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Supporting Information

Ring-Size Dependent Ratiometric Photoluminescence of Cyclophane Mechanophores

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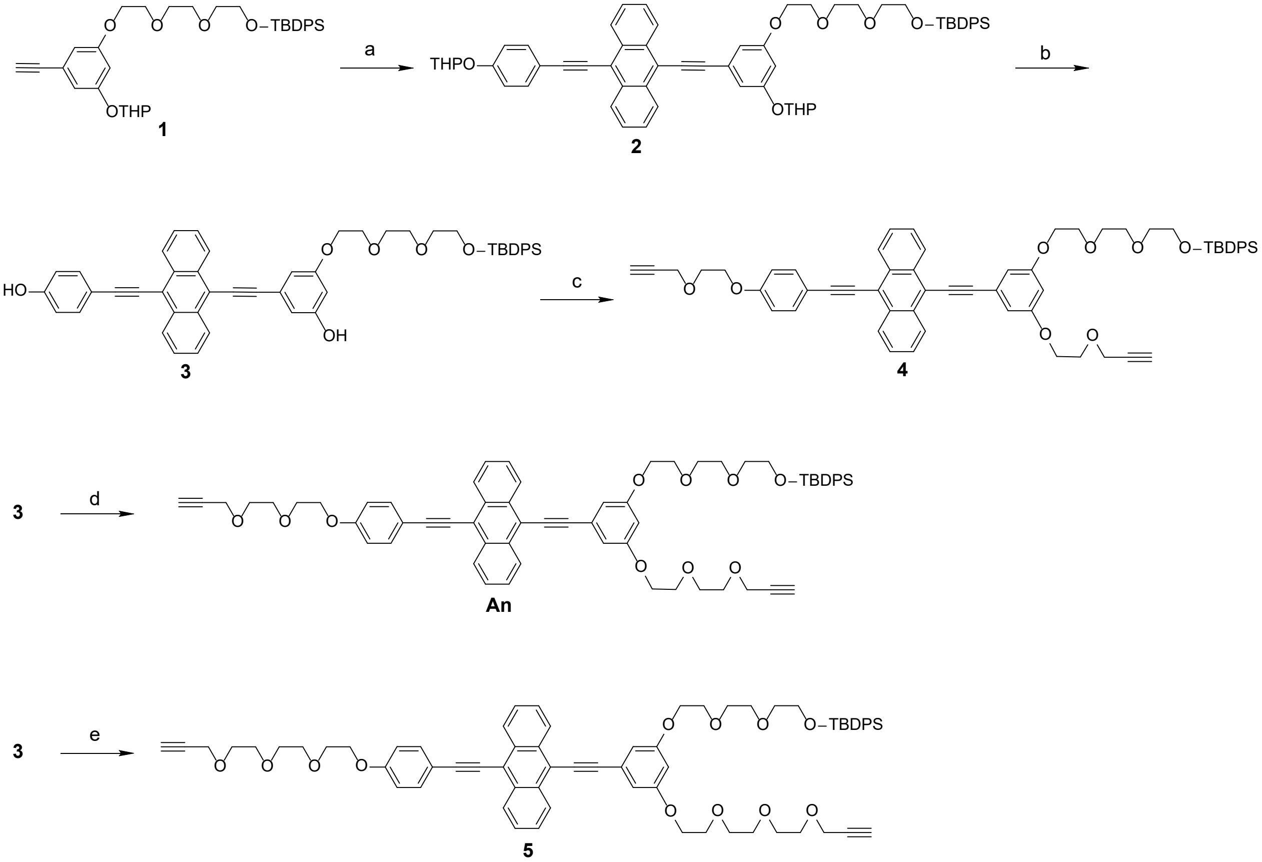
General methods

All reagents and solvents were purchased from Kanto Chemical, Merck, Tokyo Kasei, or FUJIFILM Wako Pure Chemical Corporation and were used without further purification. All reactions were carried out under nitrogen atmosphere unless specified otherwise. Flash silica gel column chromatography was conducted using a Biotage Isolera Flash system using SHOKO-scientific Purif-Pack-Ex cartridges. Silica gel from Kanto Chemicals (silica gel 60 N, spherical, 40–50 μm) was used for conventional column chromatography. Recycling preparative gel permeation chromatography (GPC) was performed using a Japan Analytical Industry LaboACE. For polymer synthesis, inhibitor-free anhydrous tetrahydrofuran (FUJIFILM Wako Pure Chemical Corporation) was used as the solvent. Hydroxyl-terminated poly(tetrahydrofuran) (M_n = 2,000 g/mol) was dried *in vacuo* at 100 °C for 2 h prior to polymer preparation. The remaining reagents for polymer synthesis, 1,4-butanediol, and 4,4'-bis(phenyl isocyanate) were distilled under vacuum and stored over molecular sieves at room temperature (r.t.) and 4 °C, respectively. Dibutyltin dilaurate was used as the catalyst for the polymerizations without any purification. ^{1}H NMR spectra were obtained using a JEOL JNM-ECZ400S/L1 spectrometer. All chemical shifts are reported on the δ-scale in parts per million (ppm) relative to the signal of tetramethylsilane (TMS at 0.00 ppm) or residual solvent protons (THF at 1.72 ppm) as an internal standard. Coupling constants (J) are denoted in Hz and relative intensities are reported. Proton-decoupled ^{13}C NMR spectra were acquired on a JEOL JNM-ECZ400S/L1 spectrometer and all chemical shifts are expressed in ppm using solvents as the internal standards ($CDCl_3$ at 77.16 ppm; DMSO-d_6 at 39.52 ppm). 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 spectra were obtained on a high performance TOF-MS system Bruker Daltonics micrOTOF II. Absorption spectra were measured using a JASCO V-750 spectrophotometer. 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 polyurethane films during stretching were monitored with an Ocean Optics QEPro-FL equipped with an LLS-365 LED light source and a Reflection/Backscattering Probe R400-7-UV-VIS; these spectra were not corrected. Time-resolved fluorescence decay measurements were carried out with a Hamamatsu Photonics Quantaurus-Tau. Quantum efficiencies were recorded with a Hamamatsu Photonics Quantaurus-QY. Size-exclusion chromatography (SEC) experiments were performed on a SHIMADZU Nexera GPC system equipped with a GPC KF–805L column (ID = 8.0 mm, L = 300 mm, particle size = 10 μm). Samples were injected using THF as the eluent at 40 °C and a flow rate of 1.0 mL/min. For the data analysis, Labsolutions software (SHIMADZU) was used and molecular weights were calculated based on narrow-molecular-weight polystyrene calibration (1100–2,500,000 g/mol). Thermogravimetric analyses (TGA) were conducted under nitrogen with a Mettler-Toledo Star^e system at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed under N_2 on a Hitachi DSC7020 at heating and cooling rates of 10 °C/min. Dynamic mechanical analyses (DMA) were carried out under N_2 with a TA Instruments DMA Q800 at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm. 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 2 mm/s. Videos and photographs were captured with a Canon EOS 9000D camera stabilized with a tripod.

Synthesis of Cy1, Cy2, Cy3, and An

The synthetic routes used to prepare compounds **Cy1**, **Cy2**, **Cy3**, and **An** are shown in the Schemes S1 and S2. 9-bromo-10-{2-[4-(tetrahydro-2*H*-pyranyloxy)phenyl]ethynyl}anthracene, 2-(prop-2-yn-1-yloxy)ethyl 4-methylbenzenesulfonate, 2-[2-(prop-2-yn-1-yloxy)ethoxy]ethyl 4-methylbenzenesulfonate, 2-{2-[2-(prop-2-yn-1-yloxy)ethoxy]ethoxy}ethyl 4-methylbenzenesulfonate, compound **1**, and compound **6** were prepared according to reported procedures.[S1–S3]

Scheme S1



Conditions: (a) 9-bromo-10-{2-[4-(tetrahydro-2*H*-pyranyloxy)phenyl]ethynyl}anthracene, $Pd(PPh_3)_4$, CuI, diisopropylamine, THF, 80 °C, 22 h; (b) pyridinium *p*-toluenesulfonate, THF, H_2O, 80 °C, 2 h; (c) 2-(prop-2-yn-1-yloxy)ethyl 4-methylbenzenesulfonate, K_2CO_3, DMF, 80 °C, 18 h; (d) 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethyl 4-methylbenzenesulfonate, K_2CO_3, DMF, 80 °C, 18 h; (e) 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate, K_2CO_3, DMF, 80 °C, 18 h.

Compound 2. A mixture of compound **1** (1.07 g, 2.14 mmol), 9-bromo-10-{2-[4-(tetrahydro-2*H*-pyranyloxy)phenyl]ethynyl}anthracene (979 mg, 2.14 mmol), $Pd(PPh_3)_4$ (124 mg, 0.107 mmol), CuI (20.4 mg, 0.107 mmol), and diisopropylamine (10 mL) in THF (30 mL) was stirred under nitrogen atmosphere at 80 °C for 22 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (200 mL) and washed with 5% aq. HCl (2 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column

chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 4:1 v/v to hexane/ethyl acetate = 1:1 v/v) and by recycling preparative GPC (eluent: chloroform) to afford compound **2** (1.03 g, 1.07 mmol, 50 %) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H), 1.61–1.76 (m, 6H), 1.87–1.92 (m, 4H), 1.99–2.07 (m, 2H), 3.62–3.75 (m, 8H), 3.83 (t, J = 5.2 Hz, 2H), 3.88–3.97 (m, 4H), 4.17–4.19 (m, 2H), 5.49–5.52 (m, 2H), 6.74 (t, J = 2.0 Hz, 1H), 6.96–6.96 (m, 1H), 7.08–7.09 (m, 1H), 7.13 (d, J = 8.8 Hz, 2H), 7.35–7.43 (m, 6H), 7.61–7.65 (m, 4H), 7.68–7.72 (m, 6H), 8.64–8.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.75, 18.78, 19.33, 25.27, 25.30, 26.94, 30.35, 30.43, 62.17, 63.57, 67.79, 69.82, 70.97, 71.05, 72.63, 85.51, 86.22, 96.33, 96.53, 102.36, 102.81, 104.80, 111.10, 112.55, 116.45, 116.73, 117.97, 119.11, 124.71, 126.80, 126.94, 127.37, 127.44, 127.76, 129.75, 132.03, 132.28, 133.22, 133.78, 135.74, 157.61, 158.21, 159.87. MS (MALDI-TOF): m/z: 964.48 (calcd. $[M]^+$ = 964.44).

Compound 3. Pyridinium *p*-toluenesulfonate (2.19 g, 8.70 mmol) was added to a solution of compound **2** (840 mg, 0.870 mmol) in a mixture of THF (20 mL) and water (10 mL) and the reaction mixture was stirred at 80 °C for 2 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (100 mL) and then washed with saturated aq. NaCl (2 × 100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and 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 = 19:1 v/v) to afford compound **3** (630 mg, 0.790 mmol, 91 %) as a yellow solid.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.98 (s, 9H), 3.55–3.64 (m, 6H), 3.75–3.80 (m, 4H), 4.15 (t, J = 4.4 Hz, 2H), 6.52 (t, J = 2.0 Hz, 1H), 6.87–6.88 (m, 1H), 6.89–6.90 (m, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.34–7.45 (m, 6H), 7.64–7.67 (m, 4H), 7.72–7.80 (m, 6H), 8.63–8.69 (m, 4H), 9.93 (s, 1H), 10.19 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.83, 26.67, 63.33, 67.44, 69.07, 70.09, 70.13, 71.76, 84.27, 85.17, 102.83, 103.74, 104.02, 108.40, 111.21, 112.48, 116.09, 116.74, 118.54, 123.57, 126.81, 127.01, 127.53, 127.75, 127.88, 129.83, 131.06, 131.47, 133.19, 133.58, 135.18, 158.77, 158.82, 159.90. MS (MALDI-TOF): m/z: 796.41 (calcd. $[M]^+$ = 796.32).

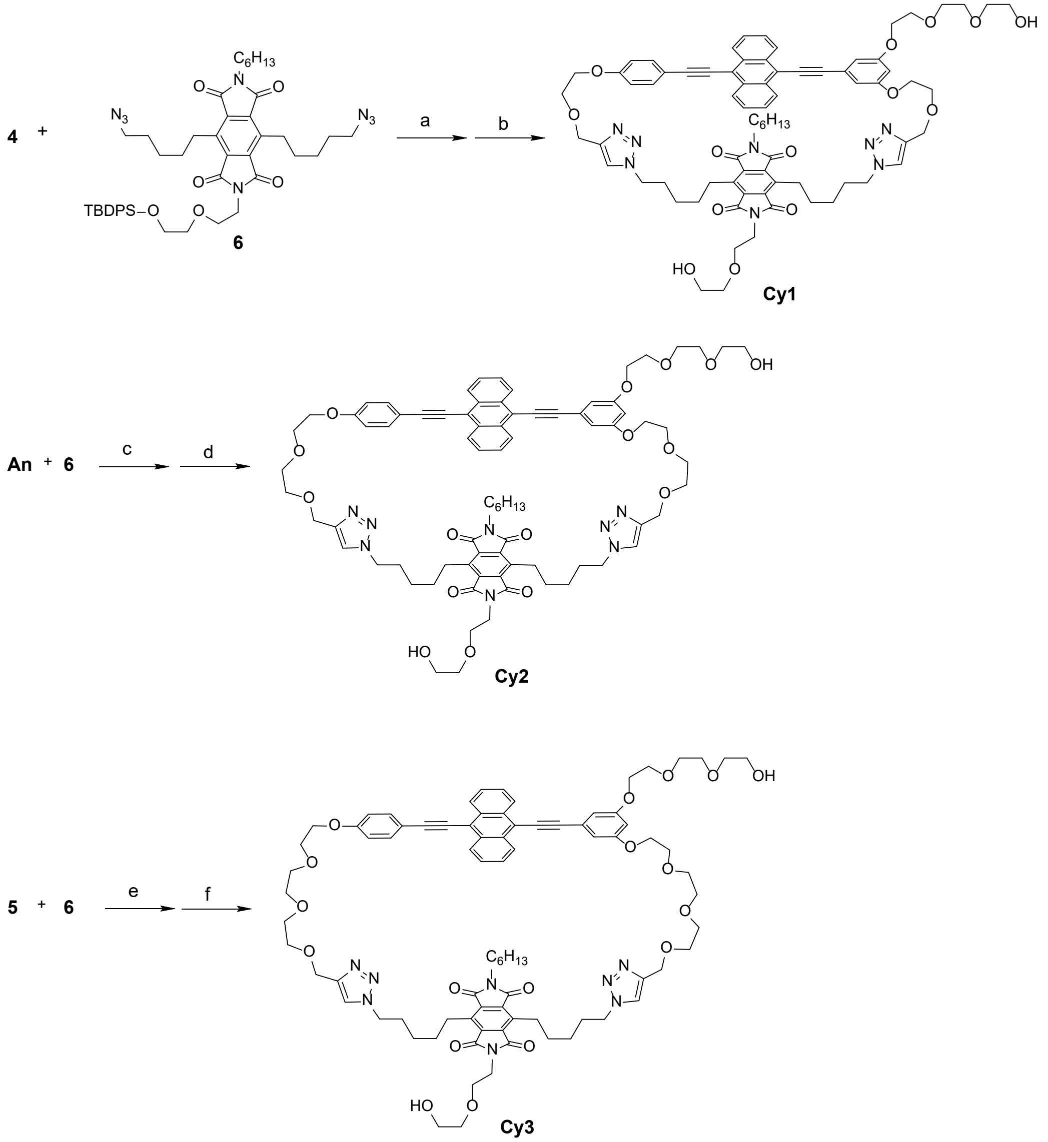
Compound 4. A mixture of compound **3** (200 mg, 0.251 mmol), 2-(prop-2-yn-1-yloxy)ethyl 4-methylbenzenesulfonate (192 mg, 0.753 mmol), and K_2CO_3 (104 mg, 0.753 mmol) in DMF (100 mL) was stirred at 80 °C for 18 h. After cooling to r.t., most of the DMF was evaporated under reduced pressure. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with saturated NH_4Cl (4 × 200 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 7:3 v/v to hexane/ethyl acetate = 9:11 v/v) to afford compound **4** (206 mg, 0.214 mmol, 85 %) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9H), 2.49 (t, J = 2.0 Hz, 2H), 3.63 (t, J = 5.2 Hz, 2H), 3.68– 3.74 (m, 4H), 3.83 (t, J = 5.2 Hz, 2H), 3.88 (t, J = 4.8 Hz, 2H), 3.91– 3.93 (m, 4H), 4.16 (t, J = 4.8 Hz, 2H), 4.19 (t, J = 4.8 Hz, 4H), 4.29 (t, J = 2.4 Hz, 4H), 6.58 (t, J = 2.4 Hz, 1H), 6.92–6.93 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.35–7.43 (m, 6H), 7.60–7.64 (m, 4H), 7.68–7.71 (m, 6H), 8.62–8.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.30, 26.92, 58.69, 58.71, 63.55, 67.35, 67.49, 67.74, 68.17, 69.76, 70.92, 71.00, 72.60, 75.07, 79.44, 79.50, 85.52, 86.29, 102.25, 102.77, 103.08, 110.47, 110.60, 114.92, 115.89, 117.81, 119.13, 124.75, 126.77, 126.94, 127.27, 127.41, 127.75, 129.73, 131.96, 132.23, 133.28, 133.75, 135.71, 159.18, 159.77, 159.92. MS (MALDI-TOF): m/z: 960.15 (calcd. $[M]^+$ = 960.41).

Compound An. A mixture of compound **3** (200 mg, 0.251 mmol), 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethyl 4-methylbenzenesulfonate (223 mg, 0.753 mmol), and K_2CO_3 (104 mg, 0.753 mmol) in DMF (100 mL) was stirred at 80 °C for 18 h. After cooling to r.t., most of the DMF was evaporated under reduced pressure. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with saturated NH_4Cl (4 × 200 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The

crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 3:2 v/v to hexane/ethyl acetate = 3:7 v/v) to afford compound **An** (166 mg, 0.158 mmol, 63%) as a yellow solid.
^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.05 (s, 9H), 2.44–2.46 (m, 2H), 3.63 (t, J = 5.2 Hz, 2H), 3.70– 3.84 (m, 14H), 3.89–3.93 (m, 6H), 4.16–4.25 (m, 10H), 6.58 (t, J = 2.0 Hz, 1H), 6.93–6.94 (m, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.35–7.43 (m, 6H), 7.62–7.65 (m, 4H), 7.68–7.72 (m, 6H), 8.65–8.70 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.33, 26.95, 58.61, 63.58, 67.65, 67.78, 69.28, 69.81, 70.80, 70.83, 70.96, 71.05, 72.63, 74.78, 79.72, 85.50, 86.27, 102.29, 102.82, 103.16, 110.54, 115.01, 115.83, 117.87, 119.17, 124.75, 126.81, 126.98, 127.32, 127.46, 127.77, 129.75, 132.02, 132.29, 133.31, 133.79, 135.74, 159.35, 159.91, 159.96. MS (MALDI-TOF): m/z: 1048.53 (calcd. [M+Na]$^+$ = 1048.46).

Compound 5. A mixture of compound **3** (200 mg, 0.251 mmol), 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (258 mg, 0.753 mmol), and K$_2$CO$_3$ (104 mg, 0.753 mmol) in DMF (100 mL) was stirred at 80 °C for 18 h. After cooling to r.t., most of the DMF was evaporated under reduced pressure. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with saturated NH$_4$Cl (4 × 200 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over MgSO$_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 1:1 v/v to hexane/ethyl acetate = 1:4 v/v) to afford compound **5** (186 mg, 0.160 mmol, 64 %) as a yellow solid.
^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.05 (s, 9H), 2.43 (t, J = 2.4 Hz, 1H), 2.44 (t, J = 2.4 Hz, 1H), 3.63 (t, J = 5.2 Hz, 2H), 3.67–3.76 (m, 20H), 3.83 (t, J = 5.2 Hz, 2H), 3.86–3.89 (m, 6H), 4.15–4.18 (m, 6H), 4.20 (d, J = 2.4 Hz, 2H), 4.21 (d, J = 2.4 Hz, 2H), 6.57 (t, J = 2.4 Hz, 1H), 6.91–6.93 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 7.35–7.43 (m, 6H), 7.60–7.65 (m, 4H), 7.68–7.71 (m, 6H), 8.62–8.70 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.25, 26.88, 58.46, 63.50, 67.55, 67.68, 69.14, 69.69, 70.51, 70.71, 70.88, 70.95, 72.55, 74.69, 79.70, 85.42, 86.20, 102.27, 102.81, 103.05, 110.41, 114.91, 115.67, 117.76, 119.09, 124.65, 126.73, 126.91, 127.22, 127.37, 127.70, 129.68, 131.91, 132.18, 133.21, 133.70, 135.65, 159.29, 159.86. MS (MALDI-TOF): m/z: 1136.57 (calcd. [M]$^+$ = 1136.51).

Scheme S2



Conditions: (a) CuI, *N,N*-diisopropylethylamine, $CHCl_3$, 55 °C, 24 h; (b) triethylamine trihydrofluoride, triethylamine, THF, 70 °C, 24 h; (c) CuI, *N,N*-diisopropylethylamine, $CHCl_3$, 55 °C, 24 h; (d) triethylamine trihydrofluoride, triethylamine, THF, 70 °C, 24 h; (e) CuI, *N,N*-diisopropylethylamine, $CHCl_3$, 55 °C, 24 h; (f) triethylamine trihydrofluoride, triethylamine, THF, 70 °C, 24 h.

Cy1. A mixture of compound **4** (226 mg, 0.236 mmol), compound **6** (200 mg, 0.236 mmol), CuI (112 mg, 0.240 mmol), and *N,N*-diisopropylethylamine (50 mL) in $CHCl_3$ (250 mL) was stirred at 55 °C for 24 h. After cooling to r.t., the reaction mixture was washed with 5% aq. HCl (3 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 TBDPS-protected precursor of **Cy1**. Triethylamine trihydrofluoride (112 mg, 0.690 mmol) was added to a solution of the precursor (150 mg, 8.29×10^{-2} mmol) and triethylamine (105 mg, 1.03 mmol) in THF (15 mL) and the mixture was stirred at 70 °C for 24 h. After cooling to r.t., the reaction mixture was poured into chloroform (100 mL), washed with saturated aq. $NaHCO_3$ (100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 = 7:3 v/v to acetone) and by recycling preparative GPC (eluent: chloroform) to afford compound **Cy1** (96.0 mg, 7.20×10^{-2} mmol, 33% in two steps) as a reddish-orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.27–1.40 (m, 14H), 1.53–1.60 (m, 2H), 1.75–1.84 (m, 4H), 2.79 (s, 1H), 2.95 (s, 1H), 3.08–3.18 (m, 4H), 3.39 (t, J = 7.6 Hz, 2H), 3.53–3.66 (m, 10H), 3.73–3.79 (m, 6H), 3.91–3.99 (m, 6H), 4.21–4.27 (m, 8H), 4.39 (t, J = 4.0 Hz, 2H), 4.77 (s, 2H), 4.85 (s, 2H), 6.60 (t, J = 2.0 Hz, 1H), 6.92 (m, 1H), 7.00 (m, 1H), 7.08 (d, J = 8.8 Hz, 2H), 7.23 (s, 1H), 7.44–7.52 (m, 5H), 7.70 (d, J = 8.8 Hz, 2H), 8.32–8.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.09, 22.60, 25.88, 25.94, 26.73, 26.91, 27.30, 28.50, 28.51, 28.91, 29.32, 29.83, 29.99, 31.37, 37.38, 38.10, 50.26, 50.68, 61.65, 61.76, 65.36, 65.48, 67.54, 67.59, 67.80, 68.16, 68.79, 69.61, 69.71, 70.16, 70.40,70.94, 72.16, 72.69, 84.90, 85.78, 102.77, 102.84, 103.69, 109.75, 112.00, 115.33, 115.67, 117.43, 118.87, 122.05, 122.44, 124.52, 126.69, 126.94, 126.98, 131.05, 131.45, 132.66, 132.72, 132.84, 132.98, 133.16, 138.64, 138.80, 145.70, 145.73, 159.58, 159.75, 159.92, 166.20, 166.22, 166.28. HRMS (ESI-TOF): m/z: 1355.5986 (calcd. $[M+Na]^+$ = 1355.5999).

Cy2. A mixture of compound **An** (111 mg, 0.106 mmol), compound **6** (90.0 mg, 0.106 mmol), CuI (50.5 mg, 0.265 mmol), and *N,N*-diisopropylethylamine (50 mL) in $CHCl_3$ (250 mL) was stirred at 55 °C for 24 h. After cooling to r.t., the reaction mixture was washed with 5% aq. HCl (3 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 = 3:1 v/v) to afford TBDPS-protected precursor of **Cy2**. Triethylamine trihydrofluoride (148 mg, 0.928 mmol) was added to a solution of the precursor (115 mg, 5.80×10^{-2} mmol) and triethylamine (93.8 mg, 0.928 mmol) in THF (15 mL) and the mixture was stirred at 70 °C for 24 h. After cooling to r.t., the reaction mixture was poured into chloroform (100 mL), washed with saturated aq. $NaHCO_3$ (100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 = 7:3 v/v to acetone) and by recycling preparative GPC (eluent: chloroform) to afford **Cy2** (60.2 mg, 4.23×10^{-2} mmol, 40% in two steps) as a reddish-orange solid.

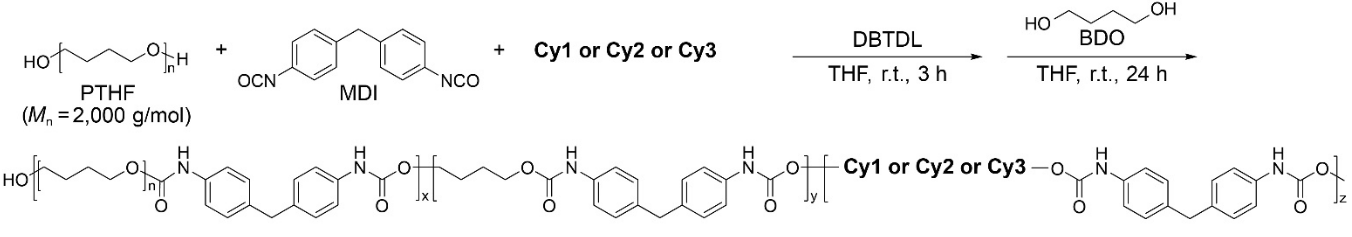
^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.26–1.35 (m, 14H), 1.51–1.58 (m, 2H), 1.74–1.81 (m, 4H), 2.67 (t, J = 5.6 Hz, 1H), 2.81 (t, J = 5.6 Hz, 1H), 3.08–3.16 (m, 4H), 3.35 (t, J = 7.6 Hz, 2H), 3.51–3.66 (m, 10H), 3.72–3.80 (m, 14H), 3.90–3.94 (m, 6H), 4.14 (t, J = 7.2 Hz, 4H), 4.23–4.28 (m, 6H), 4.78 (s, 4H), 6.67 (t, J = 2.4 Hz, 1H), 7.00 (m, 1H), 7.02–7.03 (m, 1H), 7.08 (d, J = 8.8 Hz, 2H), 7.41 (s, 1H), 7.45–7.52 (m, 4H), 7.57 (s, 1H), 7.74 (d, J = 8.8 Hz, 2H), 8.37–8.40 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 22.61, 25.93, 26.15, 26.72, 26.86, 27.11, 28.49, 28.86, 29.09, 29.47, 29.78, 31.38, 37.32, 38.06, 50.40, 50.51, 61.68, 61.80, 64.85, 65.12, 67.82, 68.03, 68.15, 68.19, 69.44, 69.55, 69.69, 69.73, 69.79, 70.46, 70.97, 71.05, 71.44, 72.19, 72.68, 85.40, 86.07, 102.81, 102.99, 103.52, 110.50, 110.65, 115.22, 115.71, 117.51, 118.89, 124.73, 126.70, 126.93, 126.99, 127.06, 131.17, 131.53, 132.84, 132.87, 133.02, 133.08, 133.51, 138.83, 138.86, 159.69, 160.04, 160.18, 166.21, 166.25, 166.28, 166.30. HRMS (ESI-TOF): m/z: 1443.6538 (calcd. $[M+Na]^+$ = 1443.6523).

Cy3. A mixture of compound **5** (123 mg, 0.106 mmol), compound **6** (90.0 mg, 0.106 mmol), CuI (50.5 mg, 0.265 mmol), and *N,N*-diisopropylethylamine (50 mL) in $CHCl_3$ (250 mL) was stirred at 55 °C for 24 h. After cooling to r.t., the reaction mixture was washed with 5% aq. HCl (3 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl

(100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 = 7:3 v/v) to afford TBDPS-protected precursor of **Cy3**. Triethylamine trihydrofluoride (195 mg, 1.22 mmol) was added to a solution of the precursor (151 mg, 7.60×10^{-2} mmol) and triethylamine (123 mg, 1.22 mmol) in THF (15 mL) and the mixture was stirred at 70 °C for 24 h. After cooling to r.t., the reaction mixture was poured into chloroform (100 mL), washed with saturated aq. $NaHCO_3$ (100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and 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 = 7:3 v/v to acetone) and by recycling preparative GPC (eluent: chloroform) to afford **Cy3** (98.3 mg, 6.49×10^{-2} mmol, 61% in two steps) as a reddish-orange solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.28–1.38 (m, 14H), 1.55 (s, 2H), 1.75–1.80 (m, 4H), 2.38 (s, 1H), 2.81 (s, 1H), 3.09–3.17 (m, 4H), 3.36 (t, J = 7.6 Hz, 2H), 3.54–3.66 (m, 10H), 3.68–3.80 (m, 22H), 3.91–3.97 (m, 6H), 4.13–4.18 (m, 4H), 4.22–4.24 (m, 6H), 4.74 (s, 2H), 4.76 (s, 2H), 6.63 (t, J = 2.0 Hz, 1H), 6.96–6.98 (m, 2H), 7.15 (d, J = 8.8 Hz, 2H), 7.46–7.52 (m, 5H), 7.60 (s, 1H), 7.69 (d, J = 8.8 Hz, 2H), 8.37–7.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.09, 22.59, 25.89, 26.04, 26.66, 26.70, 27.74, 28.47, 28.73, 28.89, 29.29, 29.76, 31.36, 37.32, 38.05, 50.03, 50.15, 61.62, 61.76, 64.87, 64.97, 67.76, 67.95, 68.06, 68.11, 69.59, 69.67, 69.71, 69.81, 70.43, 70.71, 70.81, 70.85, 70.93, 71.02, 71.03, 72.17, 72.67, 85.27, 85.98, 102.79, 103.17, 103.54, 110.46, 110.60, 115.05,115.57, 117.52, 118.87, 122.84, 124.60, 126.69, 126.91, 126.99, 127.04, 131.18, 131.55, 132.91, 132.97, 133.07, 133.15, 133.42, 138.86, 138.88, 159.53, 159.95, 160.00, 166.23, 166.25, 166.31, 166.34. HRMS (ESI-TOF): m/z: 777.3466 (calcd. $[M+2Na]^{2+}$ = 777.3470).

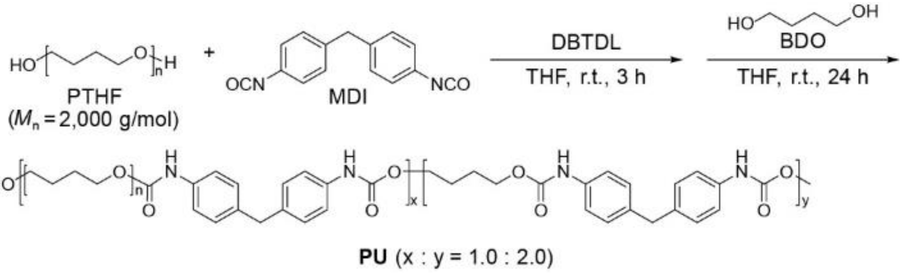
Polymer synthesis



Cy1-PU (x : y : z = 1.0 : 2.2 : 0.0037) **Cy2-PU** (x : y : z = 1.0 : 2.1 : 0.0037) **Cy3-PU** (x : y : z = 1.0 : 2.1 : 0.0037)

Synthesis of polyurethane Cy1-PU. To a stirred mixture of hydroxyl-terminated poly(tetrahydrofuran) (M_n = 2,000 g/mol, 3.00 g, 1.50 mmol), **Cy1** (8.00 mg, 6.00×10^{-3} mmol), and 4,4′-methylenebis(phenylisocyanate) (1.30 g, 5.19 mmol) in THF (30 mL), dibutyltin dilaurate (2 drops) was added and the reaction mixture was stirred at r.t. under nitrogen gas atmosphere for 3 h with a magnetic stir bar. A solution of 1,4-butanediol (297 mg, 3.26 mmol) in THF (10 mL) was added, and the reaction mixture was stirred for another 24 h at r.t. under nitrogen gas atmosphere. Methanol (5 mL) was added, and the reaction mixture was stirred for 30 min. The reaction mixture was then poured into methanol (1000 mL), and the mixture was stirred for 2 min. The pale-yellow precipitate was filtered off and dissolved in THF (200 mL). The resulting solution was directly added to hexane (900 mL) through a cotton filter. The precipitate was filtered off and dried *in vacuo* for 24 h at r.t. to afford **Cy1-PU** as a yellow rubbery solid (4.33 g, 94%, M_n = 108 kg mol^{-1}).

Synthesis of polyurethane Cy2-PU and Cy3-PU. Cy2-PU and **Cy3-PU** were prepared following the same procedure used for the synthesis of **Cy1-PU. Cy2** (8.53 mg, 6.00×10^{-3} mmol) and **Cy3** (9.06 mg, 6.00×10^{-3} mmol) were used to prepare **Cy2-PU** (yellow rubbery solid, 4.28 g, 93%, M_n = 123 kg mol^{-1}) and **Cy3-PU** (yellow rubbery solid 4.40 g, 96%, M_n = 122 kg mol^{-1}), respectively.



Synthesis of polyurethane PU. To a stirred mixture of hydroxyl-terminated poly(tetrahydrofuran) (M_n = 2,000 g/mol, 3.00 g, 1.50 mmol), and 4,4′-methylenebis(phenylisocyanate) (1.26 g, 5.04 mmol) in THF (20 mL), dibutyltin dilauate (4 drops) was added and the reaction mixture was stirred at r.t. under nitrogen atmosphere for 3 h with a magnetic stir bar. A solution of 1,4-butanediol (297 mg, 3.26 mmol) in THF (10 mL) was added, and the reaction mixture was stirred for another 24 h at r.t. under nitrogen gas atmosphere. Methanol (5 mL) was added, and the reaction mixture was stirred for 30 min. The reaction mixture was then poured into methanol (1000 mL), and the mixture was stirred for 2 min. The white precipitate was filtered off and dissolved in THF (200 mL). The resulting solution was directly added to hexane (900 mL) through a cotton filter. The precipitate was filtered off and dried *in vacuo* for 24 h at r.t. to afford **PU** as a white rubbery solid (4.24 g, 85%, M_n = 172 kg mol^{-1}).

Preparation of polyurethane films

Preparation of Cy1-PU, Cy2-PU, and Cy3-PU films. The polyurethanes (**Cy1-PU**, **Cy2-PU**, and **Cy3-PU**, 300 mg) were dissolved in THF (7–8 mL) and the solutions were divided between two square-shaped poly(tetrafluoroethylene) molds (51 × 51 × 5.0 mm). The molds were placed under an inverted funnel to reduce the evaporation rate. The solvent was slowly evaporated overnight under ambient conditions and the resulting films were further dried *in vacuo* at r.t. overnight. The slightly opaque **Cy1-PU**, **Cy2-PU**, and **Cy3-PU** films were smooth and had a thickness of 60–100 µm. The **Cy1-PU**, **Cy2-PU**, and **Cy3-PU** films were yellow in color.

Preparation of PU/5 reference films. The polyurethane **PU** (300 mg) and compound **5** (0.476 mg, 4.54 × 10^{-4} mmol) were dissolved in THF (7–8 mL) and the solution was divided between two square-shaped poly(tetrafluoroethylene) molds (51 × 51 × 5.0 mm). The molds were placed under an inverted funnel to reduce the evaporation rate. The solvent was slowly evaporated overnight under ambient conditions and the resulting films were further dried *in vacuo* at r.t. overnight. The slightly opaque yellow films were smooth and had a thickness of 60–100 µm.

Preparation of PU/Cy3 reference films. The polyurethane **PU** (300 mg) and **Cy3** (0.566 mg, 3.75 × 10^{-4} mmol) were dissolved in THF (7–8 mL) and the solution was divided between two square-shaped poly(tetrafluoroethylene) molds (51 × 51 × 5.0 mm). The molds were placed under an inverted funnel to reduce the evaporation rate. The solvent was slowly evaporated overnight under ambient conditions and the resulting films were further dried *in vacuo* at r.t. overnight. The slightly opaque yellow films were smooth and had a thickness of 60–100 µm.

Cy1-PU, **Cy2-PU**, **Cy3-PU**, **PU/5** or **PU/Cy3** films were cut into dog-bone-shaped specimens that were used in the various measurements. Typical dimensions: 8 mm × 26 mm.

^{1}H NMR spectra of Cy1, Cy2, Cy3, and An

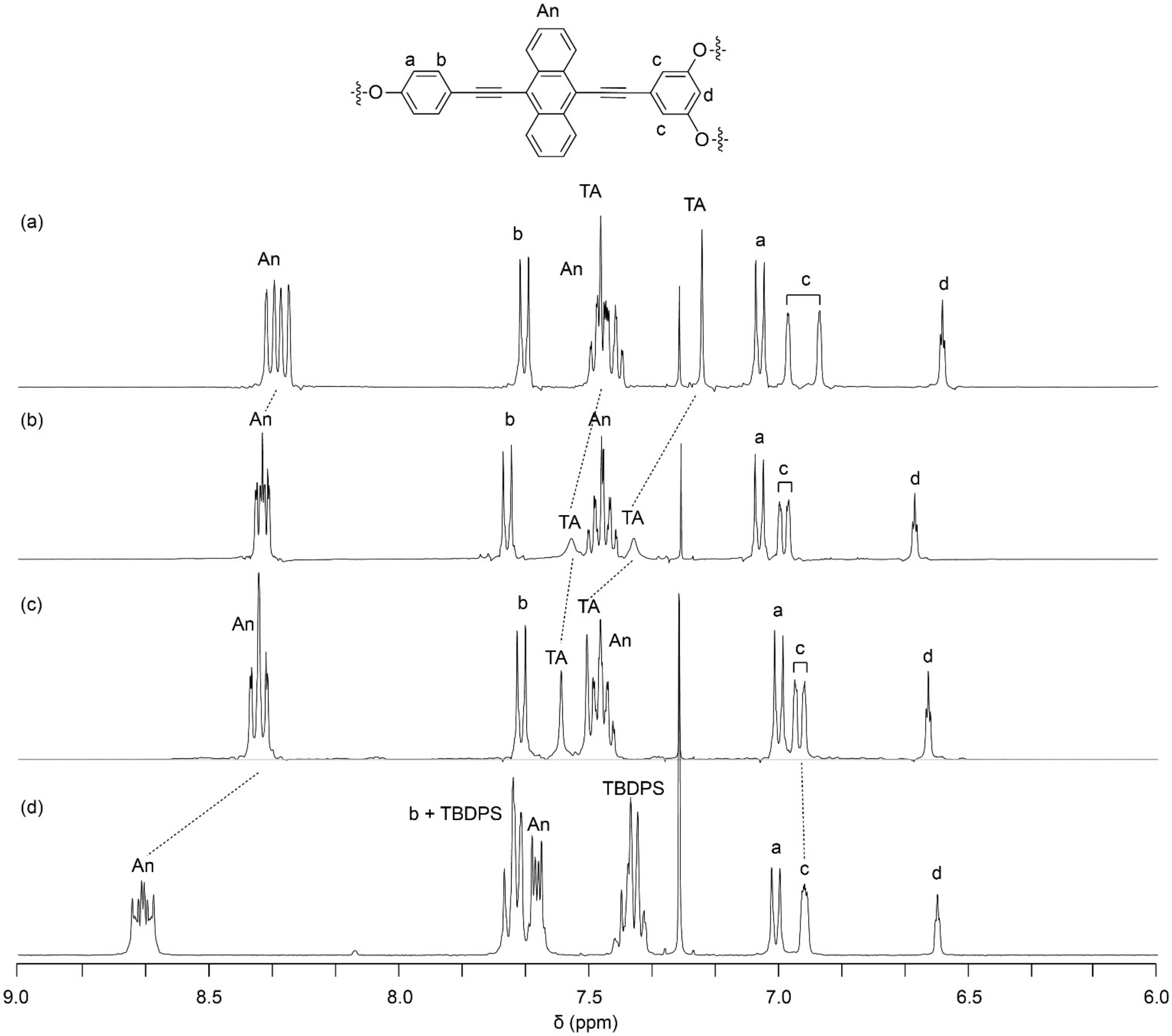


Figure S1. Partial ^{1}H NMR spectra of (a) **Cy1**, (b) **Cy2**, (c) **Cy3**, and (d) **An** in $CDCl_3$ at 293 K. The abbreviations An, TBDPS, and TA indicate the proton signals of the anthracene, *tert*-butyldiphenylsilyl, and triazole group, respectively.

Excitation spectra of Cy3 in toluene

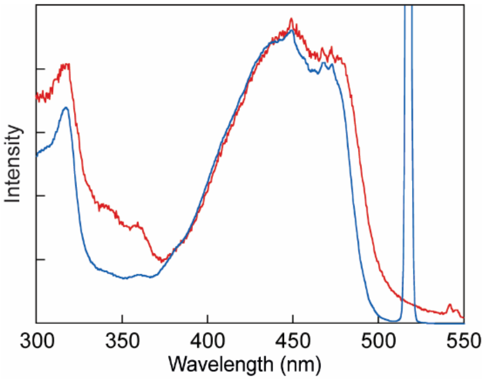


Figure S2. Excitation spectra of **Cy3** in toluene (c = 1.0 × 10^{-5} M) recorded at emission wavelengths of 650 nm (red) and 518 nm (blue).

^{1}H NMR spectra of polyurethanes

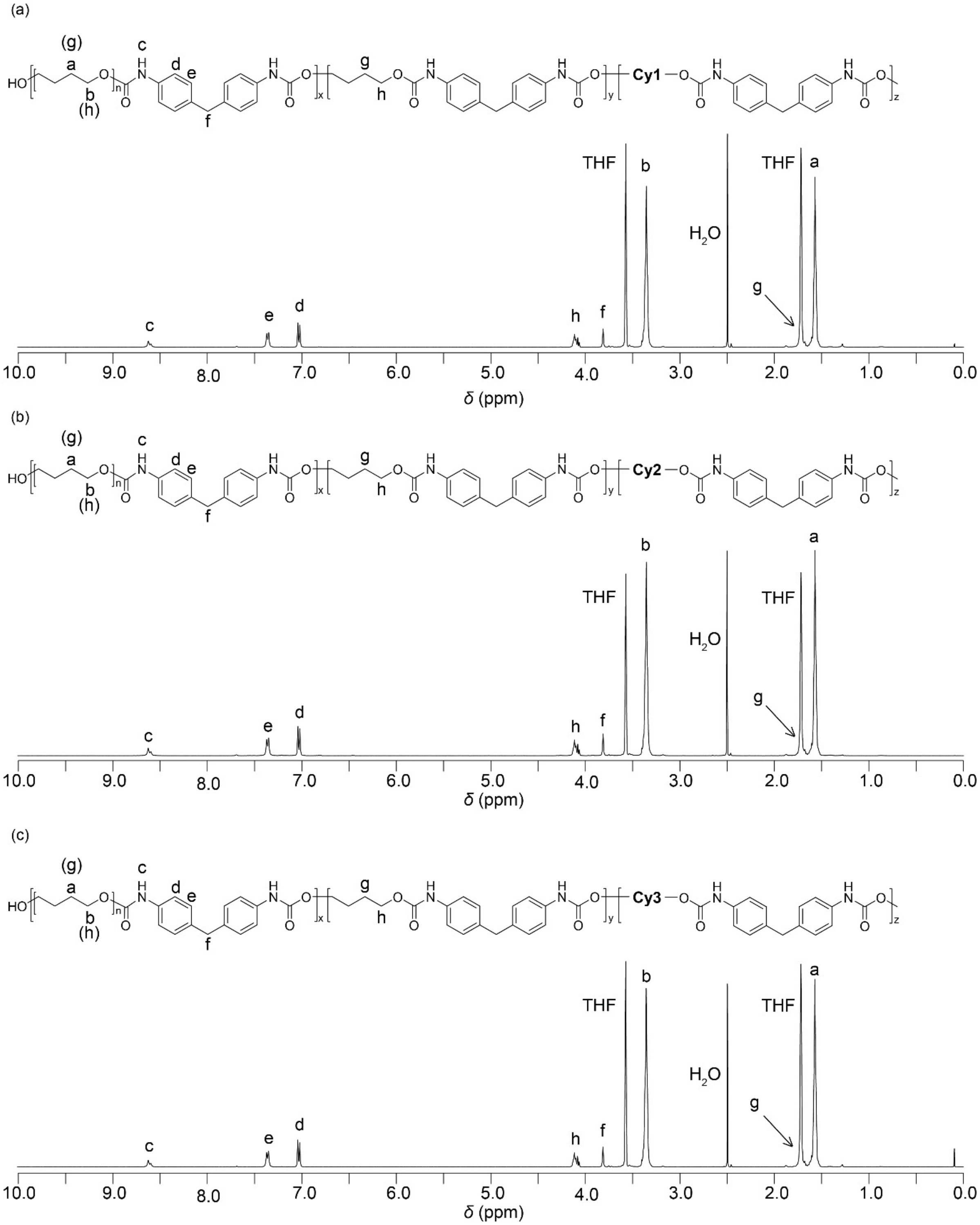


Figure S3. ^{1}H NMR spectra of (a) **Cy1-PU**, (b) **Cy2-PU**, and (c) **Cy3-PU** in THF-d_8. Signals are characterized as protons of the polyurethane chains. No signals ascribed to the residues of **Cy1**, **Cy2**, and **Cy3** are observed due to their low concentrations in **Cy1-PU**, **Cy2-PU**, and **Cy3-PU**. All spectra were measured at 293 K.

Photophysical properties of polyurethanes in solutions

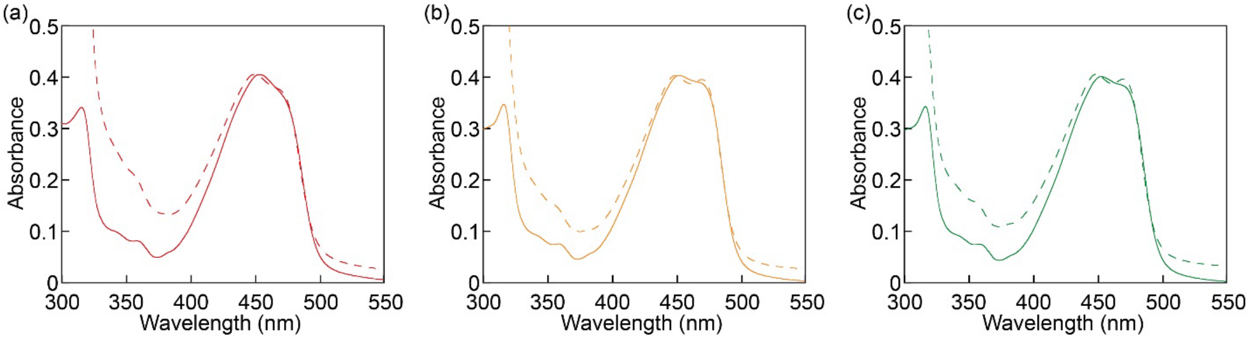


Figure S4. Absorption spectra of (a) **Cy1** (red solid line) and **Cy1-PU** (red dotted line), (b) **Cy2** (yellow solid line) and **Cy2-PU** (yellow dotted line), and (c) **Cy3** (green solid line) and **Cy3-PU** (green dotted line) in THF. The concentrations of **Cy1**, **Cy2**, and **Cy3** were $c = 1.0 \times 10^{-5}$ M. The concentrations of the **Cy1-PU**, **Cy2-PU**, and **Cy3-PU** solutions were adjusted so that the absorbances at 450 nm match those of the solutions of **Cy1**, **Cy2**, and **Cy3**, respectively.

Thermal properties of polyurethanes

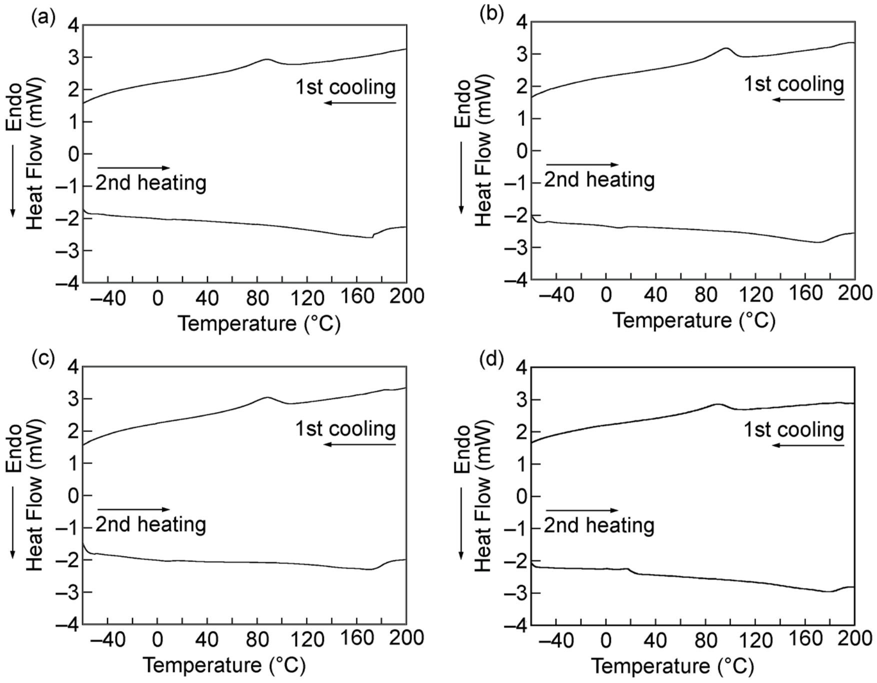


Figure S5. Differential scanning calorimetry traces of (a) **Cy1-PU**, (b) **Cy2-PU**, (c) **Cy3-PU**, and (d) **PU**. The measurements were conducted under N_2. The heating and cooling rates were 10 °C/min. Shown are the first cooling and the second heating traces.

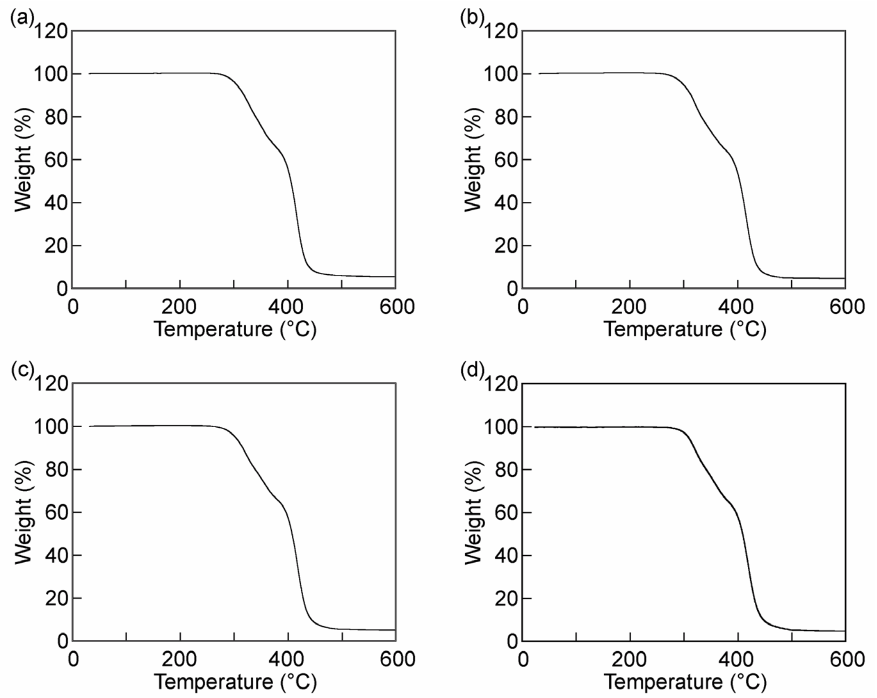


Figure S6. Thermogravimetric analysis traces of (a) **Cy1-PU**, (b) **Cy2-PU**, (c) **Cy3-PU**, and (d) **PU**. The TGA experiments were conducted under N_2 at a heating rate of 10 °C/min.

Mechanical properties of polyurethanes

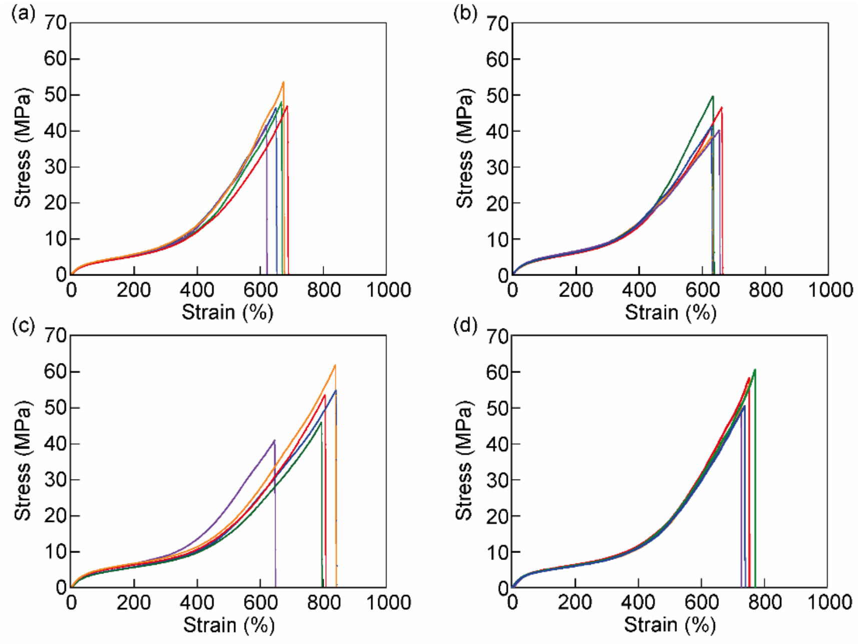


Figure S7. Stress-strain curves of (a) **Cy1-PU**, (b) **Cy2-PU**, (c) **Cy3-PU**, and (d) **PU**. Each graph shows data recorded for five different specimens. The experiments were conducted with a strain rate of 2 mm/s at r.t.

Table S1. Summary of the mechanical properties of **Cy1-PU**, **Cy2-PU**, **Cy3-PU**, and **PU** films as determined from stress-strain curves recorded during uniaxial tensile deformation (see Figure S7).[a)]

	Elongation at break (%)	**Stress at break (MPa)**	**Young's Modulus [b)] (MPa)**
Cy1-PU	660 ± 26	47 ± 4	6.0 ± 0.6
Cy2-PU	641 ± 17	44 ± 6	7.0 ± 2.0
Cy3-PU	786 ± 80	51 ± 8	12.0 ± 0.9
PU	752 ± 19	56 ± 5	11.0 ± 0.3

[a)] All data were extracted from the stress-strain curves shown in Figure S7 and represent averages of 5 measurements ± standard deviation. [b)] The Young's moduli were derived from the slopes of the stress-strain curves in the strain regime of 0.2–0.6%.

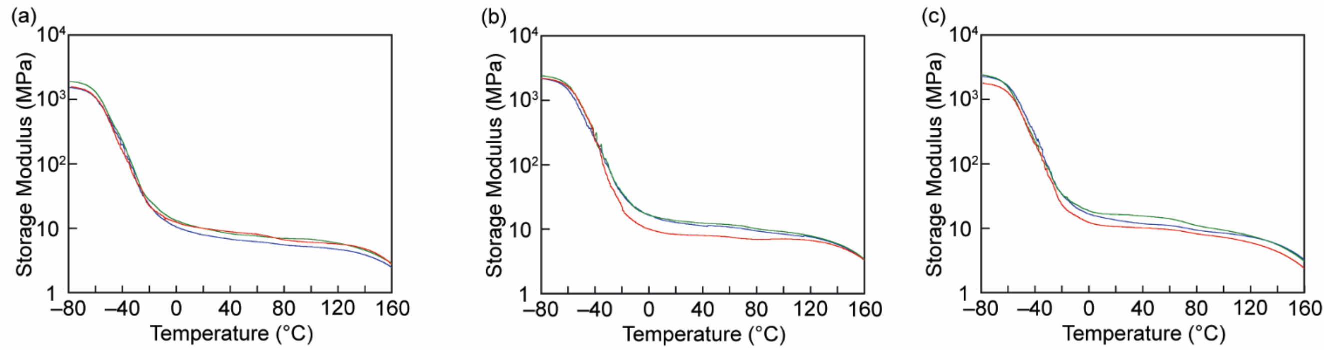


Figure S8. Dynamic mechanical analysis traces of (a) **Cy1-PU**, (b) **Cy2-PU**, and (c) **Cy3-PU**. The DMA experiments were conducted under N_2 at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 µm.

Images of polyurethane films during uniaxial deformation

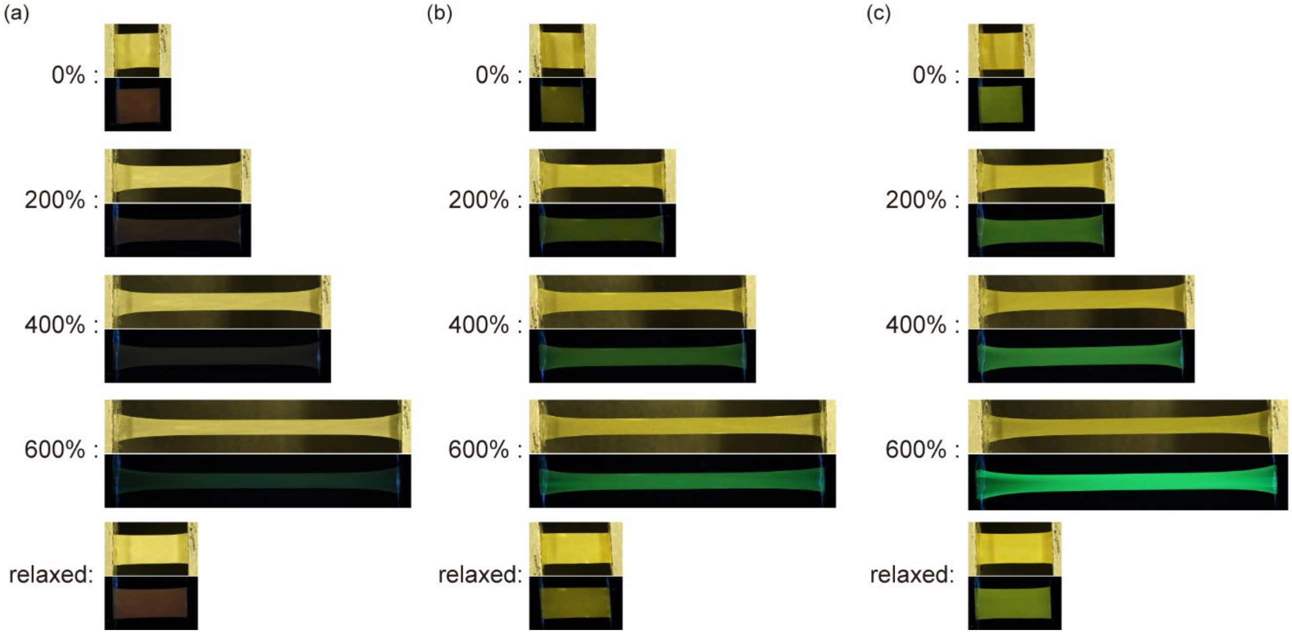


Figure S9. Photographs of **Cy1-PU**, **Cy2-PU**, and **Cy3-PU** films in cyclic uniaxial deformation tests. In each set, the bottom image shows the photoluminescence of the film taken in the dark under 365 nm excitation light; the upper image was taken under ambient illumination. All images were taken under ambient conditions at the strains indicated.

Photoluminescence spectra of Cy1, Cy2, and Cy3 in toluene

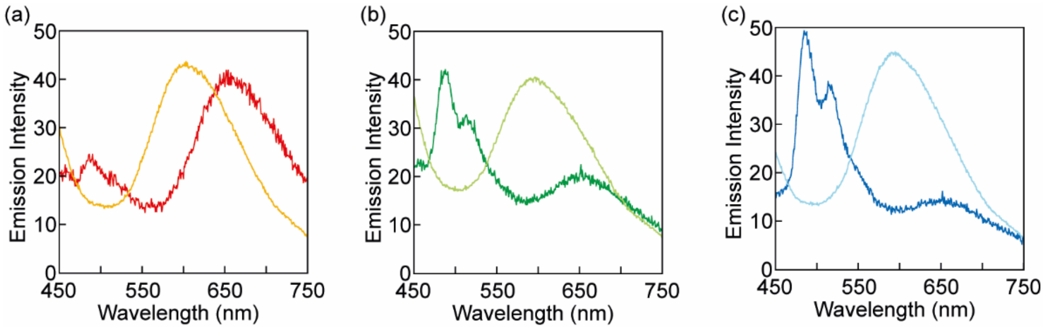


Figure S10. Photoluminescence spectra of cyclophanes (a) **Cy1** at r.t. (red line) and at 77 K (yellow line), (b) **Cy2** at r.t. (green line) and at 77 K (light green line), (c) **Cy3** at r.t. (blue line) and at 77 K (light blue line). The emission spectra were recorded with excitation at 365 nm and at $c = 1.0 \times 10^{-5}$ M in toluene.

Reversibility

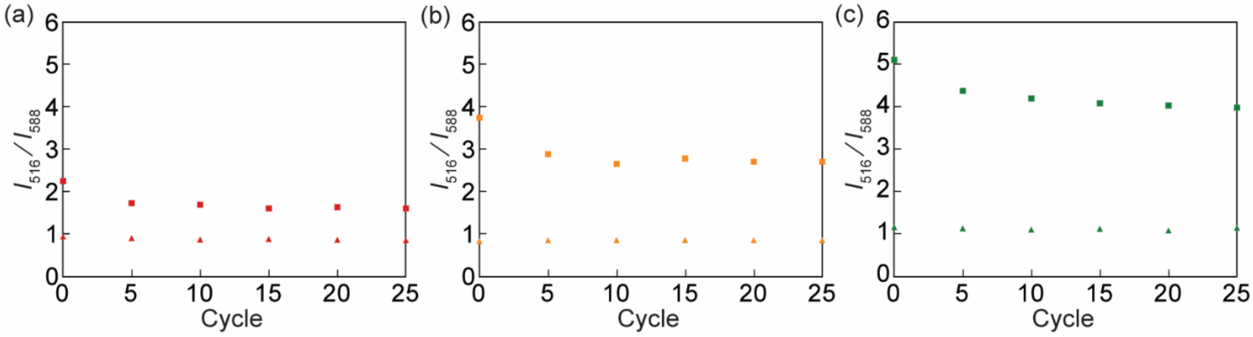


Figure S11. Plots showing the ratio I_{516}/I_{588} in the stretched (600% strain) and relaxed state of (a) **Cy1-PU**, (b) **Cy2-PU**, and (c) **Cy3-PU** films over 25 cycles. The I_{516}/I_{588} ratios were measured for every 5th cycle.

Mechanoresponsiveness of the Cy3inPU films

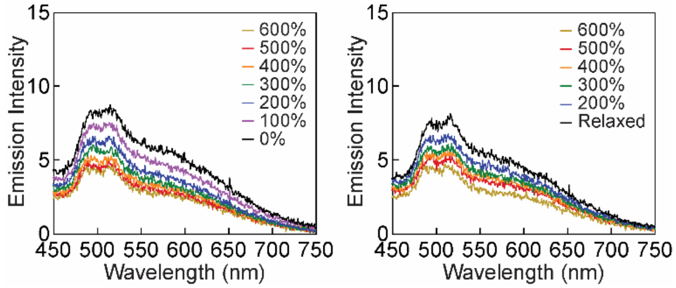


Figure S12. Change of the photoluminescence spectra of **Cy3inPU** films upon uniaxial deformation. The spectra were collected under the same experimental conditions (excitation at 365 nm) upon gradually stretching the samples (left) and subsequent relaxation from the maximum strain of 600% (right) and were not normalized. The reduction of emission intensity that is observed upon deformation is likely related to the thinning of the samples as they are elongated.

Correlation between stress relaxation and photoluminescence properties

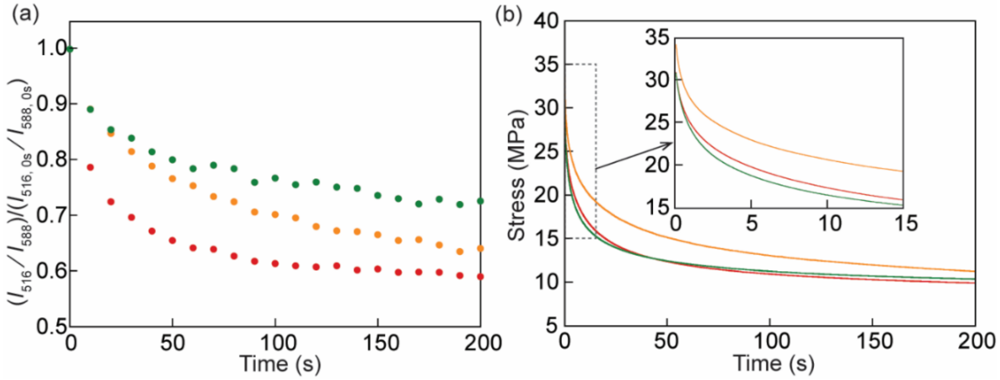


Figure S13. (a) Emission intensity ratio I_{516}/I_{588} values and (b) stress as a function of time after deforming the **Cy1-PU** (red), **Cy2-PU** (yellow), and **Cy3-PU** (green) films to 600% and keeping at the same strain.

References

[S1] T. Muramatsu, Y. Okado, H. Traeger, S. Schrettl, N. Tamaoki, W. Weder, Y. Sagara, *J. Am. Chem. Soc.* **2021**, *143*, 9884−9892.

[S2] J. Cao, Y. Liu, L. Zhang, F. Du, Y. Ci, Y. Zhang, J. Qiao, *J. Radioanal. Nucl. Chem.* **2017**, *312*, 263–276.

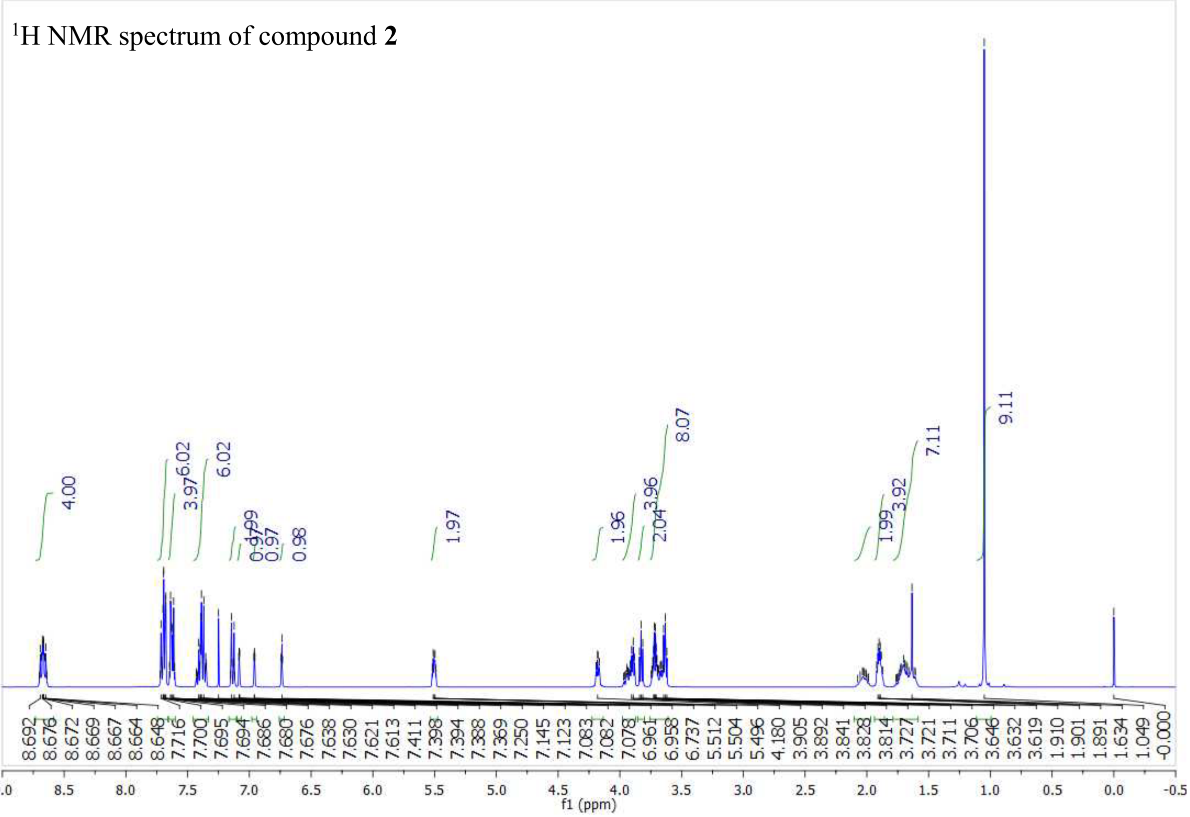
[S3] S. Thazhathethil, T. Muramatsu, N. Tamaoki, C. Weder, Y. Sagara, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209225.

Supporting Videos

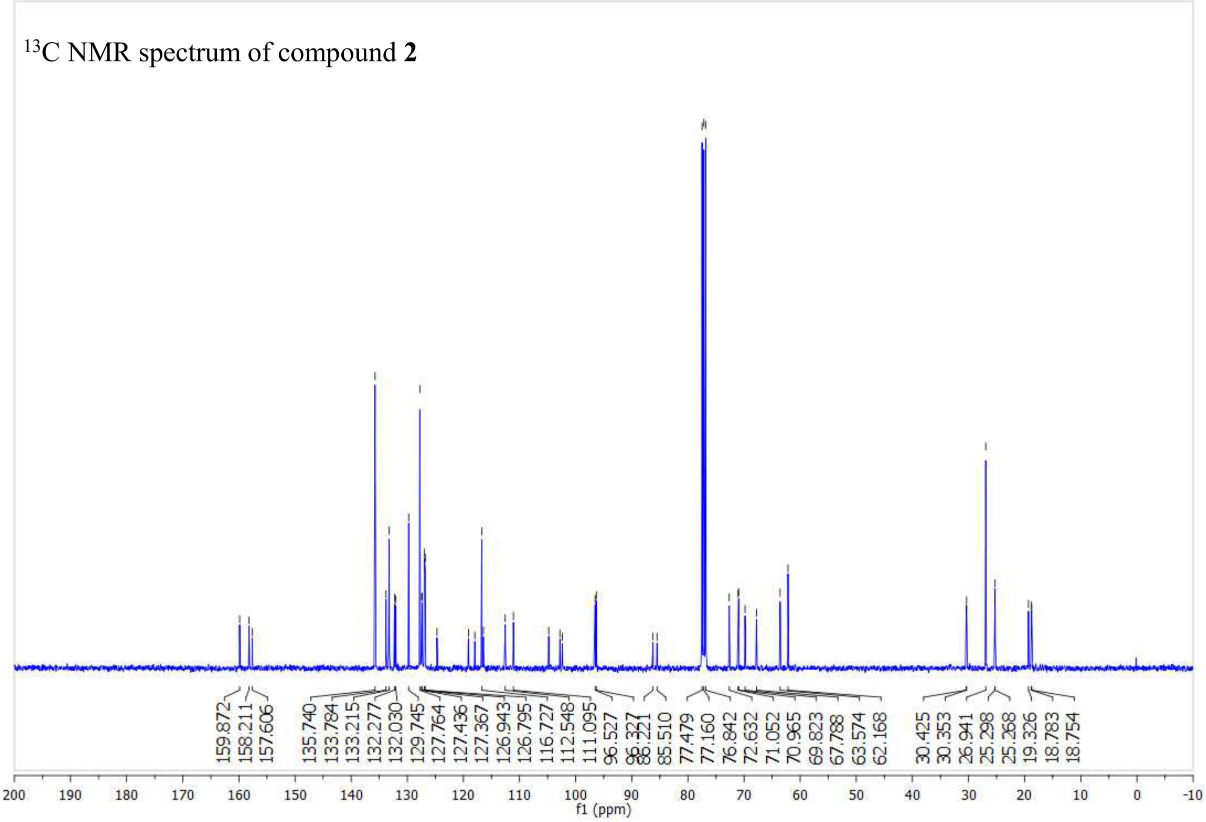
Supporting videos S1–S3. Representative videos of the mechanoresponsive luminescence behavior upon cyclic stretching and releasing of **Cy1-PU**, **Cy2-PU**, and **Cy3-PU** films. All movies were taken in the dark under excitation with 365 nm light and are shown on the original speed.

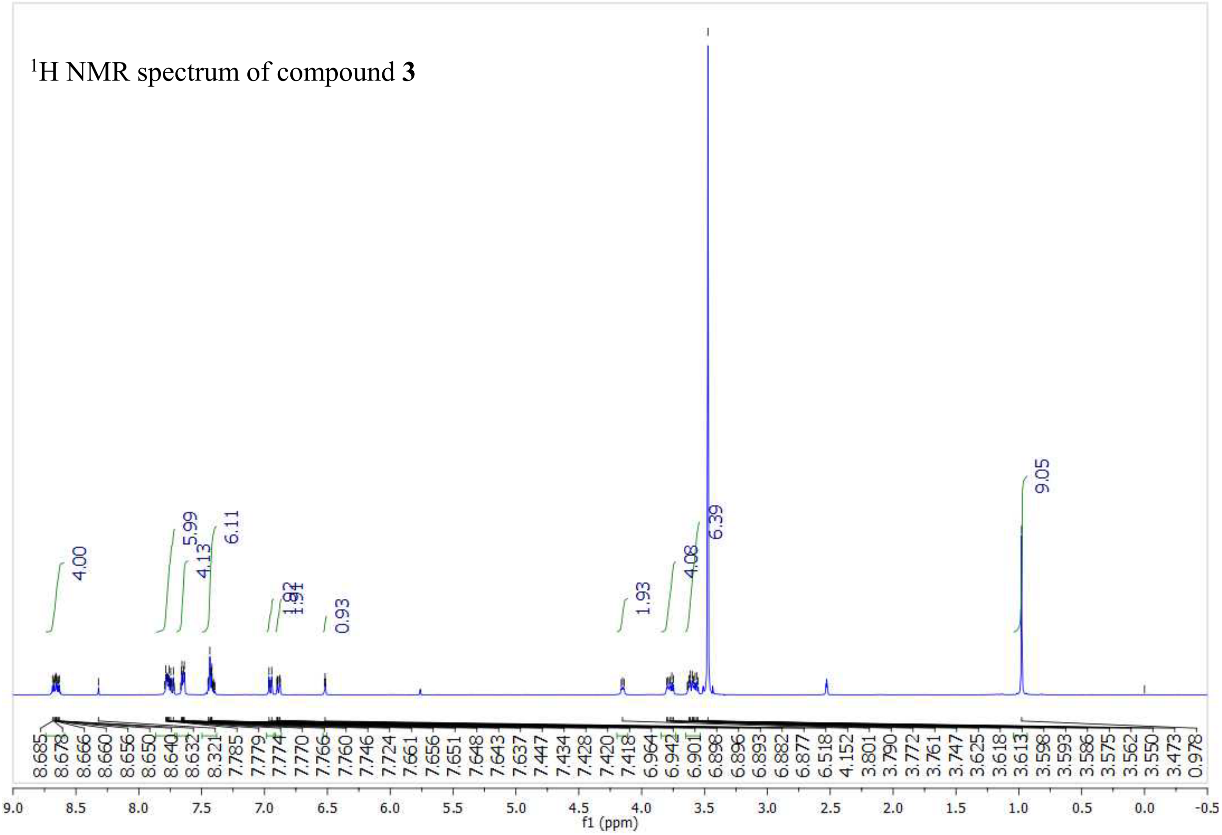
NMR Spectra

^{1}H NMR spectrum of compound **2**

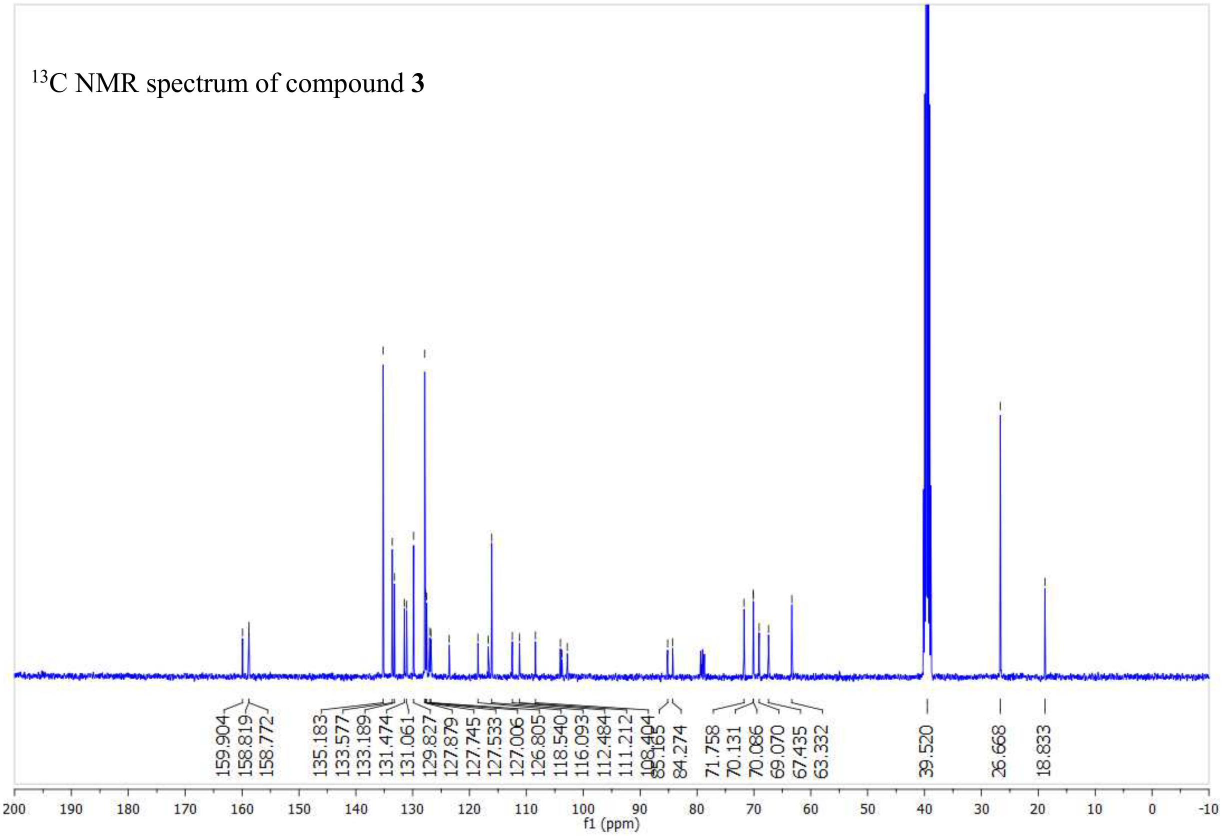


^{13}C NMR spectrum of compound **2**



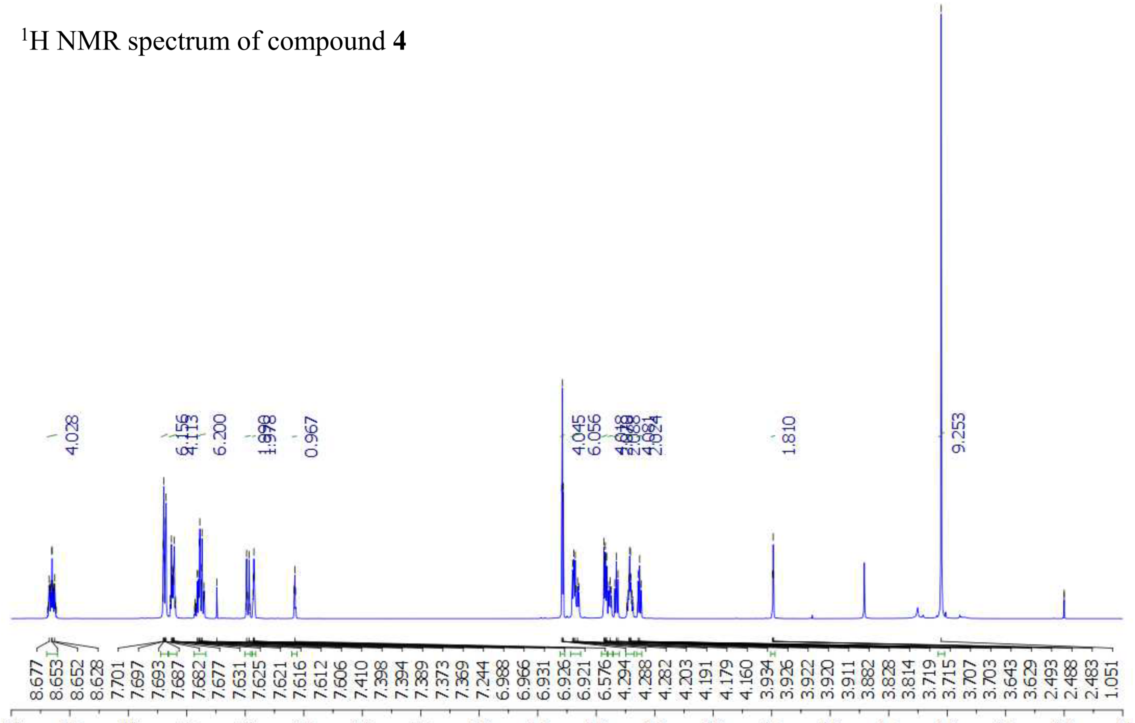


^{1}H NMR spectrum of compound **3**

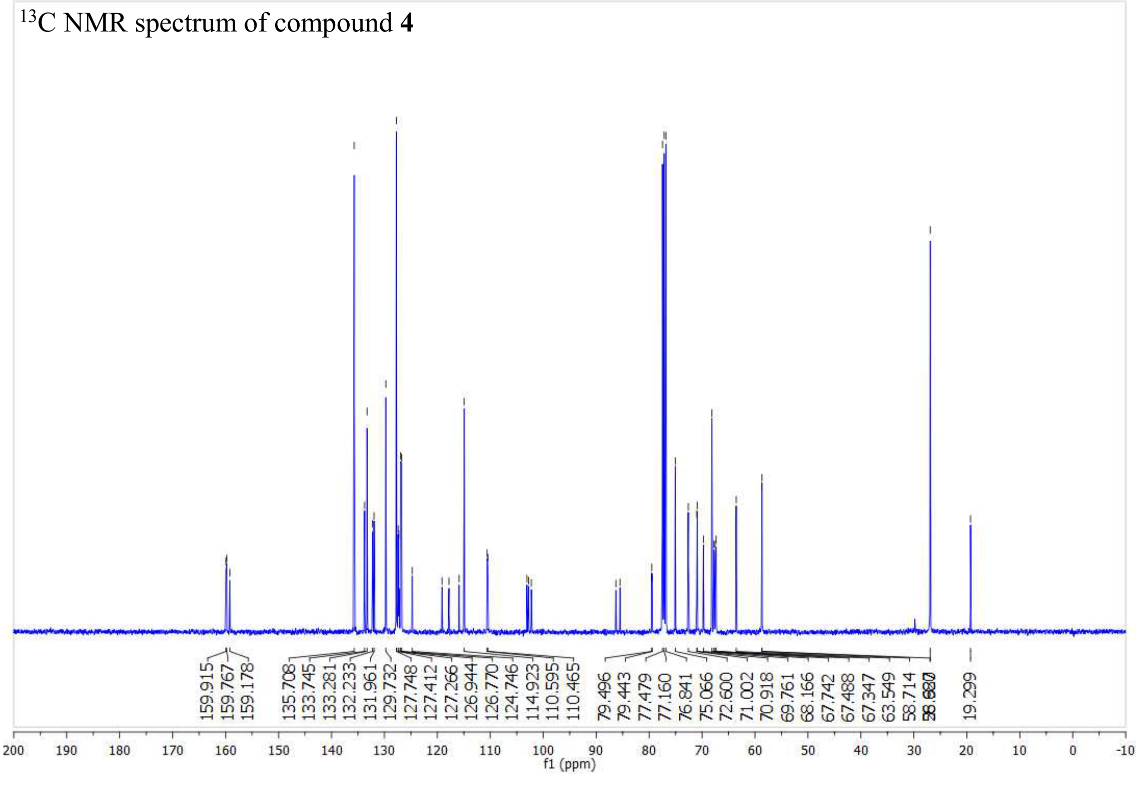


^{13}C NMR spectrum of compound **3**

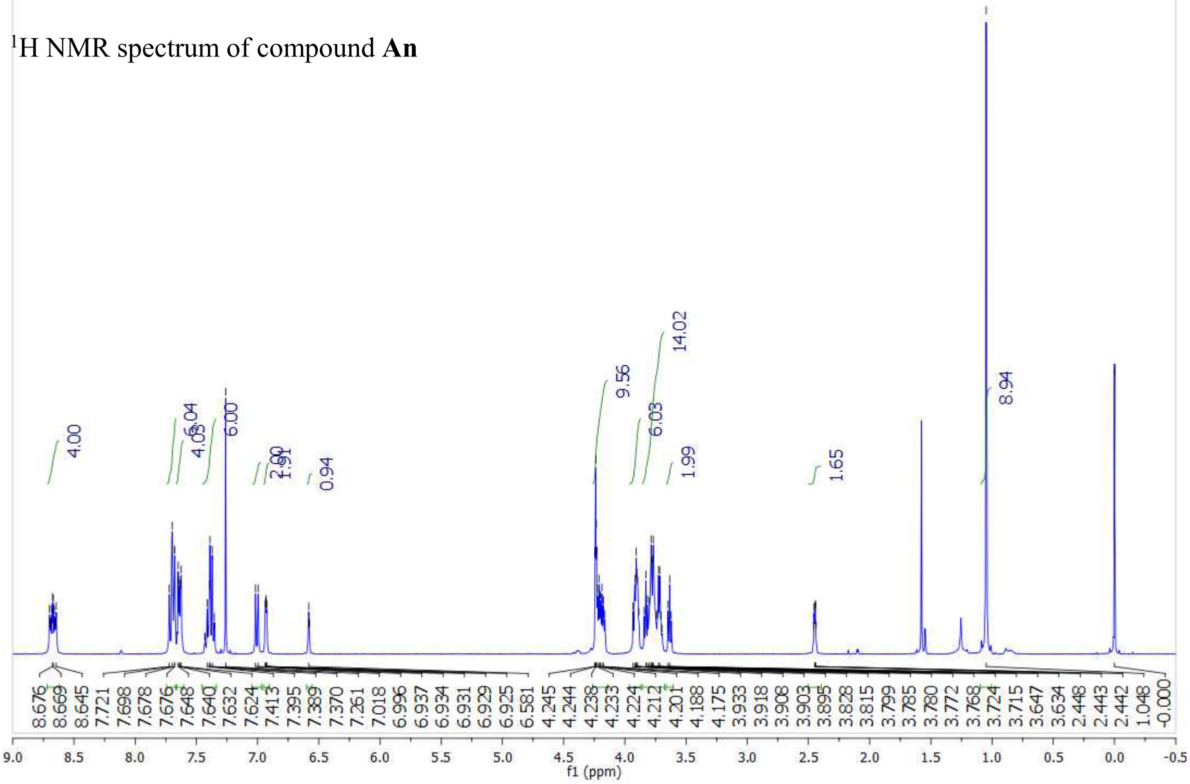
^{1}H NMR spectrum of compound **4**



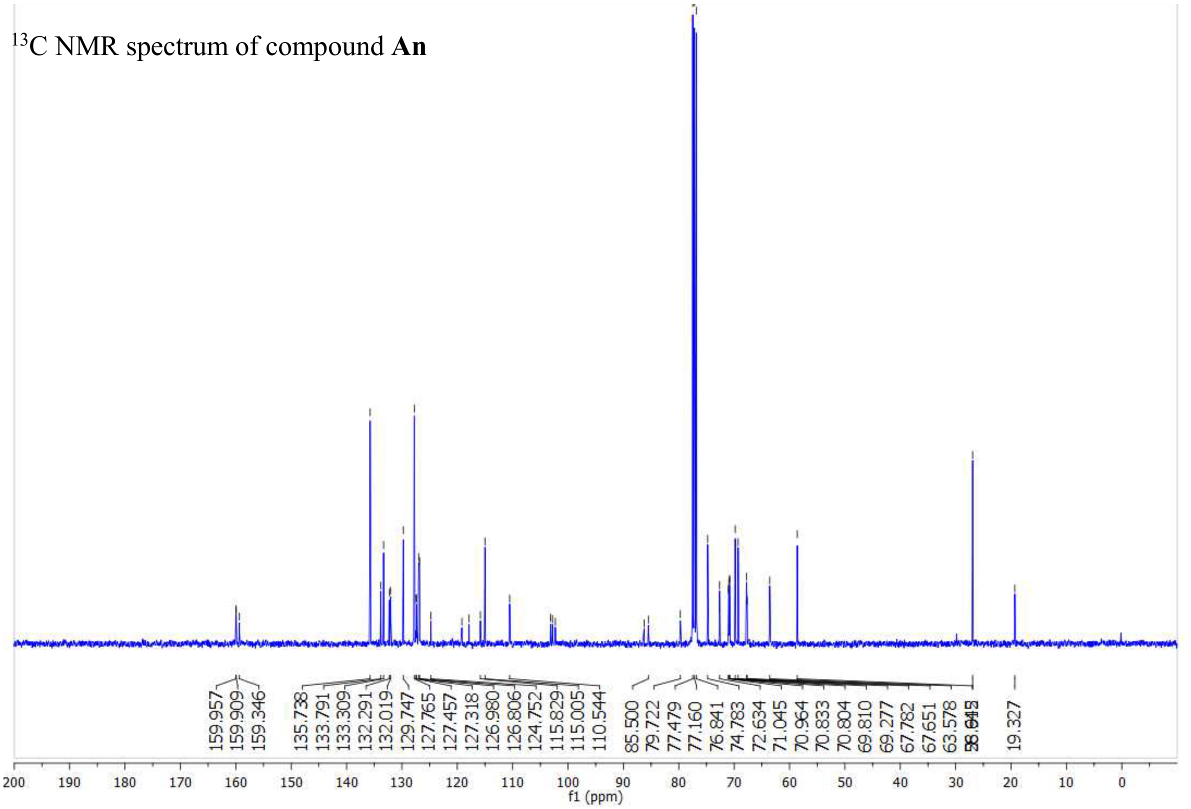
^{13}C NMR spectrum of compound **4**



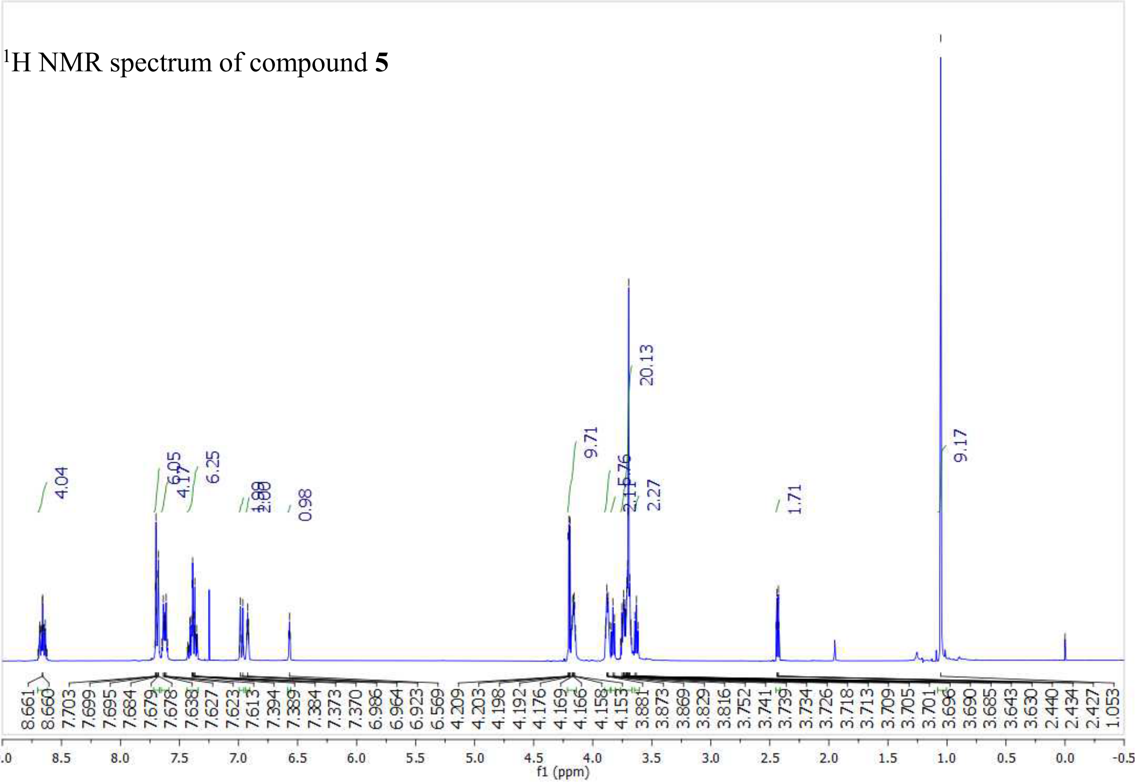
^{1}H NMR spectrum of compound **An**



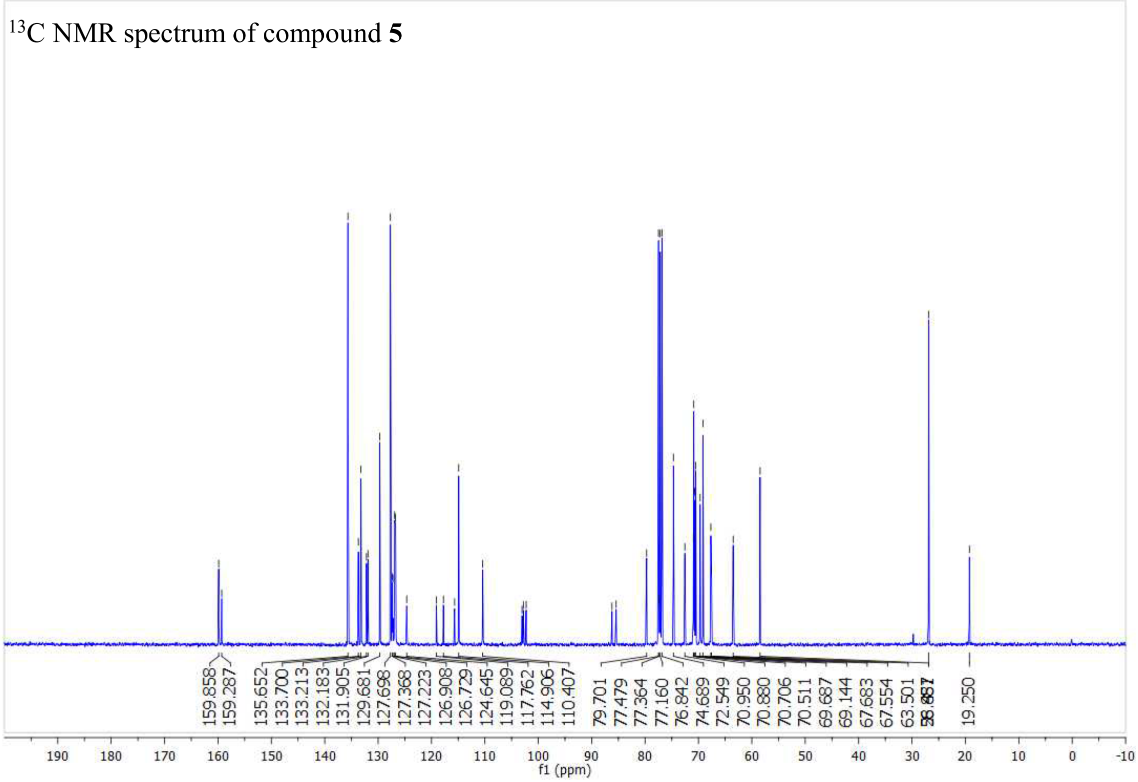
^{13}C NMR spectrum of compound **An**

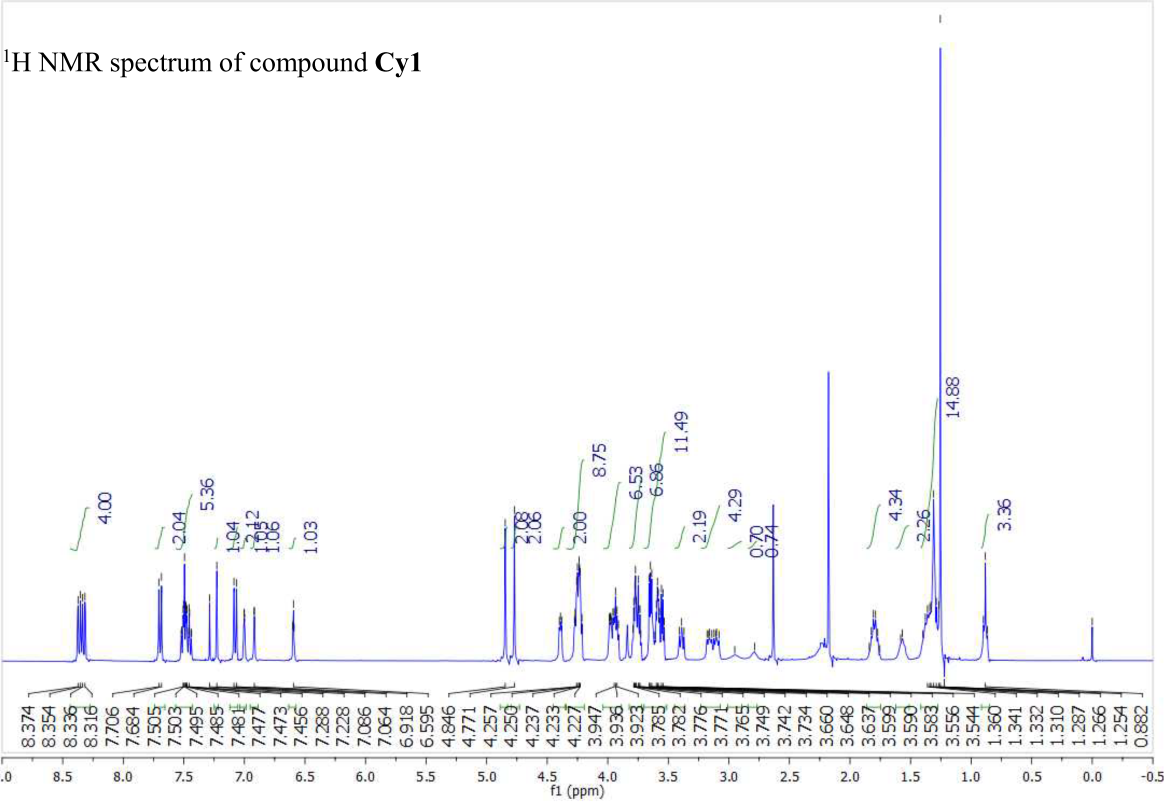


^{1}H NMR spectrum of compound **5**

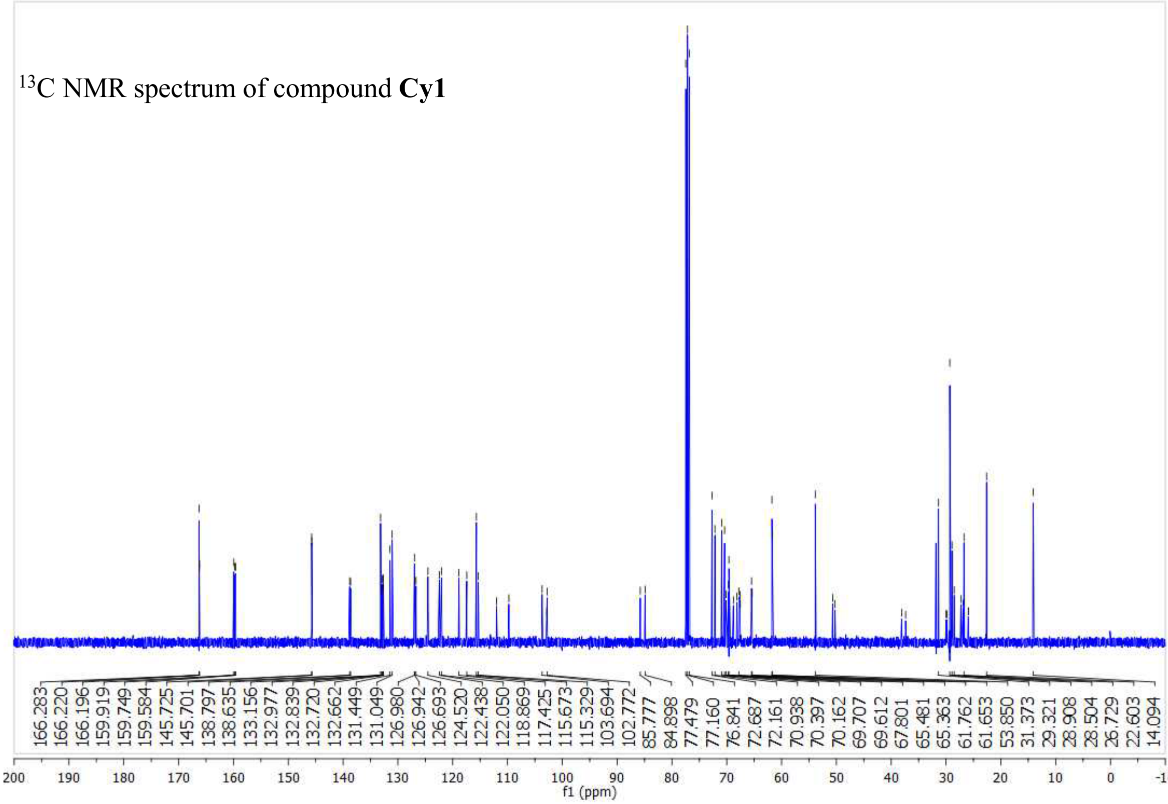


^{13}C NMR spectrum of compound **5**



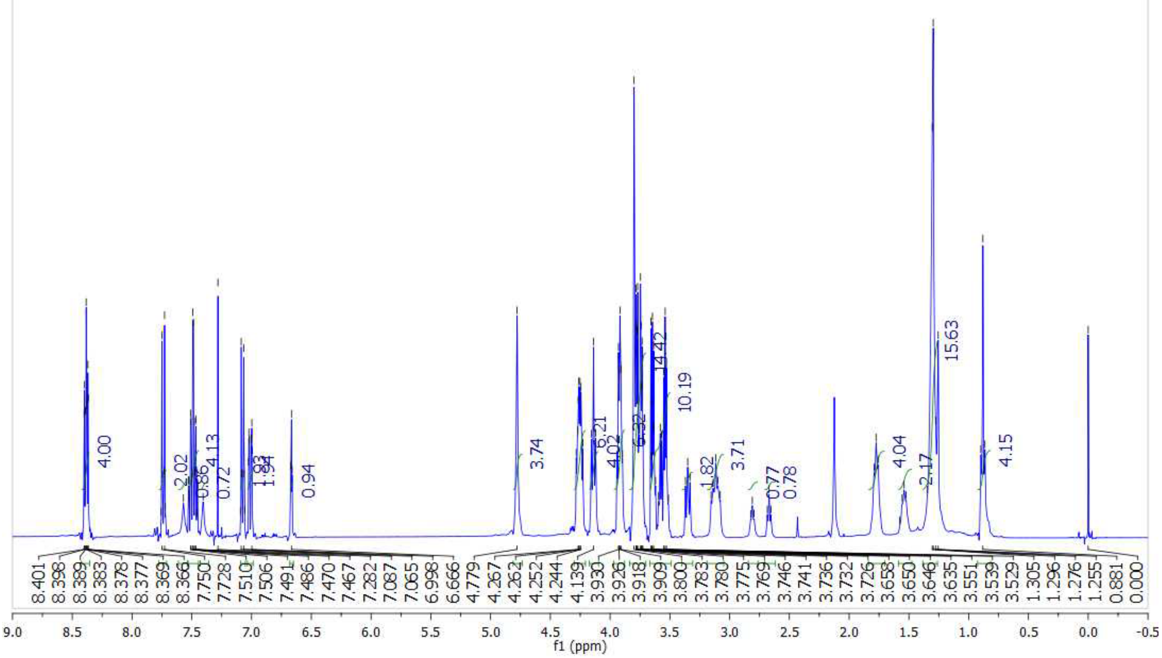


^{1}H NMR spectrum of compound **Cy1**

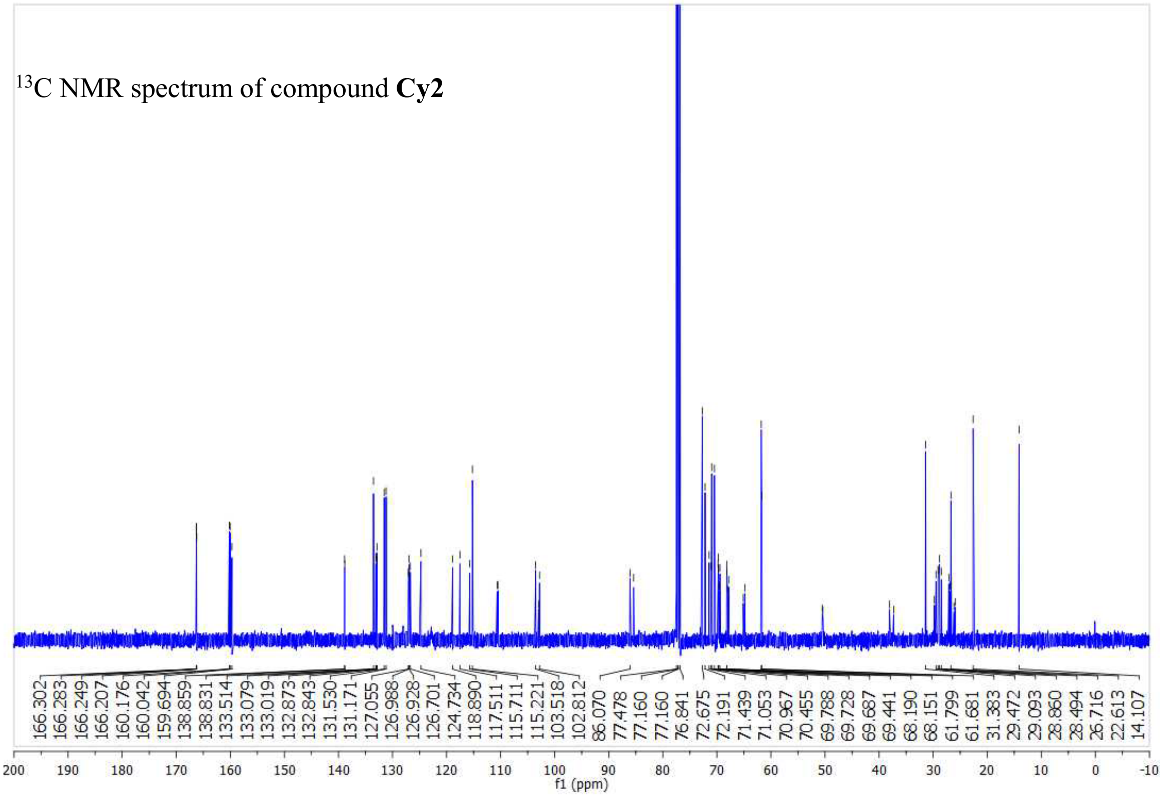


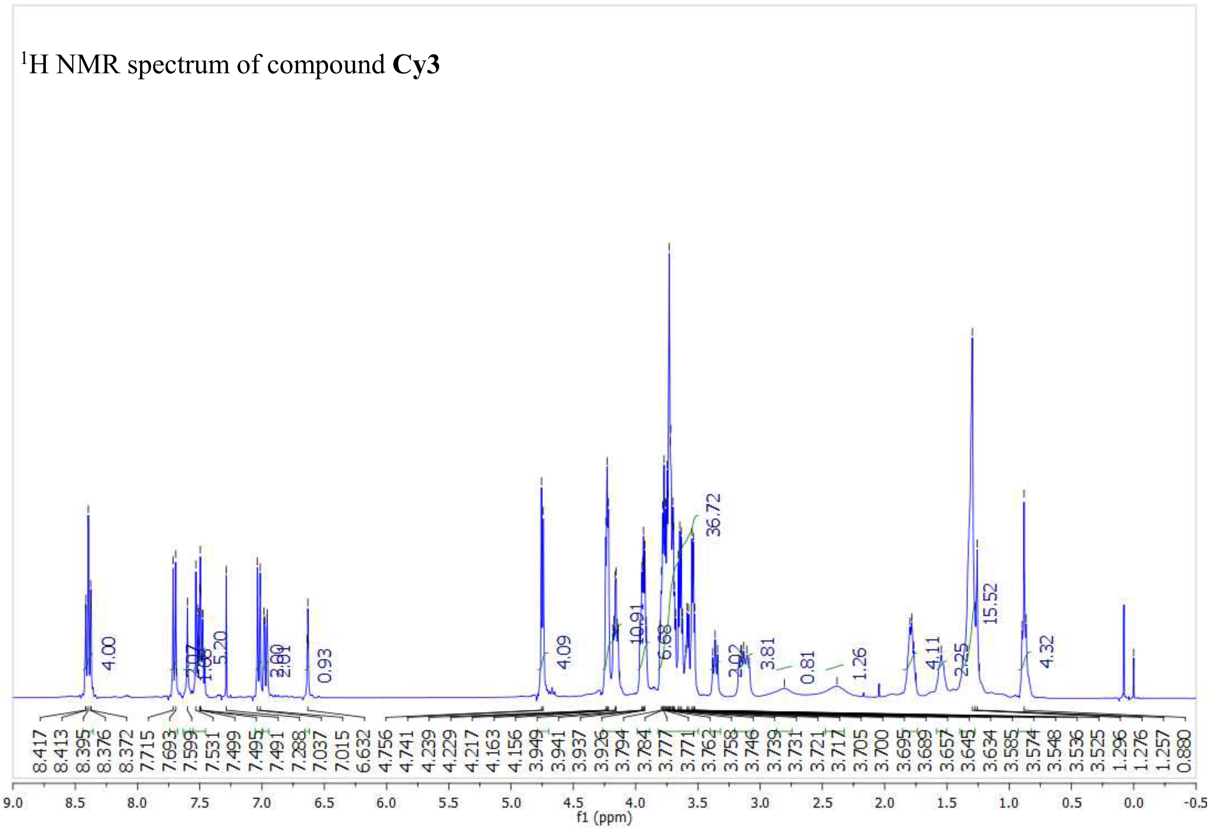
^{13}C NMR spectrum of compound **Cy1**

^{1}H NMR spectrum of compound **Cy2**

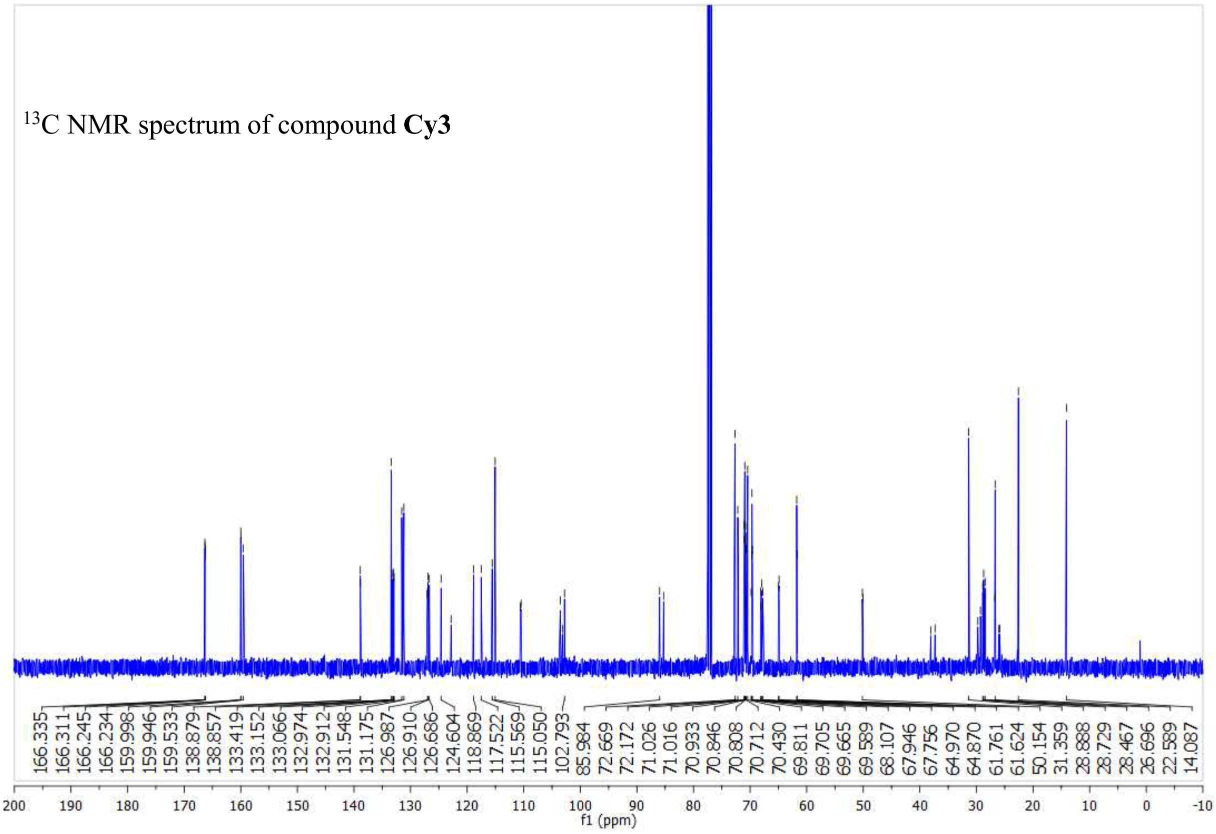


^{13}C NMR spectrum of compound **Cy2**





^{1}H NMR spectrum of compound **Cy3**



^{13}C NMR spectrum of compound **Cy3**