Chemical Science

A Redox-Active Reverse Donor-Acceptor Bistable [2]Rotaxane

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Electronic Supplementary Information

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General Methods and Materials: Starting materials and reagents were purchased from Aldrich or Fisher and used as received. Compound **6**[S1] and **9**•PF_6[S2] were prepared following procedures reported in the literature. All reactions were performed under an atmosphere of nitrogen and in dry solvents, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-F254 (Merck 5554). Flash chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. HPLC was performed on a preperative RP-HPLC instrument, using a C18 column. ^{1}H and ^{13}C NMR spectra and Double Quantum Field Correlation Spectroscopy (DQF-COSY) were recorded on either a Bruker Avance 500 MHz, or a Bruker Avance 600 MHz spectrometer. Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ 7.26 ppm, CD_3CN: δ 1.94 ppm, d_7-DMF: 8.02 ppm). Variable temperature ^{1}H NMR experiments were calibrated temperature calibrated using neat methanol. High resolution electrospray ionization (HR-ESI) mass spectra were measured on Agilent 6210 LC-TOF with Agilent 1200 HPLC introduction. High-resolution matrix-assisted laser desorption/ionization (MALDI) mass spectra were measured on a Bruker Autoflex III mass spectrometer. Electrochemical experiments were carried out at room temperature in argon-purged aqueous solutions, with a Gamry Reference 600 potentiostat interfaced to a PC. Cyclic voltammetry experiments were performed using a glassy carbon working electrode (0.071 cm^2, Cypress Systems). Its surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a standard Ag/AgCl electrode. The concentration of the sample and supporting electrolyte ($TBAPF_6$) were 1 x 10^{-3} mol L^{-1} and 0.1 mol L^{-1}, respectively. SEC experiments were made in a BASi thin layer quartz glass cell with an optical pathlength of 1 mm using a Pt gauze working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode.

Experimental Section

Compound 1: A Grignard reagent was prepared by mixing magnesium turnings (3.0 g, 123 mmol) and 4-ethylbromobenzene (21.7 g, 117 mmol) in dry THF (100 mL). Methyl-4-methoxybenzoate (8.4 g, 50 mmol) in dry THF (100 mL) was added slowly to this mixture over 20 min. The resulting reaction mixture was heated under reflux for 24 h before being cooled to RT, poured into 300 g ice-water containing conc. H_2SO_4. The aqueous solution was extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ (1 x 100 mL), dried (Na_2SO_4) and evaporated under vacuum to yield pure **1** (14 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.28–6.92 (m, 12H), 3.88 (s, 3H), 2.73 (q, J = 7.2 Hz, 4H), 1.32 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 158.7, 144.8, 143.2, 139.7, 131.5, 129.8, 129.3, 127.9,127.5, 113.2, 81.6 55.4, 28.6, 15.6 ppm. ESI-MS calcd for m/z = 329.20 $[M - OH_2]^+$, found m/z = 329.35.

Compound 2: A mixture of **1** (20 g, 58 mmol), phenol (108 g, 1.16 mol) was heated to 80^{o}C before the addition of concentrated HCl (3 mL) under N_2 atmosphere. The reaction mixture was further heated at 100^{o}C for 24 h. After the reaction completed, the mixture was diluted with PhMe, washed with 0.5 N NaOH (7 x 75 mL) and dried (Na_2SO_4). The solvent was evaporated in vacuo. The crude product was purified by column chromatography [SiO_2: EtOAc / Hexane (1:3)] to afford pure **2** (15.9 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.28–6.60 (m, 18H), 3.68 (s, 3H), 2.55 (q, J = 7.3 Hz, 4H), 1.12 (t, J = 7.3Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 157.3, 155.5, 153.3, 144.6, 141.5, 132.3, 130.9, 129.7, 126.7, 120.8, 115.3, 114.1, 112.6, 63.1, 28.2, 15.5 ppm. ESI-MS calcd for m/z = 406.22 $[M - OH_2]^+$, found m/z = 407.25.

Compound 3: A 1 M solution of BBr_3 in CH_2Cl_2 (1.5 mL, 15.6 mmol) was added dropwise to a solution of **2** (3.0 g, 7.1 mmol) in CH_2Cl_2 (50 mL) at –78^{o}C. The mixture was warmed up to the RT and stirred for 48 h under N_2. The reaction was quenched by addition of MeOH (5 mL) and H_2O

(150 mL). The organic layer was separated and the aqueous layer was washed with $CHCl_3$ (3 x 75 mL). The combined organic layer was dried (Na_2SO_4) and then evaporated in vacuo. The crude product was purified by column chromatography [SiO_2: EtOAc / Hexane (1:3)] to afford pure **3** (2.8 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.07–6.70 (m, 16H), 2.67 (q, J = 7.2 Hz, 4H), 1.28 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 153.5, 144.6, 141.6, 139.8, 132.6, 131.1, 126.9, 114.3, 28.3, 15.3 ppm. ESI-MS calcd for m/z = 391.21 $[M - OH_2]^+$, found m/z = 391.14.

Compound 5: Solid K_2CO_3 (6.4 g, 47 mmol), 5-bromopentanol (3.14 g, 18.8 mmol), 18C6 (100 mg) were added to a solution of diol **3** (1.9 g, 4.7 mmol) in dry MeCN (75 mL), and the solution was heated under reflux in an N_2 atmosphere for 12 h. The reaction was cooled to RT, and diluted with H_2O (50 mL), and then extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and filtered. The solvent was removed under reduced pressure to obtain the crude **4** product, which was subjected to tosylation without further purification. Et_3N (2 mL) and DMAP (50 mg) were added to a solution of the extended diol (1 g, 1.72 mmol) in dry CH_2Cl_2 (200 mL) and were followed by the dropwise addition of TsCl (297 mg, 1.56 mmol) in dry CH_2Cl_2 (20 mL) over 30 min at 0^{o}C. The solution was stirred at 0^{o}C and slowly warmed to RT overnight. The solvent was removed in vacuo and the resulting crude oil was purified by column chromatography [SiO_2: CH_2Cl_2 / MeOH (98:2)] to afford pure **5** as a colorless oil (1.5 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.82 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 7.15–6.74 (m, 16H), 4.08 (t, J = 6.5 Hz, 2H), 3.97 (t, J = 6.5 Hz, 2H), 3.90 (t, J = 6.5 Hz, 2H), 3.70 (t, J = 6.5 Hz, 2H), 2.65 (q, J = 7.6 Hz, 4H), 2.45 (s, 3H), 1.86–1.48 (m, 12 H), 1.26 (t, J = 7.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 156.8, 156.7, 144.8, 144.7, 141.4, 139.6, 139.5, 133.0, 132.1, 132.0, 130.9, 129.9, 127.9, 126.8, 113.1, 113.0, 70.5, 67.6,

67.2, 62.9, 62.8, 32.5, 29.1, 28.7, 28.6, 28.3, 22.4, 2.2, 21.6, 15.4 ppm. ESI-MS calcd for *m/z* = 757.35 $[M + Na]^+$, found *m/z* = 757.31.

Compound 7: Et_3N (0.1 mL) and DMAP (10 mg) were added to a solution of compound **6** (100 mg, 0.17 mmol) in dry CH_2Cl_2 (25 mL) and were followed by the dropwise addition of TsCl (33 mg, 0.17 mmol) in dry CH_2Cl_2 (20 mL) over 30 min at RT. The solution was stirred overnight. The reaction mixture was diluted with H_2O (20 mL), and then extracted with CH_2Cl_2. The combined organic layers was dried (Na_2SO_4), and the solvent was removed under reduced pressure to obtain (98 mg, 78%) compound **7** in pure form as a tan solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.92 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 6H), 7.08 (m, 8H), 6.7 (d, *J* = 9.9 Hz, 2H), 4.05 (t, *J* = 7.1 Hz, 2H), 3.87 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 1.72 (m, 4H), 1.49 (m, 2H), 1.30 (s, 27H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 157.1, 148.8, 145.2, 144.6, 140.0, 133.6, 132.7, 131.2, 130.3, 128.3, 124.5, 113.2, 70.8, 67.7, 63.5, 34.8, 31.9, 29.12, 29.07, 22.6, 22.2 ppm.

Compound 8: The compound **7** (98 mg, 0.13 mmol) was dissolved in dry DMF (10 mL) and NaN_3 (85 mg, 1.3 mmol, 10 eq.) was added to this mixture. Thereafter, the solution was heated at 80^{o}C overnight. The solvent was evaporated under vacuum and the crude product was diluted with CH_2Cl_2 and filtered. The filtrate was collected and the solvent was removed under reduced pressure to afford compound **8** (80 mg, 99%) as a tan solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.24 (d, *J* = 8.4 Hz, 6H), 7.09 (m, 8H), 6.76 (d, *J* = 9.5 Hz, 2H), 3.95, (t, *J* = 6.2 Hz, 2H), 3.31 (t, *J* = 7.0 Hz, 2H), 1.81 (m, 2H), 1.69 (m, 2H), 1.57 (m, 2H), 1.31 (s, 27H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 157.3, 148.8, 144.7, 140.1, 132.8, 131.3, 124.5, 113.4, 67.8, 63.6, 51.8, 34.8, 31.8, 29.4, 29.2, 23.9 ppm. MALDI-MS calcd for *m/z* = 638.41 $[M + Na]^+$, found *m/z* = 638.16.

Compound 10•2PF$_6$: A solution of **8** (139 mg, 0.23 mmol) in Me_2CO (20 mL) was added dropwise over 40 min to a solution of the dialkyne-functionalized compound **9**•2PF$_6$ (500 mg, 0.91 mmol), $Cu(MeCN)_4PF_6$ (42 mg, 0.11 mmol) and TBTA (60 mg, 0.11 mmol) in Me_2CO (20 mL). The resulting solution was stirred at RT overnight. The solvent was evaporated in vacuo. The crude product was purified by RP-HPLC (H_2O – MeCN / 0 – 100 % in 40 min λ = 254 nm) to afford pure **10**•2PF$_6$ (120 mg, 46%). ^{1}H NMR (500 MHz, Acetone-d$_6$, 298 K): δ = 9.50 (d, J = 6.5 Hz, 2H), 9.42 (d, J = 6.5 Hz, 2H), 8.90 (d, J = 6.5 Hz, 2H), 8.84 (d, J = 6.5 Hz, 2H), 7.89 (s, 1H), 7.34 (d, J = 8.45 Hz, 6H), 7.14 (d, J = 8.45 Hz, 2H), 7.09 (d, J = 8.75 Hz, 2H), 6.81 (d, J = 8.75 Hz, 2H), 5.30 (t, J = 6.9 Hz, 2H), 5.15 (t, J = 6.9 Hz, 2H), 4.42 (t, J = 6.9 Hz, 2H), 3.96 (t, J = 6.9 Hz, 2H), 3.63 (t, J = 6.9 Hz, 2H), 3.20 (m, 2H), 2.73 (t, J = 2.1 Hz, 2H), 1.95 (m, 2H), 1.78 (m, 2H), 1.46 (m, 2H), 1.31 (s, 27H) ppm. ^{13}C NMR (125 MHz, Acetone-d$_6$, 298 K): δ = 157.9, 151.42, 151.0, 149.2, 147.3, 147.2, 145.3, 142.4, 140.2, 132.8, 131.4, 128.1, 127.9, 125.1, 123.8, 114.0, 79.0, 75.1, 68.1, 63.9, 62.2, 61.0, 50.6, 34.9, 31.6, 30.7, 27.9, 23.8, 21.6 ppm. ESI-HRMS calcd for m/z = 1022.53 [M −PF$_6$]$^+$, found m/z = 1022.49.

Compound 11: Compound **6** (563 mg, 0.95 mmol), **5** (700 mg, 0.95 mmol), and PPh_3 (498 mg, 1.9 mmol) were added at 0^{o}C to a solution of 1,4,5,8 naphthalenetetracarboxydiimide (266 mg, 1 mmol) in dry THF (300 mL). Diethylazodicarboxylate (DEAD) (0.3 mL, 1.9 mmol) was added dropwise to this solution and the reaction mixture was stirred at RT for 48 h. The resulting suspension was filtered passed through celite, washed with CH_2Cl_2. The filtrate was concentrated under vacuum before being purified by column chromatography [SiO_2: EtOAc : Hexane (1 : 3)] to afford (250 mg) a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.78 (s, 4H), 7.80 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 7.25–6.70 (m, 32H), 4.25 (t, J = 6.5 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.98 (m, 4H), 3.88 (t, J = 6.5 Hz, 2H), 3.7 (t, J = 6.5 Hz, 2H), 2.62 (q, J = 7.6 Hz, 4H), 2.44 (s, 3H), 1.89–1.44 (m,

12 H), 1.24(t, J = 7.6 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 162.9, 156.9, 156.8, 156.7, 148.3, 144.8, 144.8, 144.1, 141.4, 139.6, 139.5, 139.4, 133.1, 132.2, 132.0, 131.0, 130.9, 130.7, 129.8, 129.4, 127.9, 126.8, 126.7, 126.6, 124.0, 114.4, 113.0, 112.9, 112.8, 70.4, 67.5, 67.2, 63.0, 62.9, 62.8, 40.8, 34.3, 32.5, 29.1, 29.0, 28.7, 28.6, 28.2, 27.9, 23.7, 22.4, 22.2, 21.6, 15.4 ppm. ESI-MS calcd for m/z = 1577.77 $[M + Na]^+$, found m/z = 1577.72. The product (235 mg, 0.15 mmol) was dissolved in dry DMF (10 mL) and NaN_3 (49 mg, 0.76 mmol, 5 eq.) was added to this mixture. Thereafter, the solution was heated at 80^{o}C for 12 h. The solvent was evaporated under vacuum and the crude product was purified by column chromatography [SiO_2: CH_2Cl_2 / MeOH (98:2)] to afford compound **11** (212 mg, 35%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.75 (s, 4H), 7.25–6.7 (m, 32H), 4.25 (m, 4H), 3.94 (m, 6H), 3.29 (t, J = 6.5 Hz, 2H), 2.62 (q, J = 7.6 Hz, 4H), 1.89–1.44 (m, 12 H), 1.22 (t, J = 7.6 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 162.9, 156.9, 156.8, 156.7, 148.3, 144.7, 144.2, 144.1, 139.5, 139.4, 132.2, 132.0, 132.0, 131.0, 130.9, 130.7, 126.8, 126.6, 124.1, 113.0, 112.9, 67.4, 67.3, 63.0, 62.9, 51.4, 40.8, 34.3, 29.7, 28.9, 28.7, 28.2, 27.8, 23.7, 23.4, 15.4 ppm. ESI-MS calcd for m/z = 1448.76 $[M + Na]^+$, found m/z = 1448.88.

Compound 12•2PF$_6$: Compound **11** (48 mg, 0.034 mmol), **10**·2PF_6 (40 mg, 0.034 mmol) dissolved in Me_2CO (1 mL), TBTA (9 mg), $Cu(MeCN)_4PF_6$ (6 mg) were added and the solution was allowed to stir at RT for 24 h. The solvent was evaporated under vacuum and the residue was purified by column chromatography (SiO_2 : 1% NH_4PF_6 in Me_2CO) to afford the dumbbell **12**•2PF_6 as a reddish-white solid (50 mg, 57 %). ^{1}H NMR (CD_3CN, 500 MHz, 298 K): δ = 8.80 (d, J = 7.2 Hz, 4H), 8.66 (s, 4H), 8.23 (d, J = 7.2 Hz, 4H), 7.34–6.71 (m, 50H), 4.95 (bs, 4H), 4.32 (t, J = 7.0 Hz, 4H), 4.16 (t, J = 7.0 Hz, 4H), 3.94 (q, J = 6.7 Hz, 4H), 3.86 (q, J = 6.7 Hz, 4H), 3.42 (bs, 4H), 2.60 (q, J = 7.5 Hz, 4H), 1.87–1.55 (m, 24H), 1.29 (s, 27H), 1.27 (s, 27H), 1.19 (t, J = 7.5 Hz, 6H) ppm. ^{13}C NMR (CD_3CN, 125 MHz, 298 K): δ = 163.9, 157.8, 149.7, 146.8,145.8, 145.5, 142.6, 132.7,

132.6, 131.5, 131.3, 131.1, 129.4, 127.9, 127.7, 125.5, 125.4, 114.2, 68.3, 63.9, 41.2, 34.9, 31.5, 29.5, 29.2, 28.7, 28.3, 24.1, 23.6, 15.9 ppm. ESI-HRMS calcd for $m/z = [M - 2PF_6]^{2+}$, found m/z = 1152.6735.

1. ^{1}H NMR Spectroscopic Characterization

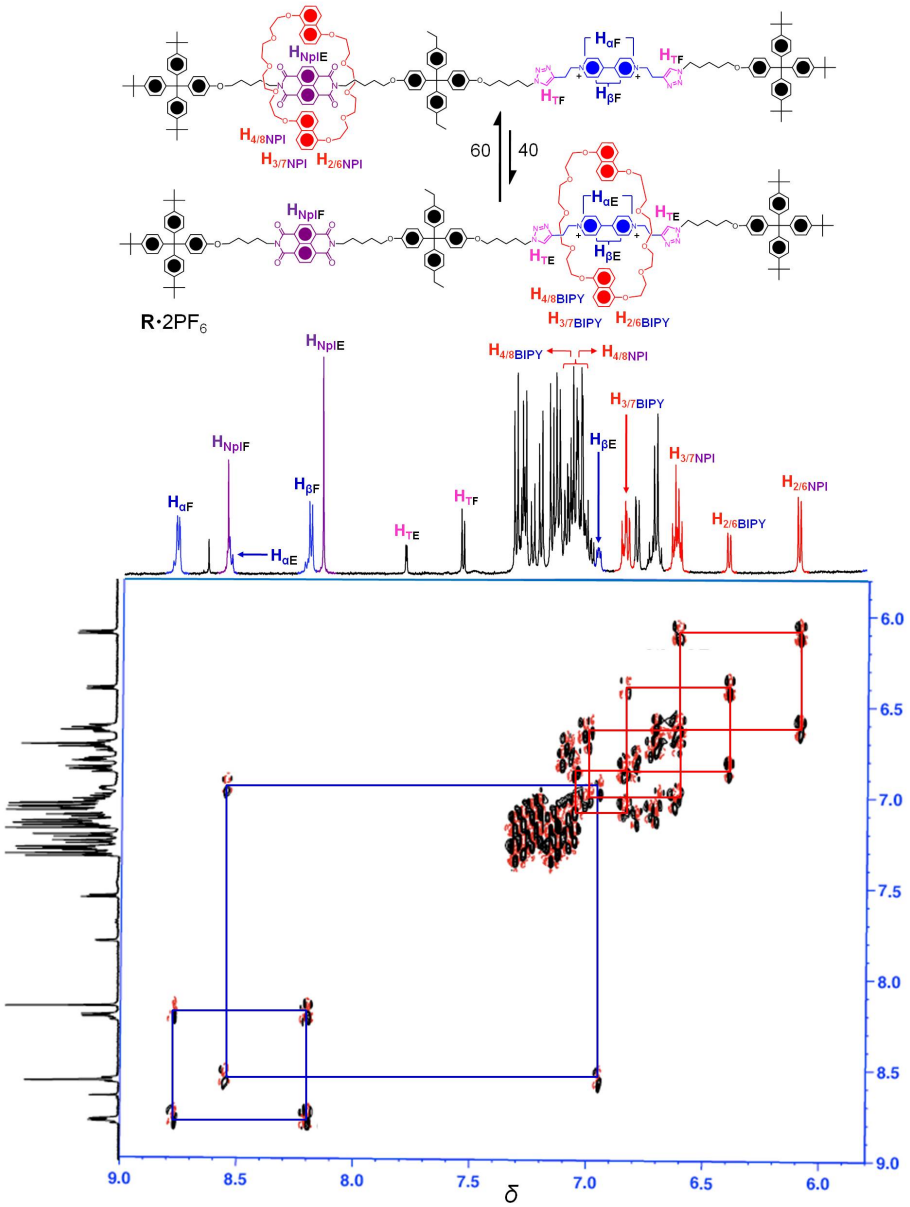


Figure S1. 600 MHz ^{1}H-^{1}H gradient selected double quantum filtered phase sensitive COSY recorded in CD_3CN of **R**•2PF_6 at 298 K.

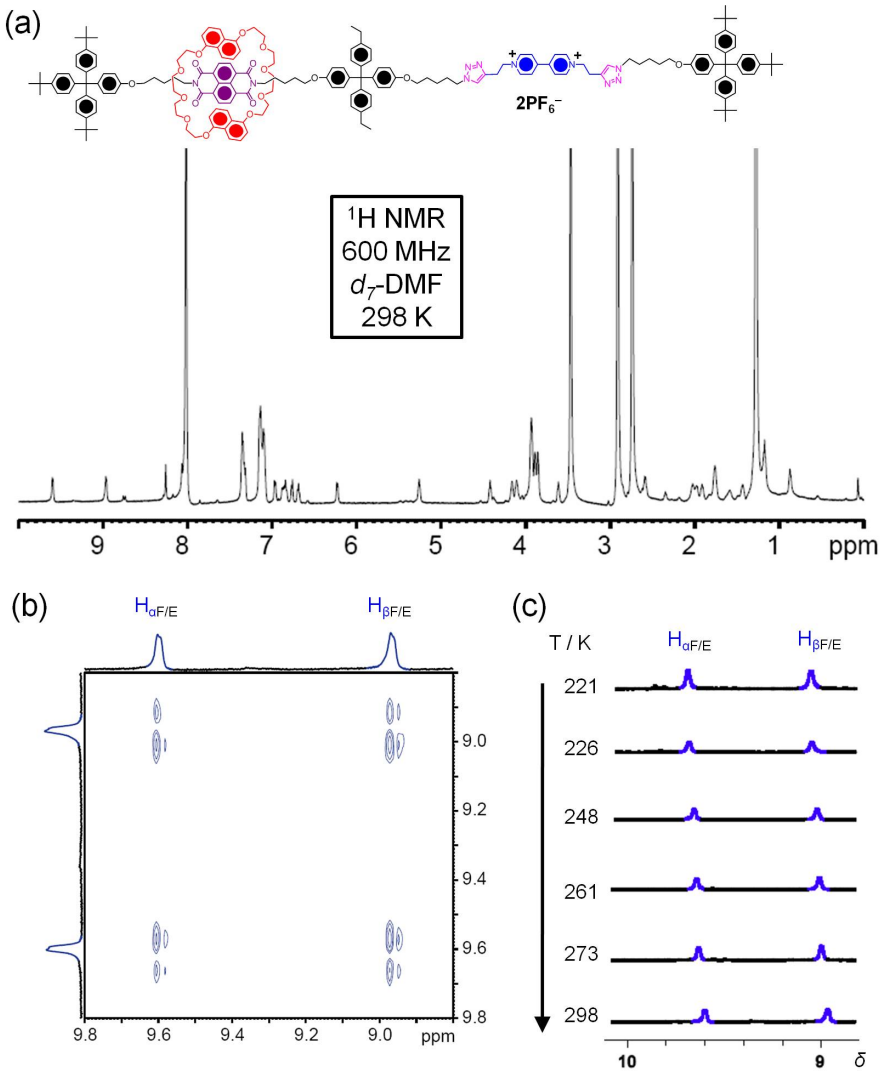


Figure S2. (a) ^{1}H NMR spectrum of **R**•2PF$_6$ in d_7-DMF at 298 K. (b) ^{1}H-^{1}H double quantum filtered phase sensitive COSY of **R**•2PF$_6$ in d_7-DMF at 298 K of the resonances arising from the H$_\alpha$ and H$_\beta$ protons. (c) Variable temperature plot of the resonances of the H$_\alpha$ and H$_\beta$ protons of **R**•2PF$_6$ in d_7-DMF.

Using the resonances arising from H$_\alpha$ and H$_\beta$ protons of **R**•2PF$_6$ as probes for the translational motion of the BDNP38C10 ring, the fact that only single resonances for the H$_\alpha$ and H$_\beta$ protons are observed points to an exchange process between translational isomers which is fast on the ^{1}H NMR timescale at least in d_7-DMF. This fast exchange persists all the way down to 221 K (Figure S2), an observation which indicates a significant decrease in the free energy barrier to translational isomerization compared to CD_3CN. We hypothesize that decrease in the free energy barrier is a consequence of the decreased affinity for the $BIPY^{2+}$ and NpI stations in DMF.

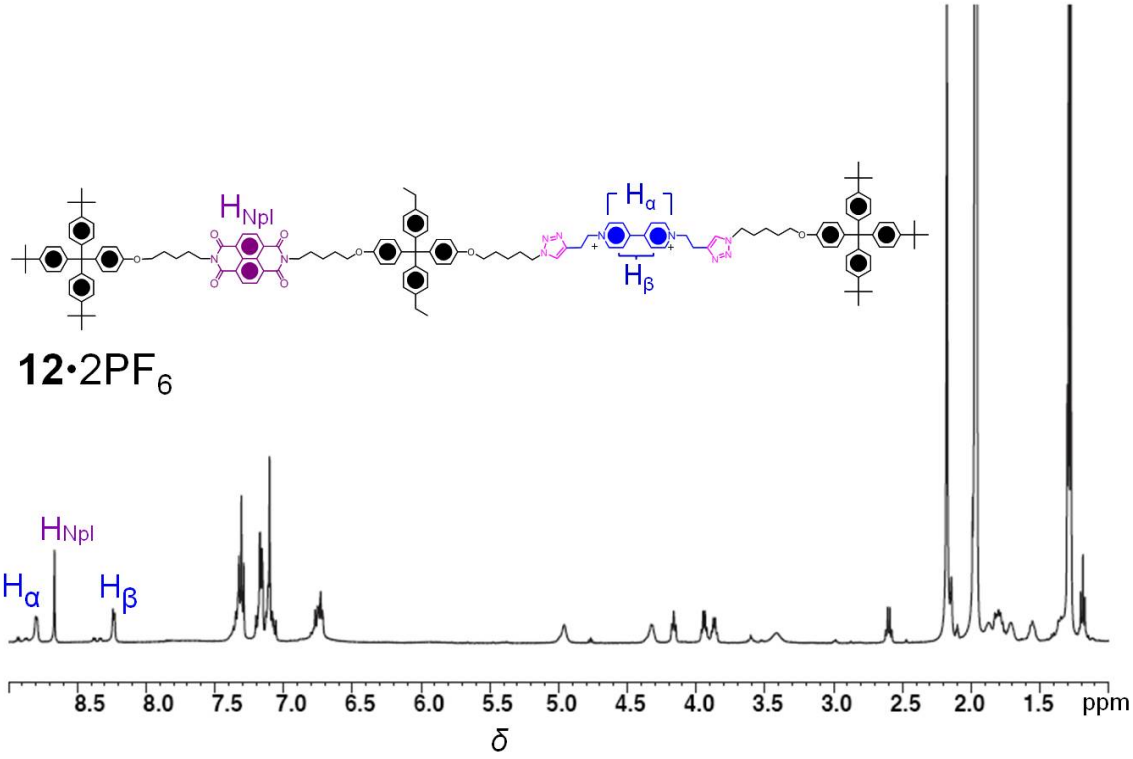


Figure S3. ^{1}H NMR spectrum of **12**•2PF_6 in CD_3CN at 298 K.

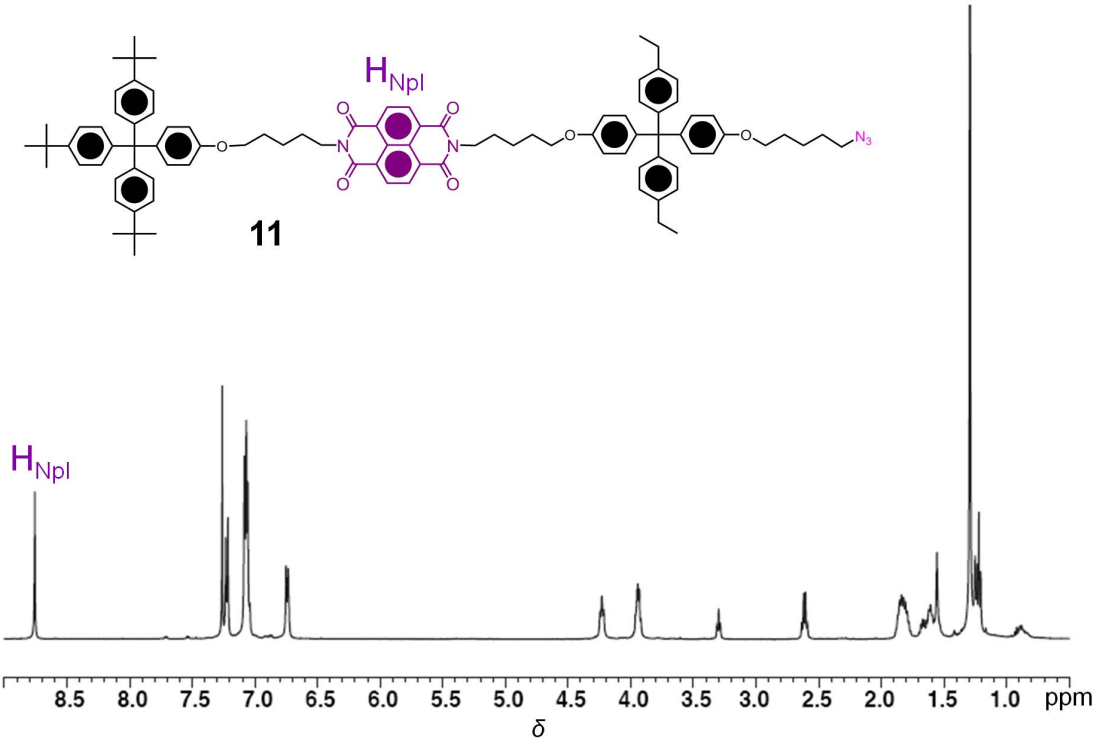


Figure S4. ^{1}H NMR spectrum of **11** in CD_3CN at 298 K.

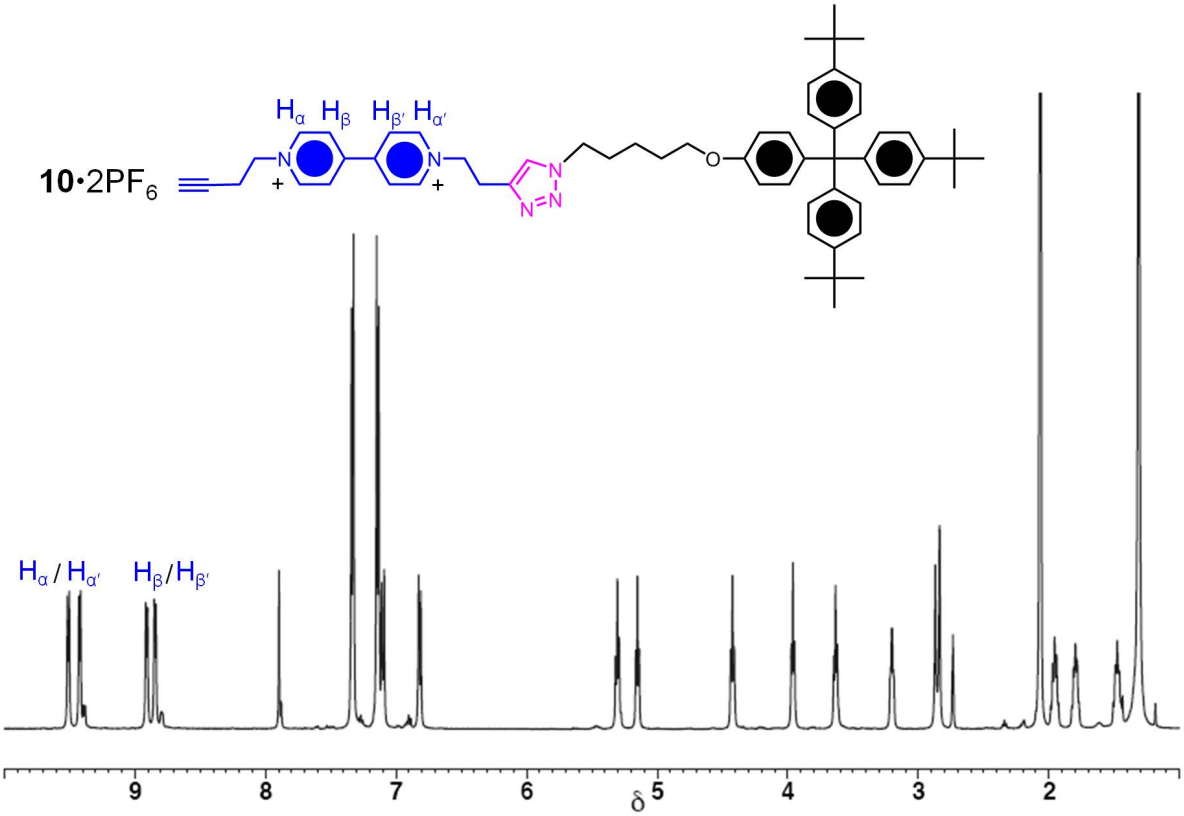


Figure S5. ^{1}H NMR spectrum of **10**•2PF_6 in CD_3CN at 298 K.

Determination of Rate (*k*) and Barrier of Relaxation ($\Delta G^{\ddagger}$) from the ^{1}H NMR Spectroscopy

The kinetic data, in particular, the rate constant for the relaxation of the BDNP38C10 ring from the NpI to the $BIPY^{2+}$ station in accordance with its equilibrium ratio, along with its associated activation barrier, were determined based on the following equilibrium –

$$\mathbf{R}^{2+}_{\text{NpI}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{R}^{2+}_{\text{BIPY}} \qquad \text{[Eq. 1]}$$

Our synthetic approach allowed us to populate (Figure S6a) only one translational isomer, in which the BDNP38C10 ring encircles exclusively the NpI station (NpI⊂BDNP38C10, $\mathbf{R}^{2+}_{\text{NpI}}$).

Equilibration to the other translational isomer, in which the BDNP38C10 ring encircles the $BIPY^{2+}$ station ($BIPY^{2+}\subset$BDNP38C10, $\mathbf{R}^{2+}_{BIPY}$) begins to proceed following the synthesis of the rotaxane $\mathbf{R}^{2+}$. From the reaction shown above (Eq. 1), we can derive the following rate law:

$$d[\mathbf{R}^{2+}_{NpI}]/dt = -k_1[\mathbf{R}^{2+}_{NpI}] + k_2[\mathbf{R}^{2+}_{BIPY}] \qquad \text{[Eq. 2]}$$

where k_1 is the rate constant for the forward reaction generating $\mathbf{R}^{2+}_{BIPY}$ and k_2 is the backwards rate constant producing $\mathbf{R}^{2+}_{NpI}$.

The solution[S3] to Eq. 2 is:

$$x_t = x_{eq} + (x_o - x_{eq})\exp[-k_1 t/(1 - x_{eq})] \qquad \text{[Eq. 3]}$$

where x_t is the mol fraction of $\mathbf{R}^{2+}_{NpI}$ $\{([\mathbf{R}^{2+}_{NpI}]/([\mathbf{R}^{2+}_{NpI}] + [\mathbf{R}^{2+}_{BIPY}])\}$ as a function of time, x_o is the mol fraction of the initial amount of $\mathbf{R}^{2+}_{NpI}$ at t = 0, and x_{eq} is the final mol fraction amount of $\mathbf{R}^{2+}_{NpI}$ at equilibrium when $t = \infty$. From ^{1}H NMR spectroscopy, x_{eq} was measured to be 0.6, and we assume that x_o is equal to 1. Fitting (Figure S6b) the data obtained from ^{1}H NMR spectroscopic experiments to this equation, we find the time constant, τ, and hence the rate constant, k_1, which is equal to 2.2 ± 0.3 x 10^{-5} s^{-1}. Using the Eyring equation, this rate constant corresponds to a free energy of activation ($\Delta G^{\ddagger}$) of 23.8 ± 0.1 kcal mol^{-1} at room temperature in CD_3CN. Errors in the rate constant and activation barrier were determined from the error of the fit to the decay curve.

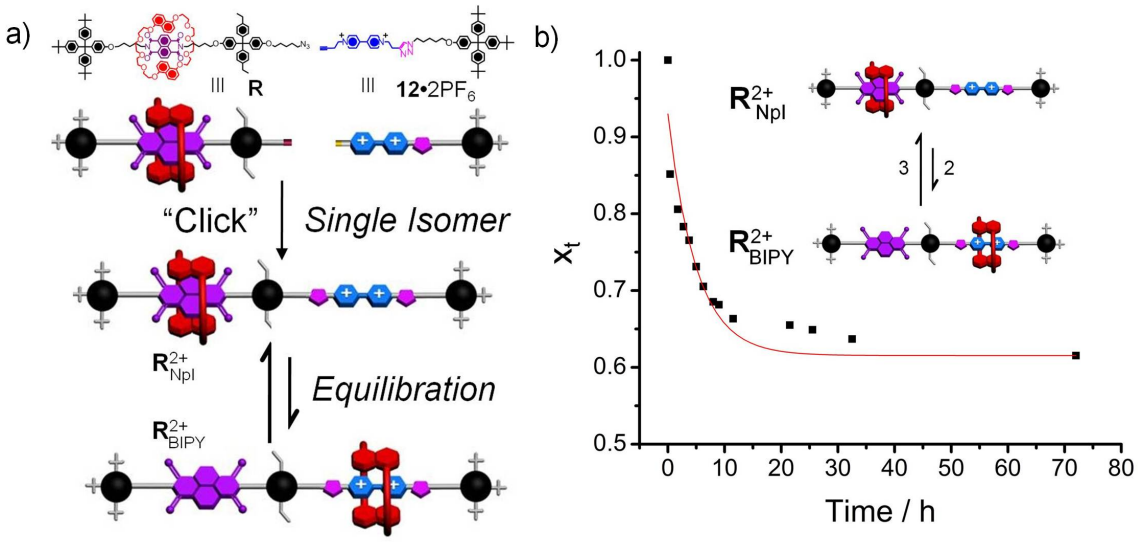
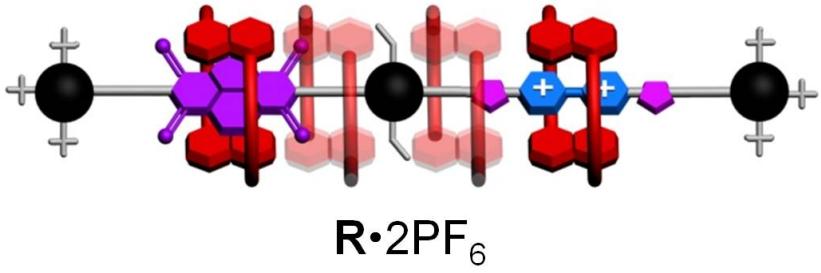


Figure S6. a) Reaction scheme illustrating the synthetic approach, which provides the ability to analyze the rate of shuttling from the BDNP38C10 ring from the NpI station to the BIPY station. Formation of the rotaxane **R** by a slippage mechanism proceeds first of all and prior to the reaction with **12**•2PF_6 containing the $BIPY^{2+}$ station. Immediately following the click reaction with **12**•2PF_6, only a single isomer exist, wherein the BDNP38C10 ring encircles the NpI station. We can then follow the equilibration process wherein the BDNP38C10 ring shuttles over the central speed-bump to encircle the $BIPY^{2+}$ station using ^{1}H NMR spectroscopy in CD_3CN at 298 K. b) First-order decay profile for the shuttling process of the BDNP38C10 ring from the NpI to $BIPY^{2+}$ station obtained from ^{1}H NMR spectroscopy in CD_3CN at 298 K and the best-fit curve (red). From these data, we can determine the time constant, τ, and hence the rate constant k_1 according to equation 3.

Differential Pulse Voltammetery (DPV) Cyclic Voltammetry (CV) Measurements and Spectroelectrochemistry (SEC)

Figure S7 shows the DPV measurement of the [2]rotaxane **R**•2PF_6 recorded in argon purged DMF ($TBAPF_6$ = 0.1 M). The observation of a shoulder peak accompanying the reduction process observed at approximately − 0.60 V, in addition to the observed broadness of the reduction processes occurring at approximately − 0.86 V support the existence of the overlapping reduction potentials.



R•2PF$_6$

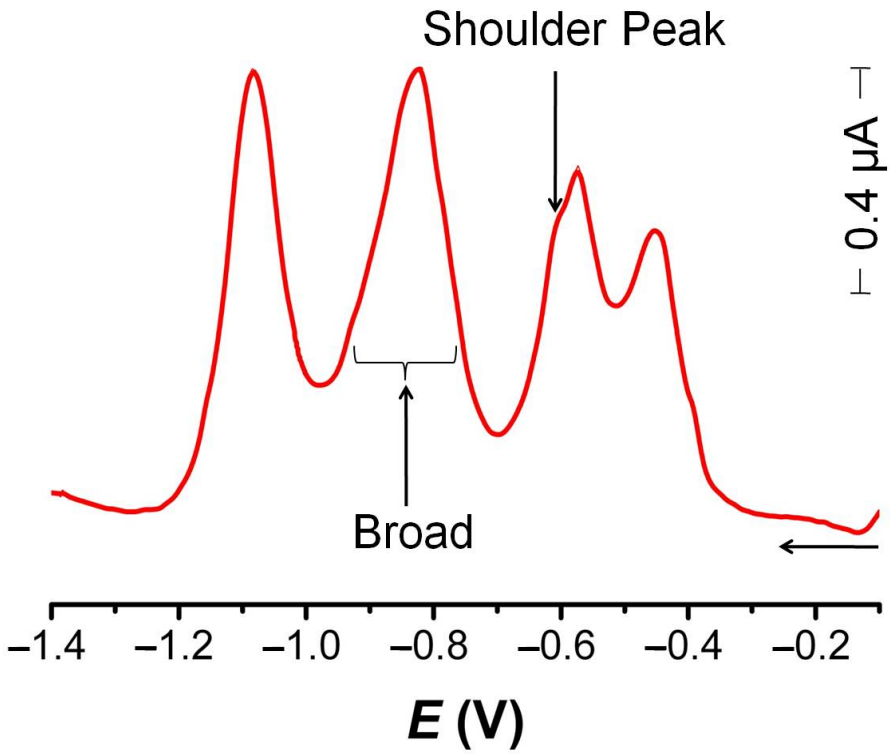


Figure S7. DPV measurement of the rotaxane **R**•2PF$_6$ recorded in argon purged DMF solution at a 1 mM concentration with TBAPF$_6$ (0.1 M) as the supporting electrolyte at 298 K.

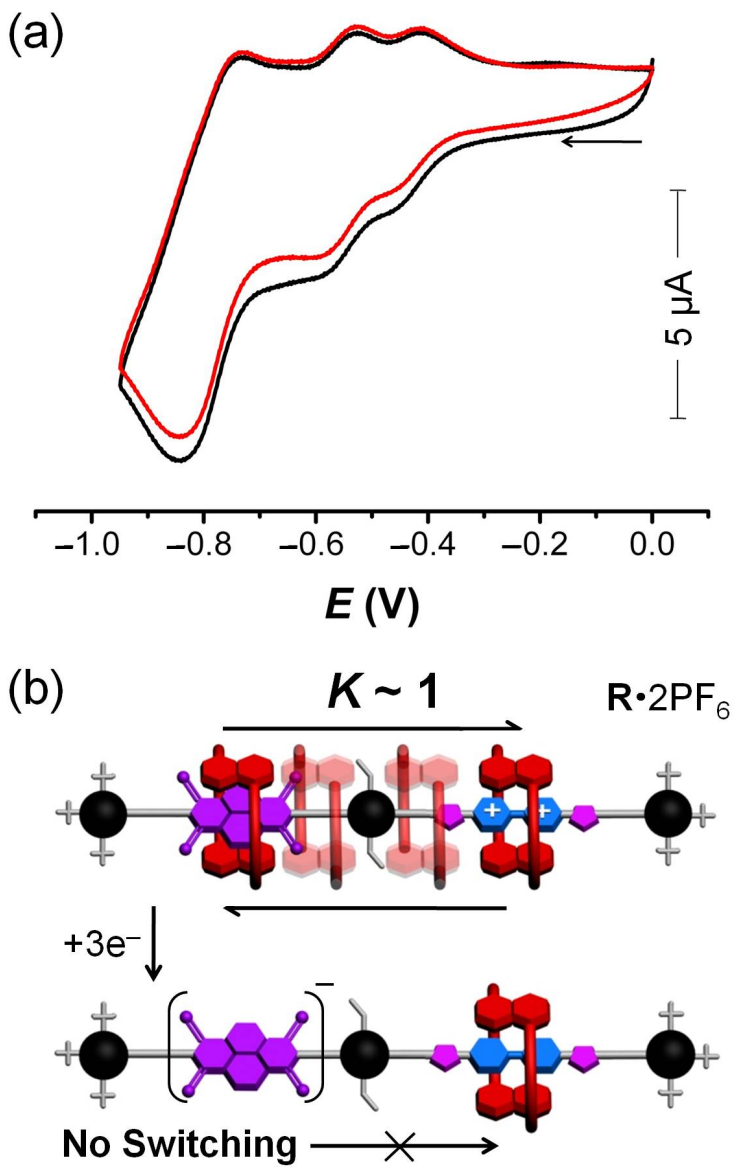


Figure S8. (a) Two sequential CV scans of the rotaxane **R**•2PF_6 recorded in argon purged DMF at 298 K. The scans started at 0 V and were taken to the limit of −0.95 V. The concentration of the solution was 1 mM supported by 0.1 M $TBAPF_6$ electrolyte. (b) Graphical representation of the proposed scheme illustrating the inability of the rotaxane to switch upon generation of the $NPI^{\bullet-}$ radical anion.

Figure S8a shows two scans of the CV of the rotaxane **R**•2PF_6 starting from 0 V and scanning to the limit of − 0.95 V. No significant change in the relative intensity of the reduction process at − 0.46 V between the first and second scans were observed. This observation indicates that the $NPI^{\bullet-}$ radical anion is not able to induce switching of the BDNP38C10 macrocycle over the central speed bump to encircle the neutral $BIPY^0$ on the timescale of the CV experiment illustrated by Figure S8b.

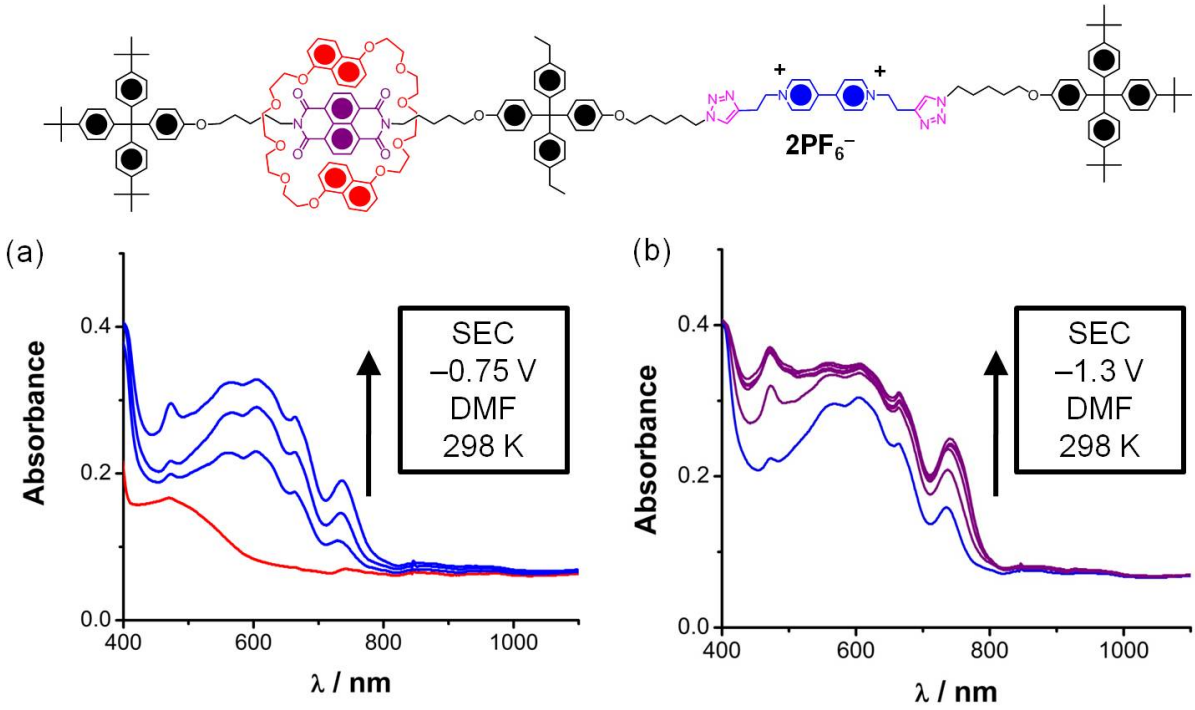


Figure S9. SEC of the rotaxane **R**•2PF_6 in DMF at 298 K at 1.2 mM concentration with 0.1 M $TBAPF_6$ electrolyte. (a) Resulting spectra that appeared over time after applying a voltage of –0.75 V starting from 0 V (red trace). (b) Resulting spetra that appeared over time following the application of a potential of –1.3 V.

SEC of the rotaxane **R**•2PF_6 results (Figure S9) in the observation of spectra consistent with the formation of the $BIPY^{\bullet+}$ radical cation and the $NPI^{\bullet-}$ radical anion after applying a potential of –0.75 V, followed by spectra that are consistent with the formation of neutral $BIPY^0$ and NPI^{2-} dianion after the application of –1.3 V. The initial spectrum taken at 0 V (red trace) shows a charge transfer band (λ_{max} = 481 nm) which is consistent with encirclment of the BDNP38C10 ring over both NPI and $BIPY^{2+}$ stations in aproximately a 1:1 ratio.

UV/Vis Spectroscopy

Determination of Binding Affinities

The binding affinities for the BDNP38C10 macrocycle with the $BIPY^{2+}$ and NpI stations were elucidated from UV/vis titration data based on model compounds. All titration studies were carried out in anhydrous DMF in a 2 mm cuvet, using a Shimadzu UV 3600 UV-Vis-NIR Spectrometer at 25°C. The calculations of binding constants for model compounds from absorbance measurements taken at 460 or 550 nm, which are close to the maxima of the charge transfer bands for the inclusion complexes formed were performed using DynaFit.

$BIPY^{2+}$ Titration Study

A 10 mM stock solution of the BDNP38C10 macrocycle was prepared in DMF. Methyl viologen bishexafluorophosphate (MV) was dissolved with the BDNP38C10 host solution, creating a 1 M guest solution of MV doped with 10 mM concentration of the macrocycle. Additionally, a 200 mM MV solution was prepared by once again diluting further with the BDNP38C10 10 mM stock solution. During the titration 5 µL aliquots of MV guest solution were sequentially added to 500 µL of the 10 mM BDNP38C10 macrocycle stock solution, while monitoring by UV/vis spectroscopy (Figure S10). Fitting the titration data reveals a binding constant (K_a) equal to 29 ± 1 M^{-1}.

NpI Titration Study

A 10 mM host solution of BDNP38C10 macrocycle was prepared in DMF. Bis-diethylene glycol naphthalene diimide (DNpI) was dissolved using the 10 mM BDNP38C10 stock solution, to generate a 100 mM solution of DNpI doped with 10 mM of the BDNP38C10 macrocycle. The solution was heated to fully solubilize the DNpI in DMF. Aliquots of 10, 20 and 50 µL of the guest

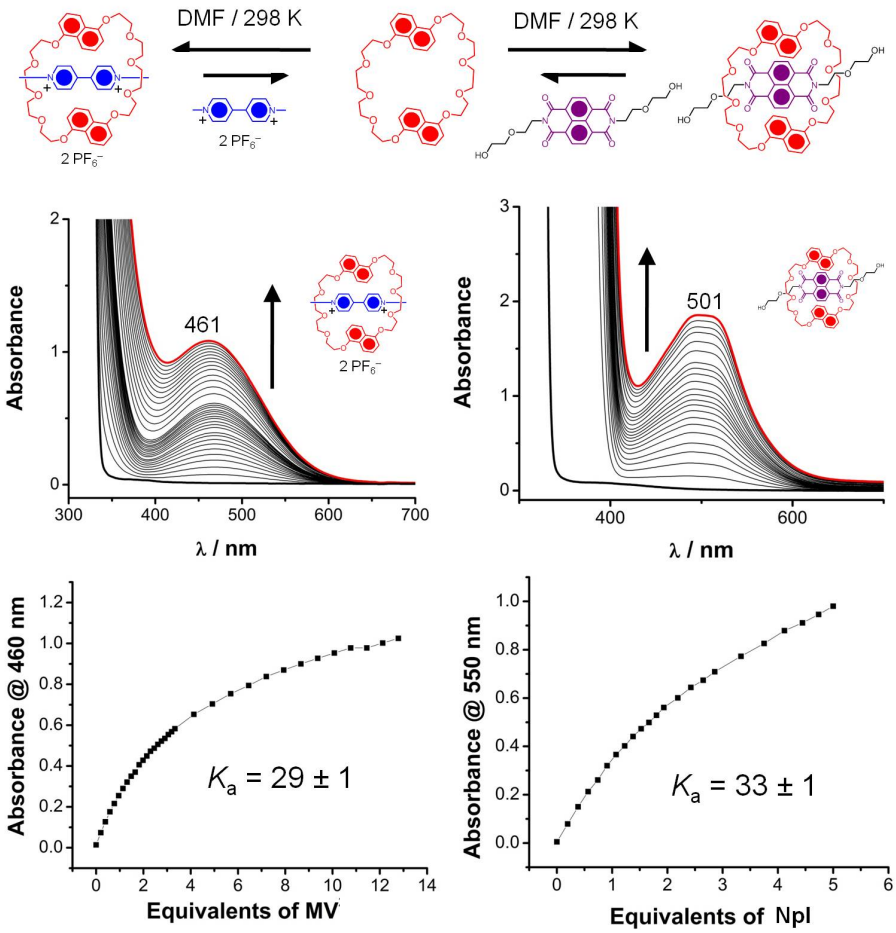


Figure S10. Titration data and binding constant plots for the 1:1 complexes formed between the BDNP38C10 ring and either methyl viologen or an NPI derivative model compound in DMF at 298 K.

solution were added sequentially to 500 μL of the 10 mM stock solution of the BDNP38C10 while monitoring by UV/vis spectroscopy (Figure S10). Fitting the titration data reveals a binding constant (K_a) equal to 33 ± 1 M^{-1}.

References

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