Electronic Supplementary Information

Fluorescent supramolecular mechanophores based on charge-transfer interaction

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Materials

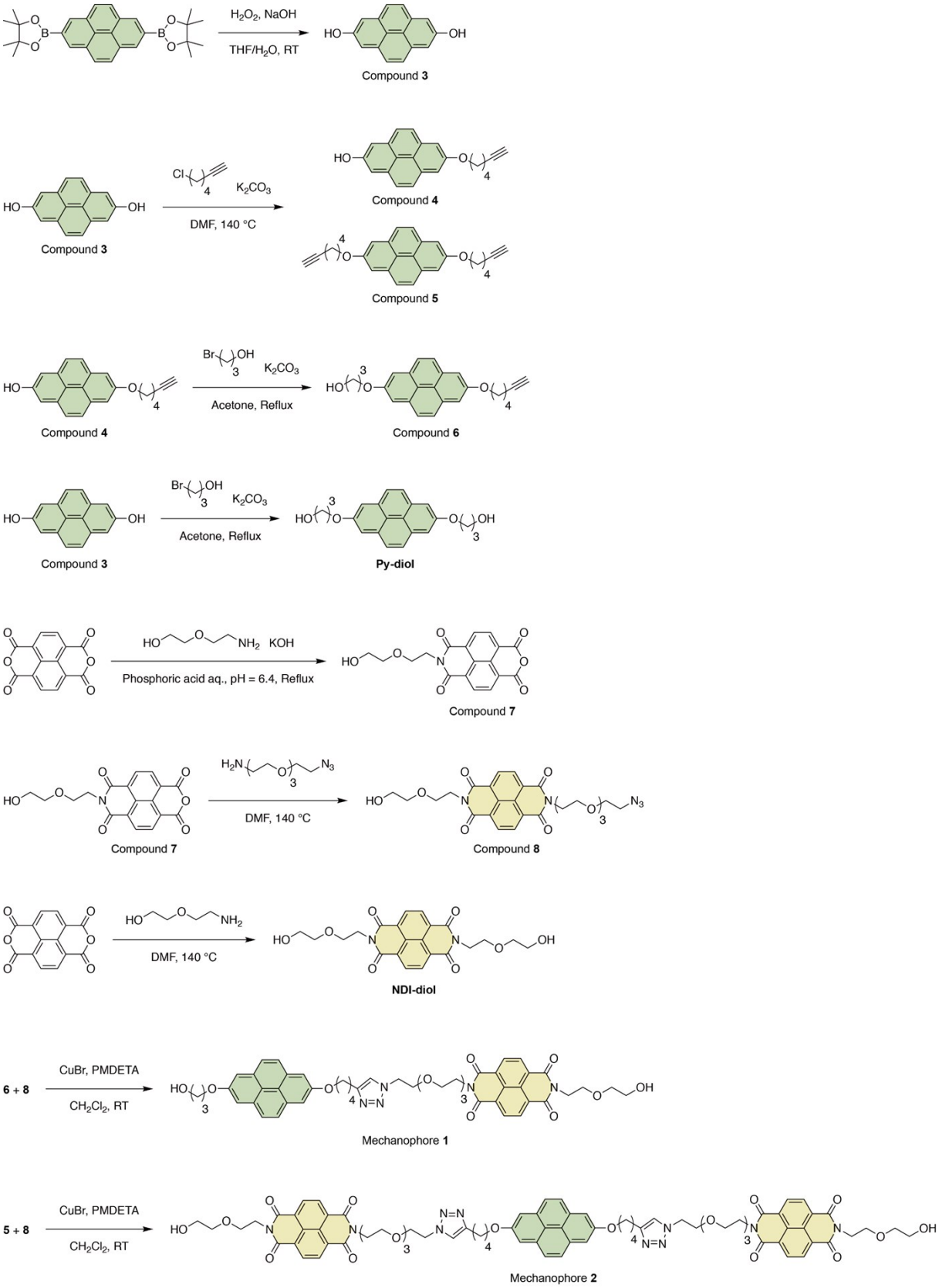
All solvents and reagents were purchased from FUJIFILM Wako Pure Chemical, Tokyo Chemical Industry, Sigma Aldrich, Kanto Chemical, or Nacalai Tesque and used as received, unless otherwise noted. ε-Caprolactone was distilled under reduced pressure.

Measurements

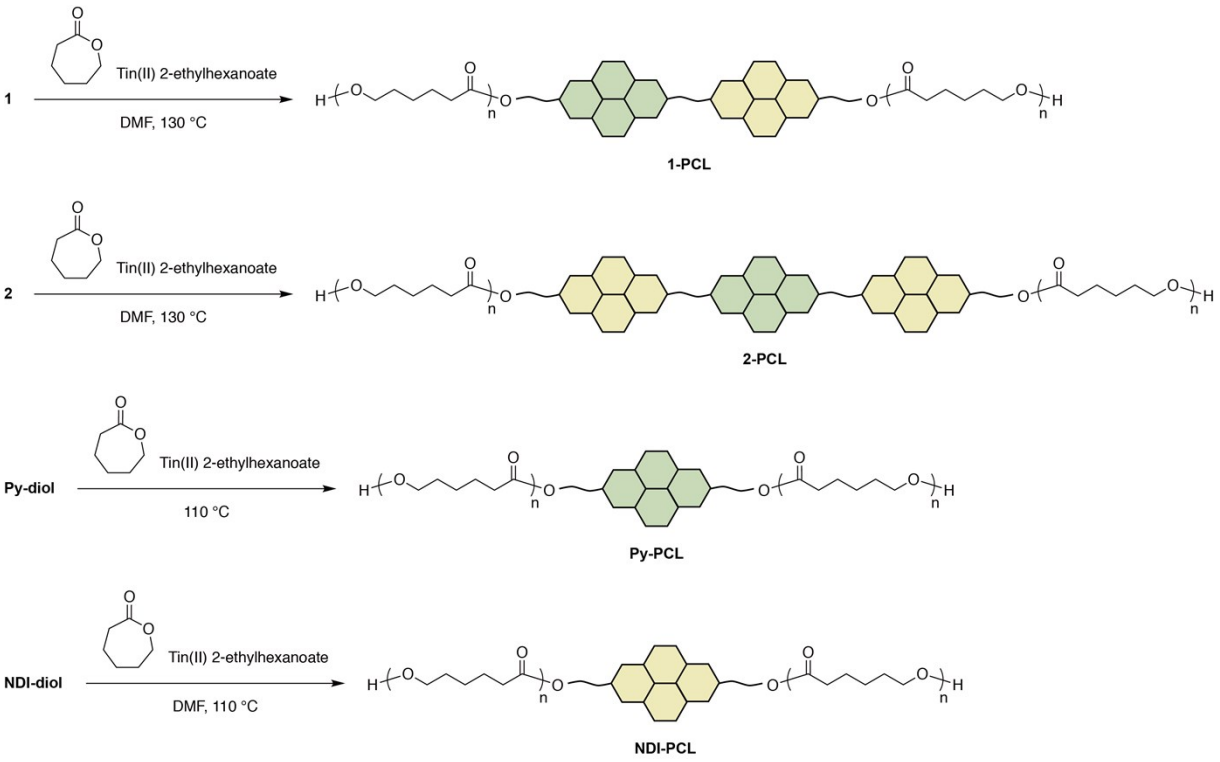
^{1}H NMR spectroscopic measurements were performed at 25 °C using a 400-MHz Varian spectrometer in $CDCl_3$ or dimethylsulfoxide (DMSO)-d_6 with tetramethylsilane as the internal standard. Low resolution mass spectral data were acquired using a Thermo Fisher Scientific LCQ Fleet ion trap mass spectrometer. Size exclusion chromatography (SEC) measurements were performed at 40 °C using a JASCO SEC system with a guard column (KF-G 4A, Shodex), two series-connected columns (KF-806L, Shodex), a UV detector, and a differential refractive index (RI) detector. Tetrahydrofuran (THF) was used as the eluent, and polystyrene standards were used to calibrate the SEC system. Number-average molecular weights (M_ns) and polydispersity indices (PDIs) for **Py-PCL** and **NDI-PCL** were determined from UV (254 nm) curves, and those for **1-PCL** and **2-PCL** were determined from RI curves. UV-vis absorption measurements were performed using a JASCO V-750 spectrometer. Fluorescence (FL) measurements were performed using a SHIMADZU RF-5300PC spectrofluorometer. UV light (365 nm, UVGL-58, UVP) for excitation were used to visualize the FL for photographs.

Syntheses

Mechanophore **1** and **2** were synthesized via the route shown in Scheme S1. Poly(ε-caprolactone)s (PCLs), **1-PCL**, **2-PCL**, **Py-PCL**, and **NDI-PCL**, were prepared via the ring-opening polymerization of ε-caprolactone initiated from hydroxyl groups, as shown in Scheme S2.



Scheme S1 Synthetic route for mechanophore **1** and **2**.



Scheme S2 Syntheses of PCLs, **1-PCL**, **2-PCL**, **Py-PCL**, and **NDI-PCL**.

Compound 3. A solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (5.00 g, 11.0 mmol), NaOH (2.65 g, 66.2 mmol), and H_2O_2 (ca. 30% aqueous solution, 6.68 mL) in THF (500 mL) was prepared and stirred at room temperature. After 4 h, 1 M HCl was added to the solution to adjust the pH to 1–2. Et_2O (500 mL) was added to the solution, and the organic layer was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated to be ca. 25 mL. The crude mixture was precipitated in hexane (400 mL). The precipitate was collected by filtration, dissolved in acetone (50 mL), and reprecipitated in hexane (500 mL). The precipitate was collected and dried in vacuo at 80 °C to give compound **3** as a dark brown solid (2.32 g, 91% yield). ^{1}H NMR (400 MHz, DMSO-d_6, Fig. S1): δ (ppm) = 9.89 (s, 2H, OH), 7.94 (s, 4H, aromatic), 7.60 (s, 4H, aromatic).

Compound 4 and 5. A solution of **3** (2.28 g, 9.72 mmol), K_2CO_3 (1.34 g, 9.71 mmol), and 6-chloro-1-hexyne (1.20 mL, 9.88 mmol) in anhydrous *N*,*N*-dimethylformamide (DMF, 90 mL) was prepared under N_2 atmosphere and stirred at 140 °C. Another 0.93 mL of 6-chloro-1-hexyne (7.69 mmol) was dropped into the solution during the reaction. After the reaction for 24 h, the solution was cooled to room temperature and filtered using acetone, and the filtrate was concentrated to be ca. 30 mL. The crude mixture was precipitated in hexane (500 mL). The precipitate was collected, washed with H_2O, and dried in vacuo at 60 °C. Finally, the crude product was purified by column chromatography (silica, CH_2Cl_2/hexane = 19/1) to give compound **4** as a white solid (0.399 g, 13% yield) and **5** as a yellow solid (1.52 g, 40% yield). **Compound 4.** ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S2): δ (ppm) = 7.96 (d, J = 9.2 Hz, 2H, aromatic), 7.92 (d, J = 9.6 Hz, 2H, aromatic), 7.69 (s, 2H, aromatic), 7.61 (s, 2H, aromatic), 5.13 (s, 1H, OH), 4.29 (t, J = 6.0 Hz, 2H, CH_2), 2.33–2.36 (m, 2H, CH_2), 2.03–2.10 (m, 2H, CH_2), 2.00 (s, 1H, CH), 1.80–1.88 (m, 2H, CH_2). **Compound 5.** ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S3): δ (ppm) = 7.95 (s, 4H, aromatic), 7.68 (s, 4H, aromatic), 4.28 (t, J = 6.2 Hz, 4H, CH_2), 2.35 (td, J = 7.0, 3.0 Hz, 4H, CH_2), 2.03–2.10 (m, 4H, CH_2), 2.00 (t, J = 2.4 Hz, 2H, CH), 1.81–1.88 (m, 4H, CH_2).

Compound 6. A solution of **4** (238 mg, 0.758 mmol), K_2CO_3 (105 mg, 0.759 mmol), and 3-bromo-1-propanol (0.07 mL, 0.774 mmol) in anhydrous acetone (7 mL) was prepared under N_2 atmosphere and refluxed at 50 °C with stirring. Another 0.28 mL of 3-bromo-1-propanol (3.23 mmol) was dropped into the solution during the reaction. After the reaction for 168 h, the solution was cooled to room temperature, and CH_2Cl_2 (50 mL) was added to the solution. The crude mixture was washed

with H_2O (50 mL) three times, dried over anhydrous $MgSO_4$, filtered, and dried in vacuo at 95 °C to give compound **6** as a yellow solid (240 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S4): δ (ppm) = 7.95 (s, 4H, aromatic), 7.70 (s, 2H, aromatic), 7.69 (s, 2H, aromatic), 4.43 (t, J = 6.0 Hz, 2H, CH_2), 4.24–4.32 (m, 3H, CH_2, OH), 3.98 (q, J = 5.6 Hz, 2H, CH_2), 2.35 (td, J = 7.0, 2.7 Hz, 2H, CH_2), 2.20 (quint, J = 5.9, 2H, CH_2), 2.03–2.10 (m, 2H, CH_2), 2.00 (t, J = 2.6 Hz, 1H, CH), 1.80–1.88 (m, 2H, CH_2).

Compound 7. Naphthalene-1,4,5,8-tetracarboxylic dianhydride (4.33 g, 16.2 mmol) was dissolved in H_2O (590 mL) and stirred at room temperature. KOH (4.50 g, 80.2 mmol) and 2-(2-aminoethoxy)ethanol (1.65 mL, 16.6 mmol) were added to the solution, and then, pH of the solution was adjusted to 6.36 using a diluted aqueous solution of phosphoric acid. The solution was stirred at 100 °C. After 36 h, the solution was cooled to room temperature, and pH of the solution was adjusted to 4.05 using acetic acid. The crude mixture was concentrated be ca. 300 mL and cooled to 4 °C. The precipitate was filtered and dried in vacuo at 85 °C to give compound **7** as a yellow solid (4.02 g, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6, Fig. S5): δ (ppm) = 8.47 (d, J = 7.6 Hz, 2H, aromatic), 7.94 (d, J = 7.6 Hz, 2H, aromatic), 4.24 (t, J = 6.4 Hz, 2H, CH_2), 3.00–4.20 (br, 6H, CH_2).

Compound 8. A solution of **7** (3.00 g, 8.44 mmol) and 11-azido-3,6,9-trioxaundecan-1-amine (0.67 mL, 3.38 mmol) in anhydrous DMF (155 mL) was prepared under N_2 atmosphere and stirred at 140 °C. After 16 h, the solution was cooled to room temperature, concentrated, and dried in vacuo at 80 °C. The crude mixture was dispersed in $CHCl_3$ (240 mL) and sonicated. After filtration, the filtrate was concentrated and dried in vacuo at 100 °C to give compound **8** as a black solid (1.41 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S6): δ (ppm) = 8.77 (d, J = 1.2 Hz, 4H, aromatic), 4.48 (q, J = 5.6 Hz, 4H, CH_2), 3.84–3.90 (m, 4H, CH_2), 3.50–3.72 (m, 14H, CH_2), 3.36 (t, J = 5.0 Hz, 2H, CH_2).

Mechanophore 1. A solution of **6** (114 mg, 0.306 mmol), **8** (168 mg, 0.303 mmol), CuBr (44.6 mg, 0.311 mmol), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 0.07 mL, 0.335 mmol) in anhydrous CH_2Cl_2 (23 mL) was prepared under N_2 atmosphere and stirred at room temperature. After 21 h, the solution was concentrated, and the crude product was purified by column chromatography (silica, CH_3CN/H_2O = 3/2) to give mechanophore **1** as a purple solid (250 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S7 and S8): δ (ppm) = 7.30–8.71 (m, 12H, charge-transfer (CT)

and non-CT pyrene (Py) and naphthalene diimide (NDI)), 3.41–4.55 (m, 30H, CH_2), 2.83–3.05 (m, 4H, CH_2, OH), 2.00–2.25 (m, 6H, CH_2). LRMS (ESI): 950.333 $[M+H]^+$, calculated for $C_{54}H_{56}N_5O_{11}$ $[M+H]^+$: 950.398.

Mechanophore 2. A solution of **5** (171 mg, 0.435 mmol), **8** (490 mg, 0.883 mmol), CuBr (62.7 mg, 0.437 mmol), and PMDETA (0.09 mL, 0.431 mmol) in anhydrous CH_2Cl_2 (46 mL) was prepared under N_2 atmosphere and stirred at room temperature. After 20 h, the solution was concentrated, and the crude product was purified by column chromatography (silica, CH_3CN/H_2O = 3/2) to give mechanophore **2** as a purple solid (605 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S9 and S10): δ (ppm) = 7.17–8.75 (m, 16H, CT and non-CT Py and NDI), 3.50–4.56 (m, 52H, CH_2), 2.65–3.04 (m, 6H, CH_2, OH), 1.98–2.23 (m, 8H, CH_2). LRMS (ESI): 1527.500 $[M+Na]^+$, calculated for $C_{80}H_{84}N_{10}O_{20}Na$ $[M+Na]^+$: 1527.576.

Py-diol. A solution of **3** (500 mg, 2.13 mmol), K_2CO_3 (210 mg, 1.50 mmol), and 3-bromo-1-propanol (0.75 mL, 8.53 mmol) in anhydrous acetone (150 mL) was prepared under N_2 atmosphere and refluxed at 50 °C with stirring. After 72 h, the solution was cooled to room temperature and concentrated. The crude mixture was dissolved in H_2O (100 mL), EtOAc (500 mL) was added to the solution, and the organic layer was washed with H_2O (100 mL) twice, collected, dried over anhydrous $MgSO_4$, filtered, concentrated, and dried in vacuo at 95 °C to give **Py-diol** as a brown solid (490 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S11): δ (ppm) = 7.96 (s, 4H, aromatic), 7.70 (d, J = 2.8 Hz, 4H, aromatic), 4.43 (t, J = 5.8 Hz, 4H, CH_2), 3.99 (q, J = 5.3 Hz, 4H, CH_2), 2.20 (quint, J = 5.8 Hz, 4H, CH_2), 1.82–1.89 (m, 2H, OH).

NDI-diol. A solution of naphthalene-1,4,5,8-tetracarboxylic dianhydride (3.00 g, 11.2 mmol) and 2-(2-aminoethoxy)ethanol (1.85 mL, 18.6 mmol) in anhydrous DMF (150 mL) was prepared under N_2 atmosphere and stirred at 140 °C. After 12 h, the solution was cooled to 4 °C. The precipitate was collected by filtration and dried in vacuo at 90 °C to give **NDI-diol** as a pink solid (2.62 g, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S12): δ (ppm) = 8.78 (s, 4H, aromatic), 4.46 (t, J = 5.6 Hz, 4H, CH_2), 3.89 (t, J = 5.6 Hz, 4H, CH_2), 3.65–3.72 (m, 8H, CH_2), 2.22 (t, J = 5.6 Hz, 2H, OH).

1-PCL. A solution of mechanophore **1** (21 mg, 22.9 μmol), ε-caprolactone (4.6 mL, 41.5 mmol), and tin(Ⅱ) 2-ethylhexanoate (1 drop) in anhydrous DMF (2 mL) was prepared under N_2

atmosphere, degassed by three freeze-pump-thaw cycles, filled with N_2, and stirred at 130 °C. After 71 h, the solution was cooled to room temperature, diluted with $CHCl_3$ to be ca. 20 mL, and precipitated in MeOH (400 mL). The precipitate was collected, dissolved in $CHCl_3$ (20 mL), and reprecipitated in hexane (400 mL). The precipitate was collected and dried in vacuo at room temperature to give **1-PCL** as a pink solid (3.99 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S13): δ (ppm) = 4.06 (t, J = 6.8 Hz, 2H, CH_2), 2.31 (t, J = 7.6 Hz, 2H, CH_2), 1.61–1.69 (m, 4H, CH_2), 1.35–1.42 (m, 2H, CH_2). M_n = 65100 g mol^{-1}, PDI = 1.85.

2-PCL. A solution of mechanophore **2** (36 mg, 23.6 μmol), ε-caprolactone (4.7 mL, 42.4 mmol), and tin(Ⅱ) 2-ethylhexanoate (1 drop) in anhydrous DMF (2 mL) was prepared under N_2 atmosphere, degassed by three freeze-pump-thaw cycles, filled with N_2, and stirred at 130 °C. After 19 h, the solution was cooled to room temperature, diluted with $CHCl_3$ to be ca. 20 mL, and precipitated in MeOH (400 mL). The precipitate was collected, dissolved in $CHCl_3$ (20 mL), and reprecipitated in hexane (400 mL). The precipitate was collected and dried in vacuo at room temperature to give **2-PCL** as a pink solid (3.92 g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S14): δ (ppm) = 4.06 (t, J = 6.8 Hz, 2H, CH_2), 2.31 (t, J = 7.4 Hz, 2H, CH_2), 1.60–1.69 (m, 4H, CH_2), 1.34–1.42 (m, 2H, CH_2). M_n = 73900 g mol^{-1}, PDI = 1.61.

Py-PCL. A solution of **Py-diol** (20 mg, 57.1 μmol), ε-caprolactone (11.6 mL, 105 mmol), and tin(Ⅱ) 2-ethylhexanoate (1 drop) was prepared under N_2 atmosphere, bubbled with N_2 for 30 min, and stirred at 110 °C. After 4.5 h, the solution was cooled to room temperature, diluted with a small volume of THF, and precipitated in MeOH. The precipitate was collected, dissolved in a small volume of THF, and reprecipitated in hexane. The precipitate was collected and dried in vacuo at room temperature to give **Py-PCL** as a light brown solid (1.90 g, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S15): δ (ppm) = 4.06 (t, J = 6.6 Hz, 2H, CH_2), 2.31 (t, J = 7.6 Hz, 2H, CH_2), 1.61–1.69 (m, 4H, CH_2), 1.34–1.42 (m, 2H, CH_2). M_n = 49000 g mol^{-1}, PDI = 1.22.

NDI-PCL. A solution of **NDI-diol** (30 mg, 67.8 μmol), ε-caprolactone (6.26 mL, 56.5 mmol), and tin(Ⅱ) 2-ethylhexanoate (1 drop) in anhydrous DMF (6 mL) was prepared under N_2 atmosphere, bubbled with N_2 for 30 min, and stirred at 110 °C. After 90 h, the solution was cooled to

room temperature, diluted with a small volume of THF, and precipitated in MeOH. The precipitate was collected, dissolved in a small volume of THF, and reprecipitated in hexane. The precipitate was collected and dried in vacuo at room temperature to give **Py-PCL** as a white solid (5.73 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. S16): δ (ppm) = 4.06 (t, J = 6.4 Hz, 2H, CH_2), 2.31 (t, J = 7.2 Hz, 2H, CH_2), 1.53–1.69 (m, 4H, CH_2), 1.34–1.42 (m, 2H, CH_2). M_n = 34800 g mol^{-1}, PDI = 1.71.

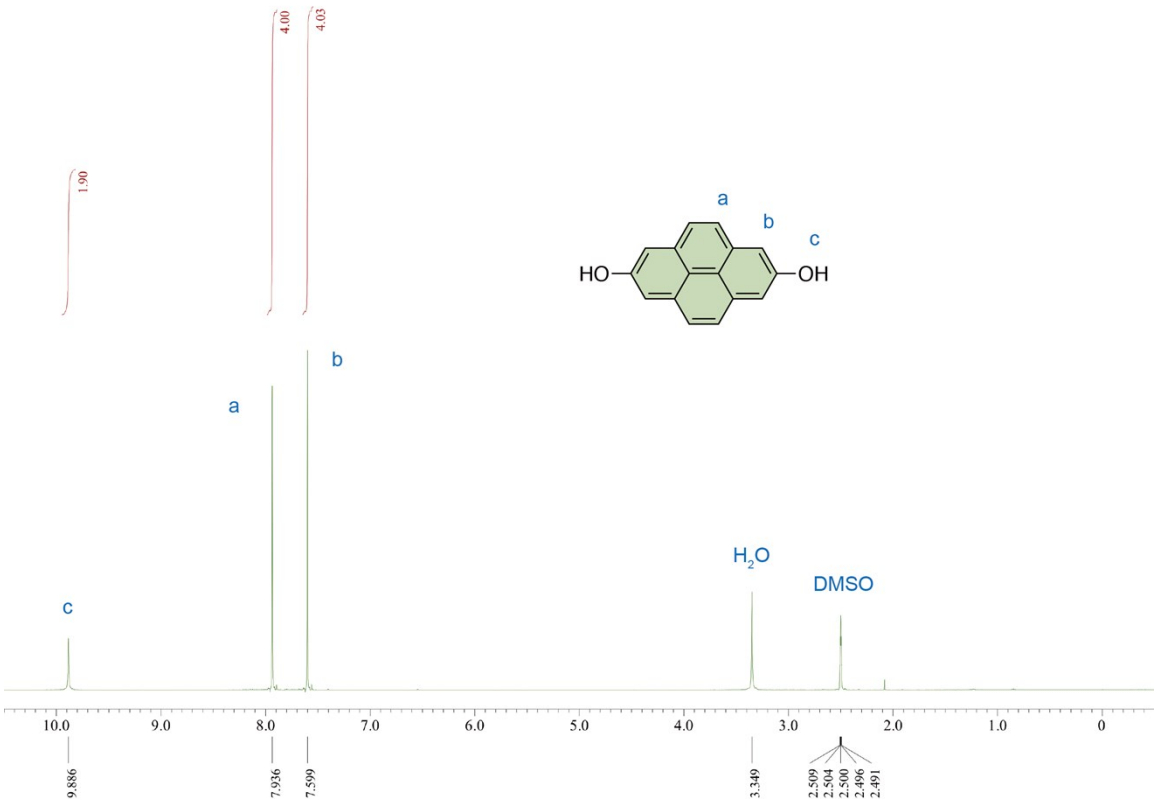


Fig. S1 [1]H NMR spectrum of compound **3** (400 MHz, DMSO-d_6).

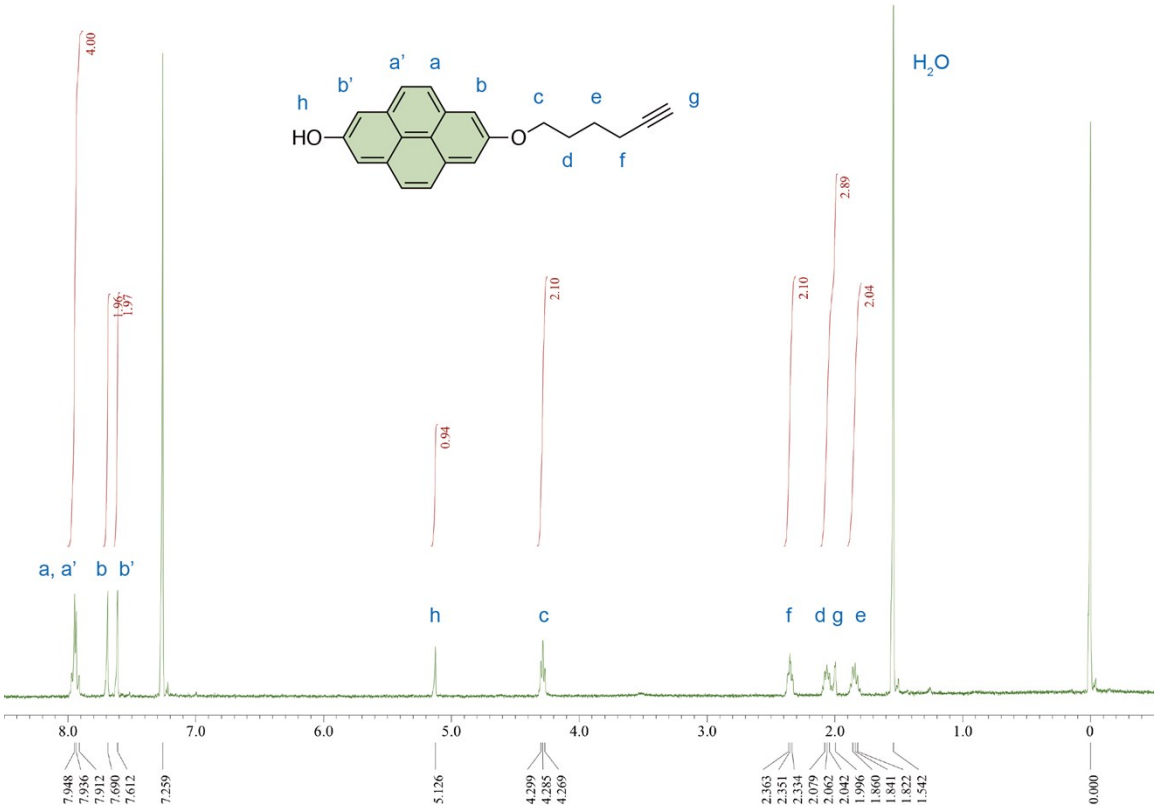


Fig. S2 [1]H NMR spectrum of compound **4** (400 MHz, $CDCl_3$).

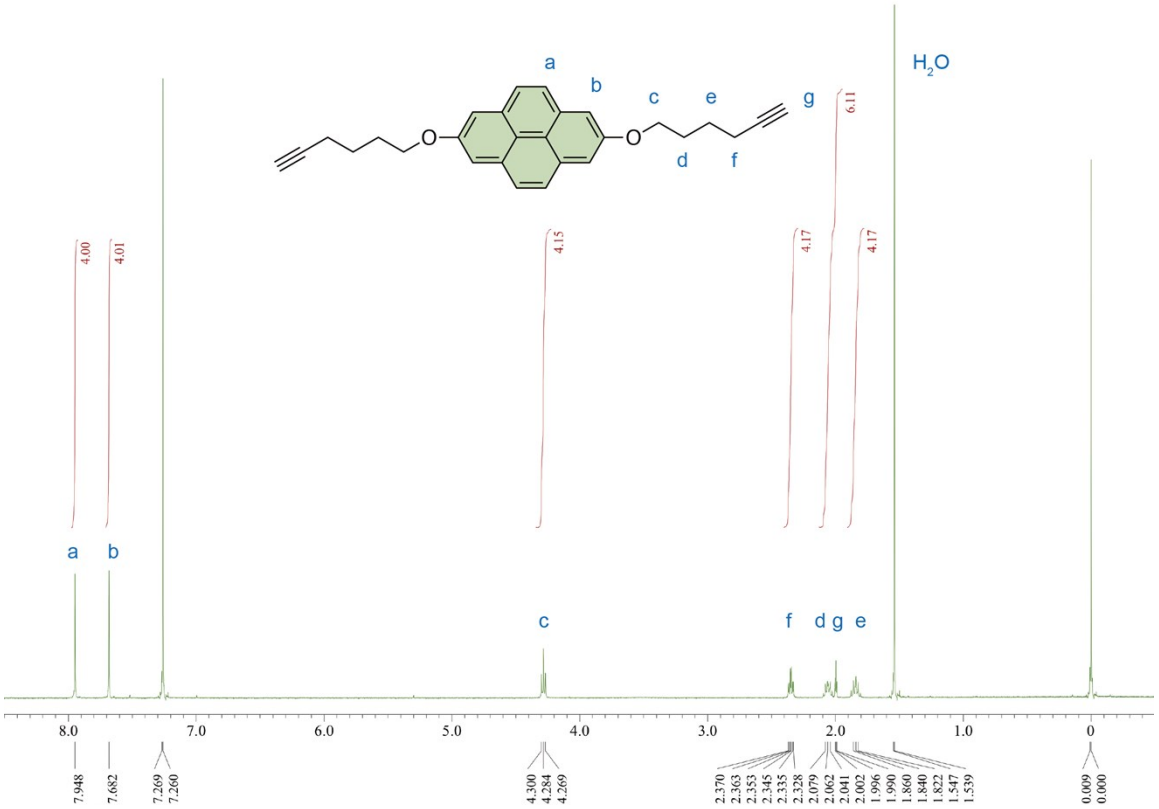


Fig. S3 ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

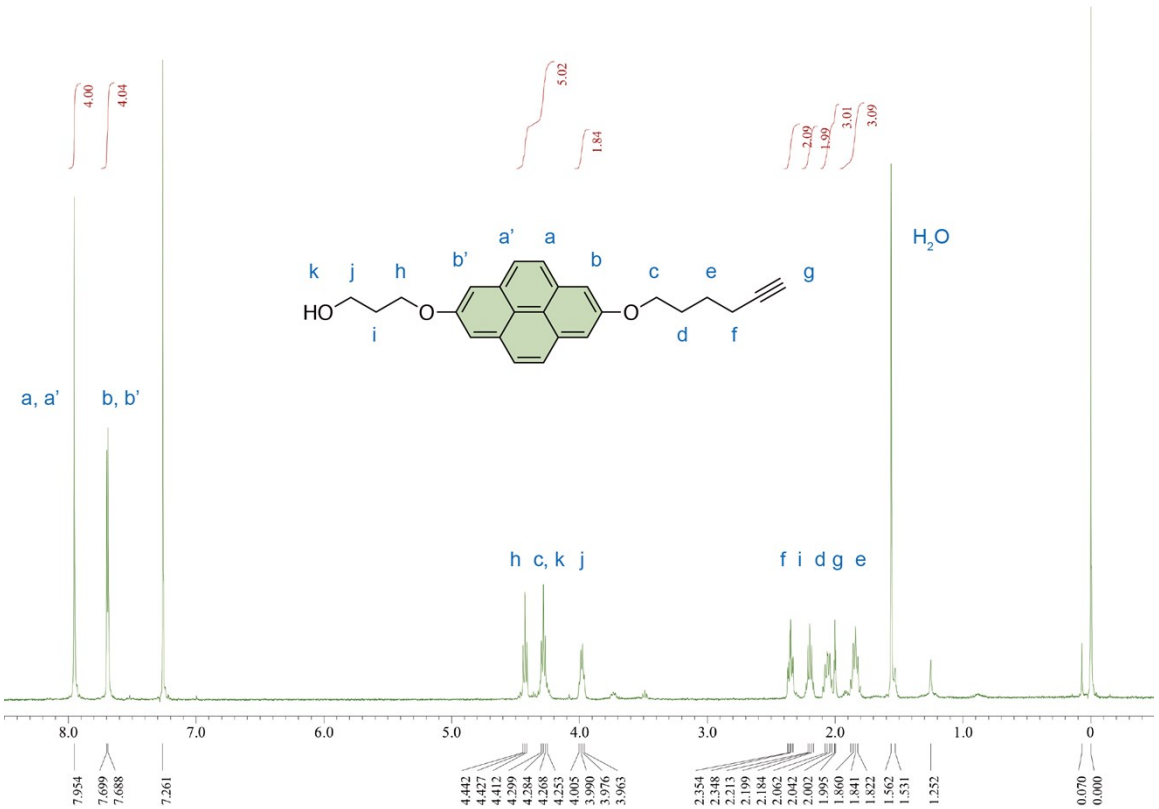


Fig. S4 ^{1}H NMR spectrum of compound **6** (400 MHz, $CDCl_3$).

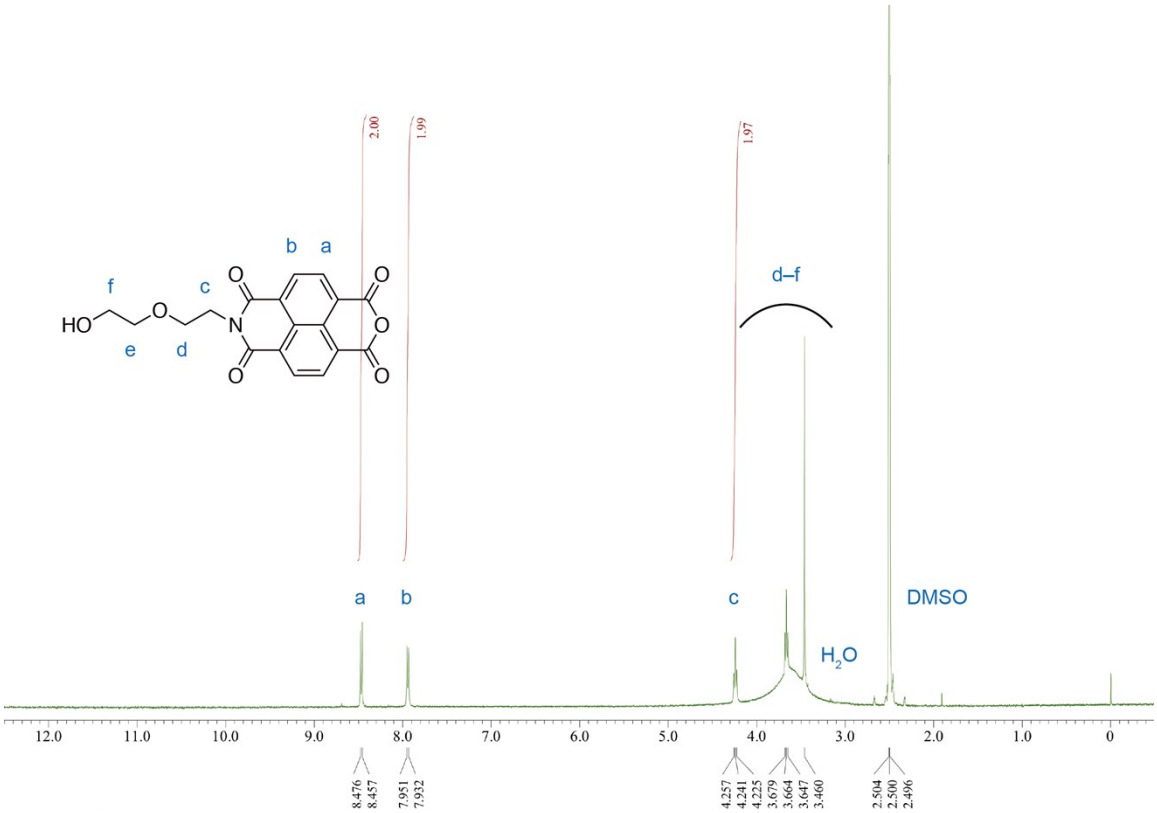


Fig. S5 ^{1}H NMR spectrum of compound **7** (400 MHz, DMSO-d_6).

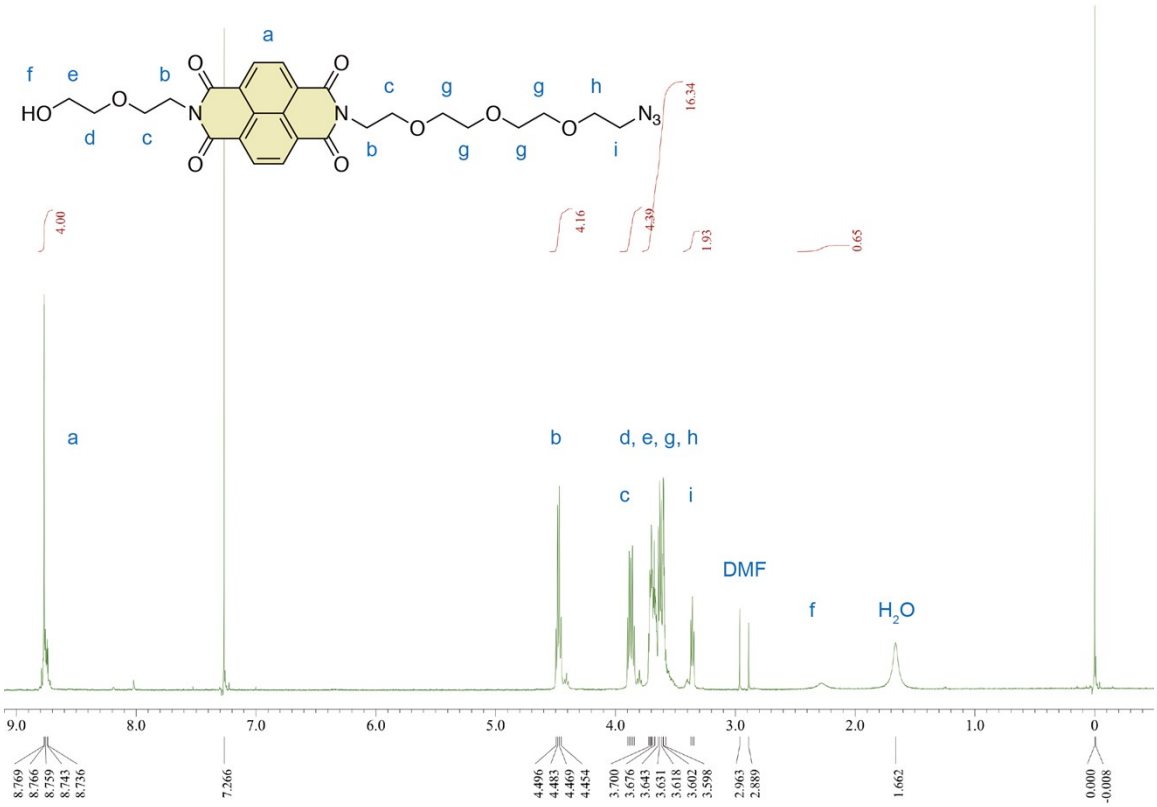


Fig. S6 ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$).

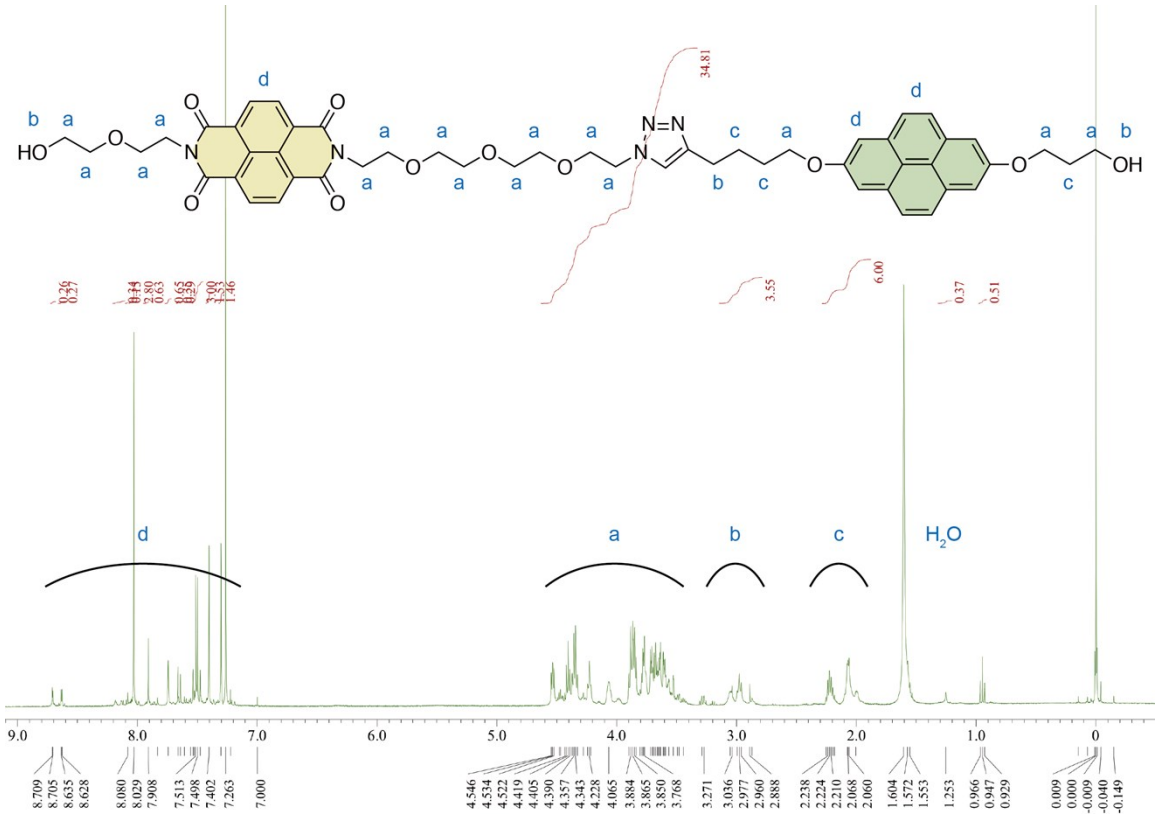


Fig. S7 ^{1}H NMR spectrum of mechanophore **1** (400 MHz, $CDCl_3$).

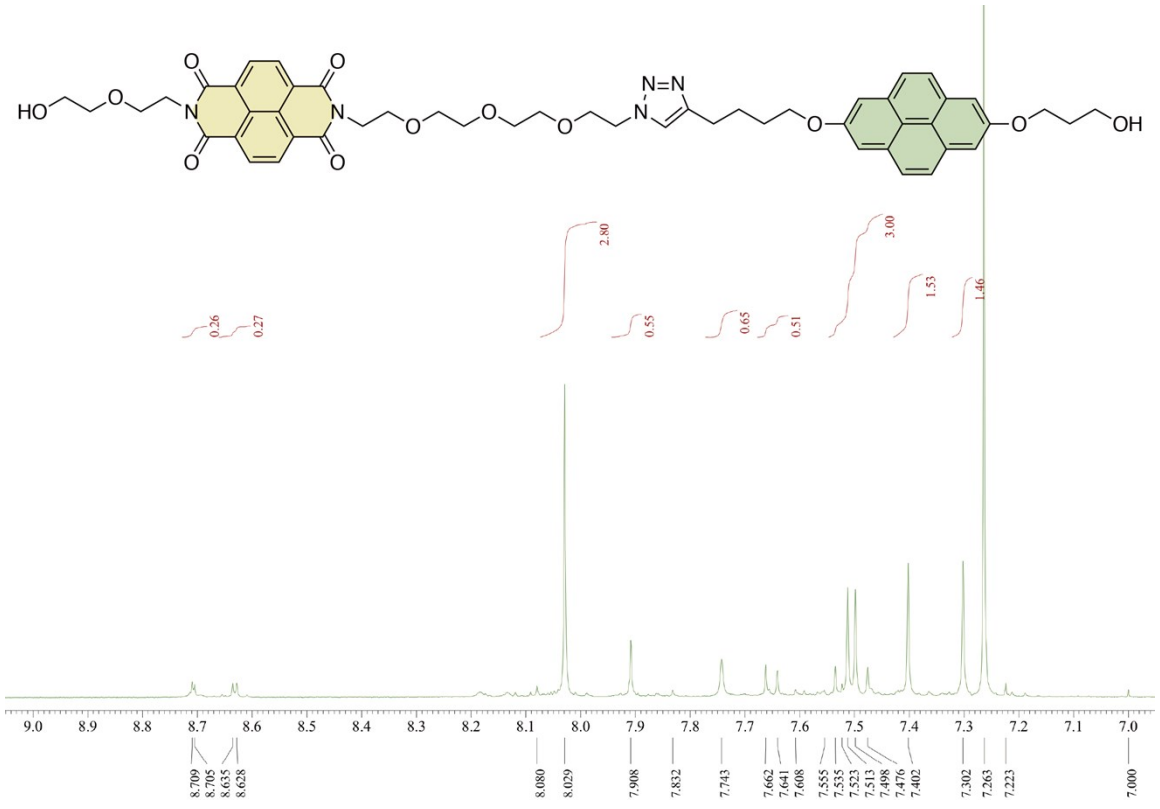


Fig. S8 Magnification of ^{1}H NMR spectrum of mechanophore **1** (400 MHz, $CDCl_3$).

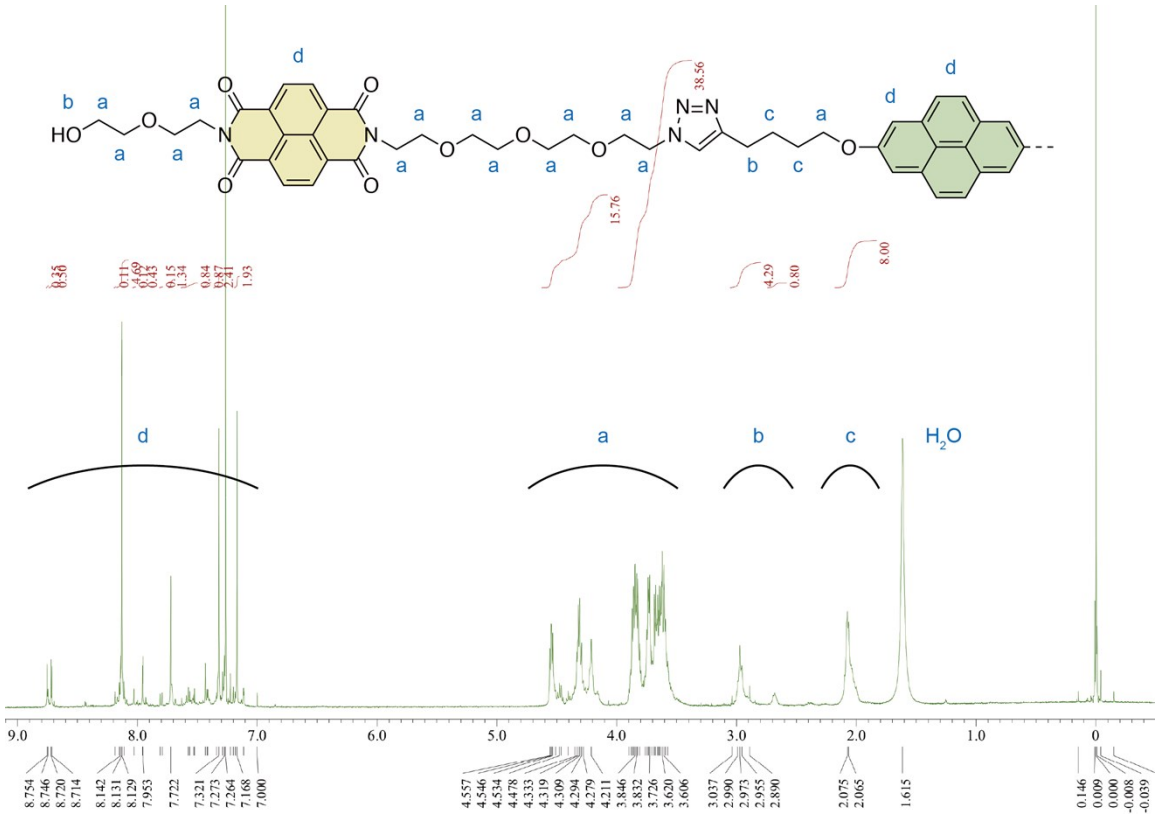


Fig. S9 [1]H NMR spectrum of mechanophore **2** (400 MHz, $CDCl_3$).

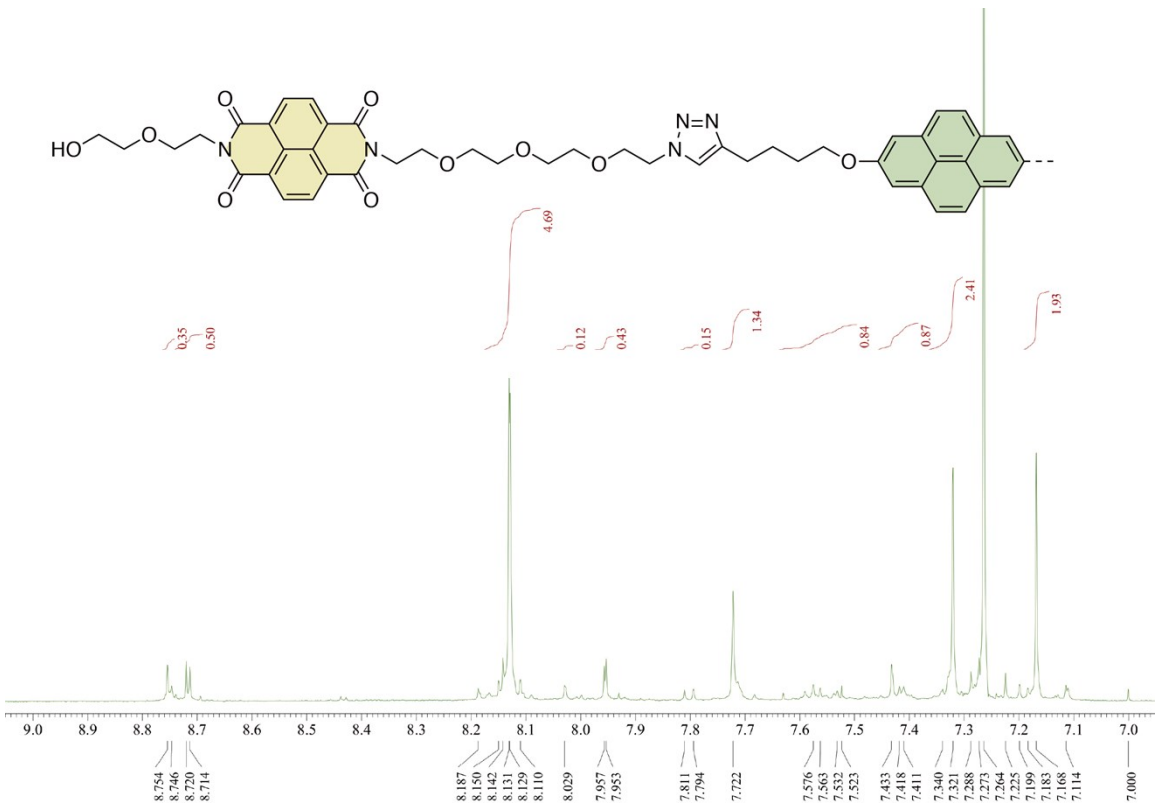


Fig. S10 Magnification of [1]H NMR spectrum of mechanophore **2** (400 MHz, $CDCl_3$).

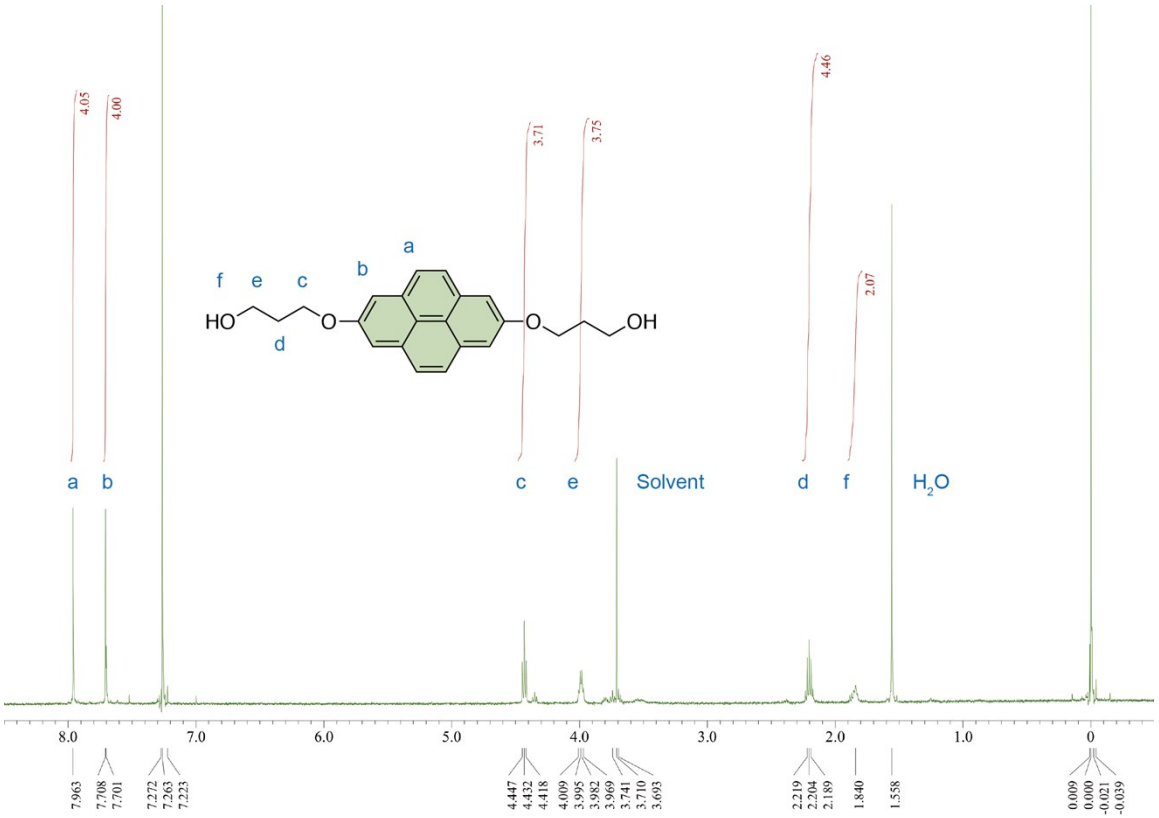


Fig. S11 ^{1}H NMR spectrum of **Py-diol** (400 MHz, $CDCl_3$).

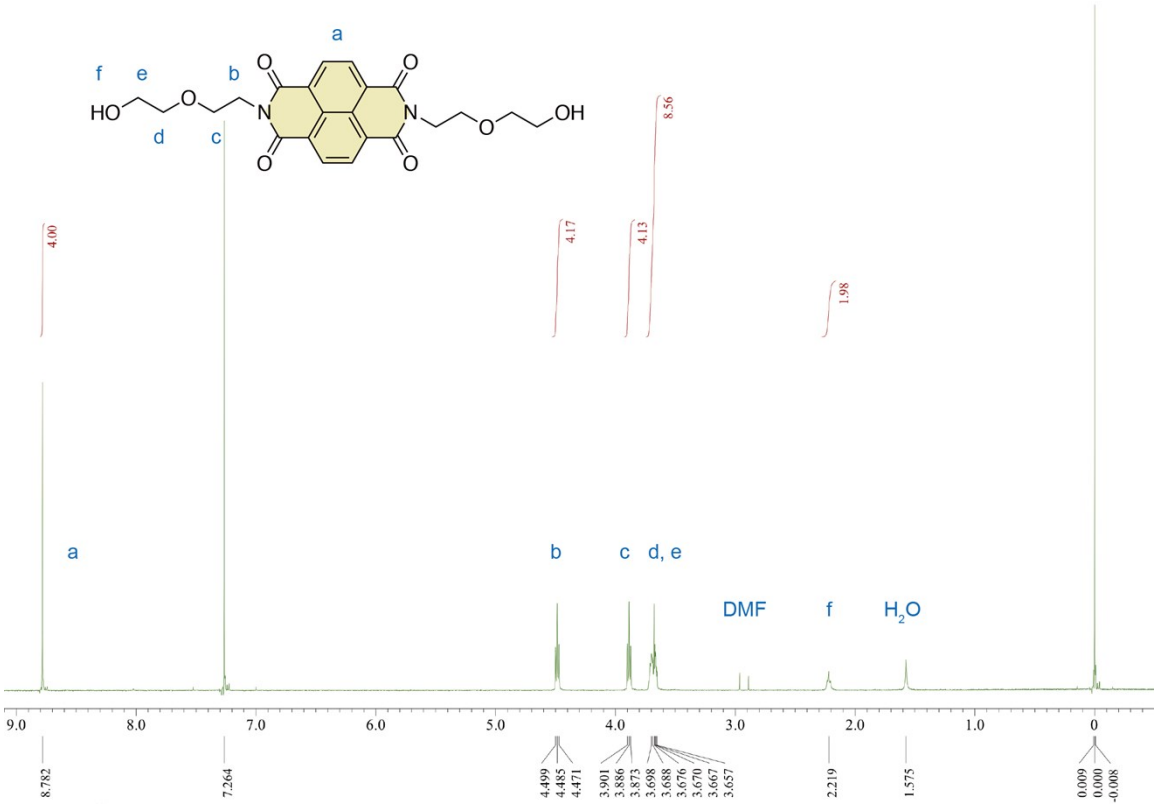


Fig. S12 ^{1}H NMR spectrum of **NDI-diol** (400 MHz, $CDCl_3$).

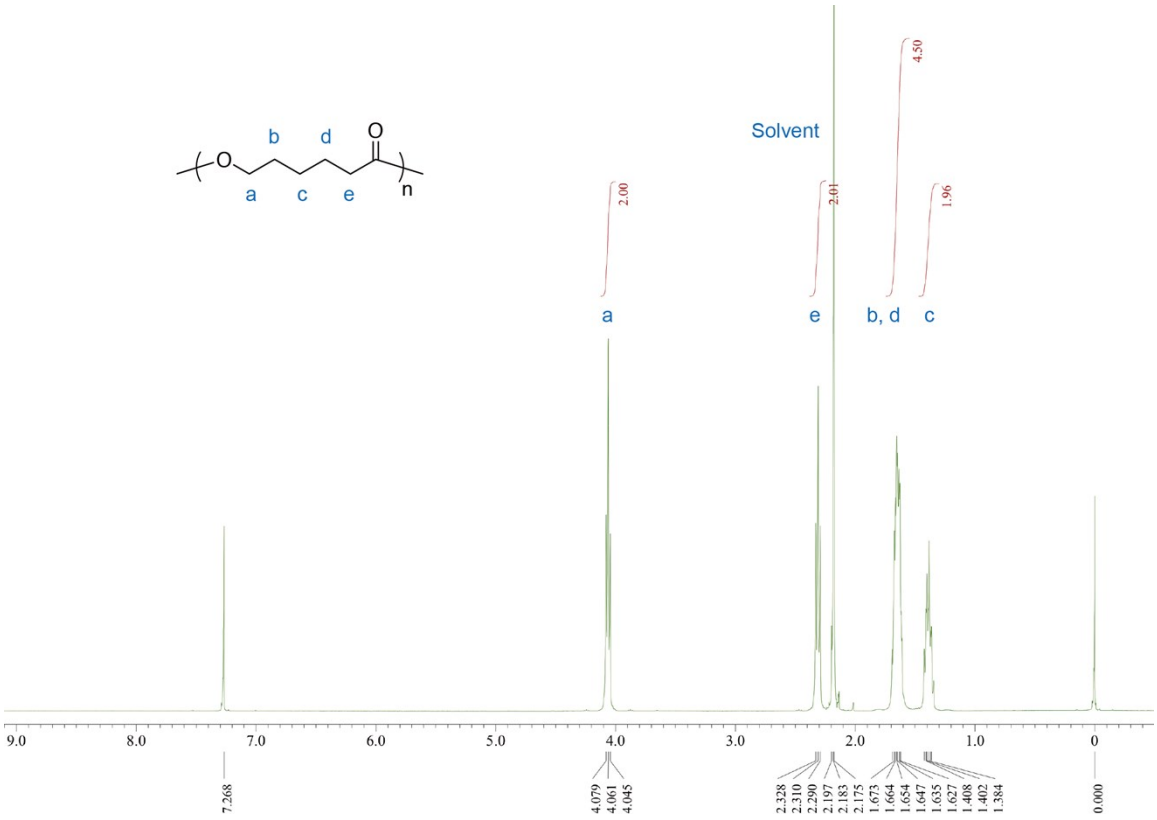


Fig. S13 ^{1}H NMR spectrum of **1-PCL** (400 MHz, $CDCl_3$).

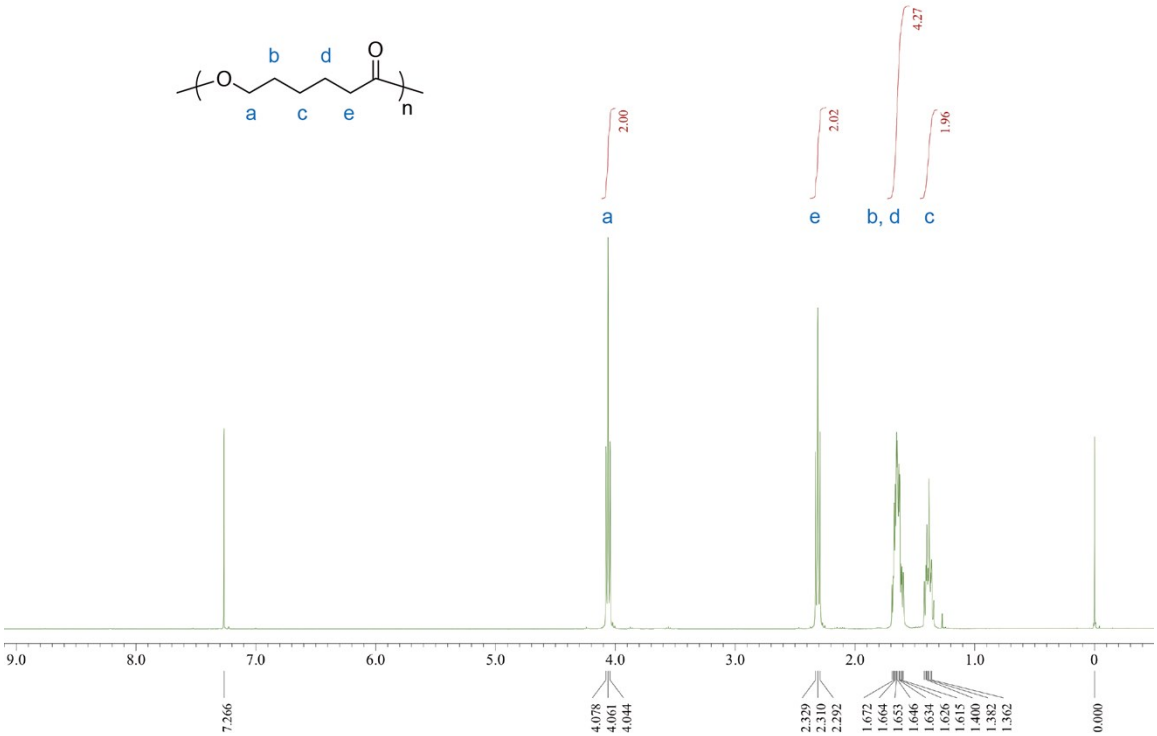


Fig. S14 ^{1}H NMR spectrum of compound **2-PCL** (400 MHz, $CDCl_3$).

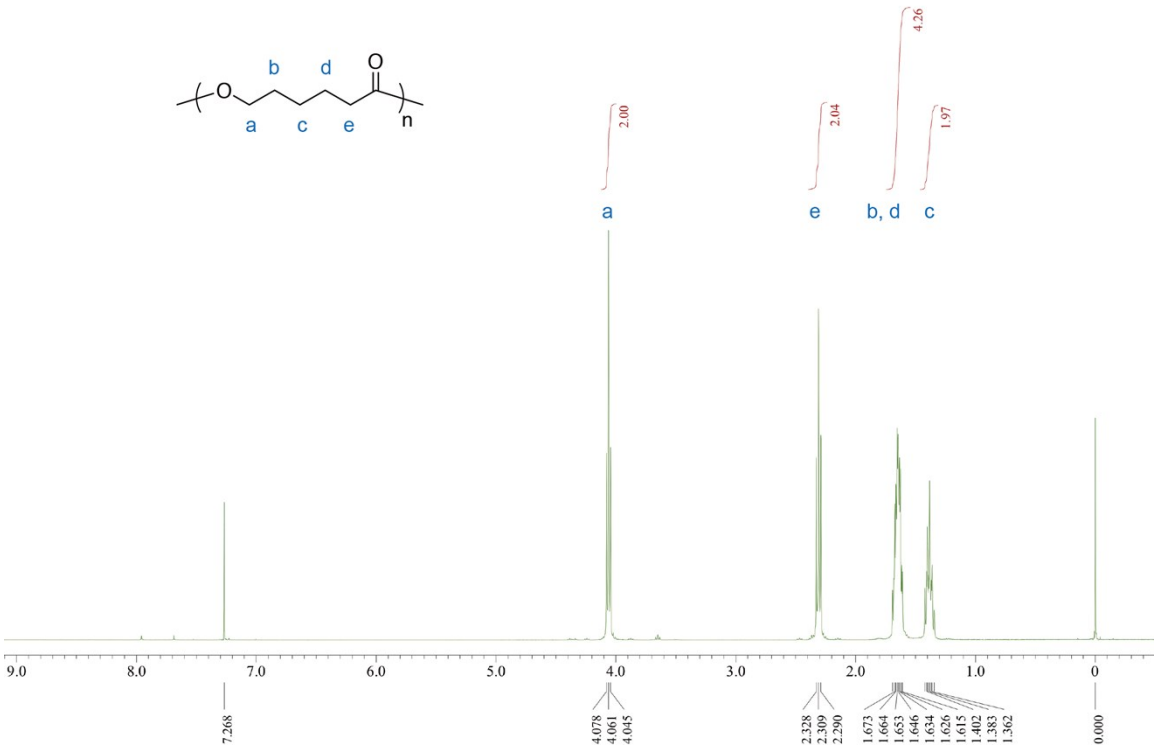


Fig. S15 ^{1}H NMR spectrum of compound **Py-PCL** (400 MHz, $CDCl_3$).

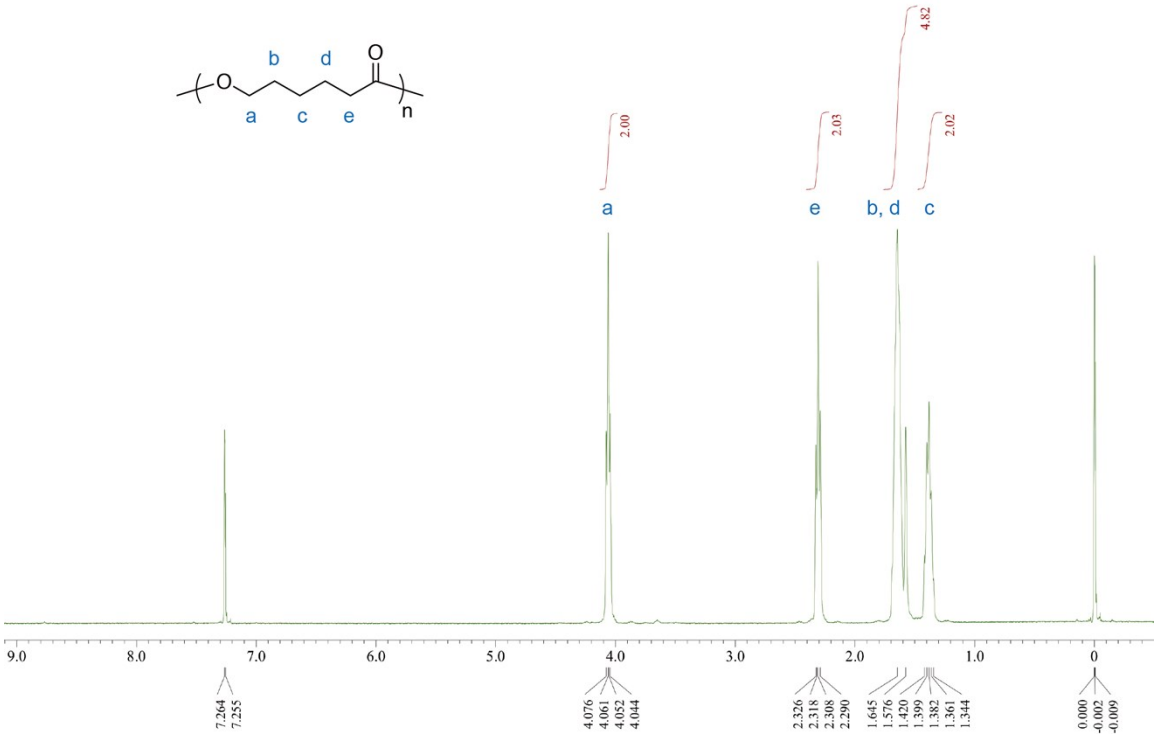


Fig. S16 ^{1}H NMR spectrum of **NDI-PCL** (400 MHz, $CDCl_3$).

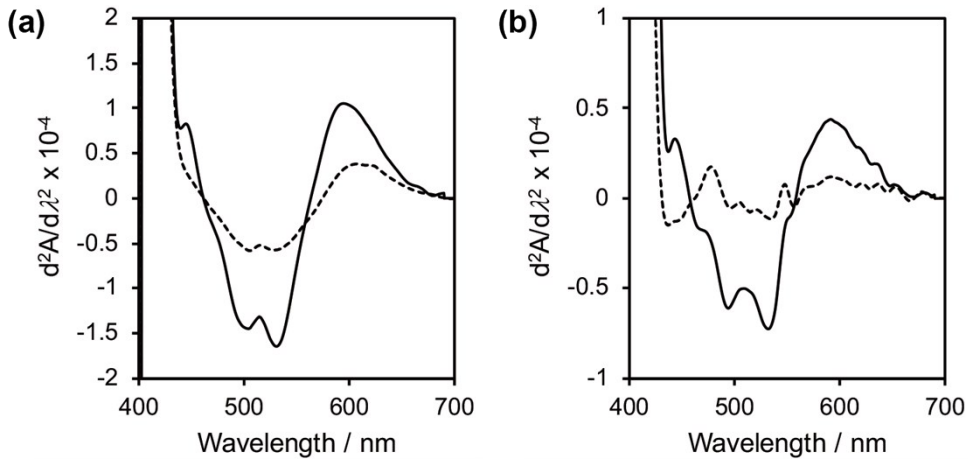


Fig. S17 Second-order derivative photoabsorption spectra of (a) **1** (dashed line), **2** (solid line), (b) **1-PCL** (dashed line), and **2-PCL** (solid line) in $CHCl_3$ (5.0×10^{-4} M).

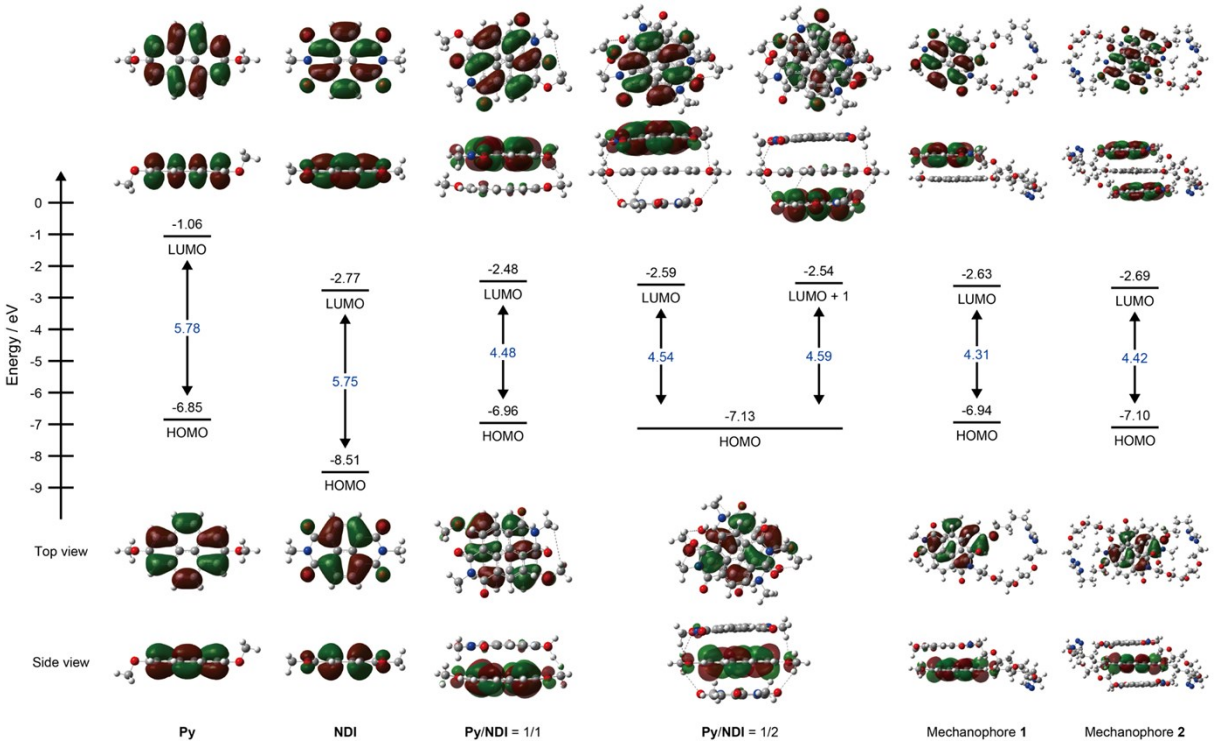


Fig. S18 Molecular orbital energy diagram of Py, NDI, their mixtures, and mechanophores by DFT calculations at the M06-2X/6-311G(d,p) level. The end groups of all molecules are displaced by methyl groups. It is apparent that the HOMOs of the complexes are located on the Py moieties, while the LUMOs are located on the NDI moieties. The HOMO-LUMO excitations of the complexes occur from the HOMOs of the Py moieties to the LUMOs of the NDI moieties, which are consistent with the photoabsorption in the long wavelength region shown in Fig. 2 and 3.

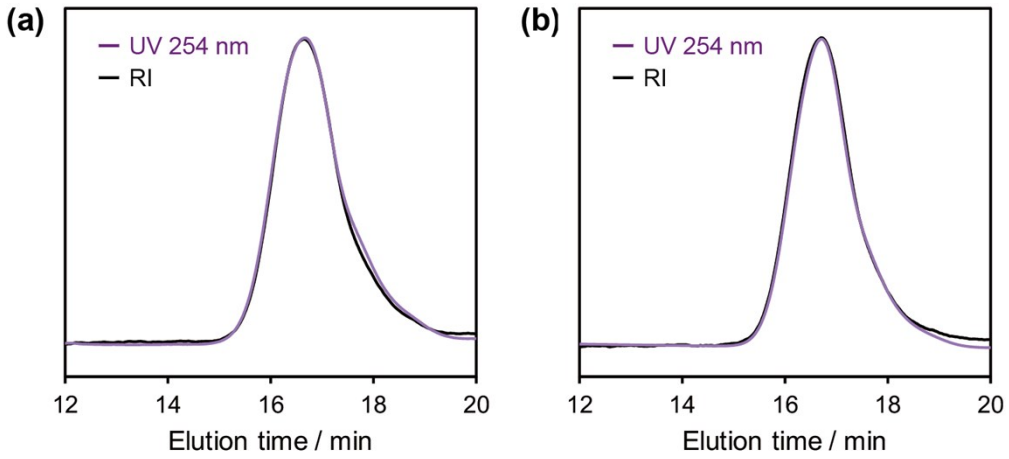


Fig. S19 SEC curves of (a) **1-PCL** and (b) **2-PCL** recorded by a UV (254 nm) detector and differential refractive index (RI) detector. The monomodal curves exclude the possibility of the polymerizations initiated from water and only from one terminal OH group in **1** and **2**, indicating the successful incorporation of the mechanophores into the polymer mid-chains.

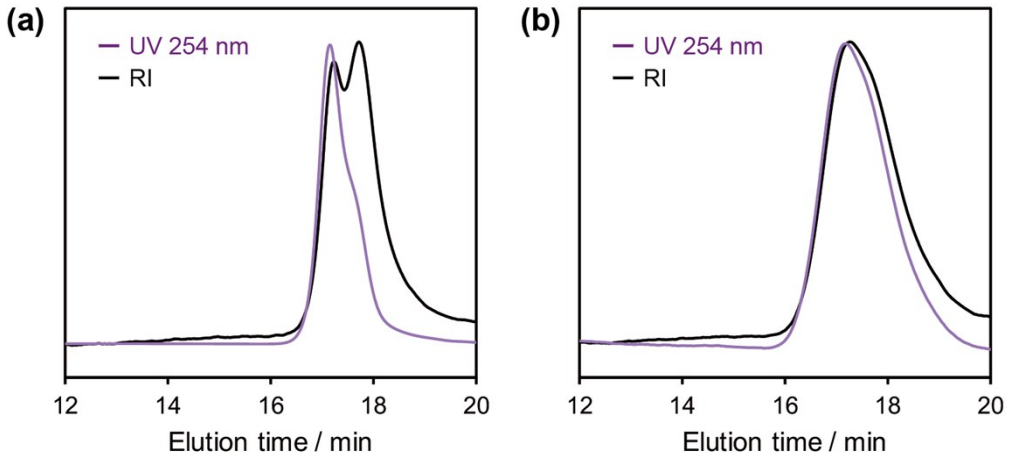


Fig. S20 SEC curves of (a) **Py-PCL** and (b) **NDI-PCL** recorded by a UV (254 nm) detector and RI detector. The bimodal RI curve of **Py-PCL** indicates the presence of polymers initiated from water and/or only from one terminal OH group in **Py-diol**. The monomodal curves of **NDI-PCL** exclude the possibility of the polymerizations initiated from water and only from one terminal OH group in **NDI-diol**.

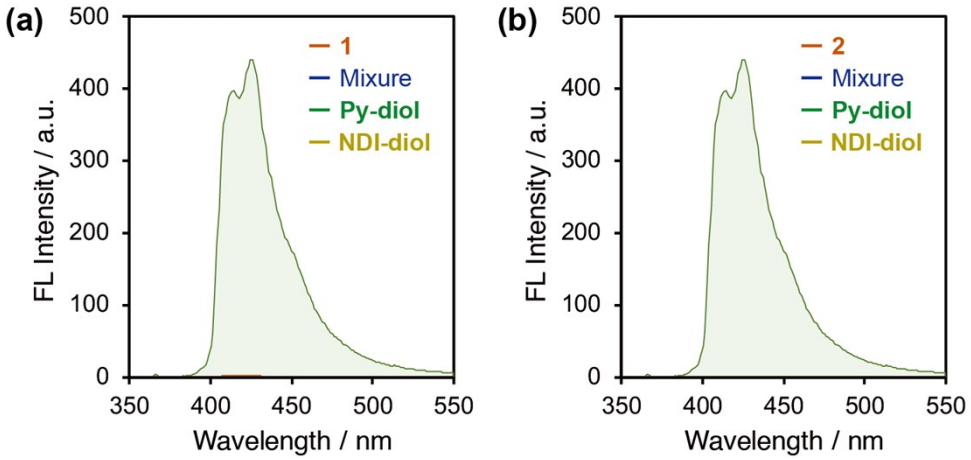


Fig. S21 FL (λ_{ex} = 365 nm) spectra of (a) **1**, a mixture of **Py-diol**/**NDI-diol** = 1/1 (mol/mol), **Py-diol**, and **NDI-diol** and (b) **2**, a mixture of **Py-diol**/**NDI-diol** = 1/2 (mol/mol), **Py-diol**, and **NDI-diol** in $CHCl_3$ (5.0×10^{-4} M). In the mixture solutions, Py concentrations were 5.0×10^{-4} M.

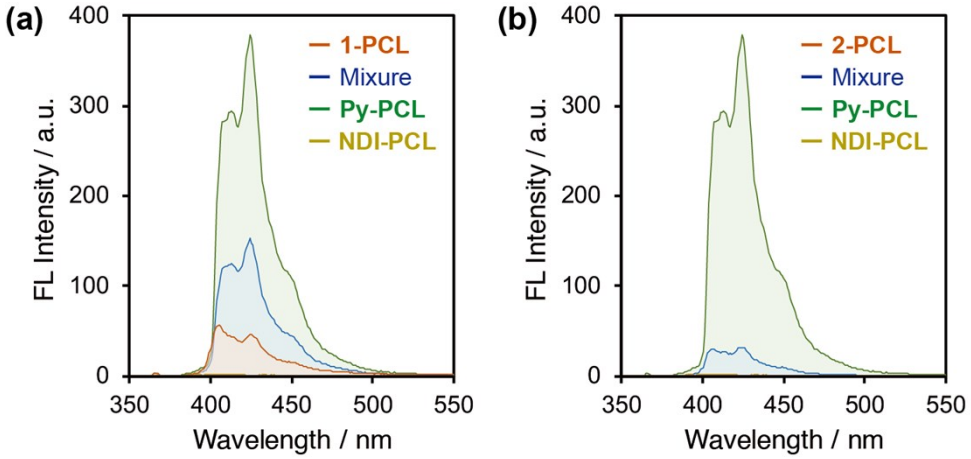


Fig. S22 FL (λ_{ex} = 365 nm) spectra of (a) **1-PCL**, a mixture of **Py-PCL**/**NDI-PCL** = 1/1 (mol/mol), **Py-PCL**, and **NDI-PCL** and (b) **2-PCL**, a mixture of **Py-PCL**/**NDI-PCL** = 1/2 (mol/mol), **Py-PCL**, and **NDI-PCL** in $CHCl_3$ (5.0×10^{-4} M). In the mixture solutions, Py concentrations were 5.0×10^{-4} M.

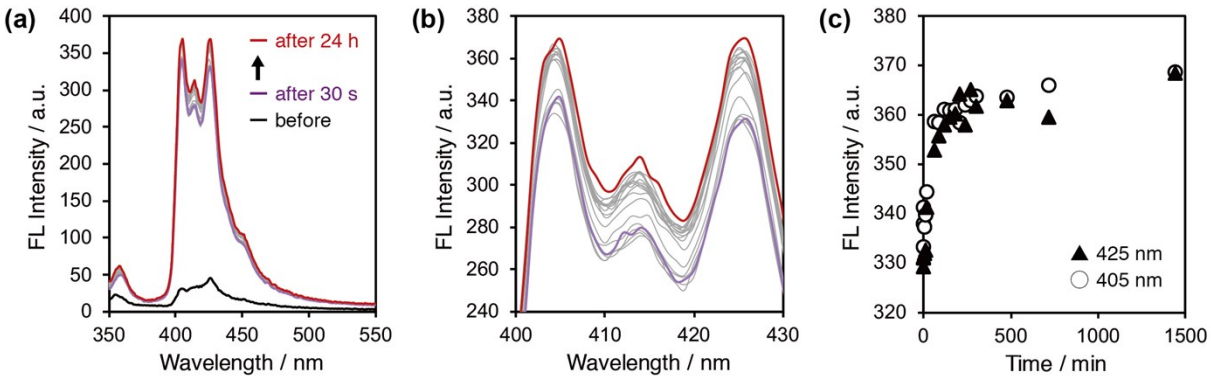


Fig. S23 (a) FL (λ_{ex} = 320 nm) spectra of a **2-PCL** cast film at the different timing after stretching and removal of the force. (b) Magnification of peak tops around 405 and 425 nm in the spectra. (c) Time course profiles of FL intensities at the peak tops around 405 and 425 nm after stretching and removal of the force.

Table S1 Quenching efficiencies (QEs) of Py FL in $CHCl_3$ solutions of **1**, **2**, **1-PCL**, **2-PCL**, and their control samples of Py/NDI mixtures (5.0×10^{-4} M) calculated from intensities at 425 nm (peak of Py FL)

Solution	QE / %	Solution	QE / %
1	94.2	**1-PCL**	83.3
2	99.9	**2-PCL**	98.7
Mixture of **Py-diol/NDI-diol** = 1/1	95.0	Mixture of **Py-PCL/NDI-PCL** = 1/1	24.7
Mixture of **Py-diol/NDI-diol** = 1/2	98.2	Mixture of **Py-PCL/NDI-PCL** = 1/2	73.9