

Supporting Information

Rotaxane-based Mechanophores Enable Polymers with Mechanically Switchable White Photoluminescence

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Table of Contents

Safety Statement and General Methods	S2
Synthesis of Cyclic Compounds and Rotaxanes	S3
Polymer Synthesis	S11
Preparation of Polyurethane Films	S11
¹H NMR Spectra of Rotaxanes	S12
White Photoluminescence of Solution	S13
¹H NMR Spectra of Polyurethanes	S14
Thermal Properties of Polyurethanes	S15
Mechanical Properties of Polyurethanes	S16
Images of Polyurethane Films During Uniaxial Deformation	S17
Photoluminescence Spectra of Polymer Solutions	S17
Reversibility of the Mechanically Induced Photoluminescence Switching	S18
Photoluminescence Spectra of the Rotaxane-Containing Polymers in Solutions After Cyclic Mechanical Tests	S18
Images of a Rot-Mix-PU Film Acquired Upon Uniaxial Deformation and After Subsequent Relaxation	S19
Photoluminescence Spectra of a Rot-Mix-PU Film Acquired Upon Releasing the Mechanical Stress from a Strained State	S19
Reversibility of the Photoluminescence Switching in a White Light Emitting Blend Film	S20
References	S21
Supporting Movies	S21

Safety Statement

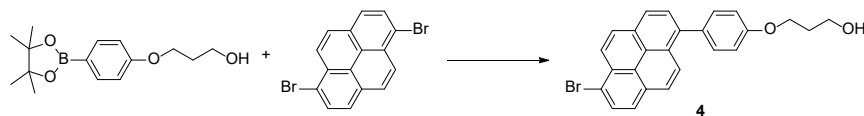
No unexpected or unusually high safety hazards were encountered in this research.

General Methods

All reagents and solvents were purchased from Tokyo Kasei, Kanto Chemical, Merck, or FUJIFILM Wako Pure Chemical Corporation. Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. Flash silica gel column chromatography was conducted with a Biotage Isolera Flash system using Biotage Flash Cartridges or SHOKO-scientific Purif-Pack-EX cartridges. Recycling preparative gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LaboACE. Inhibitor-free anhydrous tetrahydrofuran (FUJIFILM Wako Pure Chemical Corporation) was used as solvent for the synthesis of all polymers. 1,4-Butanediol and 4,4'-methylenebis(phenyl isocyanate) were distilled under vacuum and stored over molecular sieves at room temperature and 4 °C, respectively. Poly(tetrahydrofuran) ($M_n = 2,000$ g/mol) was dried *in vacuo* at 100 °C for 2 h before use. ^1H NMR spectra were conducted with a JEOL JNM-ECX 400 spectrometer and all chemical shifts are reported on the δ -scale in ppm relative to the signal of tetramethylsilane (TMS, at 0.00) or residual solvent protons (THF at 1.72) as an internal standard. Proton-decoupled ^{13}C NMR spectra were conducted with a JEOL JNM-ECX 400 spectrometer and all chemical shifts (δ) are quoted in ppm using residual solvent as the internal standard (CDCl_3 at 77.16). Coupling constants (J) are quoted in Hz and relative intensities are also shown. High resolution electrospray ionization (ESI) mass spectra were conducted with a Thermo Scientific Exactive or a JEOL JMS-T100LP. Absorption spectra were recorded on a JASCO V-550. Steady-state fluorescence spectra of solutions were measured with a JASCO FP-6500 and the obtained spectra were corrected for the detector nonlinearity. Steady-state fluorescence spectra of films during deformation experiments were monitored with an Ocean Optics QEPro-FL equipped with an LLS-365 or LLS-385 LED light source and a Reflection/Backscattering Probe R400-7-UV-VIS and the spectra were used without correction. Size-exclusion chromatography (SEC) experiments were carried out on an Agilent 1200 series HPLC system equipped with an Agilent PLgel mixed guard column (particle size = 5 μm) and two Agilent PLgel mixed-D columns (ID = 7.5 mm, L = 300 mm, particle size = 5 μm). Signals were monitored on a UV detector (Agilent 1200 series), an Optilab REX interferometric refractometer, and a miniDawn TREOS light scattering detector (Wyatt Technology Corp.). Samples were injected using THF as the eluent at 30 °C and a flow rate of 1.0 mL/min. Data analyses were conducted on Astra software (Wyatt Technology Corp.) and molecular weights were calculated based on narrow-molecular-weight polystyrene calibration (from 580 to 364,000 g/mol). Differential scanning calorimetry (DSC) measurements were performed under N_2 on Mettler-Toledo Star^e DSC at heating and cooling rates of 10 °C/min. Thermogravimetric analyses (TGA) were conducted under N_2 with a Mettler-Toledo Star^e system at a rate of 10 °C/min. Stress–strain measurements were carried out under ambient conditions with a Zwick/Roell Z010 tensile tester equipped with a 200 N load cell at a strain rate of 100 mm/min. Dynamic mechanical analyses (DMA) were conducted 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 .

Synthesis of Cyclic Compounds and Rotaxanes

Compound 4.

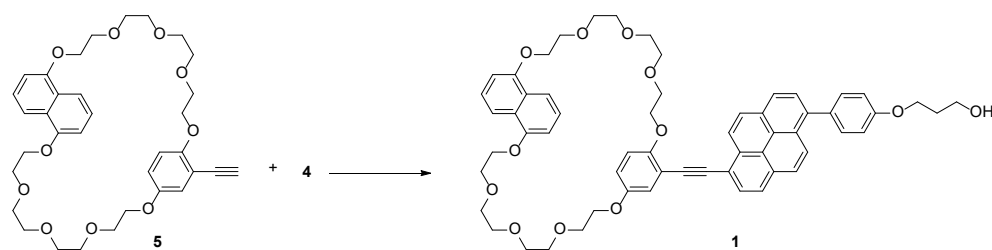


Conditions: K_2CO_3 , toluene, H_2O , EtOH, $\text{Pd}(\text{PPh}_3)_4$, reflux, 19 h.

A mixture of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)propan-1-ol^[S1] (1.84 g, 6.60 mmol), 1,6-dibromopyrene (3.56 g, 9.90 mmol), toluene (30 mL), EtOH (1 mL), K_2CO_3 (3.64 g, 26.3 mmol), H_2O (13 mL), and $\text{Pd}(\text{PPh}_3)_4$ (382 mg, 0.330 mmol) was vigorously stirred for 19 h under reflux condition. The suspension was cooled to room temperature and poured into a mixture of H_2O (100 mL) and chloroform (150 mL). The organic layer was separated off, washed with H_2O (2×100 mL), dried over MgSO_4 and filtered, before the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: chloroform) to afford compound 4 (322 mg, 0.747 mmol, 11%) as a pale yellow solid.

^1H NMR (400 MHz, CDCl_3): δ = 1.79 (t, 5.2 Hz, 1H), 2.14 (quin, J = 6.0 Hz, 2H), 3.96 (q, J = 6.0 Hz, 2H), 4.26 (t, J = 6.0 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.95–8.00 (m, 3H), 8.18–8.26 (m, 4H), 8.45 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 32.17, 60.65, 65.98, 114.56, 119.97, 124.47, 125.30, 125.32, 125.77, 125.86, 126.21, 127.10, 128.41, 128.70, 129.11, 130.02, 130.23, 130.26, 130.53, 131.80, 133.58, 138.27, 158.41. HRMS (ESI): m/z : 453.0469 (calcd. $[\text{M}+\text{Na}]^+$ = 453.0461).

Compound 1.



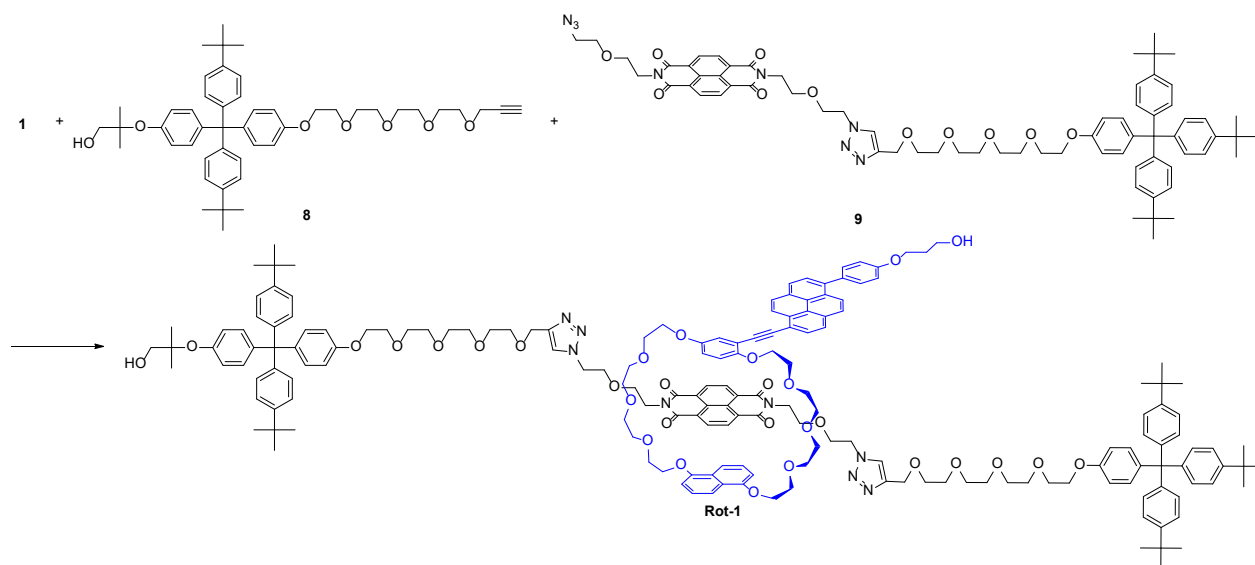
Conditions: $\text{Pd}(\text{PPh}_3)_4$, CuI, Et_2NH , THF, 80 °C, 24 h.

A mixture of compound 5^[S2] (386 mg, 0.632 mmol), compound 4 (300 mg, 0.696 mmol), $\text{Pd}(\text{PPh}_3)_4$ (36.5 mg, 3.16×10^{-2} mmol), CuI (6.0 mg, 3.2×10^{-2} mmol), and Et_2NH (20 mL) in THF (20 mL) was stirred for 24 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (100 mL) and the organic layer was washed with 5% aq. HCl (100 mL) and saturated aq. NaCl (2×100 mL). The organic layer was dried over MgSO_4 and

filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 20:1 v/v to dichloromethane/acetone = 5:1 v/v) and recycling GPC (eluent: chloroform) to afford compound **1** (351 mg, 0.365 mmol, 58%) as a yellow waxy solid.

^1H NMR (400 MHz, CDCl_3): δ = 2.05 (quin, J = 6.0 Hz, 2H), 2.23 (br, 1H), 3.61–3.78 (m, 18H), 3.83–3.86 (m, 6H), 3.95–3.98 (m, 6H), 4.10–4.19 (m, 6H), 6.50 (d, J = 8.8 Hz, 1H), 6.61 (dd, J = 2.8, 8.8 Hz, 1H), 6.66–6.71 (m, 2H), 7.02 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 2.8 Hz, 1H), 7.23–7.30 (m, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.83–7.86 (m, 2H), 7.91–7.93 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 8.14–8.19 (m, 4H), 8.78 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 32.09, 60.20, 65.67, 67.93, 68.01, 68.02, 68.86, 69.66, 69.68, 69.76, 69.82, 70.76, 70.81, 70.85, 70.87, 70.89, 70.92, 70.97, 92.05, 92.95, 105.64, 105.66, 113.55, 113.60, 114.44, 114.53, 114.69, 116.48, 118.25, 118.40, 124.30, 124.67, 124.75, 125.18, 125.20, 125.26, 125.85, 126.06, 126.71, 126.72, 127.22, 128.03, 128.69, 128.33, 129.49, 130.33, 130.99, 131.69, 132.33, 133.42, 137.96, 152.58, 154.01, 154.32, 154.34, 158.30. HRMS (ESI): m/z : 983.3998 (calcd. $[\text{M}+\text{Na}]^+$ = 983.3977).

Compound Rot-1.



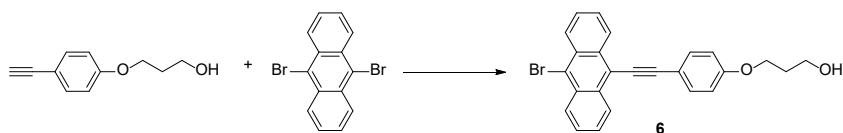
Conditions: CuSO_4 , sodium ascorbate, CHCl_3 , H_2O , 5 °C, 24 h.

A mixture of sodium ascorbate (98.2 mg, 0.496 mmol) and copper(II) sulfate (39.5 mg, 0.248 mmol) in water (1 mL) was added to a solution of compound **8**^[S2] (124 mg, 0.165 mmol), compound **9**^[S2] (200 mg, 0.165 mmol), and compound **1** (159 mg, 0.165 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 24 h at 5 °C. The suspension was poured into a mixture of water (100 mL) and chloroform (150 mL), before the organic layer was separated off, washed with saturated aq. NaCl solution (2 × 100 mL), dried over MgSO_4 and filtered, and the solvent was evaporated. The crude product thus obtained was purified by flash column chromatography on silica gel (eluent: gradient from

dichloromethane/acetone = 7:3 v/v to dichloromethane/acetone = 1:4) and recycling GPC (eluent: chloroform) to afford compound **Rot-1** (72.5 mg, 2.48×10^{-2} mmol, 15%) as a brown solid.

^1H NMR (400 MHz, CDCl_3): δ = 1.28 (s, 6H), 1.29 (s, 45H), 2.03 (t, J = 4.8 Hz, 1H), 2.11–2.17 (m, 2H), 2.29 (t, J = 6.4 Hz, 1H), 3.50–4.08 (m, 80H), 4.27 (t, J = 6.0 Hz, 2H), 4.35 (br, 4h), 4.65 (br, 4h), 5.91–5.93 (m, 2H), 6.03 (dd, J = 2.8, 8.8 Hz, 1H), 6.09–6.13 (m, 2H), 6.60–6.70 (m, 2H), 6.75 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 8.8 Hz, 2H), 6.89–6.96 (m, 2H), 7.03–7.08 (m, 16H), 7.13 (d, J = 8.8 Hz, 2H), 7.21–7.23 (m, 10H), 7.55 (d, J = 8.8 Hz, 2H), 7.69 (br, 2H), 8.00–8.03 (m, 3H), 8.11 (d, J = 8.0 Hz, 1H), 8.17–8.27 (m, 3H), 8.43 (d, J = 8.8 Hz, 1H), 8.54 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ = 23.28, 31.48, 32.19, 34.38, 34.40, 38.66, 50.38, 60.46, 63.05, 63.13, 64.63, 65.91, 67.26, 67.28, 67.52, 67.57, 67.78, 68.11, 68.59, 69.58, 69.78, 69.84, 69.99, 70.02, 70.07, 70.44, 70.59, 70.65, 70.66, 70.68, 70.84, 71.10, 71.24, 71.35, 71.42, 71.49, 71.59, 80.53, 91.05, 92.60, 103.62, 103.64, 110.26, 111.71, 113.14, 113.22, 113.92, 114.32, 114.67, 116.61, 117.90, 122.29, 123.74, 124.13, 124.21, 124.36, 124.72, 124.76, 124.93, 124.98, 125.28, 125.51, 125.71, 126.34, 127.36, 128.30, 128.50, 128.80, 129.78, 130.40, 130.75, 130.81, 131.16, 131.35, 131.80, 131.97, 132.23, 132.25, 132.30, 133.42, 138.28, 139.68, 139.83, 142.75, 144.10, 144.22, 148.38, 148.55, 151.14, 152.45, 152.51, 153.20, 153.23, 156.62, 156.71, 158.49, 163.20. HRMS (ESI): m/z : 1461.7455 (calcd. $[\text{M}+2\text{H}]^{2+}$ = 1461.7414).

Compound 6.

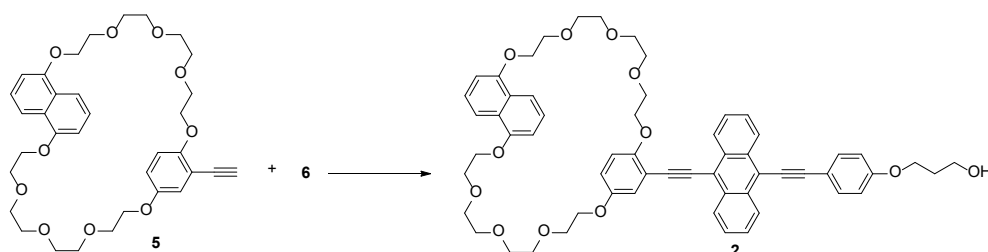


Conditions: $\text{Pd}(\text{PPh}_3)_4$, CuI , $i\text{-Pr}_2\text{NH}$, THF, 80 °C, 17 h.

A mixture of 3-(4-ethynylphenoxy)propan-1-ol^[S3] (500 mg, 2.84 mmol), 9,10-dibromoanthracene (1.43 g, 4.26 mmol), $\text{Pd}(\text{PPh}_3)_4$ (164 mg, 0.142 mmol), CuI (27.0 mg, 0.142 mmol), and $i\text{-Pr}_2\text{NH}$ (30 mL) in THF (20 mL) was stirred for 17 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into chloroform (300 mL) and the organic layer was washed with 5% aq. HCl (2×100 mL) and saturated aq. NaCl (2×100 mL). The organic layer was dried over MgSO_4 and filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography on silica gel (eluent: gradient from chloroform to chloroform/ethyl acetate = 10:1 v/v) to afford compound **6** (747 mg, 1.73 mmol, 61%) as a yellow cottony solid.

^1H NMR (400 MHz, CDCl_3): δ = 1.76 (t, J = 4.8 Hz, 1H), 2.07 (quin, J = 6.0 Hz, 2H), 3.88 (q, J = 5.2 Hz, 2H), 4.16 (t, J = 6.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.57–7.62 (m, 4H), 7.68 (d, J = 8.8 Hz, 2H), 8.51–8.54 (m, 2H), 8.64–8.67 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 32.07, 60.33, 65.78, 84.97, 102.09, 114.84, 115.72, 118.80, 123.74, 126.75, 127.43, 127.51, 128.29, 130.36, 132.92, 133.27, 159.35. HRMS (ESI): m/z : 453.0461 (calcd. $[\text{M}+\text{Na}]^+$ = 453.0471).

Compound 2.

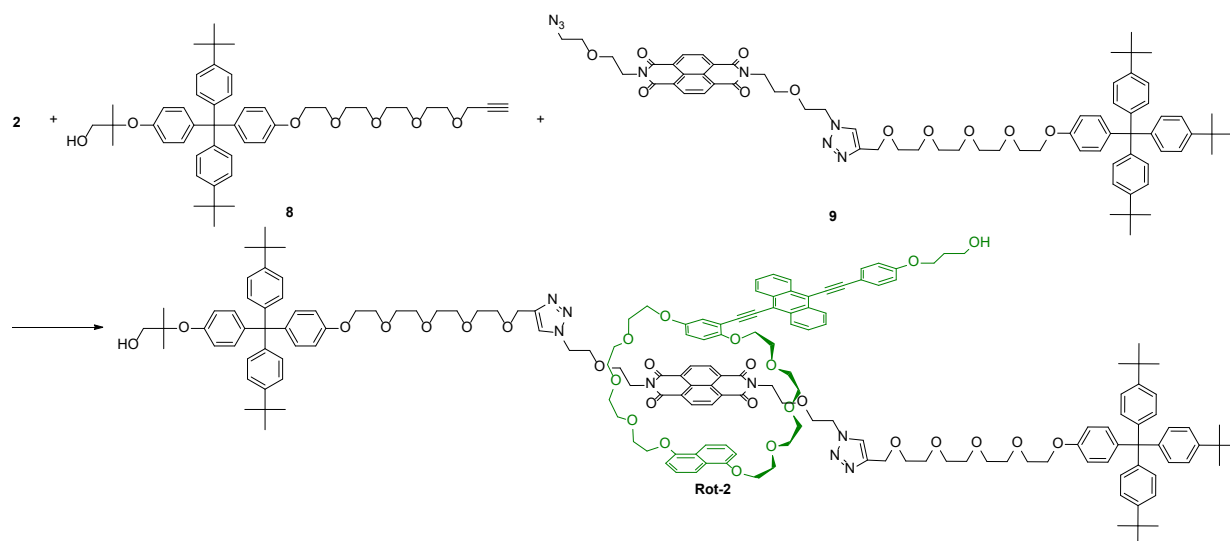


Conditions: Pd(PPh₃)₄, CuI, Et₂NH, THF, 80 °C, 20 h.

A mixture of compound **5**^[S2] (880 mg, 1.44 mmol), compound **6** (622 mg, 1.44 mmol), Pd(PPh₃)₄ (83.2 mg, 7.20 × 10⁻² mmol), CuI (13.7 mg, 7.20 × 10⁻² mmol), and Et₂NH (20 mL) in THF (20 mL) was stirred for 20 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL) and the organic layer was washed with 5% aq. HCl (100 mL), and saturated aq. NaCl (2 × 100 mL). The organic layer was dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was then purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 20:1 v/v to dichloromethane/acetone = 5:1 v/v) and recycling GPC (eluent: chloroform) to afford compound **2** (990 mg, 0.717 mmol, 72%) as an orange waxy solid.

¹H NMR (400 MHz, CDCl₃): δ = 1.72 (t, *J* = 4.8 Hz, 1H), 2.09 (quin, *J* = 6.0 Hz, 2H), 3.62–3.67 (m, 6H), 3.72–3.92 (m, 18H), 3.98–4.03 (m, 6H), 4.12 (t, *J* = 4.8 Hz, 2H), 4.18–4.23 (m, 4H), 6.52 (d, *J* = 8.8 Hz, 1H), 6.62 (dd, *J* = 3.2, 8.8 Hz, 1H), 6.67–6.73 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 3.2 Hz, 1H), 7.23–7.28 (m, 2H), 7.60–7.64 (m, 4H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.82–7.85 (m, 2H), 8.66–8.70 (m, 2H), 8.75–8.79 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 32.06, 60.25, 65.73, 67.97, 68.11, 68.16, 68.64, 69.75, 69.81, 69.89, 70.88, 70.91, 71.00, 71.05, 71.10, 85.61, 90.86, 99.35, 102.64, 105.68, 105.70, 113.27, 113.53, 114.58, 114.75, 114.84, 115.82, 116.66, 118.59, 118.65, 118.71, 125.22, 125.27, 126.78, 126.79, 127.29, 127.74, 132.04, 132.12, 133.30, 152.61, 154.10, 154.40, 154.42, 159.33. HRMS (ESI): *m/z*: 983.4003 (calcd. [M+Na]⁺ = 983.3977).

Compound Rot-2.

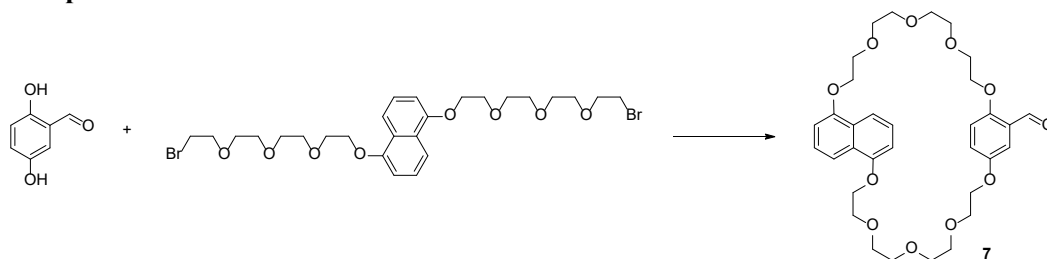


Conditions: CuSO₄, sodium ascorbate, CHCl₃, H₂O, 5 °C, 24 h.

A mixture of sodium ascorbate (98.2 mg, 0.496 mmol) and copper(II) sulfate (39.5 mg, 0.248 mmol) in water (1 mL) was added to a solution of compound **8**^[S2] (124 mg, 0.165 mmol), compound **9**^[S2] (200 mg, 0.165 mmol), and compound **2** (159 mg, 0.165 mmol) in chloroform (0.5 mL) and the mixture was vigorously stirred for 24 h at 5 °C. The suspension was poured into a mixture of water (150 mL) and chloroform (150 mL), before the organic layer was separated off, washed with saturated aq. NaCl solution (2 × 100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product thus obtained was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 7:3 v/v to dichloromethane/acetone = 1:4) and recycling GPC (eluent: chloroform) to afford compound **Rot-2** (83.2 mg, 2.85 × 10⁻² mmol, 17%) as a dark brown solid.

¹H NMR (400 MHz, CDCl₃): δ = 1.28 (s, 6H), 1.29 (s, 45H), 1.91 (br, 1H), 2.07–2.13 (m, 2H), 2.22 (br, 1H), 3.46–4.07 (m, 80H), 4.22 (t, *J* = 6.0 Hz, 2H), 4.46 (br, 4h), 4.68 (br, 4h), 5.98 (d, *J* = 8.8 Hz, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 6.05–6.08 (m, 2H), 6.11 (dd, *J* = 3.2, 8.8 Hz, 1H), 6.54–6.67 (m, 2H), 6.76 (d, *J* = 8.8 Hz, 4H), 6.82–6.95 (m, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.03–7.08 (m, 16H), 7.20–7.23 (m, 10H), 7.61–7.73 (m, 8H), 8.37–8.39 (m, 2H), 8.46 (s, 4H), 8.68–8.70 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 23.28, 31.49, 32.11, 34.40, 38.51, 50.60, 60.06, 63.05, 63.14, 63.14, 64.68, 65.69, 67.27, 67.30, 67.49, 67.62, 67.67, 68.63, 69.57, 69.79, 69.85, 69.96, 70.02, 70.07, 70.46, 70.61, 70.66, 70.85, 71.09, 71.16, 71.24, 71.29, 71.40, 71.44, 80.54, 85.58, 90.40, 98.29, 103.04, 103.58, 103.63, 110.19, 111.73, 113.15, 113.23, 113.98, 114.25, 114.38, 115.00, 115.55, 117.36, 118.02, 118.79, 122.30, 123.75, 124.14, 124.22, 124.94, 124.96, 124.98, 125.25, 126.95, 127.01, 127.26, 127.49, 130.76, 130.82, 131.26, 131.91, 131.98, 132.24, 132.31, 133.34, 139.69, 139.69, 139.84, 139.84, 142.76, 144.11, 144.23, 148.39, 148.39, 148.56, 151.23, 152.46, 153.20, 156.63, 156.72, 159.53, 163.04. HRMS (ESI): *m/z*: 1461.7436 (calcd. [M+2H]²⁺ = 1461.7414).

Compound 7.

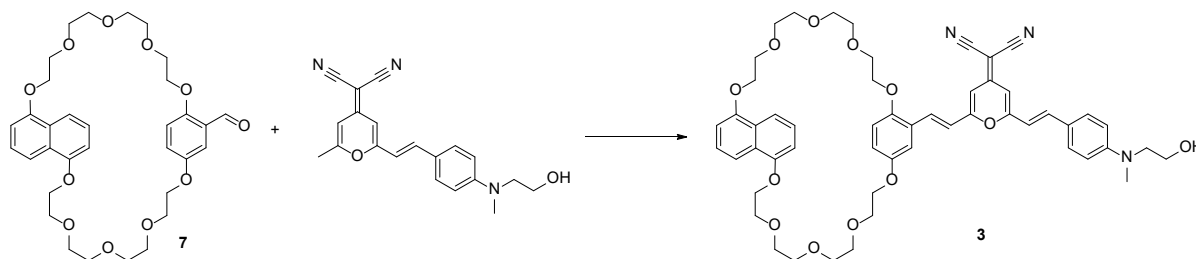


Conditions: K_2CO_3 , DMF, 80 °C, 30 h.

A solution of 2,5-dihydroxybenzaldehyde (325 mg, 2.35 mmol) and 1,5-bis(2-(2-(2-bromoethoxy)ethoxy)ethoxy)naphthalene (1.50 g, 2.35 mmol) in DMF (20 mL) was added over the course of 6 h and under vigorous stirring to a suspension of K_2CO_3 (3.25 g, 23.5 mmol) in DMF (250 mL) at 80 °C. After further stirring for 24 h at 80 °C, the solvent was evaporated. Ethyl acetate (250 mL) was added and the organic layer was washed with saturated aq. NH_4Cl (3 × 100 mL) and saturated aq. NaCl (100 mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. The crude product thus isolated was purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 20:1 v/v to dichloromethane/acetone = 17:3) to afford compound 7 (581 mg, 0.945 mmol, 40%) as a white solid.

1H NMR (400 MHz, $CDCl_3$): δ = 3.65–3.81 (m, 22H), 3.88–3.90 (m, 2H), 3.97–4.01 (m, 4H), 4.16–4.22 (m, 4H), 6.31 (d, J = 9.2 Hz, 1H), 6.69–6.75 (m, 2H), 6.84 (dd, J = 9.2, 3.2 Hz, 1H), 7.12 (d, J = 3.2 Hz, 1H), 7.24–7.29 (m, 2H), 7.80–7.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.98, 68.02, 68.09, 68.66, 69.59, 69.64, 69.78, 69.85, 70.67, 70.83, 70.91, 70.94, 70.98, 71.00, 71.07, 71.22, 76.84, 77.16, 77.48, 105.53, 105.57, 110.68, 114.52, 114.58, 114.64, 124.08, 124.95, 125.16, 125.19, 126.66, 126.71, 152.77, 154.33, 154.38, 156.01, 189.68. HRMS (ESI): m/z : 637.2617 (calcd. $[M+Na]^+$ = 637.2619).

Compound 3.



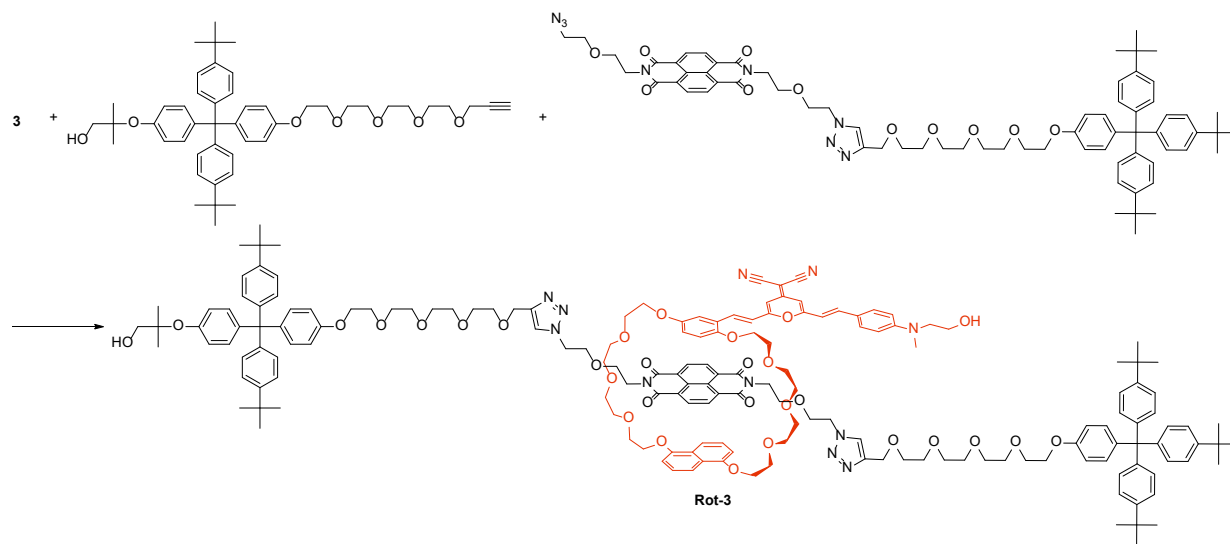
Conditions: piperidine, MeCN, reflux, 15 h.

A mixture of compound 7 (489 mg, 0.795 mmol), (E)-2-(2-(4-((2-hydroxyethyl)(methyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile^[S4] (265 mg, 0.795 mmol), and piperidine (1 mL) in MeCN (50 mL) was stirred under

reflux condition for 15 h. After cooling to room temperature, the reaction mixture was poured into ethyl acetate (150 mL) and the organic layer was washed with H₂O (200 mL), saturated aq. NH₄Cl (3 × 100 mL), and saturated aq. NaCl (100 mL). The organic layer was dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product thus isolated was then purified by flash column chromatography on silica gel (eluent: gradient from dichloromethane/acetone = 10:1 v/v to dichloromethane/acetone = 13:7) and recycling GPC (eluent: chloroform) to afford compound **3** (355 mg, 0.382 mmol, 48%) as a dark red solid.

¹H NMR (400 MHz, CDCl₃): δ = 1.99 (t, *J* = 1.6 Hz, 1H), 3.09 (s, 3H), 3.58 (t, *J* = 5.6 Hz, 2H), 3.67–3.77 (m, 14H), 3.81–3.93 (m, 14H), 3.98–4.01 (m, 2H), 4.08–4.11 (m, 2H), 4.17–4.20 (m, 2H), 6.43–6.50 (m, 4H), 6.60–6.69 (m, 3H), 6.75–6.80 (m, 3H), 6.82 (d, *J* = 2.8 Hz, 1H), 7.20–7.24 (m, 2H), 7.35 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 16.0 Hz, 1H), 7.76–7.82 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 39.07, 54.66, 57.16, 60.14, 67.99, 68.04, 68.11, 68.31, 69.78, 69.80, 69.87, 70.69, 70.87, 70.92, 70.96, 70.98, 71.02, 71.04, 71.06, 105.54, 105.57, 105.64, 107.06, 112.19, 113.05, 113.67, 114.10, 114.59, 114.62, 116.06, 116.18, 117.80, 119.58, 122.79, 124.24, 125.20, 125.23, 126.64, 126.70, 129.91, 132.86, 138.51, 151.31, 151.99, 152.89, 154.30, 154.36, 156.16, 158.65, 159.45. HRMS (ESI): *m/z*: 952.3995 (calcd. [M+Na]⁺ = 952.3991).

Compound Rot-3.



Conditions: CuSO₄, sodium ascorbate, CHCl₃, H₂O, 5 °C, 24 h.

A mixture of sodium ascorbate (98.2 mg, 0.495 mmol) and copper(II) sulfate (39.5 mg, 0.248 mmol) in water (1 mL) was added to a solution of compound **8** (126 mg, 0.168 mmol), compound **9** (200 mg, 0.168 mmol), and compound **3** (156 mg, 0.168 mmol) in chloroform (1 mL) and the mixture was vigorously stirred for 24 h at 5 °C. The suspension was poured into a mixture of water (100 mL) and chloroform (100 mL), before the organic layer was separated off, washed with saturated aq. NaCl solution (2 × 100 mL), dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product thus obtained was purified by flash column chromatography on silica gel (eluent: gradient from

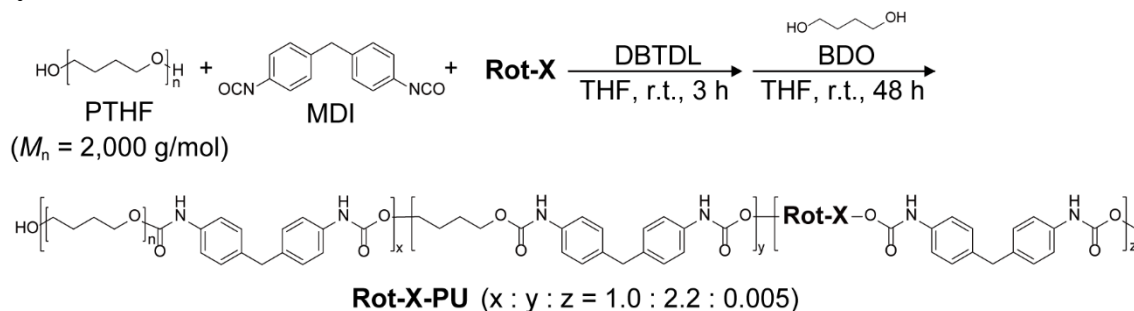
dichloromethane/acetone = 2:1 v/v to acetone) and recycling GPC (eluent: chloroform) to afford compound **Rot-3** (147 mg, 5.08×10^{-2} mmol, 30%) as a dark red solid.

^1H NMR (400 MHz, CDCl_3): δ = 1.28 (s, 6H), 1.29 (s, 45H), 2.24 (t, J = 6.4 Hz, 1H), 2.76 (br, 1H), 3.12 (s, 3H), 3.57–4.00 (m, 74H), 4.08 (t, J = 4.8 Hz, 4H), 4.16–4.30 (m, 4H), 4.54 (br, 4H), 4.67 (br, 4H), 5.70 (d, J = 2.8 Hz, 1H), 5.90 (d, J = 8.8 Hz, 1H), 6.00 (dd, J = 2.8, 8.8 Hz, 1H), 6.12 (d, J = 7.6 Hz, 2H), 6.46 (d, J = 2.0 Hz, 1H), 6.54 (d, J = 16.0 Hz, 1H), 6.61–6.71 (m, 5H), 6.76 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.89–6.95 (m, 2H), 7.03–7.08 (m, 16H), 7.20–7.24 (m, 10H), 7.37 (d, J = 16.0 Hz, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.77 (br, 2H), 8.46 (s, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ = 23.25, 31.44, 31.45, 34.35, 34.36, 38.60, 39.16, 50.54, 54.65, 57.65, 59.91, 62.99, 63.00, 63.01, 63.02, 63.08, 63.08, 63.09, 64.58, 67.00, 67.24, 67.27, 67.52, 67.97, 68.67, 69.45, 69.52, 69.78, 69.80, 69.81, 69.88, 70.04, 70.38, 70.55, 70.60, 70.63, 70.64, 70.81, 71.00, 71.03, 71.13, 71.18, 71.35, 71.39, 80.49, 103.51, 103.63, 105.45, 107.33, 110.61, 112.24, 112.82, 113.10, 113.19, 114.20, 114.28, 114.30, 114.46, 121.00, 122.26, 122.41, 122.45, 123.71, 123.74, 124.09, 124.18, 124.65, 124.89, 124.92, 125.02, 129.95, 130.71, 130.77, 131.35, 131.93, 132.07, 132.19, 132.27, 138.73, 139.65, 139.80, 142.69, 144.06, 144.17, 144.18, 148.33, 148.34, 148.49, 148.51, 150.76, 151.35, 151.42, 153.15, 153.19, 155.96, 156.58, 156.67, 158.37, 159.50, 163.12.

HRMS (ESI): m/z : 1468.2209 (calcd. $[\text{M}+2\text{Na}]^{2+}$ = 1468.2246).

Polymer Synthesis



Synthesis of polyurethane Rot-1-PU. Dibutyltin dilaurate (4 drops) was added to a stirred mixture of **Rot-1** (20 mg, 6.8×10^{-3} mmol), 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 (30 mL) and the mixture was stirred at room temperature for 3 h. A solution of 1,4-butanediol (297 mg, 3.30 mmol) in THF (10 mL) was then added and the reaction mixture was stirred at room temperature for an additional 24 h. EtOH (2 mL) was added to the reaction mixture and after stirring for another 30 min the reaction mixture was poured into EtOH (500 mL). The pale yellow precipitate was collected by filtration, dissolved in THF (300 mL), the solution was filtrated through a cotton filter while approximately half of solvent evaporated, and the polymer was precipitated into hexane (400 mL). The precipitate was filtered off and dried *in vacuo* for 24 h at room temperature to afford **Rot-1-PU** as a pale yellow rubbery solid (4.26 g, 93%, $M_n = 79,400$ g/mol).

Synthesis of polyurethane Rot-2-PU and Rot-3-PU. Following the synthetic procedure used for **Rot-1-PU**, polyurethanes **Rot-2-PU** and **Rot-3-PU** were prepared and obtained as a yellow rubbery solid (**Rot-2-PU**: 3.98 g, 87%, $M_n = 43,900$ g/mol) and a red rubbery solid (**Rot-3-PU**: 4.10 g, 90%, $M_n = 67,300$ g/mol), respectively. The concentration of the rotaxane was the same for all polyurethanes.

Preparation of Polyurethane Films

Preparation of Rot-1-PU, Rot-2-PU, or Rot-3-PU films. The polyurethane (**Rot-1-PU**, **Rot-2-PU**, or **Rot-3-PU**, 300 mg) were dissolved in THF (10 mL) and the solutions were divided between three round poly(tetrafluoroethylene) molds (32×3.5 mm). The molds were placed in a well-ventilated hood under an inverted funnel so that the evaporation rate was controlled. The solvent was evaporated overnight under ambient conditions and the resulting films were further dried *in vacuo* at room temperature overnight. The films thus obtained are smooth and transparent. The thickness of the films is 80-100 μm , which were measured by a digital caliper.

Preparation of Rot-Mix-PU, Rot-2-PU, or Rot-3-PU films. The polyurethanes **Rot-1-PU**, **Rot-2-PU**, and **Rot-3-PU** (weight ratio: 8:16:5, total amount: 300 mg) were dissolved in THF (10 mL) and the same procedure was adapted as the above films. The films thus obtained are smooth and transparent. The thickness of the films is 80-100 μm .

^1H NMR Spectra of Rotaxanes

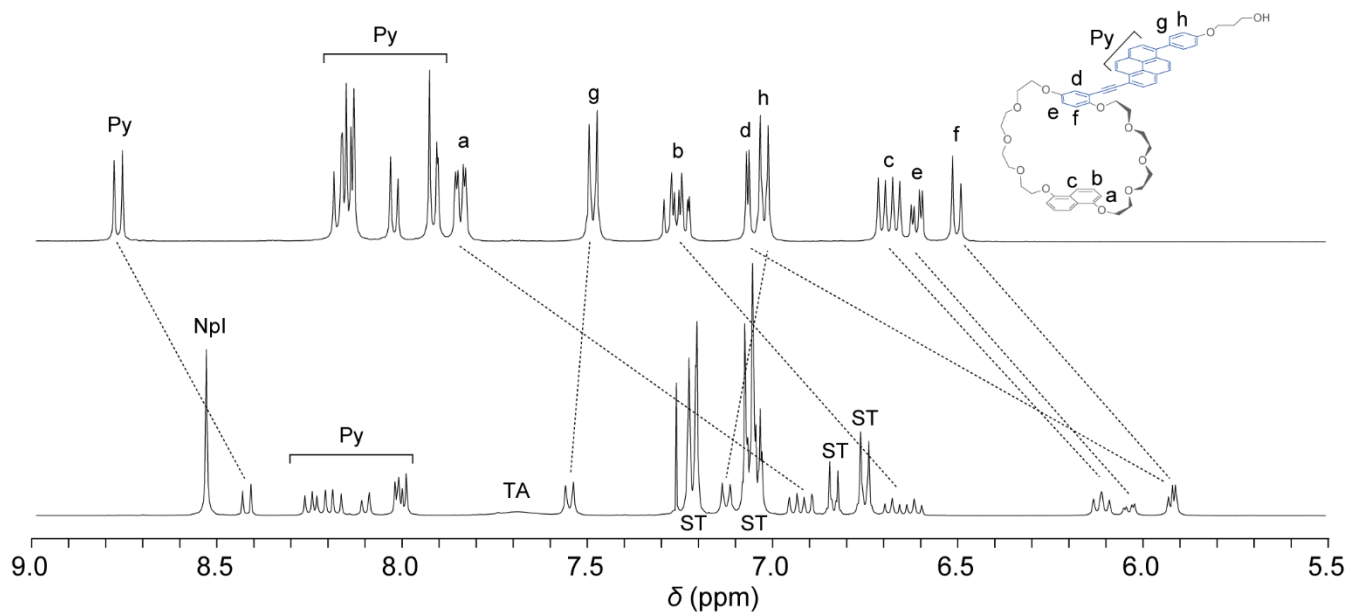


Figure S1. Partial ^1H NMR spectrum of pyrene-based, cyclic luminophore **1** (top) and the corresponding rotaxane **Rot-1** (bottom). The abbreviations “PY”, “ST”, “TA” and “Npl” indicate signals ascribed to the pyrene, stoppers, triazole and quencher moieties. Both spectra were measured in CDCl_3 at 293 K.

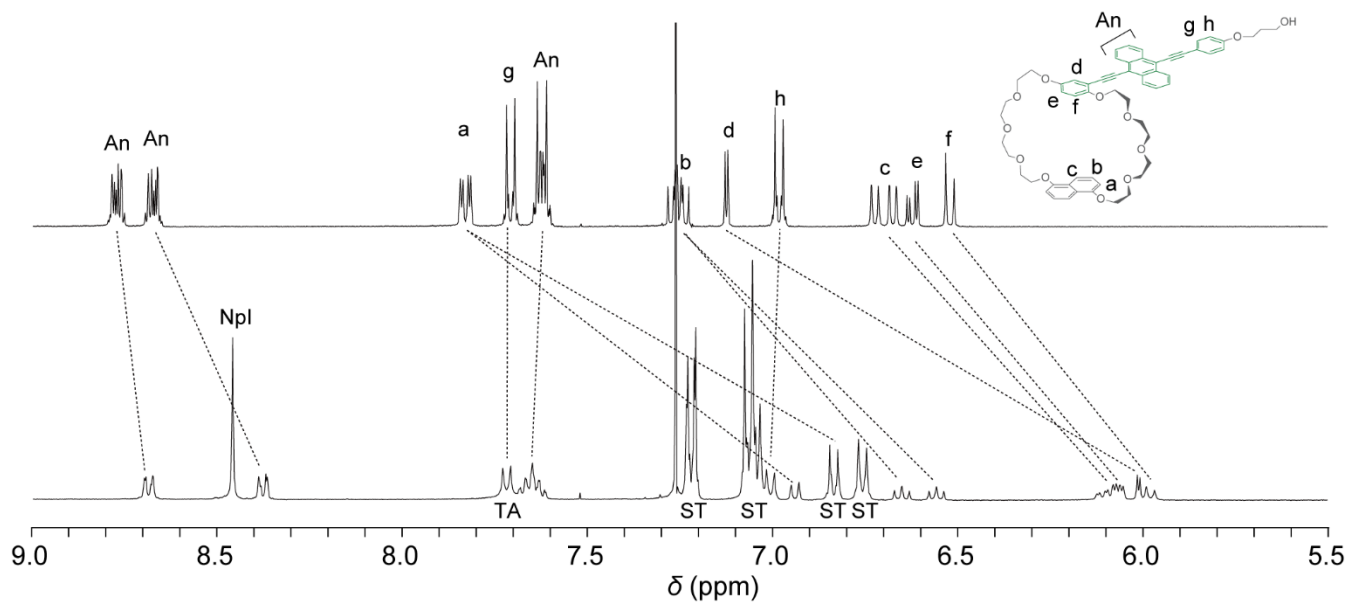


Figure S2. Partial ^1H NMR spectrum of anthracene-based, cyclic luminophore **2** (top) and the corresponding rotaxane **Rot-2** (bottom). The abbreviation “An” indicates signals ascribed to the anthracene group. Both spectra were measured in CDCl_3 at 293 K.

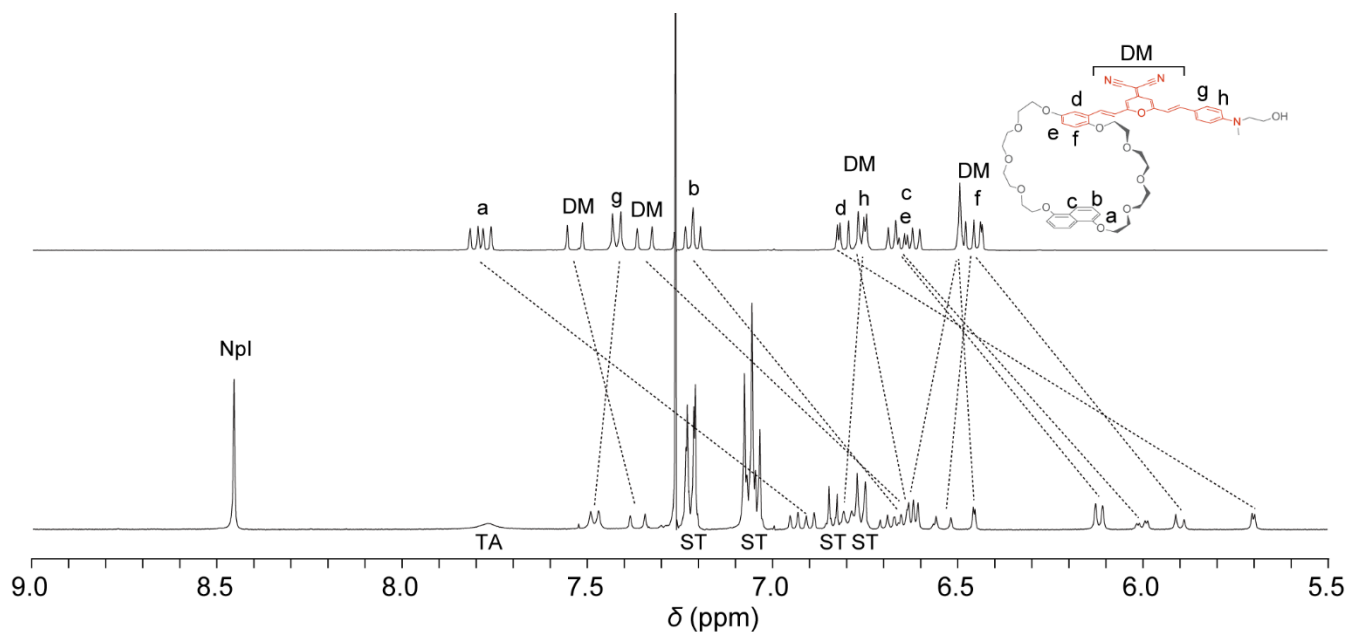


Figure S3. Partial ^1H NMR spectrum of DCM-based, cyclic luminophore **3** (top) and the corresponding rotaxane **Rot-3** (bottom). The abbreviations “DM” indicate signals ascribed to the central aromatic ring and alkene groups of DCM moieties. Both spectra were measured in CDCl_3 at 293 K.

White Photoluminescence in Solution

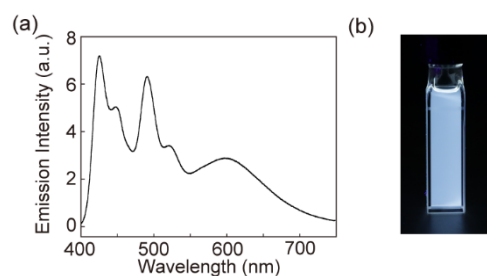


Figure S4. (a) Fluorescence spectrum of a hexane/chloroform (3:2 v/v) solution of a mixture of the cyclic compounds **1-3**. The molar ratio of **1**, **2**, and **3** was 1 : 6 : 10 and the concentration of compound **1** was ca. 1×10^{-6} M. $\lambda_{\text{ex}} = 380$ nm. (b) Photograph documenting the white photoluminescence exhibited by the same solution under excitation with 365 nm UV light.

^1H NMR Spectra of Polyurethanes

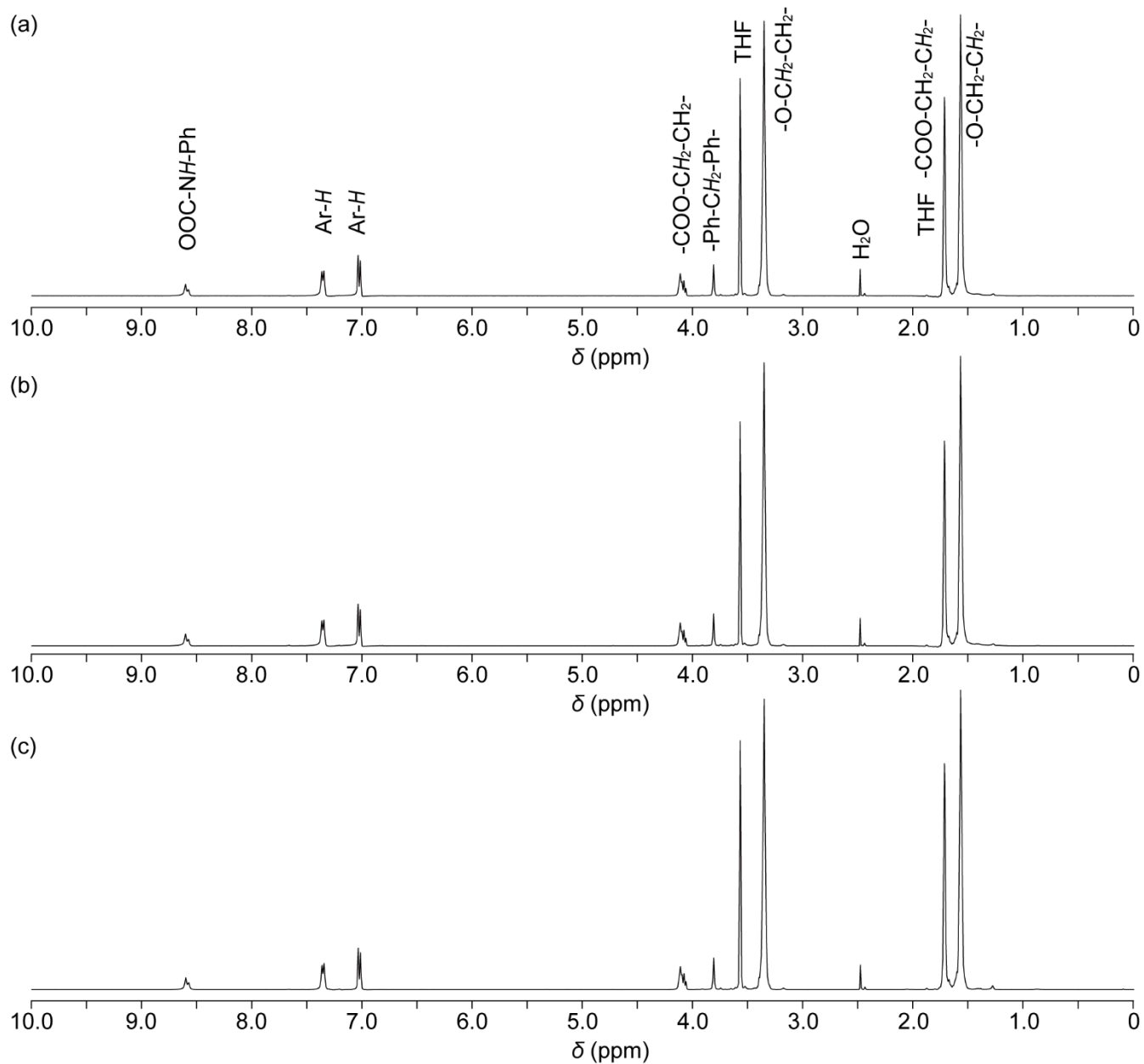


Figure S5. ^1H NMR spectra of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU** in $\text{THF-}d_8$. Signals are characterized as protons of the polyurethane chains. No signals ascribed to the rotaxane mechanophores are observed due to their very low concentration. All spectra were measured at 293 K.

Thermal Properties of Polyurethanes

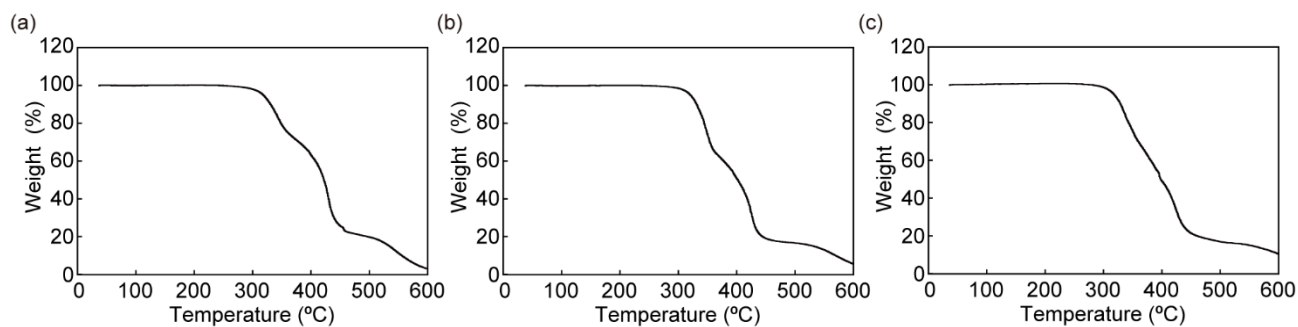


Figure S6. Thermogravimetric analyses (TGA) traces of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU**. The TGA experiments were conducted under N₂ at a heating rate of 10 °C/min.

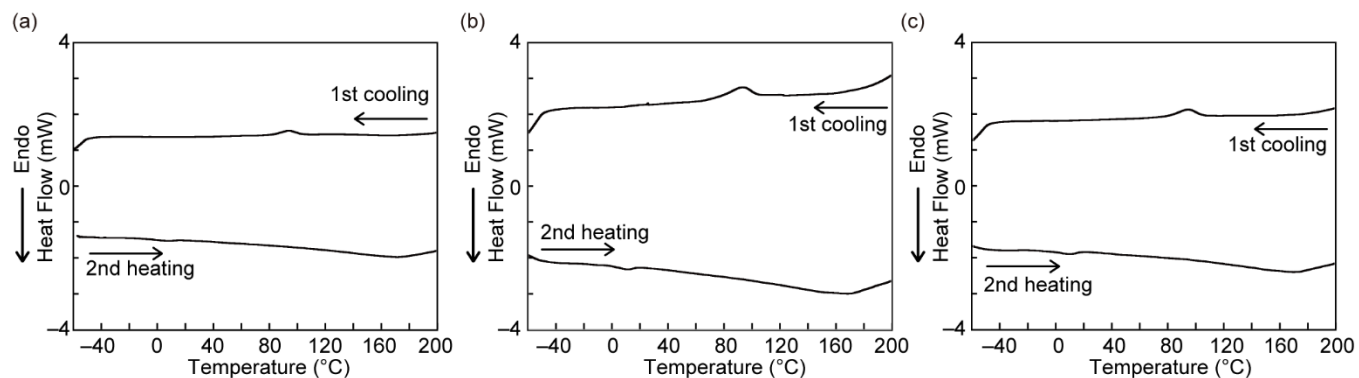


Figure S7. Differential scanning calorimetry (DSC) traces of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU**. The heating and cooling rates were 10 °C/min.

Mechanical Properties of Polyurethanes

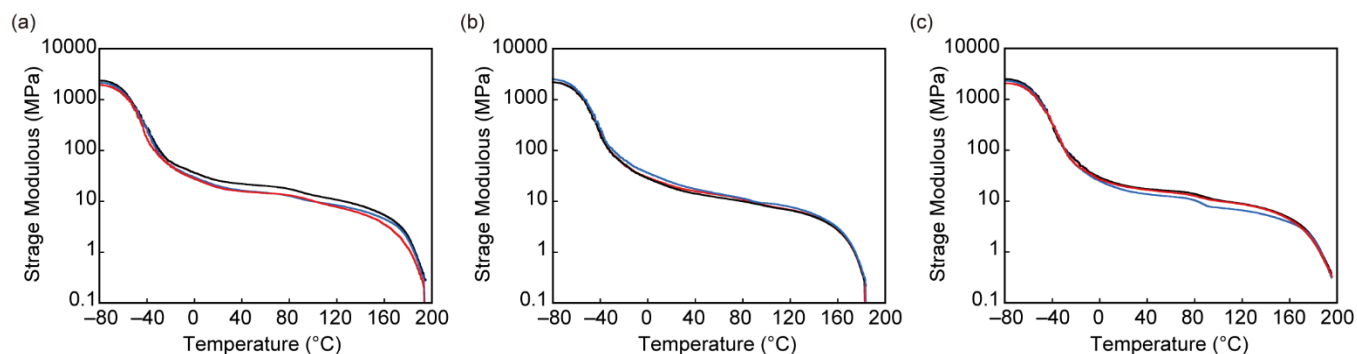


Figure S8. Dynamic mechanical analysis (DMA) traces of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU**. Each graph shows data obtained from three different samples. The measurements were conducted under N₂ at a heating rate of 3 °C/min, a frequency of 1 Hz, and an amplitude of 15 μm.

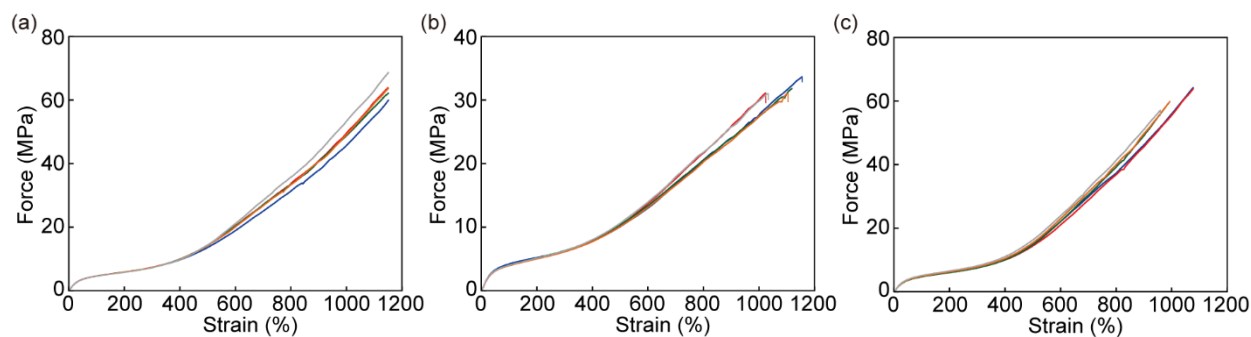


Figure S9. Stress-strain curves of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU**. Each graph shows data obtained from five different specimen. The experiments were conducted with a strain rate of 100 mm/min at room temperature.

Table S1. Mechanical data of the polyurethanes extracted from tensile tests.^{a)}

	Elongation at break (%)	Stress at break (MPa)	Young's modulus ^{b)} (MPa)
Rot-1-PU	1168 ± 22	65.3 ± 3.4	14.2 ± 0.29
Rot-2-PU	1086 ± 57	31.8 ± 1.1	12.8 ± 0.19
Rot-3-PU	1018 ± 56	60.8 ± 3.2	13.8 ± 0.48

^{a)}All data were extracted from the stress-strain curves shown in Figure S9 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 0.5–1.0 %

Images of Polyurethane Films During Uniaxial Deformation

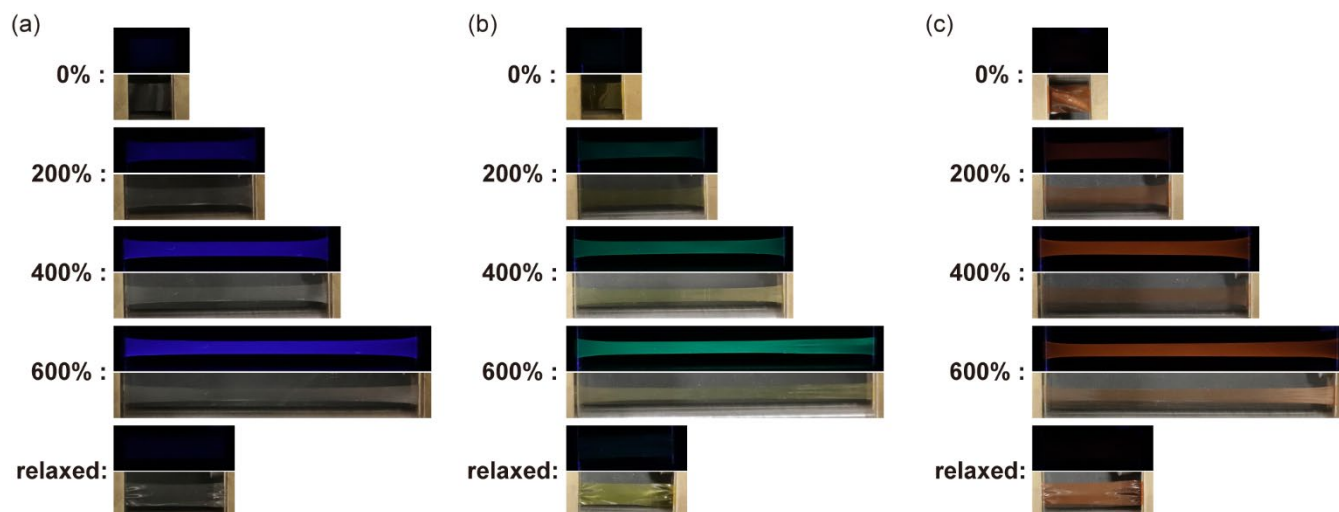


Figure S10. Pictures of (a) **Rot-1-PU**, (b) **Rot-2-PU**, and (c) **Rot-3-PU** under cyclic uniaxial deformation test. For each strained state, the top image shows the photoluminescence of the film; these pictures were taken in the dark under excitation with 365 nm UV light. The bottom image was taken under ambient illumination. All images were taken under the same ambient conditions.

Photoluminescence Spectra of Polymer Solutions

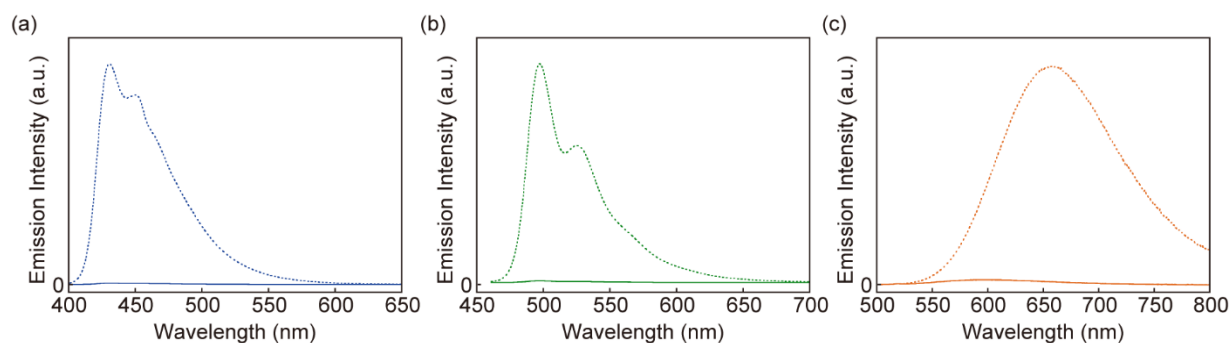


Figure S11. Fluorescence spectra of (a) **1** and **Rot-1-PU** ($\lambda_{\text{ex}} = 380$ nm), (b) **2** and **Rot-2-PU** ($\lambda_{\text{ex}} = 450$ nm), and (c) **3** and **Rot-3-PU** ($\lambda_{\text{ex}} = 450$ nm) in THF. Dotted lines represent the fluorescence spectra of **1-3**, while solid lines represent those of polymers. Concentration of luminophores and rotaxanes embedded in polymers are 1.0×10^{-5} M.

Reversibility of the Mechanically Induced Photoluminescence Switching

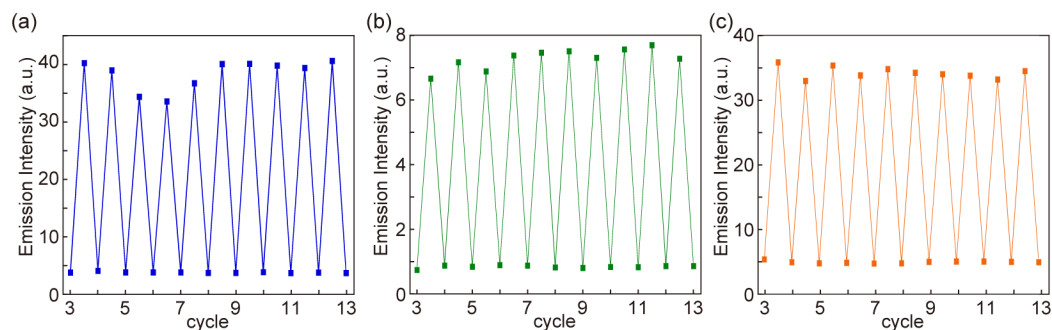


Figure S12. Plots of the emission intensities of the (a) **Rot-1-PU** film monitored at 450 nm ($\lambda_{ex} = 365$ nm), (b) **Rot-2-PU** film monitored at 500 nm ($\lambda_{ex} = 380$ nm), and (c) **Rot-3-PU** film monitored at 600 nm ($\lambda_{ex} = 365$ nm). The intensities were recorded at the strain rate was 600% and the relaxed states over ten cycles.

Photoluminescence Spectra of the Rotaxane-Containing Polymers in Solutions After Cyclic Mechanical Tests

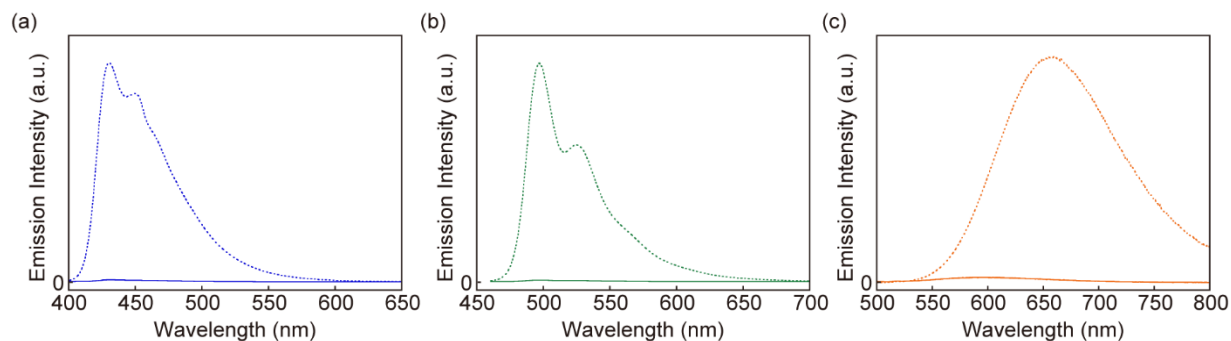


Figure S13. Fluorescence spectra of (a) **1** and **Rot-1-PU** ($\lambda_{ex} = 380$ nm), (b) **2** and **Rot-2-PU** ($\lambda_{ex} = 450$ nm), and (c) **3** and **Rot-3-PU** ($\lambda_{ex} = 450$ nm) in THF. The polymer samples used for the cyclic tests shown in Figure 12 were redissolved for photoluminescence spectroscopic measurements. Dotted lines represent the fluorescence spectra of **1-3**, while solid lines represent those of polymers. The concentration of all luminophores and rotaxanes embedded in the polymers are 1.0×10^{-5} M.

Images of a Rot-Mix-PU Film Acquired Upon Uniaxial Deformation and After Subsequent Relaxation

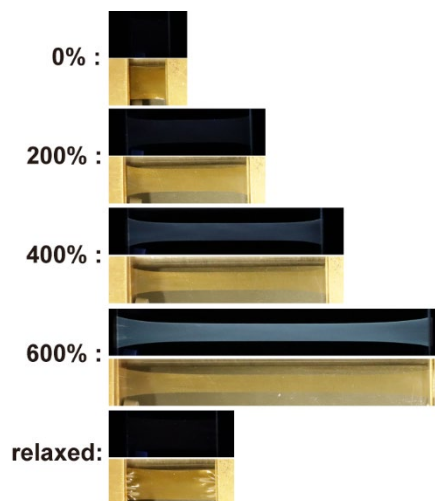


Figure S14. Pictures of a **Rot-Mix-PU** film taken upon step-wise uniaxial deformation to the strain indicated and after subsequent relaxation. For each strained state, the top image shows the photoluminescence of the film; these pictures were taken in the dark under excitation with 365 nm UV light. The bottom images were taken under ambient illumination.

Photoluminescence Spectra of a Rot-Mix-PU Film Acquired Upon Releasing the Mechanical Stress from a Strained State

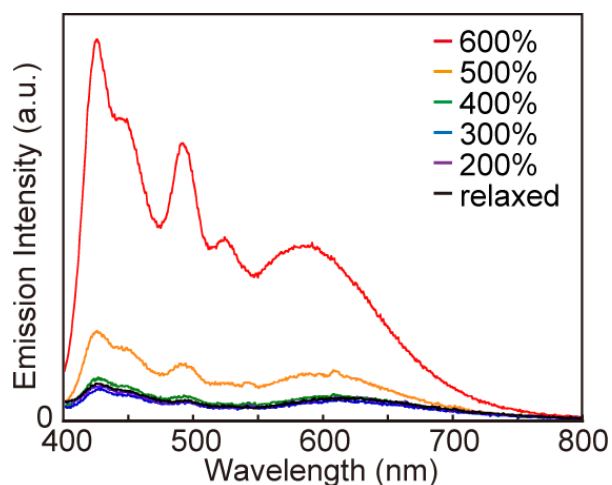


Figure S15. Change of the photoluminescence spectra of a **Rot-Mix-PU** ($\lambda_{\text{ex}} = 365 \text{ nm}$) film upon relaxing the sample from an initial strain of 600% in a step-wise manner to the strains indicated.

Reversibility of the Photoluminescence Switching in a White Light Emitting Blend Film

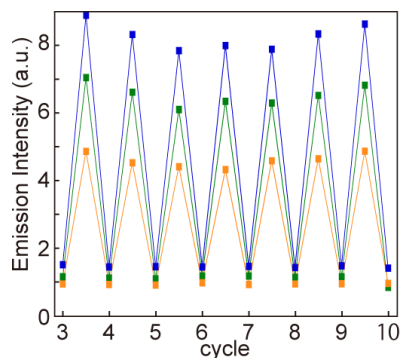


Figure S16. Plots of the emission intensities of a **Rot-Mix-PU** ($\lambda_{\text{ex}} = 365$ nm) film monitored at 450 nm (blue), 500 nm (green), and 600 nm (orange). The intensities were recorded at a strain of 600% and in the relaxed states over seven cycles of stretching and relaxing. The initial two cycles were omitted due to hysteresis.

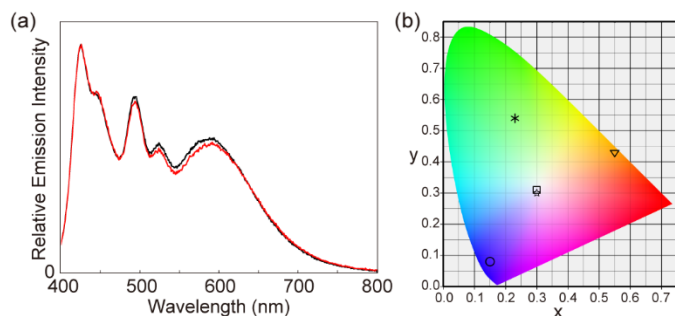


Figure S17. (a) Photoluminescence spectra of a **Rot-Mix-PU** film acquired during the first uniaxial deformation to a strain of 600% (black line) and after 20 cycles of stretching to 600% and releasing the strain (red line, the spectrum was recorded at a strain of 600%). The emission spectra were normalized to display the same intensity at 425 nm ($\lambda_{\text{ex}} = 365$ nm). (b) CIE coordinates (☆) of the **Rot-Mix-PU** film used in (a) after 20 stretch and release cycles, recorded at a strain of 600% ($\lambda_{\text{ex}} = 365$ nm); the other symbols represent the CIE coordinates depicted in Figure 6b.

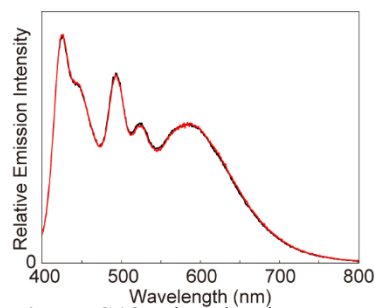


Figure S18. Photoluminescence spectra of the **Rot-Mix-PU** film used to create the data shown in Figure S17 after 20 cycles of stretching to 600% and releasing the strain (black line, the spectrum was recorded at a strain of 600%) and the same film after another 20 cycles of stretching to 800% and releasing the strain (red line, the spectrum was recorded at a strain of 800%). The emission spectra were normalized to display the same intensity at 425 nm ($\lambda_{\text{ex}} = 365$ nm).

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Supporting Movies

Supporting Movies S1-S3. Representative movie of the mechanoresponsive luminescent behavior upon cyclic stretching of **Rot-1-PU**, **Rot-2-PU** and **Rot-3-PU** films.

Supporting Movies S4 and S5. Representative movies of mechanoresponsive luminescent behavior upon cyclic stretching a white-light-emitting polyurethane film made from the blend **Rot-Mix-PU**.

All movies were taken in the dark under excitation with 365 nm UV light.