An electrochemically driven molecular shuttle controlled and monitored by C₆₀.

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Synthesis and Characterisation

NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or on a Jeol (400 MHz) at room temperature. Chemical shifts reported in ppm are referred to TMS. Signals on thread **1** and rotaxane **2** were assigned by COSY experiments.

Infrared spectra were recorded on a Jasco FTIR-200 spectrometer.

Mass Spectroscopy: MALDI experiments were recorded at Université Louis Pasteur.

UV-Vis-NIR measurements were recorded on a Varian 5000 UV-Vis-NIR spectrometer.

Commercial compounds were used as received.

EDC (N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride), HOBt (1-Hydroxybenzotriazole hydrate).





Thread 1.

EDC (211 mg, 1.069 mmol) was added in small portions to a solution of S1,^[1] (0.486 mmol) S2,^[2] (262 mg, 0.972 mmol), HOBt (144 mg, 1.069 mmol) in chloroform (anhydrous stabilized with amylenes, 50 mL). The solution was stirred for 10 min and NEt₃ (3 mL) was added. The resulting solution was stirred at room temperature overnight.

Solvent was evaporated under vaccum and thread **1** (351 mg, 63 %) was purified by flash chromatography (CHCl₃:MeOH 99:1).

¹H NMR (400 MHz, CDCl₃): 7.35-7.20 (m, 10H, H_A); 6.59 (t, 1H, J = 5.7 Hz, H_B); 6.45 (t, 1H, J = 4.9 Hz, H_C); 4.94 (s, 1H, H_D); 4.50 (s, 4H, H_E); 4.07-3.98 (m, 4H, H_F+H_G); 3.83-3.77 (m, 2H, H_I); 3.74-3.70 (m, 2H, H_I); 3.60 (t, 2H, J = 5.3 Hz, H_J); 3.45 (c, 2H, J = 5.2 Hz, H_K); 3.36 (t, 2H, J = 5.7 Hz, H_L).

¹³C NMR (50 MHz, CDCl₃): 172.12, 168.24, 154.83, 147.22, 146.16 145.98, 145.93, 145.59, 145.32, 145.21, 144.46, 142.55, 142.10, 141.98, 141.81, 140.06, 138.99, 136.09, 128.77, 127.31, 70.74, 70.54, 70.25, 69.63, 68.44, 58,87, 54.35, 43.34, 39.54.
MS (MALDI): 1144 (M⁺).
IR (NaCl): 3305, 2927, 1793, 1720, 1655, 1537, 1431, 1215, 1032, 752, 702.

IR (NaCl): 3305, 2927, 1793, 1720, 1655, 1537, 1431, 1215, 1032, 752, 70. UV (THF): 244, 324, 428, 700.

Rotaxane 2.

A solution of *p*-xylylenediamine (625 mg, 4.585 mmol) in chloroform (anhydrous stabilized with amylenes, 40 mL) containing NEt₃ (0.663 mL, 9.180 mmol) and a separate solution of isophthaloyl chloride (1 g, 4.585 mmol) in chloroform (anhydrous stabilized with amylenes, 40 mL) were added simultaneously for 4 hours to a stirred solution of thread **1** (351 mg, 0.306 mmol) in CHCl₃ (anhydrous stabilized with amylenes, 50 mL) under argon. After the addition the reaction mixture was stirred overnight at room temperature. The solution was filtered through celite, concentrated to dryness. Rotaxane **2** (172 mg, 34%) was separated from the unreacted thread **1** by chromatography (CHCl₃:MeOH 199:1) followed by reprecipitation (CH₂Cl₃/Ether, ×3).

¹H NMR (400MHz, CDCl₃): 8.28 (s, 2H, H_a); 8.19 (d, 4H, J = 7.28 Hz, H_b); 7.62 (t, 2H, J = 7.36 Hz, H_c); 7.43 (bs, 4H, H_d); 7.32-7.16 (m, 10H, H_A); 7.16-7.09 (m, 1H, H_B); 6.97 (s, 8H, H_E); 5.68 (bs, 1H, H_C); 4.58-4.48 (m, 4H, H_f); 4.37 (s, 5H, H_E+H_D); 4.35-4.27 (m, 4H, H_f); 3.94-3.86 (m, 2H, H_F); 3.73 (bs, 2H, H_I); 3.63 (bs, 2H, H_I); 3.45 (bs, 2H, H_J); 3.20 (bs, 4H, HK+H_L); 2.79 (bs, 2H, H_G).

MS (MALDI): 1701 (M+Na⁺); 1677 (M+H⁺).

IR (NaCl): 3440, 2920, 1728, 1645, 1535, 1518, 1454, 1269, 1084, 1030, 926, 821, 739. UV (THF): 244, 301, 321, 429, 703.



Figure S1 COSY spectrum of rotaxane 2 in CDCl₃.



Figure S2 COSY spectrum of rotaxane 2 in DMSO-*d*₆.

Photophysics

Absorption spectra were measured on a Perkin Elmer UV/VIS Spectrometer Lambda 2. Steady state emissions spectra were recorded on a FluoroMax[®] 3 Fluorometer (HORIBA). The measurements were carried out at 20.0 °C. Fluorescence lifetimes were measured with a laser strobe fluorescence lifetime spectrometer (Photon Technology International) with 337 laser pulses from a nitrogen laser fiber coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the laser strobe systems are described on the manufacture's web site. Femtosecond transient absorption studies were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width) from amplified Ti:Sapphire laser system (Clark-MXR, Inc.).



Figure S3 Absorption spectra of rotaxane 2 in dichloromethane (black spectrum), dichloromethane / hexafluoroisopropanol (grey spectrum), DMF (purple spectrum) and DMSO (brown spectrum) at room temperature.



Figure S4 Steady-state fluorescence spectra of rotaxane **2** in dichloromethane (black spectrum), dichloromethane / hexafluoroisopropanol (grey spectrum), DMF (purple spectrum) and DMSO (brown spectrum) with matching absorption at the excitation wavelength of 325 nm.



Figure S5 Upper part – differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (387 nm) of rotaxane 2 ($\sim 10^{-5}$ M) in nitrogen saturated dichloromethane solutions with several time delays between 0 and 1500 ps at room temperature – arrows indicate the temporal evolution of the intersystem crossing. Lower part – time-absorption profiles of the spectra shown above at 900 nm (open circles) and 690 nm (closed circles), monitoring the decay of the singlet excited and the growth of the excited triplet state, respectively.



Figure S6 Upper part – differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (387 nm) of rotaxane 2 ($\sim 10^{-5}$ M) in nitrogen saturated dichloromethane / hexafluoroisopropanol solutions with several time delays between 0 and 1500 ps at room temperature – arrows indicate the temporal evolution of the intersystem crossing. Lower part – time-absorption profiles of the spectra shown above at 900 nm (open circles) and 690 nm (closed circles), monitoring the decay of the singlet excited and the growth of the excited triplet state, respectively.



Figure S7 Upper part – differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (387 nm) of rotaxane $2 (\sim 10^{-5} \text{ M})$ in nitrogen saturated DMF solutions with several time delays between 0 and 1500 ps at room temperature – arrows indicate the temporal evolution of the intersystem crossing. Lower part – time-absorption profiles of the spectra shown above at 900 nm (open circles) and 690 nm (closed circles), monitoring the decay of the singlet excited and the growth of the excited triplet state, respectively.

Figure S8 Upper part – differential absorption spectra (visible and near infrared) obtained upon femtosecond flash photolysis (387 nm) of rotaxane 2 ($\sim 10^{-5}$ M) in nitrogen saturated DMSO solutions with several time delays between 0 and 1500 ps at room temperature – arrows indicate the temporal evolution of the intersystem crossing. Lower part – time-absorption profiles of the spectra shown above at 900 nm (open circles) and 690 nm (closed circles), monitoring the decay of the singlet excited and the growth of the excited triplet state, respectively.

Electrochemistry

Tetrahydrofuran employed for electrochemical measurements (from Fluka) was treated according to a procedure described elsewhere.^[3] Dimethylsulfoxide was dried over basic alumina and molecular sieves prior to use.

The cyclic voltammetry experiments were performed in a one-compartment electrochemical cell of airtight design, with high-vacuum glass stopcocks fitted with either Teflon or Viton (DuPont) O-rings, to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Teflon O-rings. The cell, containing the supporting electrolyte and the electroactive compound, was dried under vacuum at 363 K for at least 48 h. Afterwards the solvent was distilled by a trap-to-trap procedure into the electrochemical cell just before performing the electrochemical experiment. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically $(1.0-2.0) \times 10^{-5}$ mbar. The working electrode was a Pt disk ultramicroelectrode (diameter, 0.125 mm) sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrodes were separated from the working electrode by ~0.5 cm. Potentials were measured with respect to the decamethylferrocene standard. $E_{1/2}$ values correspond to $(E_{pc} + E_{pa})/2$ from CV. Voltammograms were recorded with a home-made fast potentiostat controlled by an AMEL Model 568 function generator. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Digital simulations of the cyclic voltammetric curves were carried out by the DigiSim 3.0 software by Bioanalytical Systems Inc.

Figure S9: Cyclic voltammograms (0.5 mM of the substrate in 0.05 M TBAPF₆ in solvent, scan rate 1 V/s) in a) THF b) DMSO and simulations of the voltammograms in c) THF d) DMSO of thread 1 (black) and rotaxane 2 (red). Potentials reported *versus* Fc/Fc^+ .

	AB ^[a]	A ⁻ B ^{-[a]}	$\mathbf{A^{2-}B^{2-[a]}}$	$\mathbf{A^{3-}B^{3-[a]}}$	AB ^[b]	A ⁻ B ^{-[b]}	$\mathbf{A^{2-}B^{2-[b]}}$	$\mathbf{A^{3-}B^{3-[b]}}$
K _{EQ}	1×10 ⁻²	1×10 ⁻¹	1	8	9.5×10 ²	1×10 ³	2.8×10 ³	1.5×10 ⁴
$k_{\rm f}$ (s ⁻¹)	1×10 ⁻³	1×10^{2}	1×10 ³	1×10 ⁵	1×10 ⁶	1×10 ⁹	1.5×10 ⁹	3×10 ¹²
$k_{\rm b}({\rm s}^{-1})$	1×10 ⁻¹	1×10 ³	1×10 ³	1.25×10^4	1.05×10^{3}	1×10 ⁶	5.4×10 ⁵	2×10 ⁸

^[a] 0.5 mM of the substrate in 0.05 M TBAPF₆ in THF, scan rate 1 V/s.

^[b] 0.5 mM of the substrate in 0.05 M TBAPF₆ in DMSO, scan rate 1 V/s.

Table S1 Kinetic and thermodinamic constants of 2 obtained by simulation.

	AA	BB ⁻	A ⁻ A ²⁻	B ⁻ B ²⁻	A ²⁻ A ³⁻	$\mathbf{B}^{2} \cdot \mathbf{B}^{3} \cdot$
$E_{1/2}$ (V) ^[a]	-0.621	-0.562	-1.180	-1.121	-1.790	-1.737
$E_{1/2}$ (V) ^[b]	-0.381	-0.379	-0.816	-0.789	-1.436	-1.393

^[a] 0.5 mM of the substrate in 0.05 M TBAPF₆ in THF, scan rate 1 V/s.

^[b] 0.5 mM of the substrate in 0.05 M TBAPF₆ in DMSO, scan rate 1 V/s.

Table S2 Theoretical reduction potentials of 2 obtained by simulation.

References

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