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Supporting Information

Mechanochromic luminescence of phase-separated hydrogels that contain cyclophane mechanophores

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General methods

All reagents and solvents were purchased from Tokyo Kasei, Kanto Chemical, FUJIFILM WAKO Pure Chemical Corporation, or Merck. Inhibitor-free anhydrous dimethyl sulfoxide (DMSO) was used as a solvent for free radical polymerization to prepare DMSO gels. Acrylamide monomer was purified by recrystallization from acetone and dried in vacuum at room temperature (r.t.) for 12 h. Ethyl acrylate was used after polymerization inhibitor was removed with activated alumina. Flash silica gel column chromatography was carried out with a Biotage Isorela flash system using SHOKO-scientific Purif-Pack-EX cartridges. Recycling preparative gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LaboACE. ^{1}H NMR spectra were measured with a JEOL JNM-ECZ400S/L1 spectrometer at r.t. and all chemical shifts are reported on the δ-scale in ppm relative to the signal of tetramethylsilane (TMS, at 0.00) as an internal standard. Coupling constants (J) are quoted in Hz and relative intensities are reported. Proton-decoupled ^{13}C NMR spectra were acquired on a JEOL JNM-ECZ400S/L1 spectrometer at r.t. or 45 ºC and all chemical shifts are expressed in ppm using solvents as the internal standards ($CDCl_3$, at 77.16; DMSO-*d*6, at 39.52). Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) mass spectroscopy was performed with a SHIMADZU AXIMA-Performance. High-resolution electrospray ionization (ESI) mass spectroscopy was performed with a Bruker Daltonics micrOTOF II. Gel preparation was conducted in a UNICO UN-800L-TKS glovebox. Stress-strain measurements were conducted under ambient conditions with a SHIMADZU AGS-100NX equipped with a 100 N load cell at a strain rate of 0.2 s^{-1}. SANS experiments were conducted with the SANS-U spectrometer of the Institute for Solid State Physics, the University of Tokyo, located at the JRR-3M research reactor of Japan Atomic Energy Agency in Tokai, Japan. The neutron wavelength λ was 7.0 Å with $\Delta\lambda/\lambda$ = 10% full width at half maximum, and the sample-to-detector distances were 16 m, 8 m, and 1 m. The scattered neutrons were collected with a two-dimensional detector (model 2660N, Ordela). After air and cell scattering subtractions, the scattered intensity was normalized to the absolute intensity using a polyethylene file as a standard sample. The 2-D scattering pattern was converted into a 1-D profile by the circular averaging, followed by the incoherent scattering subtraction. The scattering intensity was plotted against the magnitude of the scattering vector, Q. The temperature of the sample was 25 °C. Absorption spectra were measured on a JASCO V-750. Steady-state fluorescence spectra of solutions were recorded with a JASCO FP-6500 and the spectra were corrected for the detector nonlinearity. Steady-state fluorescence spectra of gels were monitored with an Ocean Optics QEPro-FL equipped with an LLS-385 LED light source and a Reflection/Backscattering Probe R400-7-UV-VIS. These spectra were not corrected. Time-resolved fluorescence microscopy was performed with a Hamamatsu Photonics Quantaurus-Tau. Fluorescence quantum yields measurements were carried out with a Hamamatsu Photonics Quantaurus-QY. Photographs were taken with a Canon EOS 9000D stabilized with a tripod.

Swelling ratio of hydrogels at r.t. was determined by a following equation (1), where W_s is mass of hydrogels and W_d is mass of dry polymers.

$$\text{Swelling ratio} = (W_s - W_d) / W_d \quad (1)$$

Net volume of gels swollen with the mixture of water and DMSO was determined by an equation (2), where d is a thickness of the gels and d_h is a thickness of the initial hydrogel.

$$\text{Net volume} = (d/d_h)^3 \quad (2)$$

Synthesis of compounds 1, 2, and 3

The synthetic procedures used to prepare compounds **1**, **2**, and **3** are shown in Schemes S1 and S2. Compounds **4**, **7**, and *N*-propargylacrylamide were prepared according to reported procedures.[S1,S2]

Compound 5. *p*-Toluenesulfonyl chloride (131 mg, 0.689 mmol) was added to a mixture of **4** (80.0 mg, 5.74×10^{-2} mmol), 4-dimethylaminopyridine (0.7 mg, 6×10^{-3} mmol), and Et_3N (139 mg, 1.38 mmol) in CH_2Cl_2 (30 mL). The mixture was then stirred under nitrogen atmosphere for 14 h at r.t. The reaction mixture was poured into CH_2Cl_2 (50 mL), and the organic layer was washed with 5% aq. HCl (50 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent wa1s evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 9/1 v/v) to afford **5** (56.2 mg, 3.30×10^{-2} mmol, 58%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 3.65–3.68 (m, 4H), 3.71–3.75 (m, 8H), 3.80 (s, 8H), 3.88–3.94 (m, 12H), 4.13 (t, J = 4.8 Hz, 4H), 4.17–4.22 (m, 12H), 6.61 (t, J = 2.4 Hz, 2H), 6.85–6.89 (m, 6H), 6.91–6.92 (m, 2H), 7.29–7.32 (m, 6H), 7.44 (d, J = 8.4 Hz, 4H), 7.66 (d, J = 8.0 Hz, 2H), 7.71–7.81 (m, 10H), 7.86 (d, J = 9.2 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.77, 67.70, 67.80, 68.93, 69.42, 69.93, 70.95, 70.99, 71.29, 87.27, 88.87, 95.27, 95.46, 102.88, 110.35, 110.81, 114.81, 115.81, 117.61, 118.54, 123.51, 123.70, 124.79, 125.11, 125.63, 125.69, 127.04, 128.12, 129.23, 129.79, 129.97, 130.42, 130.88, 131.12, 131.92, 133.05, 133.24, 144.97, 159.04, 159.90, 160.05. MS (MALDI-TOF): m/z: 1701.04 (calcd. $[M]^+$ = 1700.56).

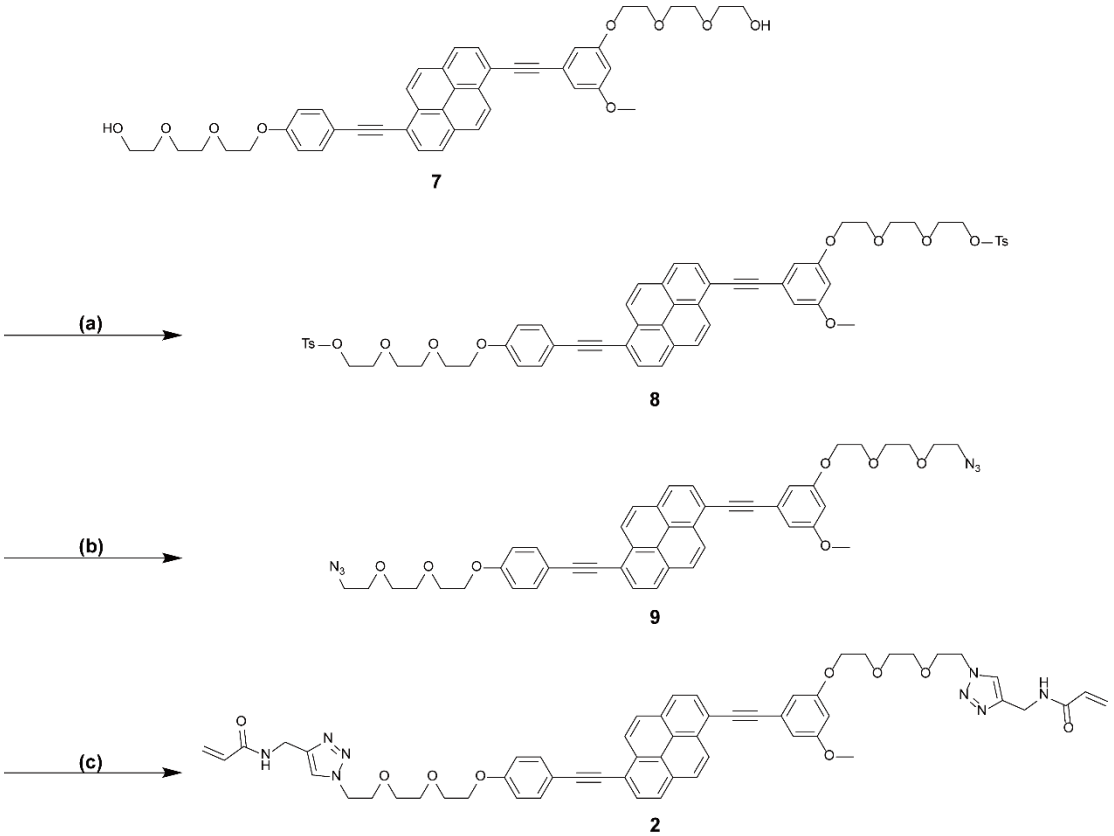
Compound 6. Sodium azide (106 mg, 0.823 mmol) was added to a mixture of **5** (70.0 mg, 4.11×10^{-2} mmol) in DMF (10 mL). The mixture was then stirred under nitrogen atmosphere for 24 h at 60 °C. The reaction mixture was poured into ethyl acetate (50 mL), and the organic layer was washed with saturated aq. NH_4Cl (4 × 50 mL) and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 4/1 v/v) to afford **6** (53.1 mg, 3.68×10^{-2} mmol, 89%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.43 (t, J = 5.2 Hz, 4H), 3.71–3.75 (m, 8H), 3.79–3.81 (m, 12H), 3.91–3.96 (m, 12H), 4.12–4.15 (m, 4H), 4.17–4.20 (m, 4H), 4.23–4.25 (m, 4H), 6.62 (t, J = 2.4 Hz, 2H), 6.86–6.88 (m, 6H), 6.92–6.93 (m, 2H), 7.31 (d, J = 9.2 Hz, 2H), 7.44 (d, J = 8.8 Hz, 4H), 7.66 (d, J = 7.6 Hz, 2H), 7.71–7.79 (m, 6H), 7.86 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.85, 67.70, 67.81, 69.95, 70.30, 70.94, 71.08, 71.31, 87.28, 88.86, 95.27, 95.46, 102.91, 110.42, 110.77, 114.81, 115.83, 117.62, 118.54, 123.52, 123.71, 124.79, 125.11, 125.63, 125.70, 127.05, 128.08, 129.23, 129.79, 130.43, 130.88, 131.13, 131.92, 133.24, 159.04, 159.92, 160.03. MS (MALDI-TOF): m/z: 1442.22 (calcd. $[M]^+$ = 1442.56).

Mechanophore 1. Cupper iodide (5.80 mg, 3.05×10^{-2} mmol) was added to a mixture of **6** (22.0 mg, 1.52×10^{-2} mmol), *N*-propargylacrylamide (49.9 mg, 0.457 mmol), and Et_3N (1 mL) in $CHCl_3$ (5 mL). The mixture was then stirred under nitrogen atmosphere for 3 d at r.t. The reaction mixture was poured into $CHCl_3$ (200 mL), and the organic layer was washed with 5% aq. HCl (30 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced

pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2/acetone = 4/1 v/v to acetone) and recycling GPC (eluent: chloroform) to afford **1** (10.5 mg, 6.32×10^{-3} mmol, 40%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*6): δ = 3.60–3.67 (m, 16H), 3.76–3.86 (m, 16H), 4.11–4.13 (m, 4H), 4.20–4.22 (m, 8H), 4.40 (d, J = 5.6 Hz, 4H), 4.52 (t, J = 5.2 Hz, 4H), 5.58 (dd, J = 10.0 , 2.0 Hz, 2H), 6.12 (dd, J = 17.2, 2.0 Hz, 2H), 6.25 (dd, J = 17.2, 10.0 Hz, 2H), 6.67–6.73 (br, 2H), 6.90–6.95 (m, 8H), 7.42 (d, J = 8.8 Hz, 4H), 7.59–7.65 (m, 4H), 7.82 (d, J = 9.2 Hz, 2H), 7.92–7.98 (m, 6H), 8.03 (d, J = 9.2 Hz, 2H), 8.10 (d, J = 7.6 Hz, 2H), 8.47–8.51 (m, 4H). ^{13}C NMR (100 MHz, DMSO-*d*6, 45 ºC): δ = 34.05, 49.20, 67.38, 67.46, 67.48, 68.67, 68.72, 68.81, 69.52, 69.68, 70.07, 70.08, 86.42, 87.92, 95.21, 95.26, 102.61, 109.65, 110.63, 114.28, 114.71, 116.91, 117.55, 122.62, 122.82, 123.05, 123.86, 124.85, 124.94, 125.05, 125.13, 127.20, 128.08, 128.88, 129.55, 129.83, 130.19, 130.26, 131.01, 131.47, 132.74, 144.34, 158.78, 159.67, 159.70, 164.36. HRMS (ESI-TOF): m/z: 853.3213 (calcd. $[M+2Na]^{2+}$ = 853.3207.

Scheme S1



Conditions: (a) *p*-toluenesulfonyl chloride, 4-dimethylaminopyridine, Et_3N, CH_2Cl_2, r.t., 40 h; (b) sodium azide, DMF, 60 °C, 18 h; (c) *N*-propargylacrylamide, CuI, Et_3N, $CHCl_3$, r.t., 2 d.

Compound 8. *p*-Toluensulfonyl chloride (367 mg, 1.93 mmol) was added to a mixture of **7** (234 mg, 0.321 mmol), 4-dimethylaminopyridine (3.90 mg, 3.21×10^{-2} mmol), and Et_3N (390 mg, 3.85 mmol) in CH_2Cl_2 (10 mL). The mixture was then stirred under nitrogen atmosphere for 40 h at r.t. The reaction mixture was poured into CH_2Cl_2 (50

mL), and the organic layer was washed with 5% aq. HCl (50 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 9/1 v/v) to afford **8** (286 mg, 0.276 mmol, 86%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.42 (s, 3H), 3.63–3.65 (m, 4H), 3.68–3.73 (m, 8H), 3.86–3.87 (m, 7H), 4.16–4.19 (m, 8H), 6.55 (s, 1H), 6.87 (s, 2H), 6.97 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 8.8 Hz, 4H), 7.64 (d, J = 8.4 Hz, 2H), 7.78–7.82 (m, 4H), 8.12–8.21 (m, 6H), 8.62–8.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.74, 21.77, 55.67, 67.60, 67.74, 68.88, 69.38, 69.84, 70.93, 87.44, 88.28, 95.51, 95.76, 102.62, 109.91, 110.14, 114.91, 115.80, 118.20, 119.03, 124.33, 124.78, 125.17, 125.35, 126.17, 126.54, 128.10, 128.35, 129.94, 129.96, 130.09, 131.00, 131.37, 131.92, 132.22, 133.04, 133.30, 144.94, 144.97, 159.15, 159.92, 160.75. MS (MALDI-TOF): m/z: 1036.26 (calcd. $[M]^+$ = 1036.32).

Compound 9. Sodium azide (179 mg, 2.76 mmol) was added to a mixture of **8** (143 mg, 0.138 mmol) in DMF (20 mL). The mixture was then stirred under nitrogen atmosphere for 18 h at 60 °C. The reaction mixture was poured into ethyl acetate (50 mL), and the organic layer was washed with saturated aq. NH_4Cl (4 × 50 mL) and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 4/1 v/v) to afford **9** (105 mg, 0.135 mmol, 98%) as a yellow solid.

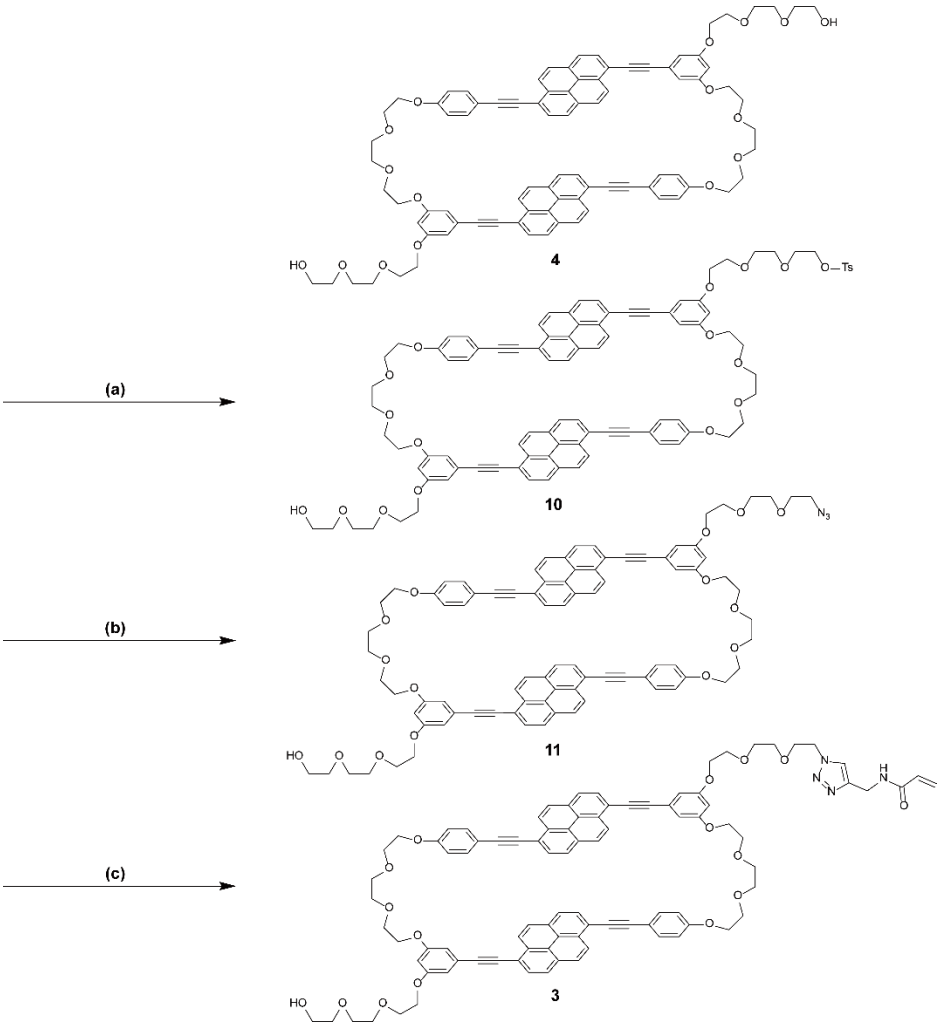
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (t, J = 4.8 Hz, 4H), 3.68–3.72 (m, 8H), 3.75–3.78 (m, 4H), 3.86 (s, 3H), 3.90 (t, J = 4.8 Hz, 4H), 4.17–4.20 (m, 4H), 6.55 (t, J = 2.4 Hz, 1H), 6.87–6.89 (m, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8Hz, 2H), 8.10–8.15 (m, 4H), 8.18 (dd, J = 8.0, 4.0 Hz, 2H), 8.61–8.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.79, 55.64, 67.60, 67.75, 69.87, 70.23, 70.86, 71.02, 87.42, 88.27, 95.50, 95.75, 102.62, 109.88, 110.16, 114.90, 115.78, 118.19, 119.01, 124.29, 124.77, 125.14, 125.31, 126.13, 126.51, 128.07, 128.30, 129.89, 130.05, 130.96, 131.34, 131.89, 132.19, 133.28, 159.15, 159.92, 160.72. MS (MALDI-TOF): m/z: 778.04 (calcd. $[M]^+$ = 778.31).

Compound 2. Cupper iodide (38.0 mg, 0.200 mmol) was added to a mixture of **9** (52.0 mg, 6.68×10^{-2} mmol), *N*-propargylacrylamide (36.0 mg, 0.334 mmol), and Et_3N (1 mL) in $CHCl_3$ (10 mL). The mixture was then stirred under nitrogen atmosphere for 2 d at r.t. The reaction mixture was poured into $CHCl_3$ (200 mL), and the organic layer was washed with 5% aq. HCl (30 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2/acetone = 1/1 v/v to acetone) and recycling GPC (eluent: chloroform) to afford **2** (37.0 mg, 1.81 mmol, 55%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64–3.66 (m, 4H), 3.70–3.72 (m, 4H), 3.85–3.89 (m, 11H), 4.17–4.20 (m, 4H), 4.51–4.54 (m, 4H), 4.57–459 (m, 4H), 5.61–5.66 (m, 2H), 6.06–6.16 (m, 2H), 6.26–6.33 (m. 2H), 6.54–6.58 (m, 3H), 6.88 (t, J = 2.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 6.4 Hz, 2H), 8.13–8.22 (m, 6H), 8.63–8.68 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.83, 35.03, 50.43, 55.69, 67.63, 67.80, 69.58, 69.83, 69.84, 70.64, 70.74, 70.76, 70.87, 87.49, 88.35, 95.46, 95.72, 102.70, 109.89, 110.21, 114.91, 115.89, 118.18, 119.03,

123.53, 123.55, 124.36, 124.83, 125.20, 125.37, 126.18, 126.58, 126.95, 126.97, 128.14, 128.38, 129.96, 130.11, 130.65, 131.02, 131.41, 131.94, 132.23, 133.35, 144.36, 159.09, 159.88, 160.77, 165.59. HRMS (ESI-TOF): m/z: 1019.4081 (calcd. $[M+Na]^+$ = 1019.4063).

Scheme S2



Conditions: (a) *p*-toluenesulfonyl chloride, 4-dimethylaminopyridine, Et_3N, CH_2Cl_2, r.t., 40 h; (b) sodium azide, DMF, 60 °C, 18 h; (c) *N*-propargylacrylamide, CuI, Et_3N, $CHCl_3$, r.t., 2 d.

Compound 10. *p*-Toluenesulfonyl chloride (16.4 mg, 8.62×10^{-2} mmol) was added to a mixture of **4** (60.0 mg, 4.31×10^{-2} mmol), 4-dimethylaminopyridine (0.5 mg, 4×10^{-3} mmol), and Et_3N (1.0 mL) in CH_2Cl_2 (120 mL). The mixture was then stirred under nitrogen atmosphere for 40 h at r.t. The reaction mixture was poured into CH_2Cl_2 (50 mL), and the organic layer was washed with 5% aq. HCl (50 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 65/35 v/v) to afford **10** (25.1 mg, 1.62×10^{-2} mmol, 37%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 3.65–3.68 (m, 4H), 3.71–3.81 (m, 20H), 3.88–3.95 (m, 12H), 4.12–

4.15 (m, 4H), 4.18–4.25 (m, 8H), 6.61 (t, J = 2.4 Hz, 1H), 6.63 (t, J = 2.4 Hz, 1H), 6.86–6.89 (m, 6H), 6.91–6.93 (m, 2H), 7.29–7.32 (m, 4H), 7.44 (d, J = 8.8 Hz, 4H), 7.65–7.67 (m, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.75–7.82 (m, 6H), 7.84–7.87 (m, 2H), 8.01 (d, J = 8.0 Hz, 2H), 8.43–8.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.78, 61.96, 67.70, 67.80, 68.93, 69.42, 69.86, 69.94, 70.59, 70.95, 71.00, 71.03, 71.31, 72.63, 87.27, 88.86, 95.26, 95.45, 102.88, 102.94, 110.35, 110.39, 110.78, 114.80, 115.80, 117.59, 117.61, 118.54, 123.50, 123.69, 124.79, 125.10, 125.63, 125.69, 127.04, 128.09, 128.12, 129.22, 129.79, 129.97, 130.42, 130.87, 131.12, 131.92, 133.04, 133.24, 144.97, 159.04, 159.85, 159.89, 160.04. MS (MALDI-TOF): m/z: 1546.90 (calcd. $[M]^+$ = 1546.55).

Compound 11. Sodium azide (10.5 mg, 0.162 mmol) was added to a mixture of **10** (25.1 mg, 1.62×10^{-2} mmol) in DMF (20 mL). The mixture was then stirred under nitrogen atmosphere for 18 h at 60 °C. The reaction mixture was poured into ethyl acetate (50 mL), and the organic layer was washed with saturated aq. NH_4Cl (4 × 50 mL) and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 50/50 v/v) to afford **11** (15.0 mg, 1.06×10^{-2} mmol, 66%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 1H), 3.43 (t, J = 5.2 Hz, 2H), 3.65–3.68 (m, 2H), 3.71–3.82 (m, 20 H), 3.91–3.96 (m, 12H), 4.13 (t, J = 4.4 Hz, 4H), 4.19 (t, J = 4.4 Hz, 4H), 4.24 (t, J = 4.4 Hz, 4H), 6.62–6.64 (m, 2H), 6.85–6.88 (m, 6H), 6.93 (t, J = 0.8 Hz 2H), 7.30 (d, J = 9.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 4H), 7.66 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.75–7.79 (m, 4H), 7.86 (d, J = 9.2 Hz), 8.01 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.83, 61.97, 67.69, 67.76, 67.80, 69.85, 69.95, 70.30, 70.58, 70.94, 71.03, 71.08, 71.31, 72.64, 87.27, 88.86, 95.26, 95.45, 102.90, 102.93, 110.39, 110.73, 110.79, 114.79, 115.81, 117.61, 118.53, 123.50, 123.69, 124.78, 125.10, 125.11, 125.63, 125.69, 127.04, 128.08, 129.22, 129.78, 130.42, 130.87, 131.12, 131.92, 132.24, 159.03, 159.84, 159.91, 160.03. MS (MALDI-TOF): m/z: 1417.14 (calcd. $[M]^+$ = 1417.55).

Compound 3. Cupper iodide (4.03 mg, 2.11×10^{-2} mmol) was added to a mixture of **11** (15.0 mg, 1.06×10^{-2} mmol), *N*-propargylacrylamide (34.6 mg, 0.317 mmol), and Et_3N (1.0 mL) in $CHCl_3$ (20 mL). The mixture was then stirred under nitrogen atmosphere for 2 d at r.t. The reaction mixture was poured into $CHCl_3$ (200 mL), and the organic layer was washed with 5% aq. HCl (30 mL), saturated aq. $NaHCO_3$ (50 mL), and saturated aq. NaCl (50 mL). The organic layer was dried over $MgSO_4$ and filtered before the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2/acetone = 1/1 v/v to acetone) and recrystallized from chloroform and hexane to afford **3** (5.0 mg, 3.3×10^{-3} mmol, 31%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*6): δ = 3.45–3.47 (m, 2H), 3.50–3.54 (m, 2H), 3.58–3.60 (m, 6H), 3.63–3.67 (m, 10H), 3.77–3.86 (m, 14H), 4.10–4.12 (m, 4H), 4.16–4.27 (br, 8H), 4.40 (d, J = 6.0 Hz, 2H), 4.53 (t, J = 5.2 Hz, 2H), 4.64 (t, J = 5.4 Hz, 1H), 5.60 (dd, J = 10.0, 2.4 Hz, 1H), 6.12 (dd, J = 17.2, 2.4 Hz, 1H), 6.26 (dd, J = 17.2, 10.0 Hz, 1H), 6.71–6.72 (m, 2H), 6.93–6.97 (m, 8H), 7.43 (d, J = 8.4 Hz, 4H), 7.64 (d, J = 8.4 Hz, 4H), 7.84 (d, J = 9.2 Hz, 2H), 7.96–8.02 (m, 5H), 8.07 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 7.6 Hz, 2H), 8.53 (d, J = 9.2 Hz, 2H), 8.65 (t, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d*6, 45 ºC): δ = 34.05, 49.20, 60.15, 67.39, 67.47, 67.53, 68.68, 68.72, 68.82, 69.52,

69.69, 69.89, 70.08, 72.26, 86.41, 87.92, 95.22, 95.26, 102.61, 109.66, 110.62, 114.27, 114.71, 116.91, 117.55, 122.62, 122.82, 123.07, 123.85, 124.85, 124.93, 125.05, 125.12, 127.20, 128.08, 128.88, 129.55, 129.83, 130.20, 130.25, 131.01, 131.47, 132.74, 158.78, 159.70, 164.35. HRMS (ESI-TOF): m/z: 786.2928 (calcd. $[M+2Na]^{2+}$ = 786.2911).

Preparation of DMSO gels and hydrogels

DG1 and **HG1**. A solution of acrylamide (455 mg, 6.40 mmol), ethyl acrylate (961 mg, 9.60 mmol), *N*,*N*'-methylenebisacrylamide (1.67 mg, 1.08 × 10^{-2} mmol), **1** (2.0 mg, 1.2 × 10^{-3} mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (6.4 μL) in DMSO (3.5 mL) was degassed using freeze-pump-thaw cycles and purged with N_2. A solution of ammonium persulfate (APS, 40.5 mg, 0.177 mmol) in DMSO (3.0 mL) was also degassed using freeze-pump-thaw cycles and purged with N_2. After adding 0.5 mL of the APS solution to the reaction mixture in a glovebox, free radical polymerization proceeded at ambient temperature for 3 d in the template (cuboid, ca. 68 mm × ca. 18 mm × 1 mm). After the polymerization, the resultant DMSO gel **DG1** was immersed into deionized water (5 × 30 mL, over 1 h), resulting in hydrogel **HG1** (swelling ratio: 0.67). The complete replacement with water was confirmed by the NMR spectrum of the solvent after 5th replacement. No peaks corresponding to DMSO were observed.

DG2 and **HG2**. A solution of acrylamide (455 mg, 6.40 mmol), ethyl acrylate (961 mg, 9.60 mmol), *N*,*N*'-methylenebisacrylamide (1.48 mg, 9.60 × 10^{-3} mmol), **2** (2.4 mg, 2.4 × 10^{-3} mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (6.4 μL) in DMSO (3.5 mL) was degassed using freeze-pump-thaw cycles and purged with N_2. A solution of APS (40.5 mg, 0.177 mmol) in DMSO (3.0 mL) was also degassed using freeze-pump-thaw cycles and purged with N_2. After adding 0.5 mL of the APS solution to the reaction mixture in glovebox, free radical polymerization proceeded at ambient temperature for 3 d in the template (cuboid, ca. 68 mm × ca. 18 mm × 1 mm). After the polymerization, the resultant DMSO gel **DG2** was immersed into deionized water (5 × 30 mL, over 1 h), resulting in hydrogel **HG2** (swelling ratio: 0.68).

DG3 and **HG3**. A solution of acrylamide (455 mg, 6.40 mmol), ethyl acrylate (961 mg, 9.60 mmol), *N*,*N*'-methylenebisacrylamide (1.85 mg, 1.20 × 10^{-2} mmol), **3** (2.0 mg, 1.3 × 10^{-3} mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (6.4 μL) in DMSO (3.5 mL) was degassed using freeze-pump-thaw cycles and purged with N_2. A solution of APS (40.5 mg, 0.177 mmol) in DMSO (3.0 mL) was also degassed using freeze-pump-thaw cycles and purged with N_2. After adding 0.5 mL of the APS solution to the reaction mixture in glovebox, free radical polymerization proceeded at ambient temperature for 3 d in the template (cuboid, ca. 68 mm × ca. 18 mm × 1 mm). After the polymerization, the resultant DMSO gel **DG3** immersed into deionized water (5 × 30 mL, over 1 h), resulting in hydrogel **HG3** (swelling ratio: 0.64).

DG4 and **HG4**. A solution of acrylamide (455 mg, 6.40 mmol), ethyl acrylate (961 mg, 9.60 mmol), *N*,*N*'-methylenebisacrylamide (1.85 mg, 1.20 × 10^{-2} mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (6.4 μL) in DMSO (3.5 mL) was degassed using freeze-pump-thaw cycles and purged with N_2. A solution of APS (40.5 mg, 0.177 mmol)

in DMSO (3,0 mL) was also degassed using freeze-pump-thaw cycles and purged with N_2. After adding 0.5 mL of the APS solution to the reaction mixture in glovebox, free radical polymerization proceeded at ambient temperature for 3 d in the template (cuboid, ca. 68 mm × ca. 18 mm × 1 mm). After the polymerization, the resultant DMSO gel **DG4** immersed into deionized water (5 × 30 mL, over 1 h), resulting in hydrogel **HG4** (swelling ratio: 0.75).

Polyacrylamide gels. A solution of acrylamide (1.13 g, 16.0 mmol), *N*,*N*'-methylenebisacrylamide (24.7 mg, 0.160 mmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (6.4 μL) in DMSO (3.5 mL) was degassed using freeze-pump-thaw cycles and purged with N_2. A solution of APS (24.7 mg, 0.16 mmol) in DMSO (3.0 mL) was also degassed using freeze-pump-thaw cycles and purged with N_2. After adding 0.5 mL of the APS solution to the reaction mixture in a glovebox, free radical polymerization proceeded at ambient temperature for 3 d in the template (cuboid, ca. 68 mm × ca. 18 mm × 1 mm). After the polymerization, the resultant DMSO gel of polyacrylamide was immersed into deionized water (5 × 30 mL, over 1 h), resulting in polyacrylamide hydrogel.

Emission spectra in solution

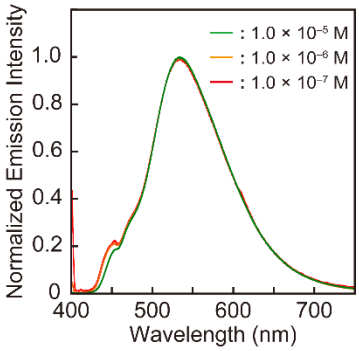


Fig. S1. Photoluminescence spectra of compound **1** varying the concentrations in DMSO. The excitation wavelength was 400 nm.

Emission lifetime measurements in solution

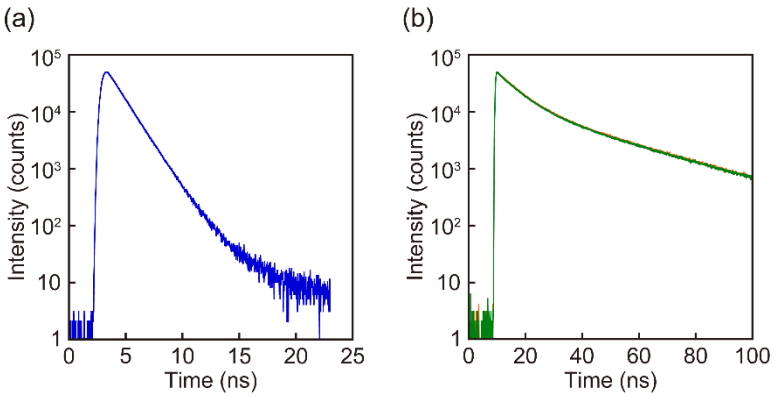


Fig. S2. (a) Emission decay profile of compound **2** (monitored at 430 nm) in DMSO (c = 1.0 × 10^{-6} M). (b) Emission decay profiles of mechanophore **1** (green) and compound **3** (orange) (monitored at 530 nm) in DMSO (c = 1.0 × 10^{-6} M). The excitation wavelength was 405 nm.

Fluorescence quantum yields of compounds and gels

Table S1. Quantum yields of compounds in DMSO and hydrogels. The excitation wavelength was 380 nm.

	1	**2**	**3**	**HG1**	**HG2**	**HG3**	**HG4** swollen with an aqueous solution of ANS	Polyacrylamide gel swollen with an aqueous solution of ANS
QY	0.65	0.85	0.77	0.63	0.77	0.55	0.38	0.02

Small-angle neutron scattering (SANS) measurement

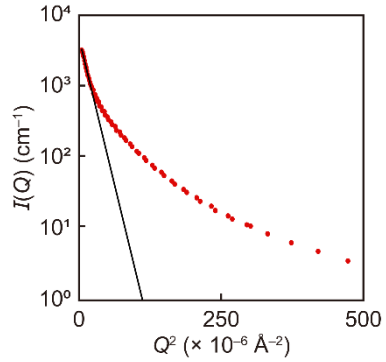


Fig. S3. SANS profile of **HG1** (red dot) and a fitting line (black line) according to Guinier plot in the range from 2.22 to 3.99 ×10^{-3} (Å^{-1}). ln$I(Q)$ = –75996Q^2 + 8.49 was given as the equation of the fitting line.

Mechanical properties of hydrogels

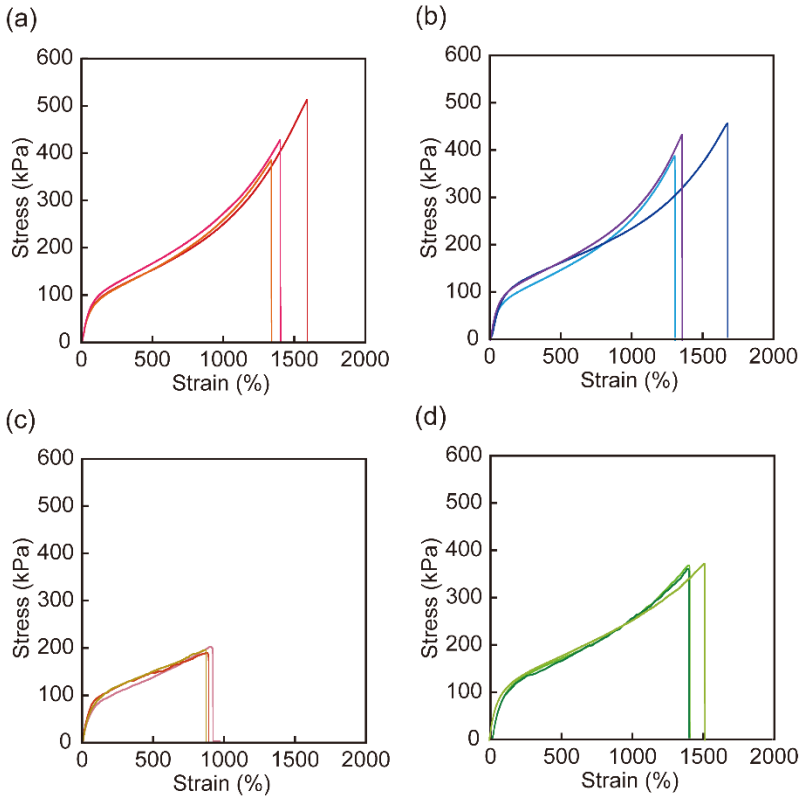


Fig. S4. Stress-strain curves of (a) **HG1**, (b) **HG2**, (c) **HG3**, and (d) **HG4**. Each graph shows data obtained from three different specimen. The experiments were conducted with a strain rate of 0.2 s^{-1}.

Table S2. Mechanical properties of hydrogels derived from tensile tests.[a)]

	Elongation at break (%)	Stress at break (kPa)	Young's modulus[b)] (kPa)
HG1	1444 ± 148	442 ± 71	1.59 ± 0.11
HG2	1445 ± 231	427 ± 37	1.46 ± 0.83
HG3	892 ± 24	195 ± 6	1.81 ± 0.33
HG4	1431 ± 91	370 ± 9	2.02 ± 0.20

a) All data were extracted from the strain-stress curves shown in Fig. S4 and represent averages of 3 measurements ± standard derivation. b) The Young's moduli were derived from the slopes of the strain-stress curves in the strain regime between 4–6%.

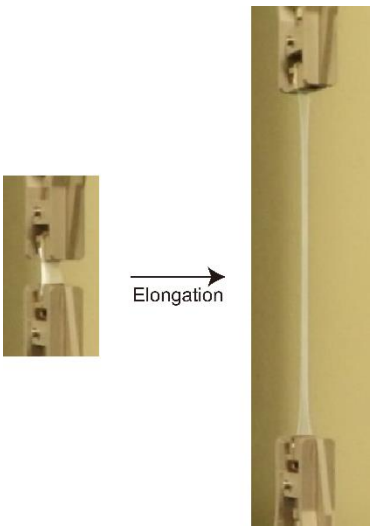


Fig. S5. Photographs of **HG4** during the tensile test at 0% (left) and 1400% (right).

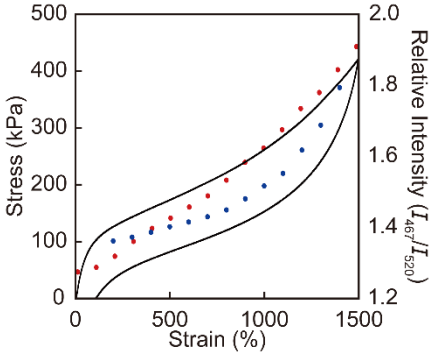


Fig. S6. Stress-strain curve of **HG1** (black line) and the relative monomer to excimer emission intensity (stretching; red dot, relaxing; blue dot).

Fig. S7. Pictures of **HG1** under excitation light of 365 nm (top) and under room light (bottom) at 0% (left) and 1500% (right).

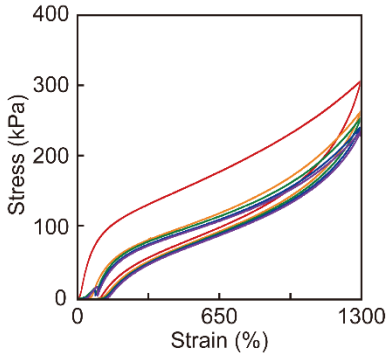


Fig. S8. Stress-strain curves during the cycle test (1st; red line, 2nd; orange line, 3rd; green line, 4th; blue line, 5th; purple line).

Photophysical properties of gels and dry films

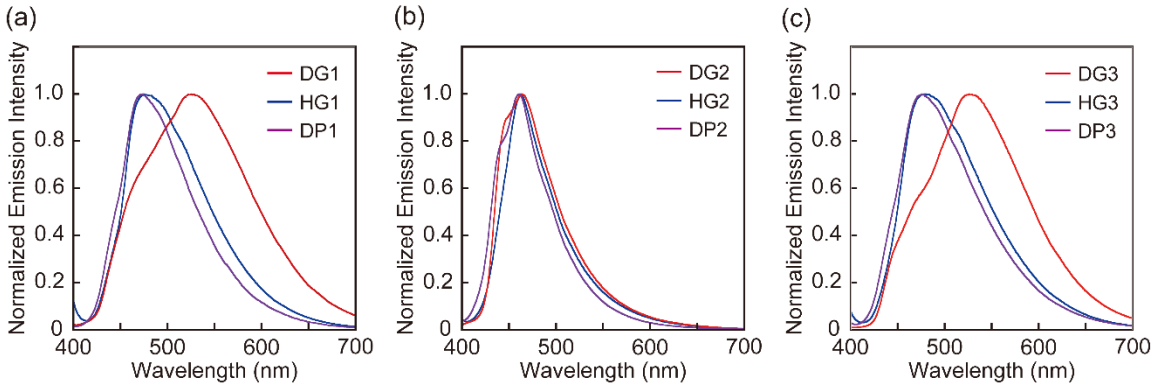


Fig. S9. Fluorescence spectra of DMSO gels (red line), hydrogels (blue line), and dry polymers (purple line) having compound (a) **1**, (b) **2**, or (c) **3**. The excitation wavelength was 385 nm.

Photophysical properties of HG2 and HG3 upon deformation

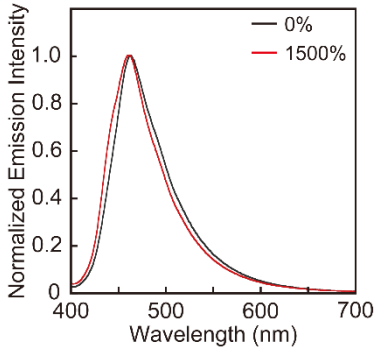


Fig. S10. Emission spectra of **HG2** before stretching (black line) and at strain of 1500% (green line). The excitation wavelength was 385 nm.

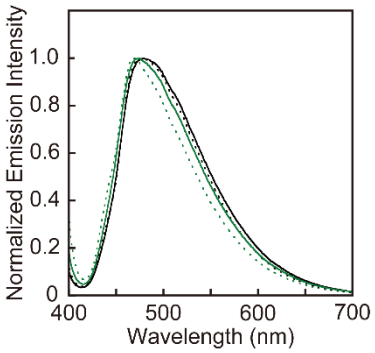


Fig. S11. Emission spectra of **HG3** before stretching (black line) and at strain of 900% (green line). Emission spectra of **HG1** before stretching (black dotted line) and at strain of 900% (green dotted line) are superimposed for reference purpose. The excitation wavelength was 385 nm.

Emission decay profiles of HG1 upon stretching

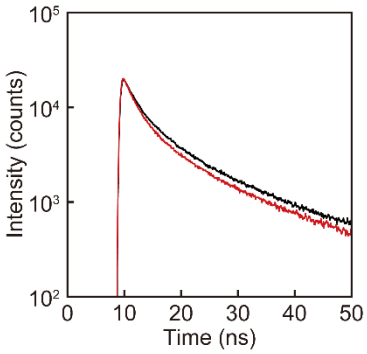


Fig. S12. Emission decay profiles of **HG1** recorded in the force-free state (black) and at strain of 1000% (red). The decays were monitored at 530 nm with excitation light of 405 nm.

Changes of the fluorescence intensity ratio during stress relaxation

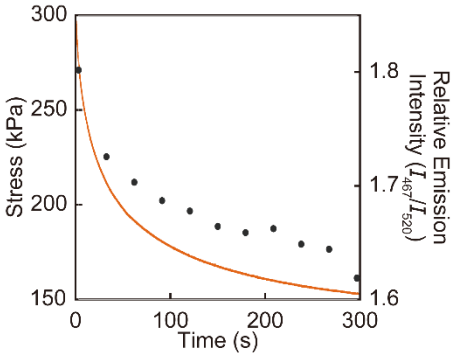


Fig. S13. Time-dependent stress curve (orange line) and the relative monomer to excimer intensity (dot) of **HG1** kept at strain of 1300%.

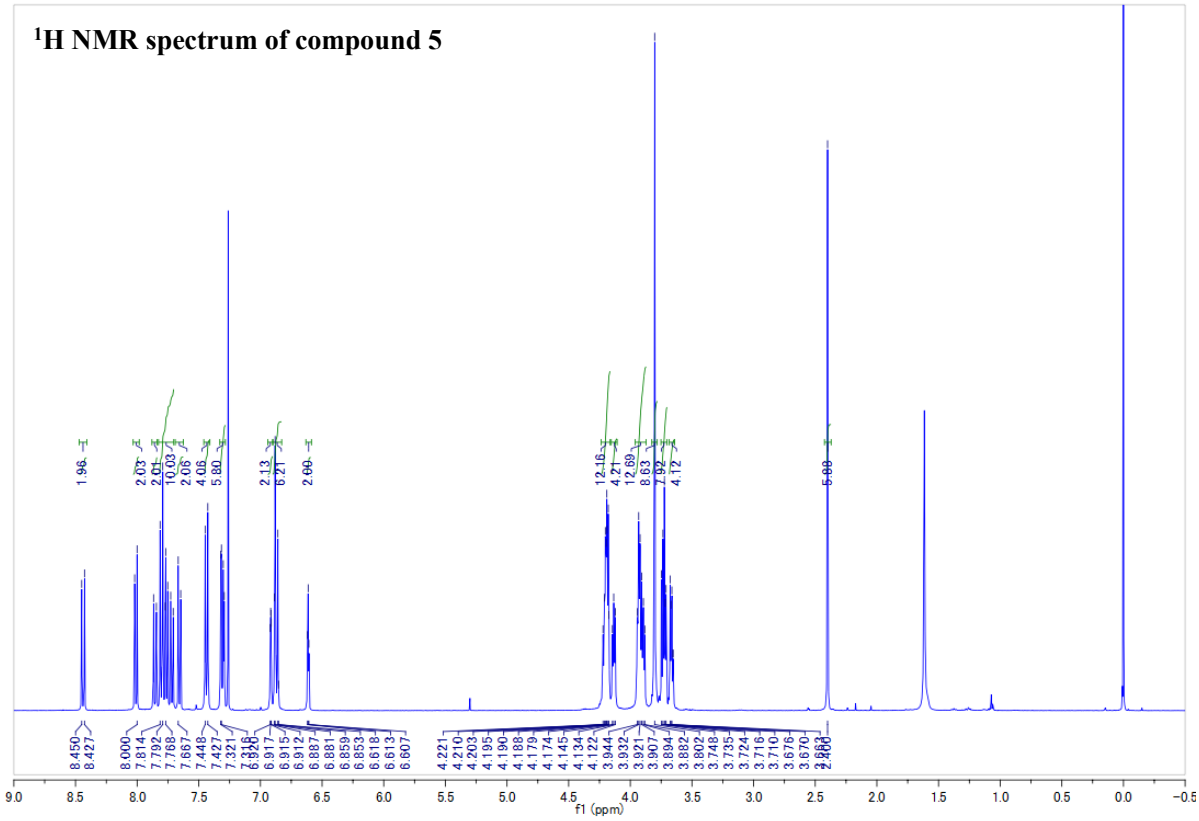
References

S1. Y. Sagara, H. Traeger, J. Li, Y. Okado, S. Schrettl, N. Tamaoki and C. Weder, Mechanically Responsive Luminescent Polymers Based on Supramolecular Cyclophane Mechanophores, *J. Am. Chem. Soc.*, 2021, **143**, 5519–5525.

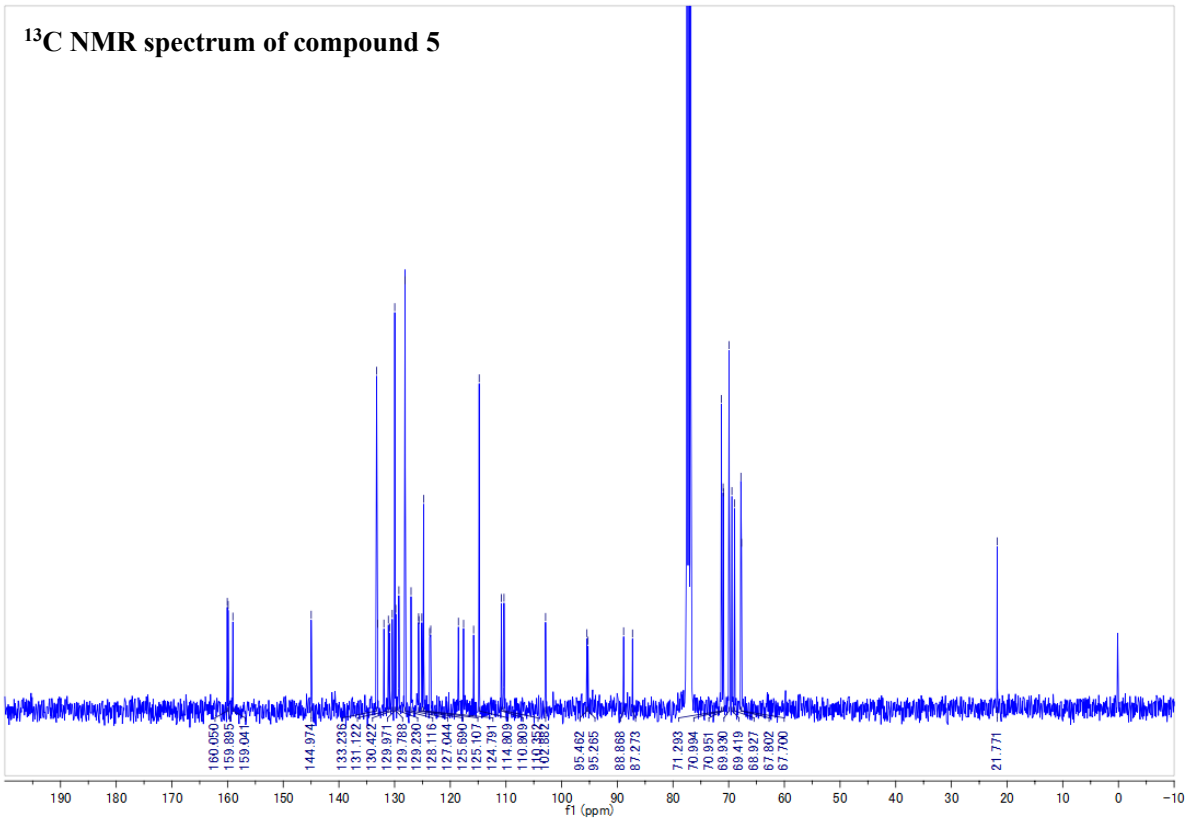
S2. Z. Chen, T. Sun and G. Qing, cAMP-modulated biomimetic ionic nanochannels based on a smart polymer, *J. Mater. Chem. B*, 2019, **7**, 3710–3715.

NMR spectra

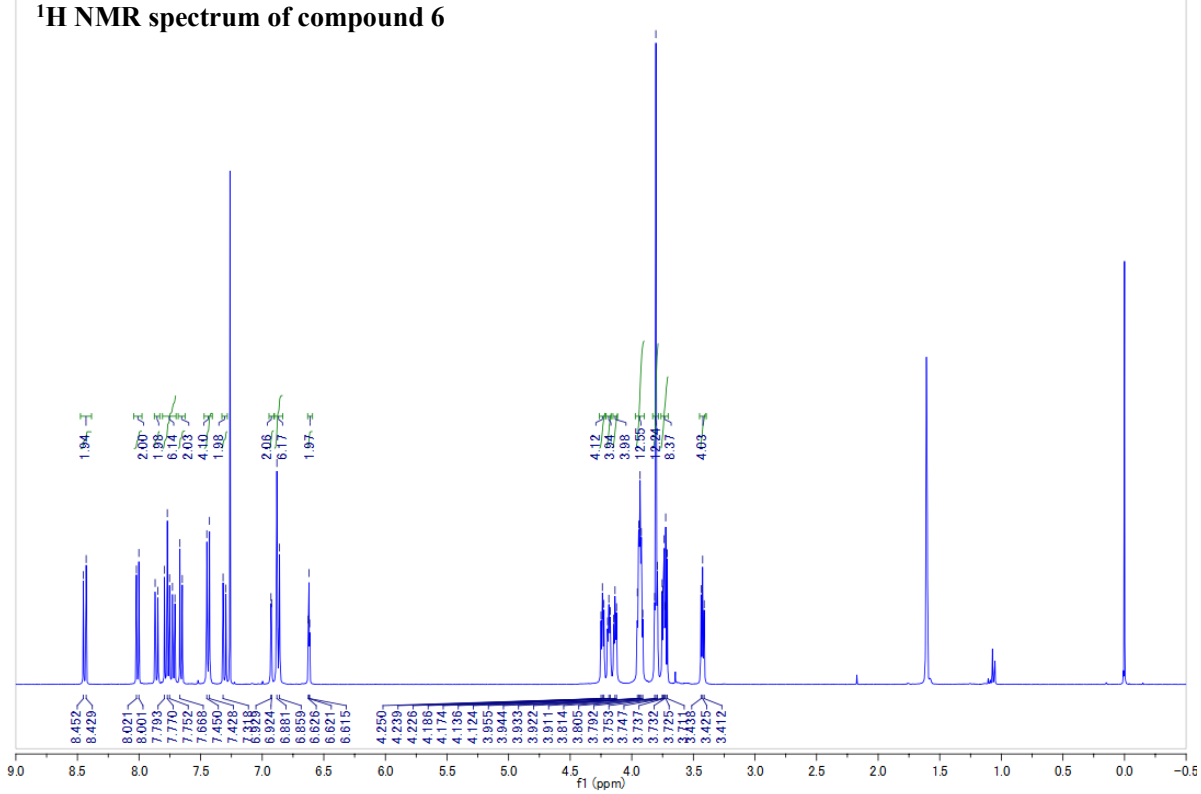
^{1}H NMR spectrum of compound 5



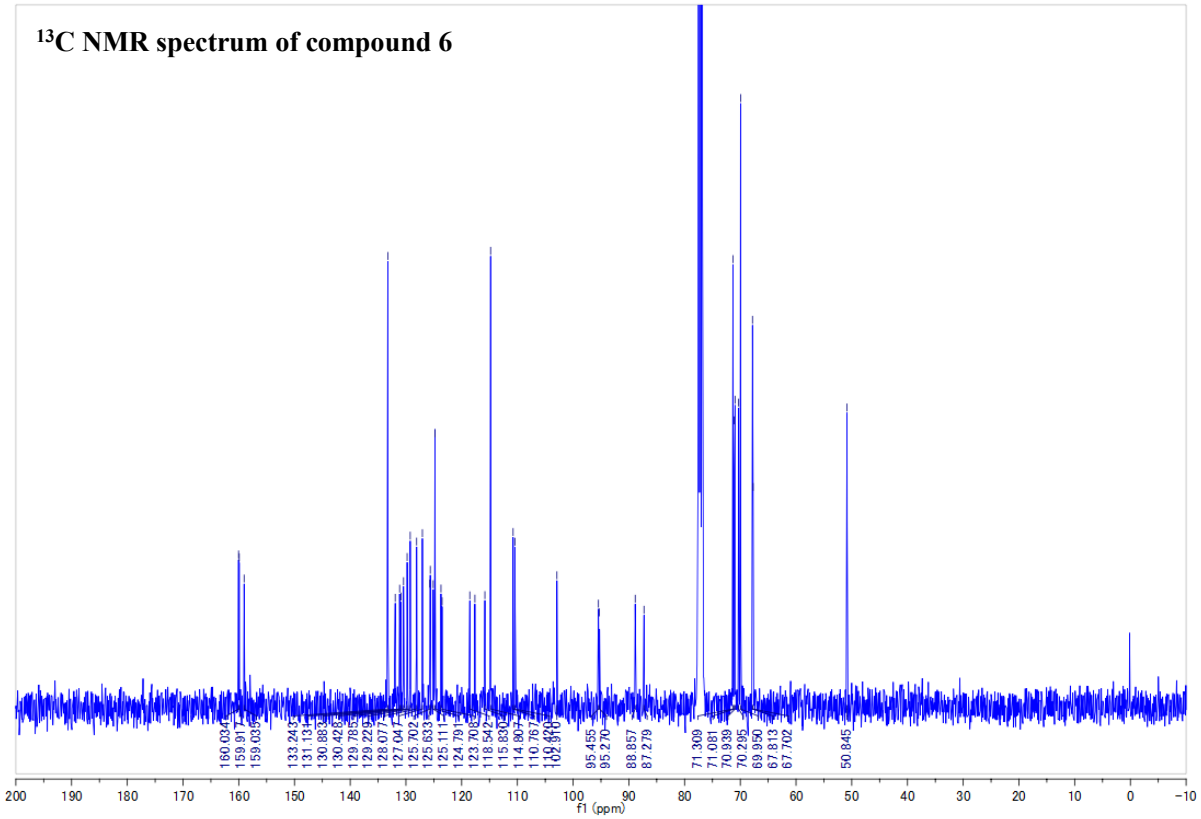
^{13}C NMR spectrum of compound 5



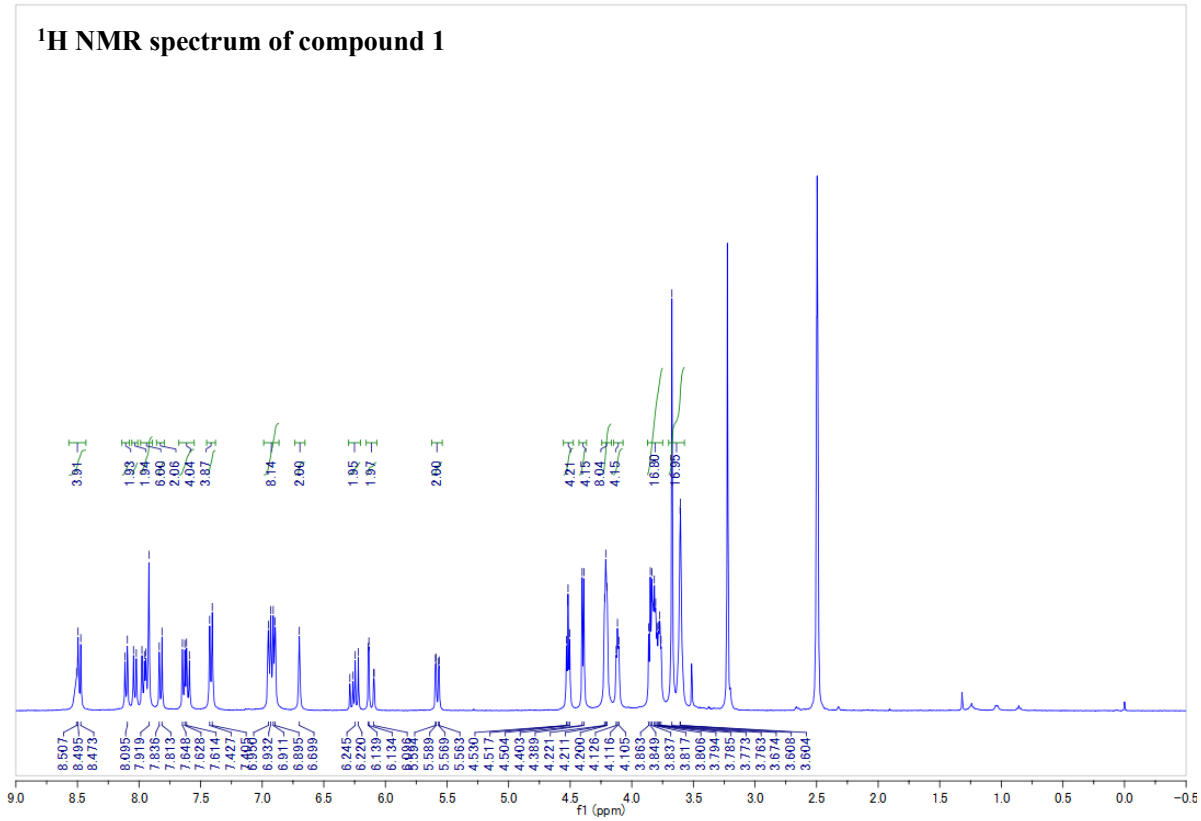
^{1}H NMR spectrum of compound 6



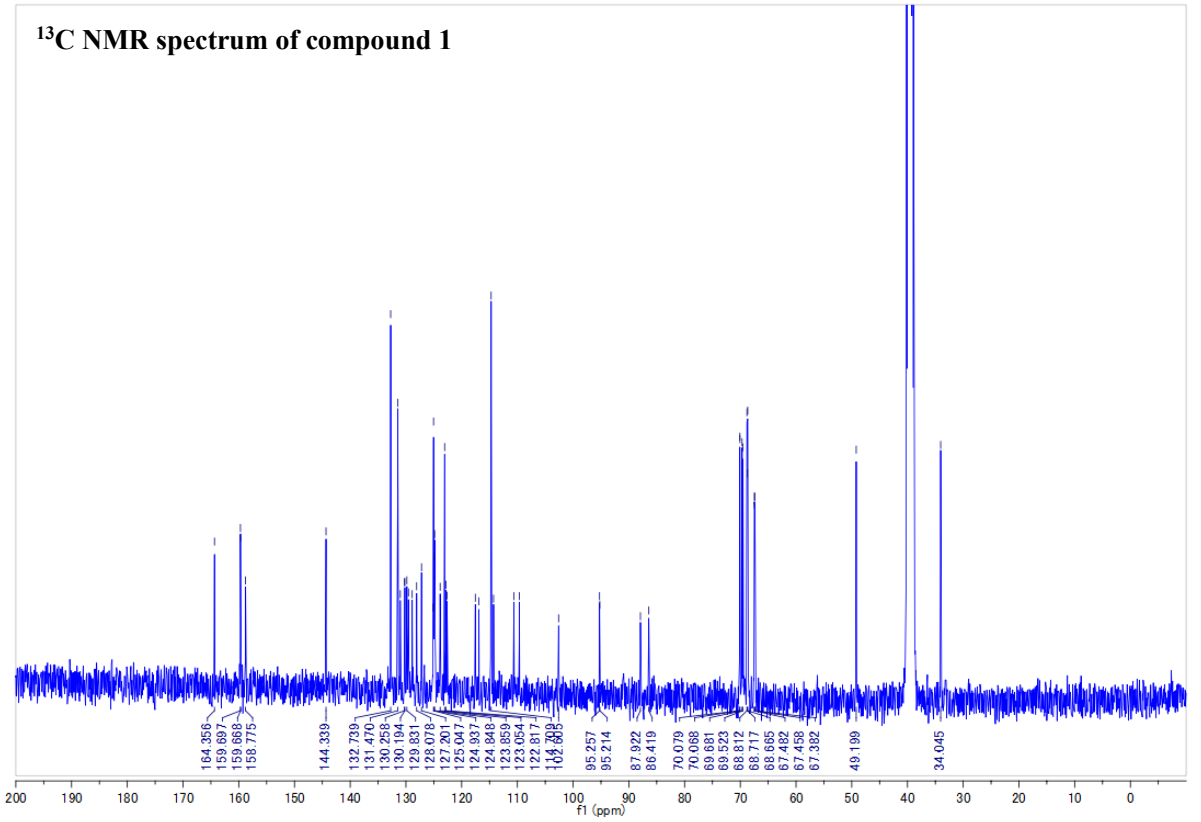
^{13}C NMR spectrum of compound 6



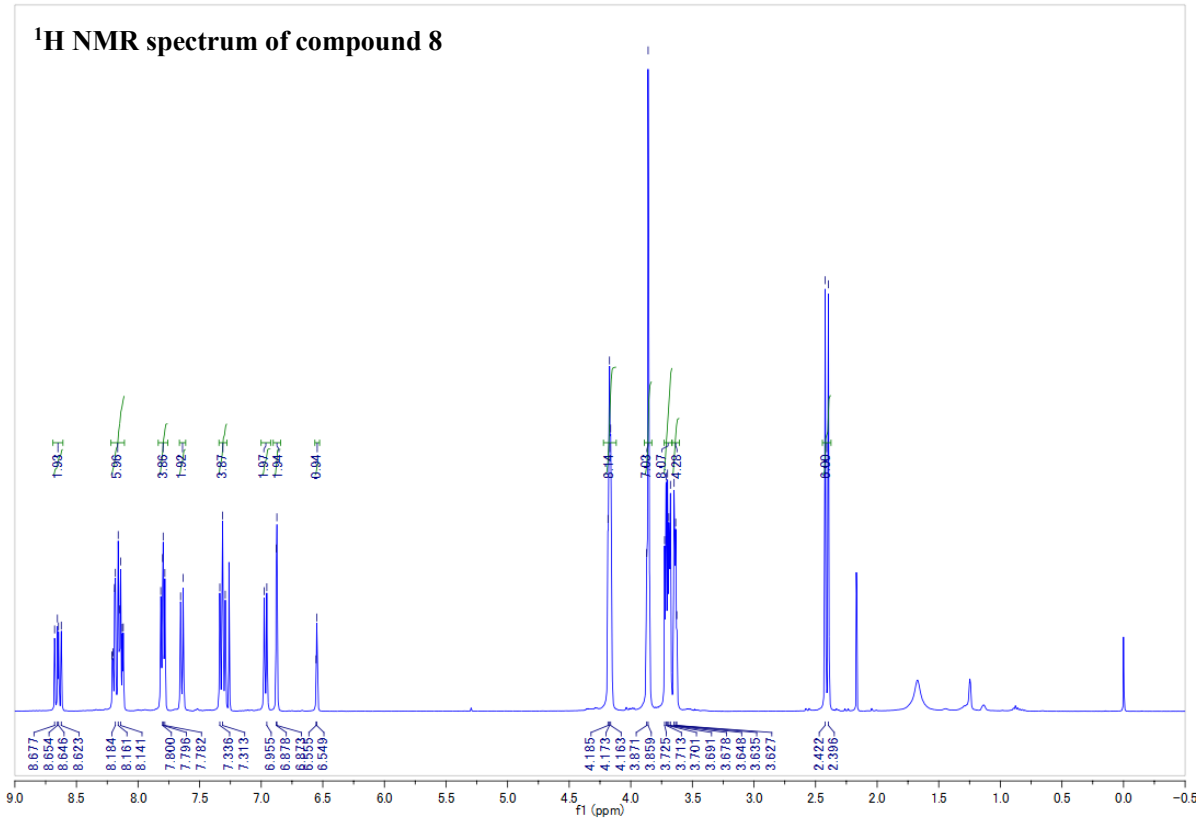
^{1}H NMR spectrum of compound 1



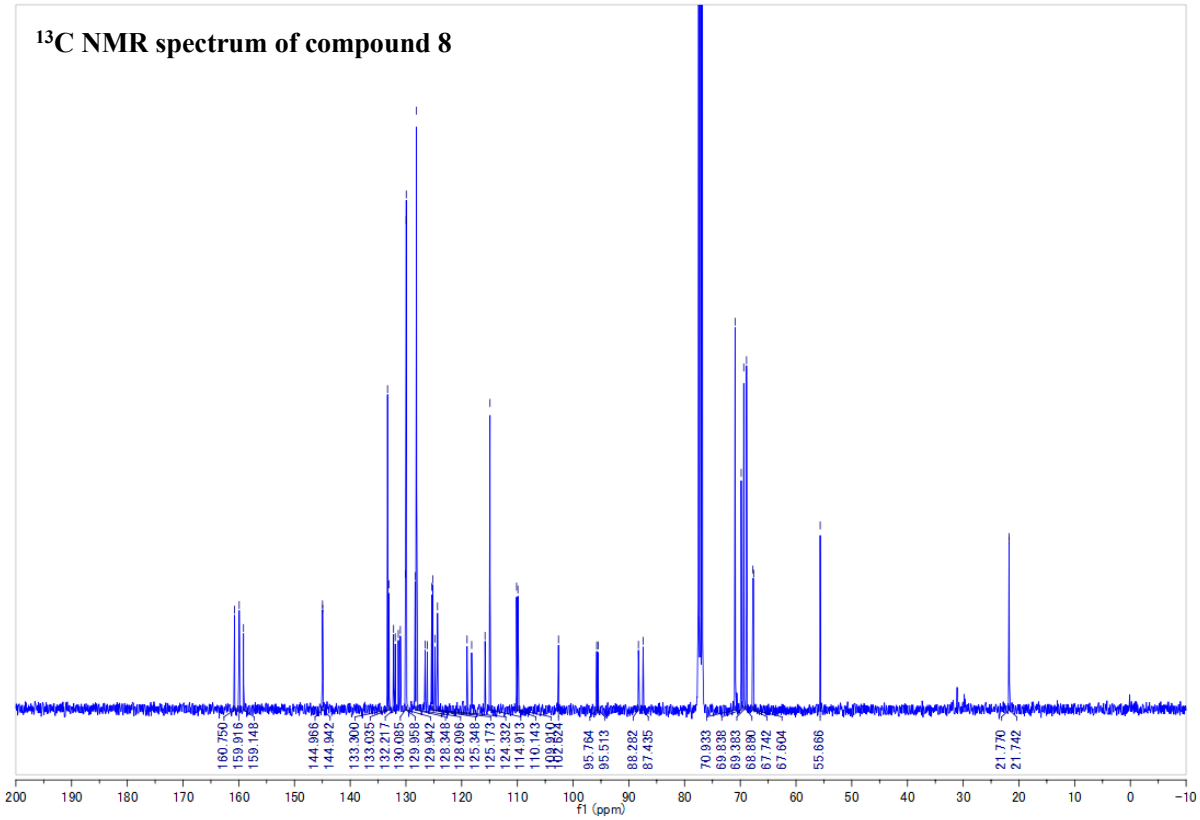
^{13}C NMR spectrum of compound 1



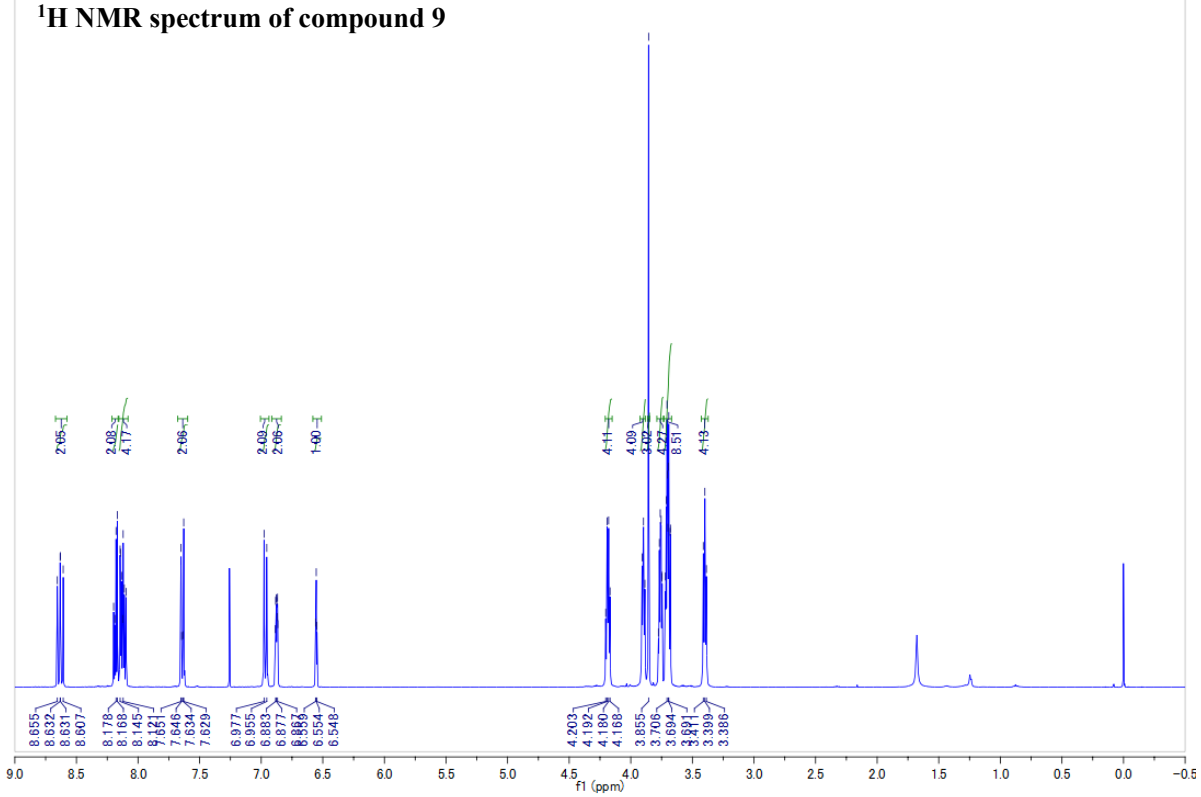
^{1}H NMR spectrum of compound 8



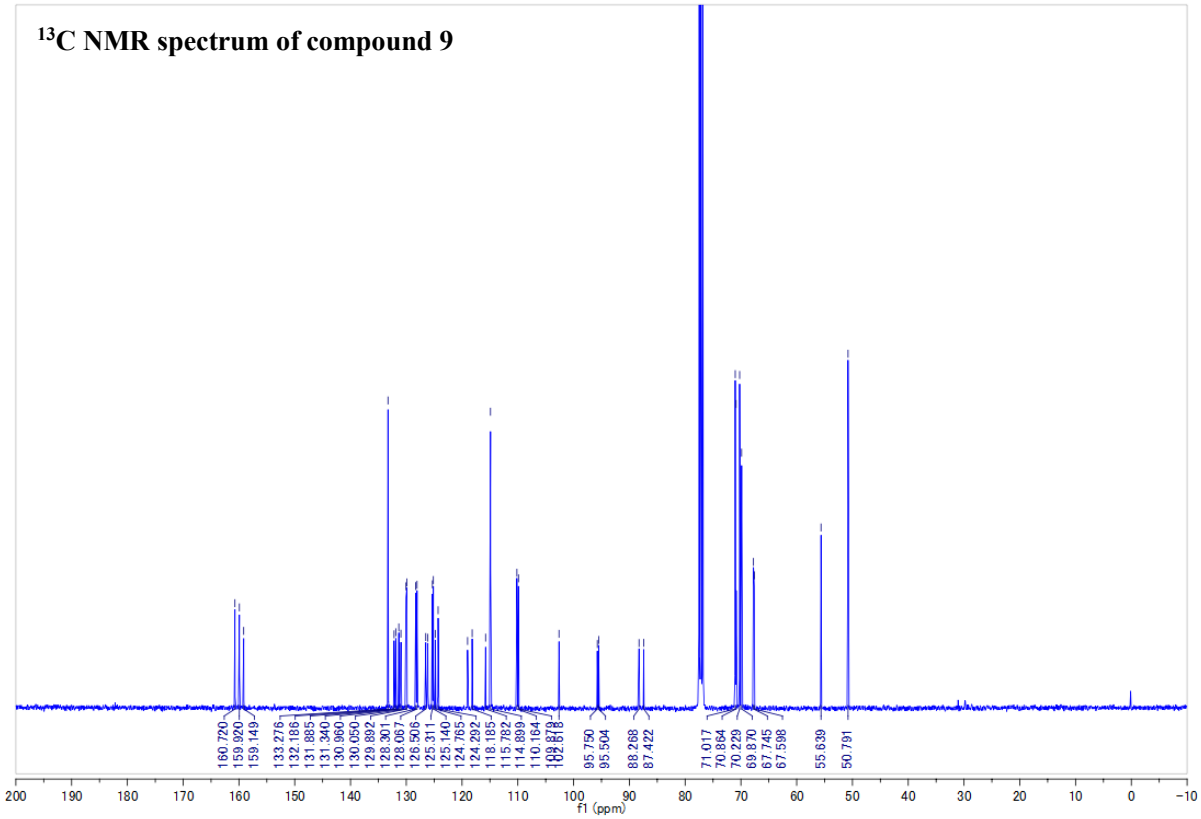
^{13}C NMR spectrum of compound 8



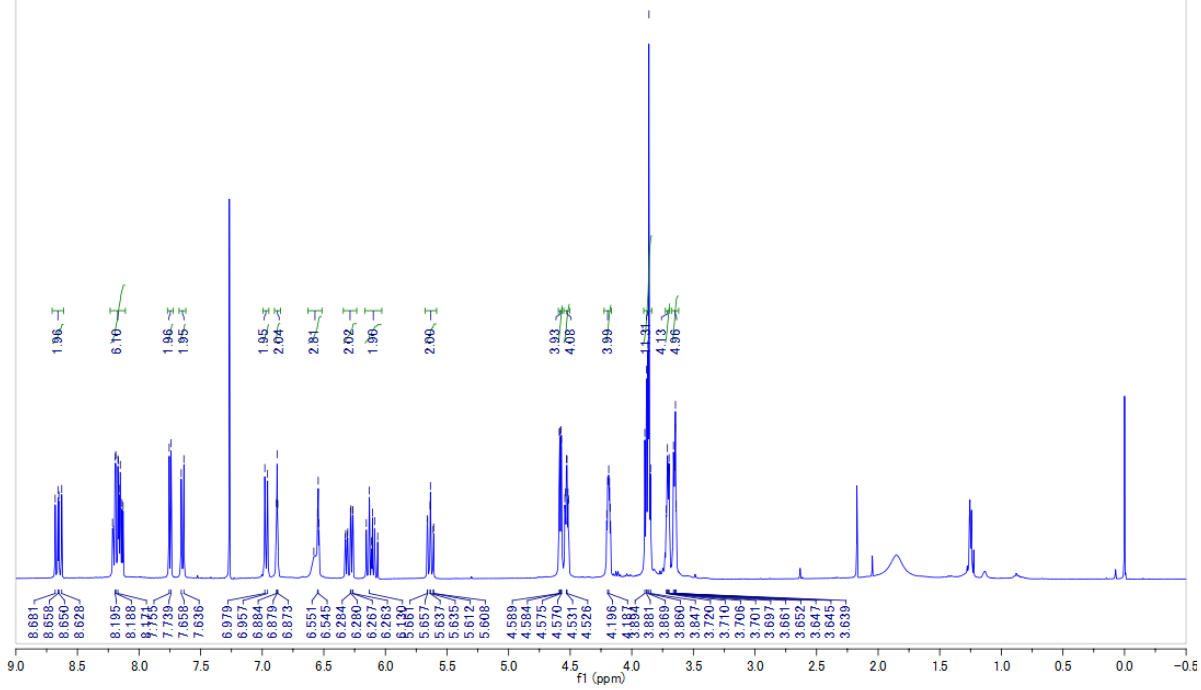
^{1}H NMR spectrum of compound 9



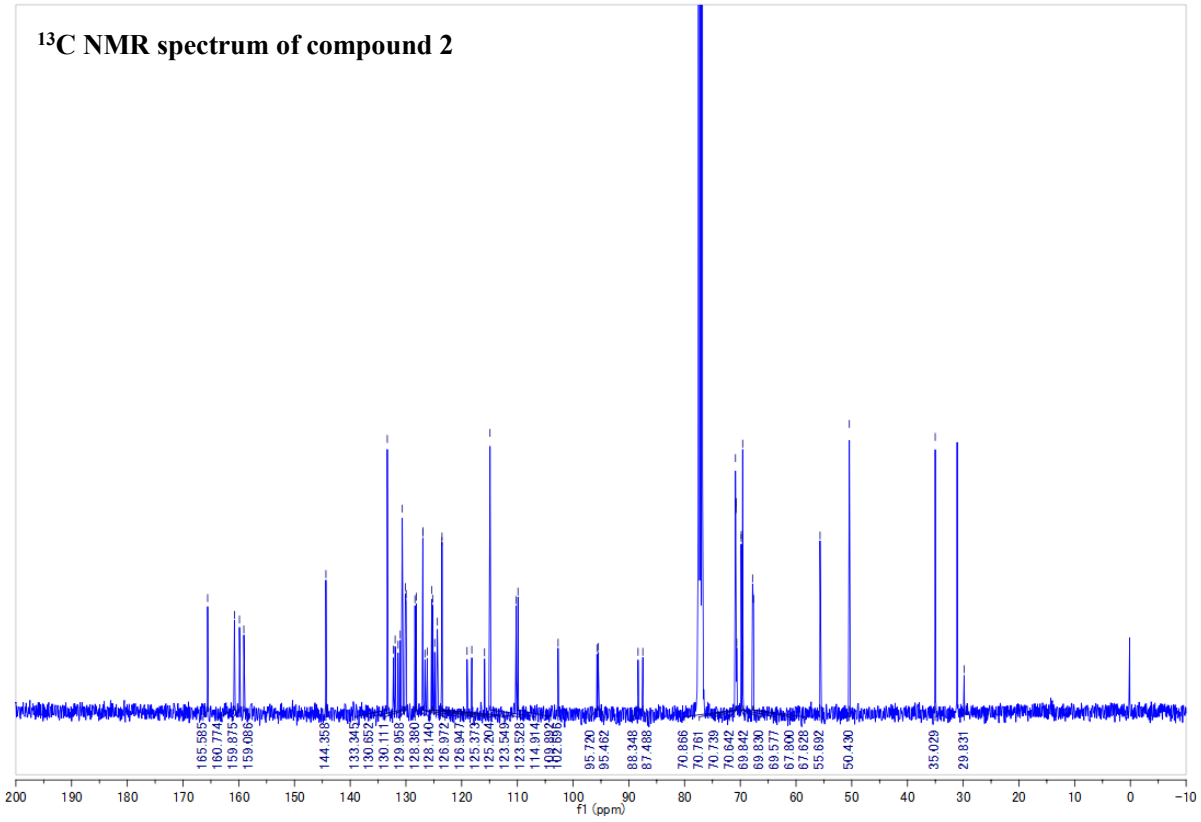
^{13}C NMR spectrum of compound 9



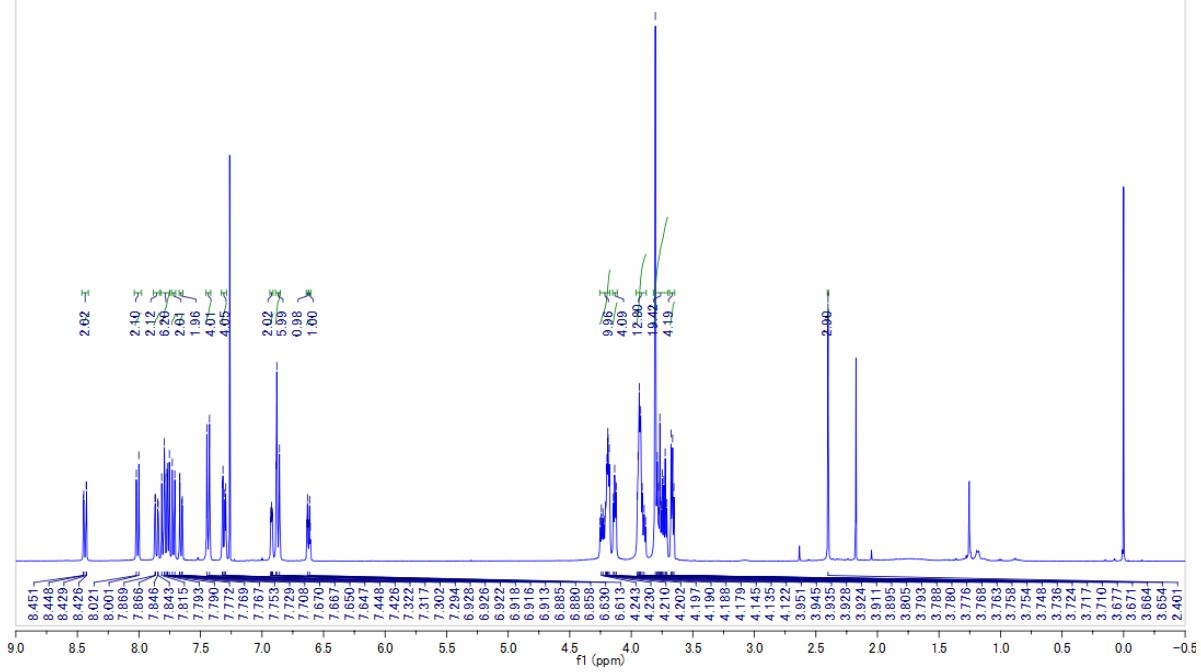
^{1}H NMR spectrum of compound 2



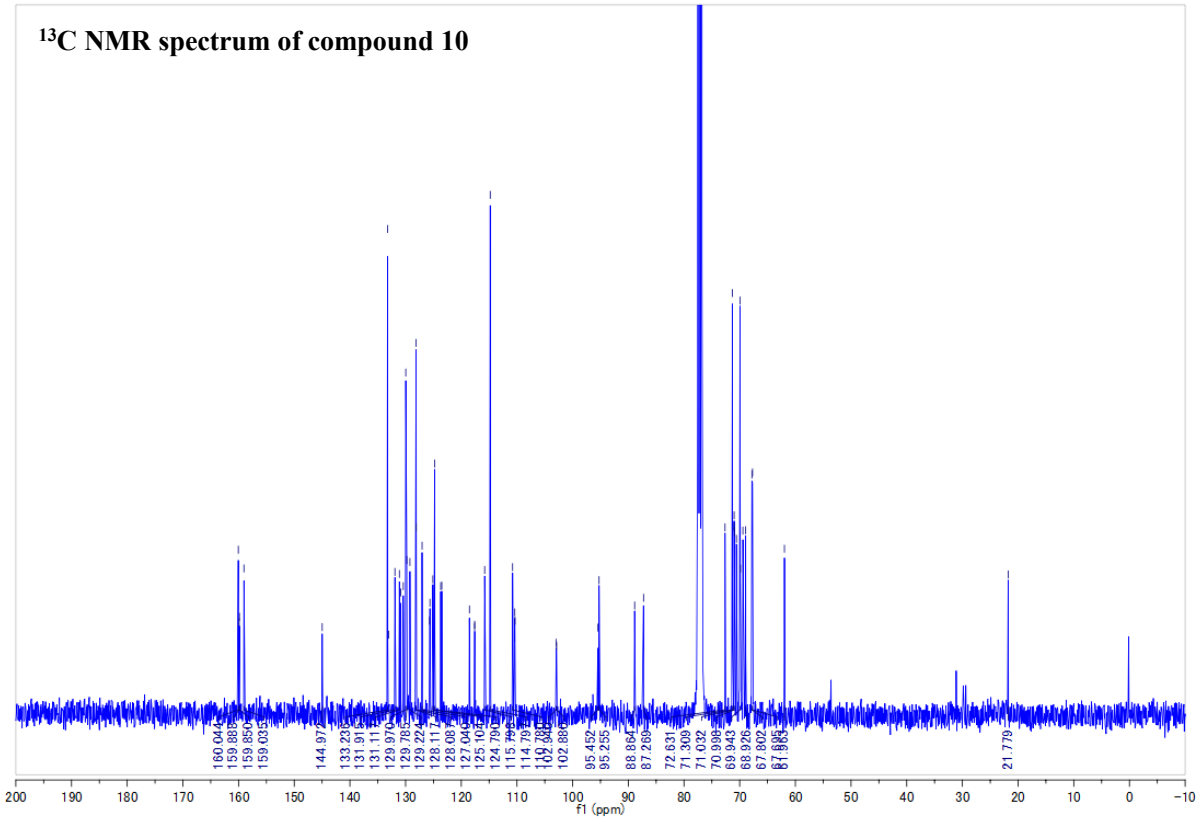
^{13}C NMR spectrum of compound 2



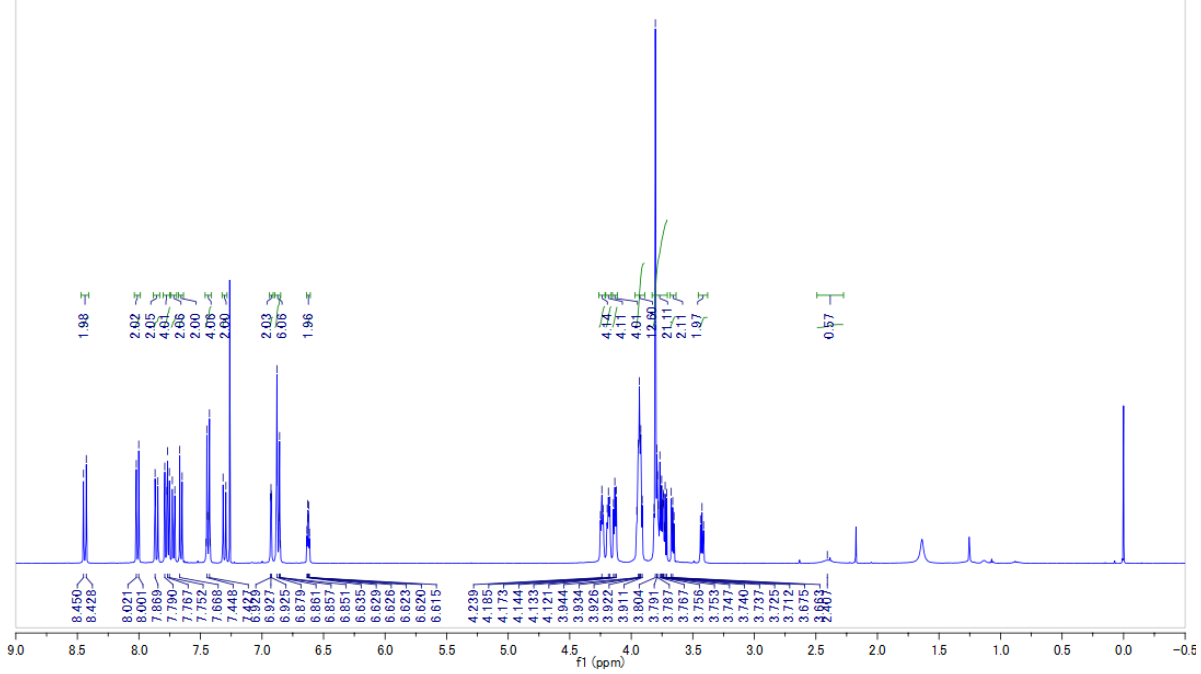
^{1}H NMR spectrum of compound 10



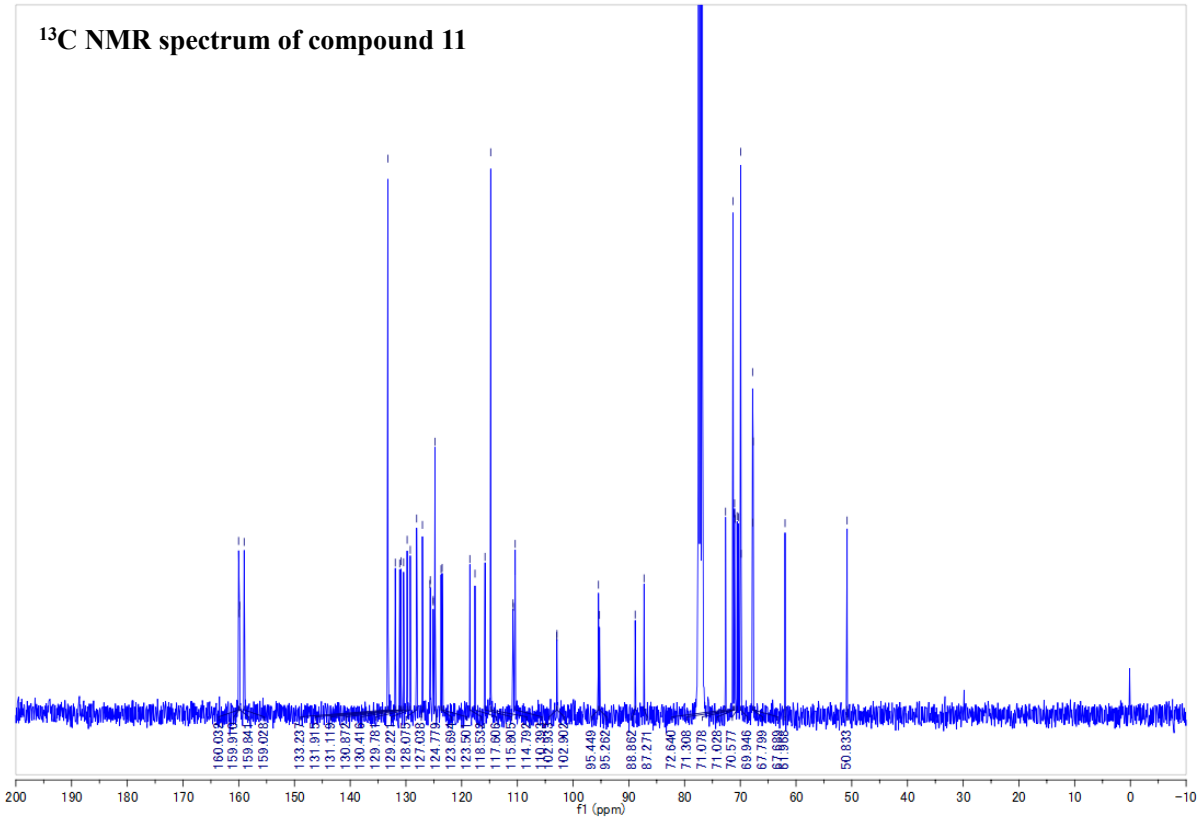
^{13}C NMR spectrum of compound 10



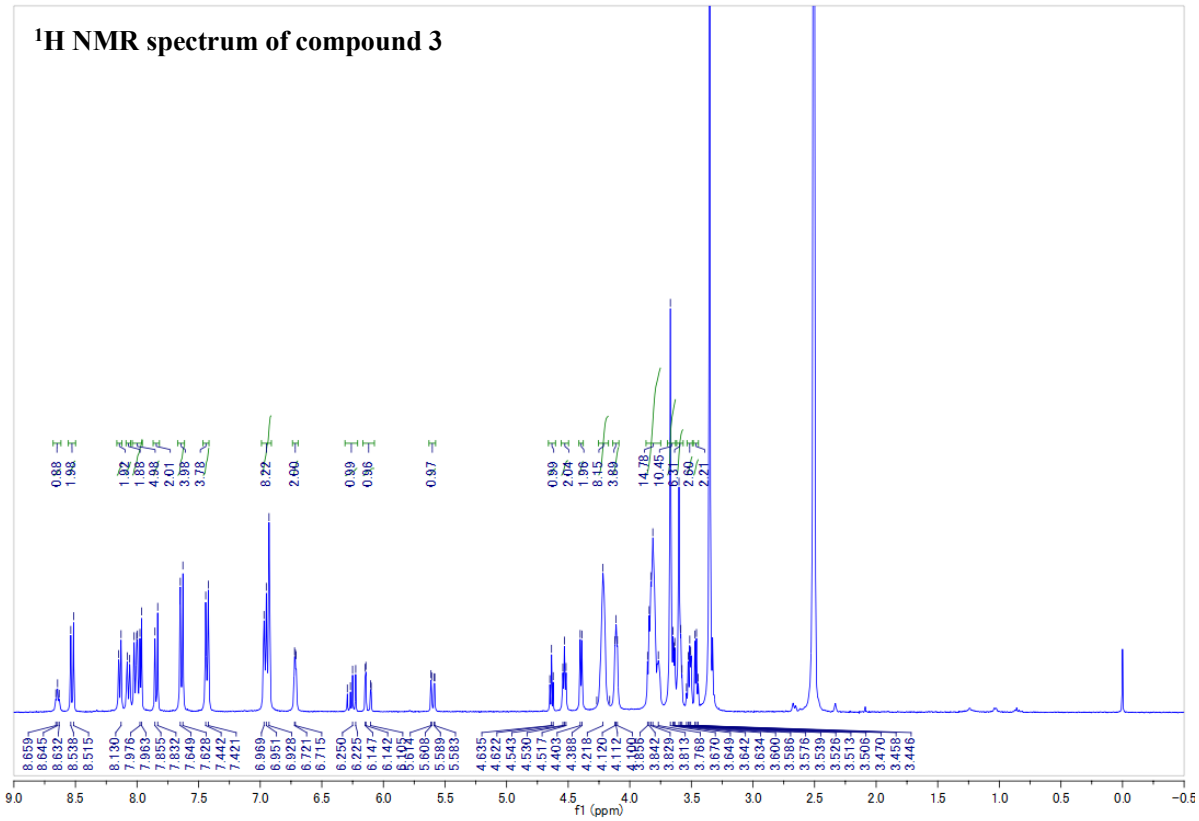
^{1}H NMR spectrum of compound 11



^{13}C NMR spectrum of compound 11



^{1}H NMR spectrum of compound 3



^{13}C NMR spectrum of compound 3