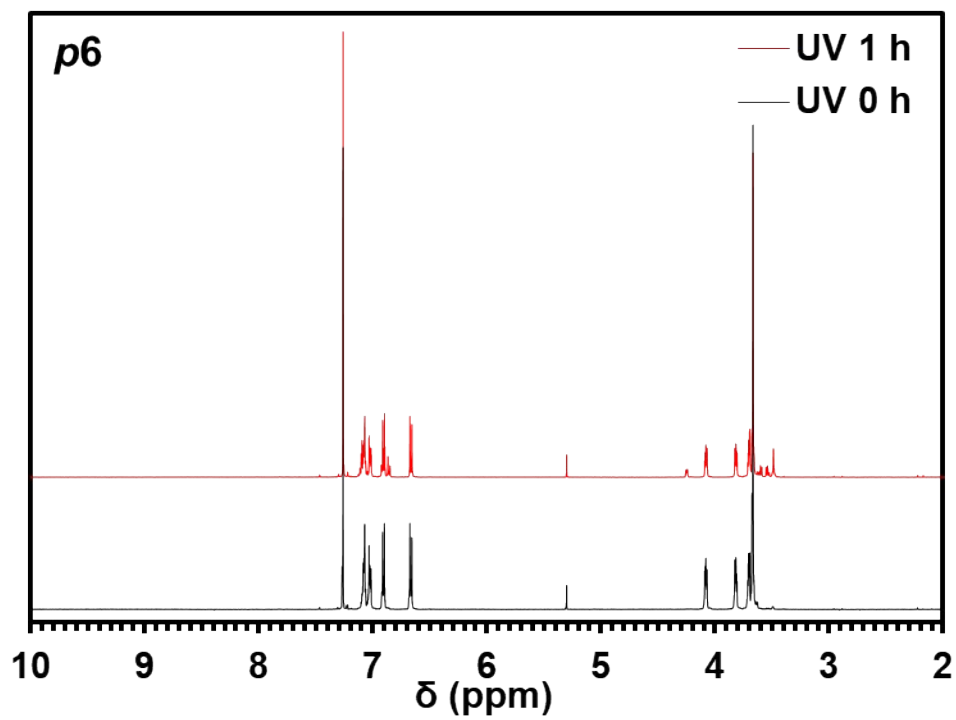


Fig. S36 ¹H NMR spectra of *p6* upon photoirradiation.

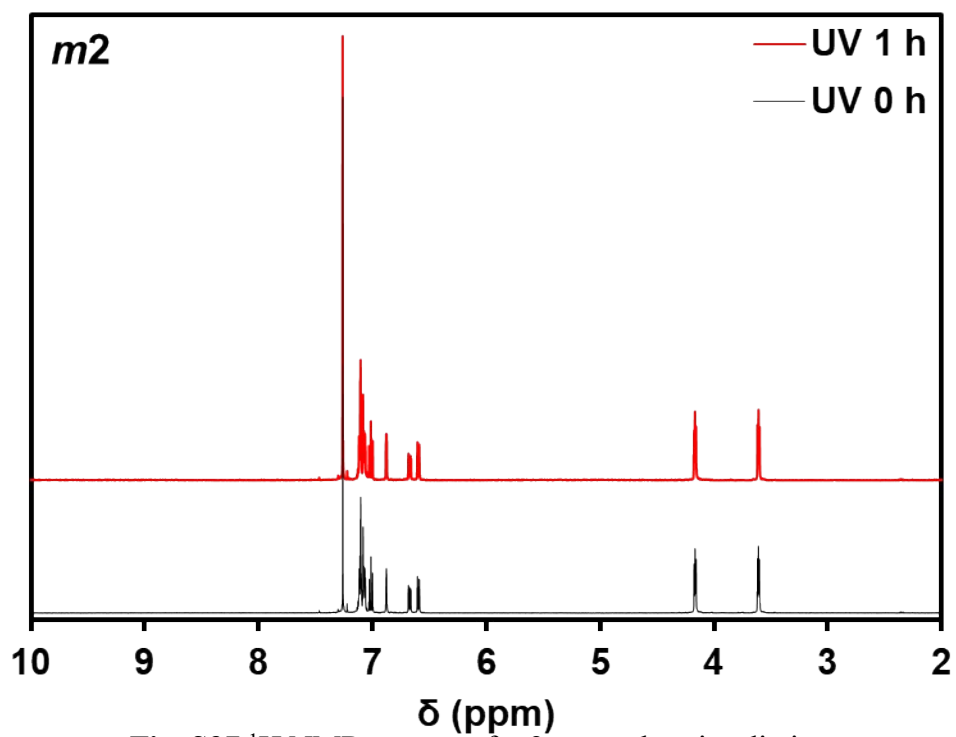


Fig. S37 ¹H NMR spectra of *m2* upon photoirradiation.

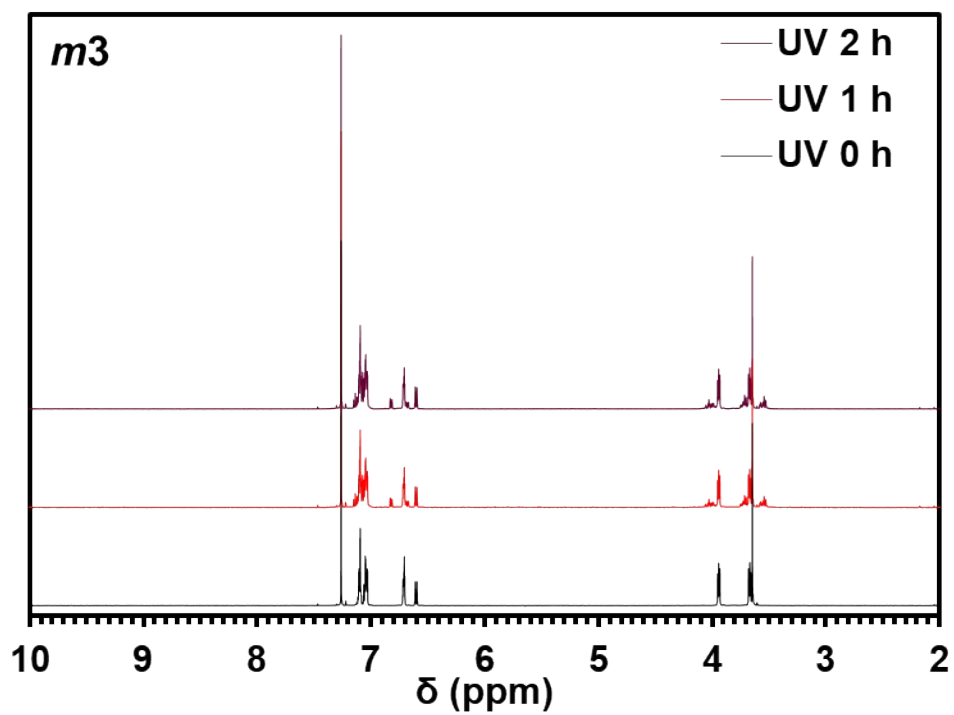


Fig. S38 ¹H NMR spectra of *m3* upon photoirradiation.

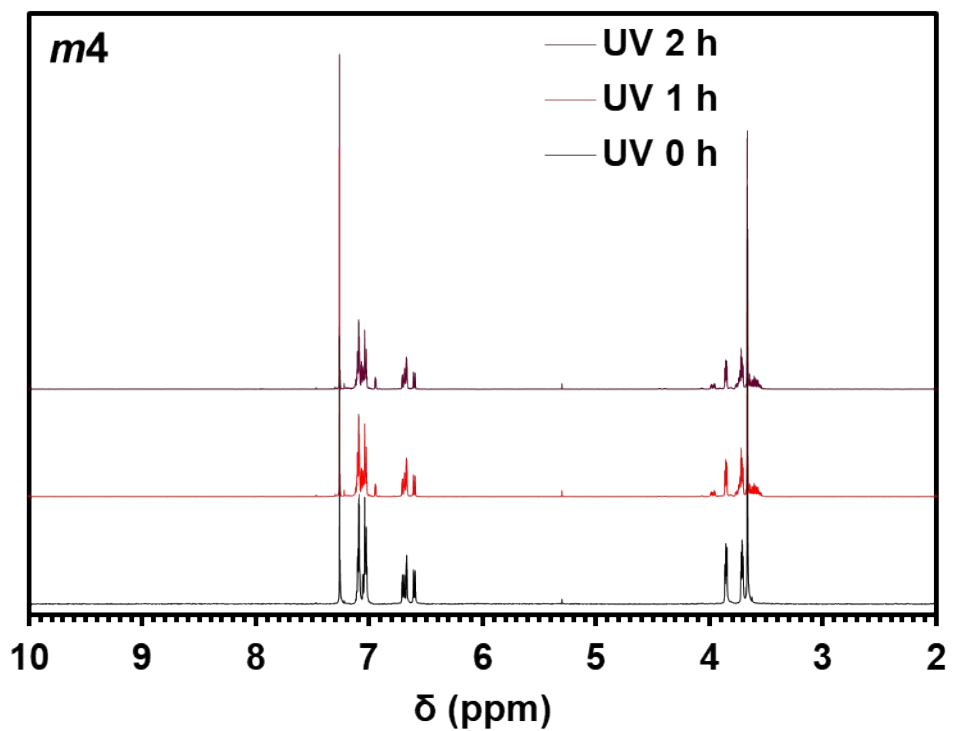


Fig. S39 ¹H NMR spectra of *m4* upon photoirradiation.

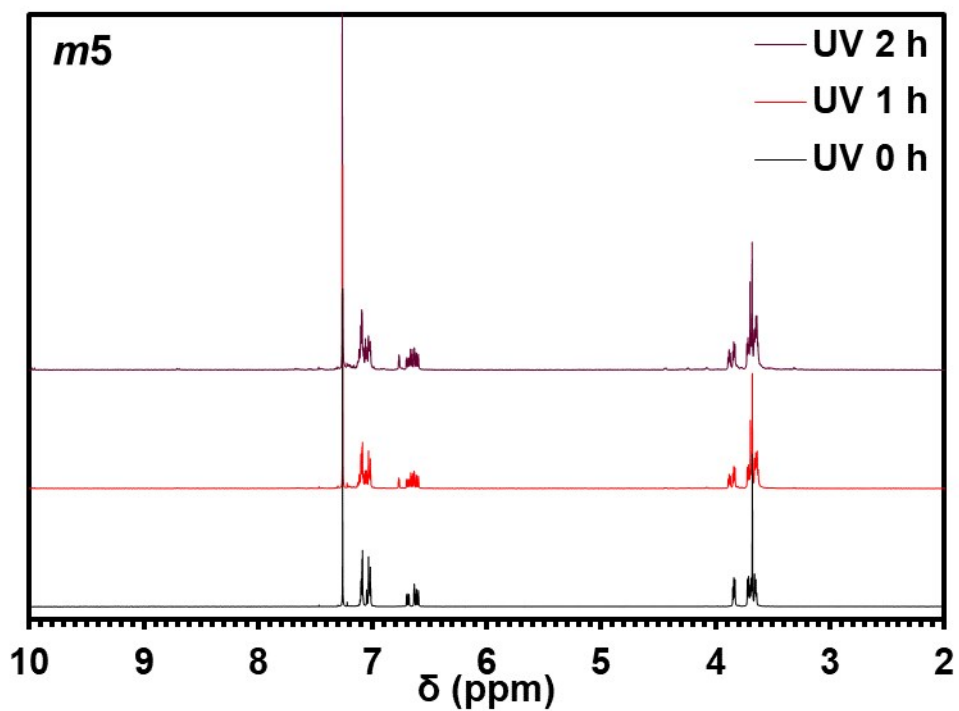


Fig. S40 ¹H NMR spectra of *m5* upon photoirradiation.

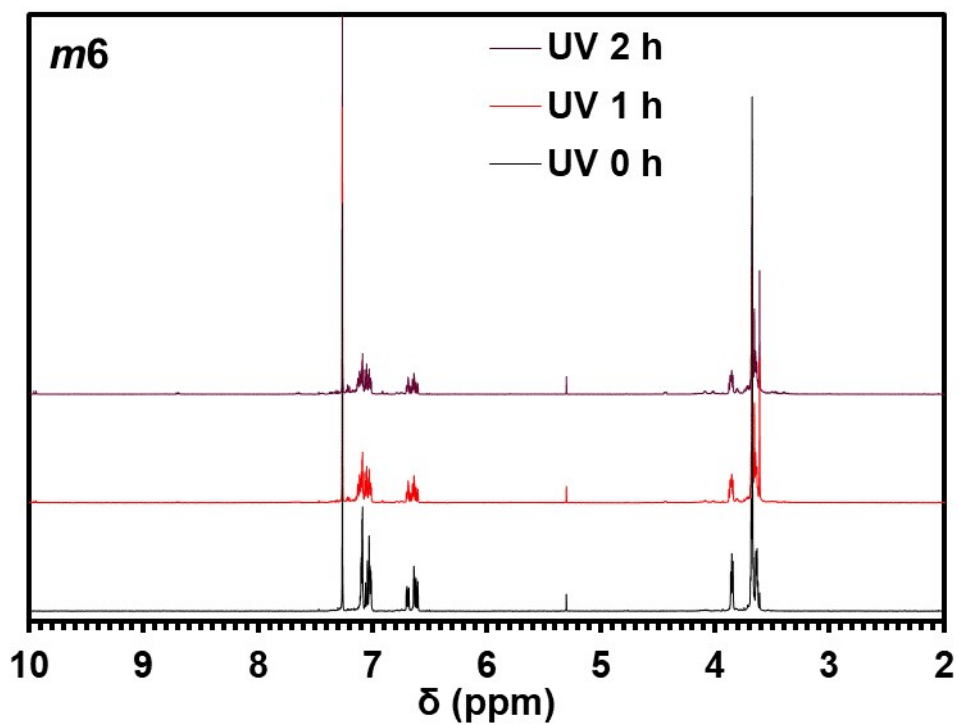


Fig. S41 ¹H NMR spectra of *m6* upon photoirradiation.

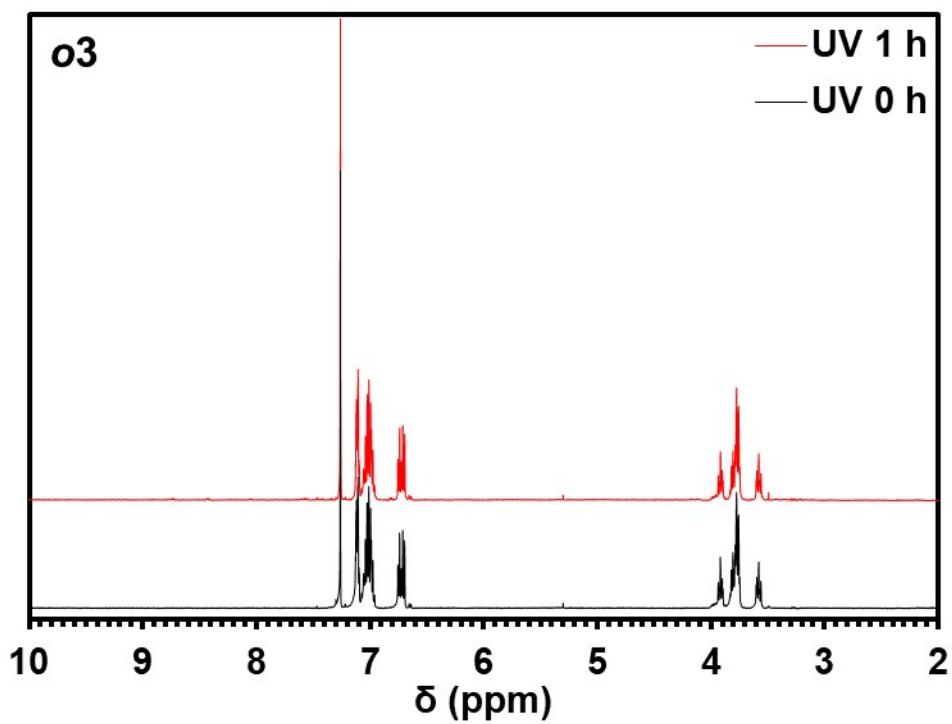


Fig. S42 ¹H NMR spectra of *o3* upon photoirradiation.

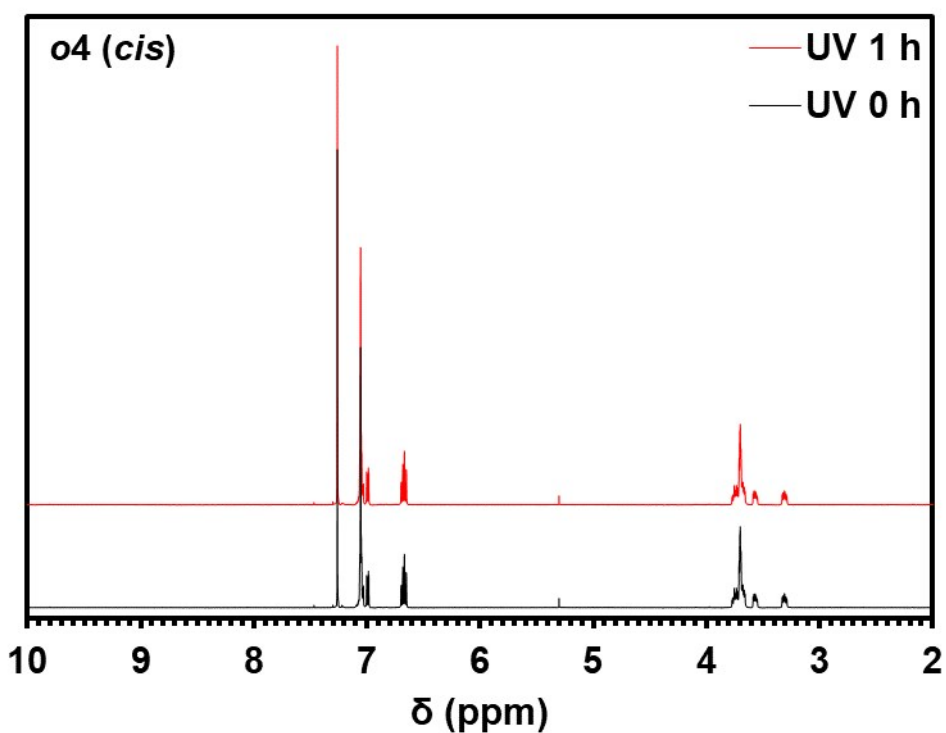


Fig. S43 ¹H NMR spectra of *o4 (cis)* upon photoirradiation.

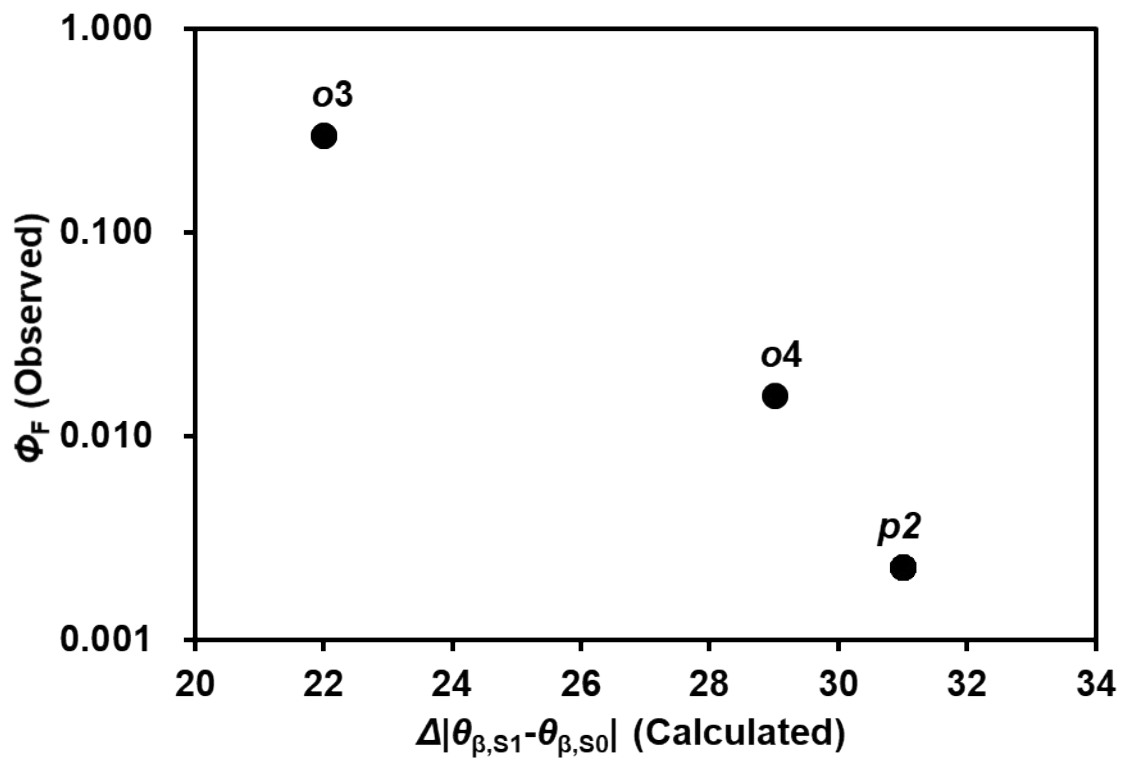
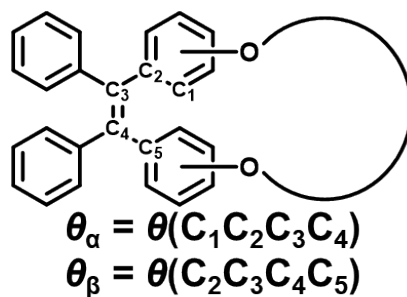


Figure S44. The relationship between $\Delta|\theta_{\beta,S1}-\theta_{\beta,S0}|$ (calculated) and Φ_F (observed).

Table S4. The calculated dihedral angle (θ_α) and bond lengths (C_3-C_4 and C_2-C_3) for TPE macrocycles at S_0 min and S_1 min at the B3LYP/6-31G(d) level.



Molecule	θ_{α,S_0} (°) ^a	θ_{α,S_1} (°) ^b	$\Delta \theta_{\alpha,S_1}-\theta_{\alpha,S_0} $ (°)	C_3-C_4 (Å)		C_2-C_3 (Å)	
				S_0 min	S_1 min	S_0 min	S_1 min
<i>p2</i>	59	34	25	1.369	1.473	1.499	1.458
<i>p3</i>	54	30	24	1.369	1.473	1.497	1.454
<i>p4</i>	47	16	31	1.368	1.477	1.492	1.443
<i>p5</i>	48	19	29	1.369	1.475	1.492	1.445
<i>p6</i>	46	16	30	1.369	1.475	1.493	1.443
<i>m2</i>	53	12	41	1.364	1.484	1.497	1.466
<i>m3</i>	46	3	43	1.366	1.488	1.496	1.457
<i>m4</i>	49	8	41	1.367	1.486	1.496	1.451
<i>m5</i>	53	10	43	1.365	1.489	1.496	1.450
<i>m6</i>	50	8	42	1.366	1.475	1.496	1.459
<i>o3 (cis)</i>	83	37	46	1.360	1.485	1.504	1.452
<i>o3 (trans)</i>	116	135	19	1.358	1.457	1.497	1.454
<i>o4 (cis)</i>	67	30	37	1.361	1.487	1.500	1.448
<i>o4 (trans)</i>	129	140	11	1.363	1.465	1.495	1.452

^a θ_α at S_0 min. ^b θ_α at S_1 min.

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2. *SHELXS-2013 and SHELXL-2013*: G. M. Sheldrick, Short History of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
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