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Three state redox-active molecular shuttle that switches in solution and on a surface

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Published in:
Journal of the American Chemical Society

DOI:
[10.1021/ja077223a](https://doi.org/10.1021/ja077223a)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Fioravanti, G., Haraszkiwicz, N., Kay, E. R., Mendoza, S. M., Bruno, C., Marcaccio, M., ... Brouwer, A. M. (2008). Three state redox-active molecular shuttle that switches in solution and on a surface. *Journal of the American Chemical Society*, 130(8), 2593-2601. DOI: 10.1021/ja077223a

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Supporting Information

A Three State Redox-Active Molecular Shuttle that Switches in Solution and on a Surface

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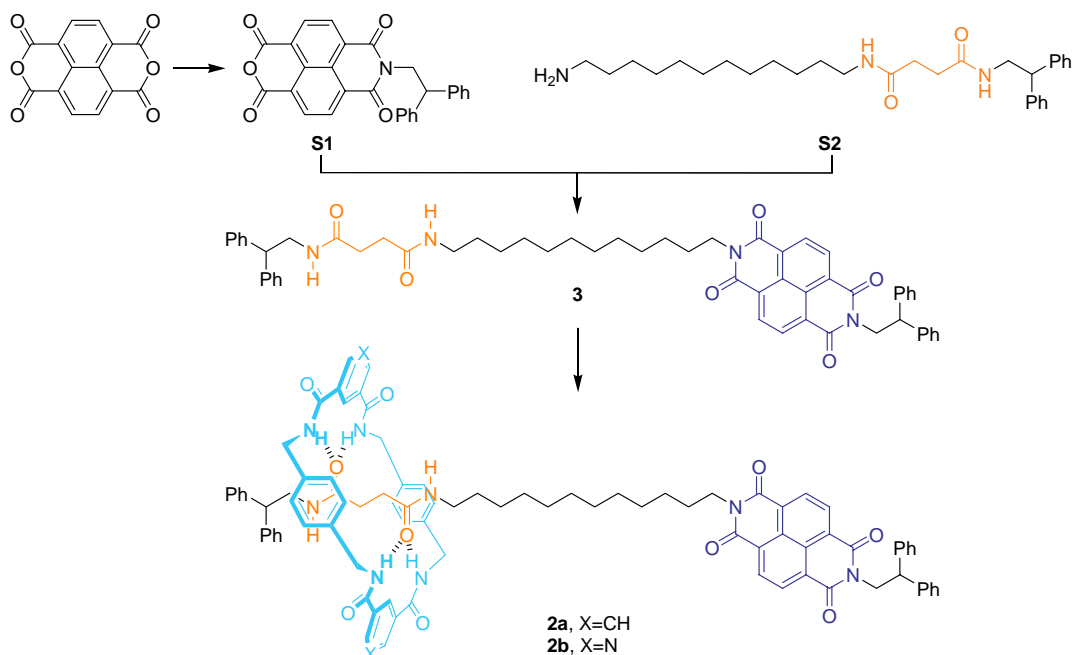
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1. Synthesis and characterization of new compounds

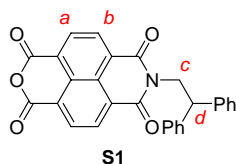
General

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. Dry chloroform and *N,N*-dimethylformamide (DMF) were obtained by passing these solvents (free of stabilizers) through activated alumina columns on a PureSolvTM solvent purification system (Innovative Technologies, Inc., MA). Column chromatography was carried out using Kiesegel C60 (Fisher) as the stationary phase, and thin-layer chromatography (TLC) was performed on precoated silica gel plates (0.25 mm thick, 60F₂₅₄, Merck, Germany) and observed under UV light. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 25 °C. Chemical shifts are reported in parts per million from low to high field and referenced to the literature values of chemical shifts, with respect to tetramethylsilane, of residual non-deuterated solvent. Standard abbreviations indicating multiplicity were used as follows: m = multiplet, br = broad, d = doublet, q = quartet, t = triplet, s = singlet. All melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected. FAB mass spectrometry was carried out by the services at the University of Edinburgh.



Scheme S1. Synthetic sequence for the synthesis of thread **3** and [2]rotaxanes **2a** and **2b**.

7-(2,2-Diphenylethyl)-2-oxa-7-azapyrene-1,3,6,8-tetraone (S1)

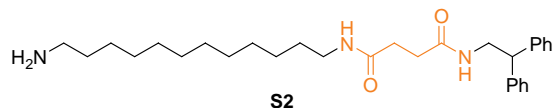


To a suspension of naphthalene-1,4,5,8-tetracarboxylic dianhydride (6.43 g, 24.0 mmol) in DMF (150 mL) at 150 °C was added dropwise 2,2-diphenylethylamine (788 mg, 4.00 mmol) in DMF (50 mL). Following addition, a clear solution was obtained, which was stirred at 150 °C for a further 5 hours. The dark colored reaction mixture was then poured into water (600 mL). The resulting precipitate was recovered by filtration, washed with water and dried in a desiccator at 90 °C overnight. This solid was then stirred in chloroform, the remaining solids (unreacted anhydride starting material) removed by filtration and then the filtrate concentrated under reduced pressure. The yellow/brown residue was powdered as finely as possible, washed with ether (25 mL) then dried, yielding **S1** as a yellow solid (1.28 g, 74%); ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ = 8.69 (d,

$J = 7.6$ Hz, 2H, H_k or H_l), 8.63 (d, $J = 7.6$ Hz, 2H, H_k or H_l), 7.37 (d, $J = 7.2$ Hz, 4H, *ortho*-PhH), 7.26 (t, $J = 7.2$ Hz, 4H, *meta*-PhH), 7.17 (t, $J = 7.2$ Hz, 2H, *para*-PhH), 4.80 (d, $J = 7.6$ Hz, 2H, H_c), 4.65 (t, $J = 7.6$ Hz, 1H, H_d).

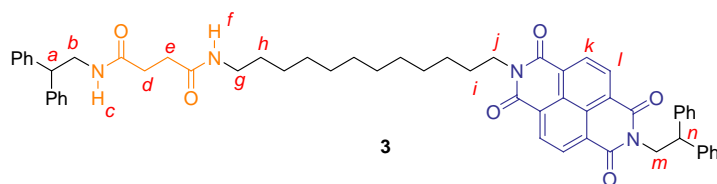
This material was used in the next step without further characterization or purification.

N' -(12-Aminododecyl)- N' -(2,2-diphenylethyl)succinamide (S2)



S2 was prepared as described by Altieri et al.¹

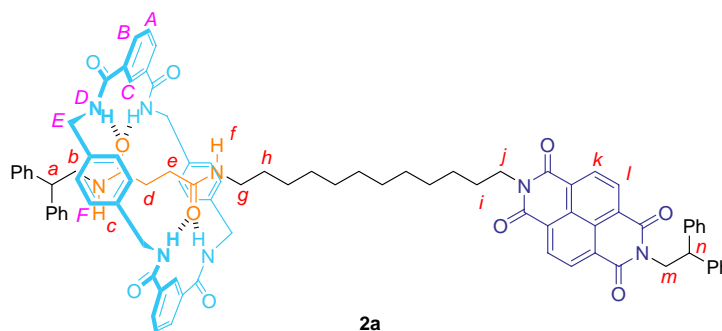
N -(2,2-Diphenylethyl)- N' -(12-{[4-(2,2-diphenylethylamino)-4-oxobutanoyl]amino}dodecyl)naphthalene-1,4,5,8-tetracarboxylic diimide (3)



Anhydride **S1** (223 mg, 0.500 mmol) and N -(12-aminododecyl)- N' -(2,2-diphenylethyl)succinamide (**S2**)¹ (240 mg, 0.500 mmol) in DMF (10 mL) were heated at 150 °C for 4 h. The mixture was then allowed to cool overnight, yielding a precipitate. The reaction mixture was warmed again to obtain a clear solution which was poured into water. The resulting precipitate was too fine to be recovered efficiently by filtration, so the suspension was extracted several times with chloroform. The combined organics were dried ($MgSO_4$) and then evaporated under reduced pressure. The residue was then washed with a small amount of ethanol, before drying to give thread **3** as an off-white solid (405 mg, 89%). ¹H NMR (400 MHz, $CDCl_3$): $\delta = 8.71$ (d, $J = 7.7$ Hz, 2H, H_k or l), 8.65 (d, $J = 7.6$ Hz, 2H, H_k or l), 7.35-7.13 (m, 20H, H_{Ph}), 5.90-5.83 (m, 2H, H_c & H_j), 4.87 (d, $J = 8.1$ Hz, 2H, H_m), 4.78 (t, $J = 8.1$ Hz, 1H, H_n), 4.18-4.15 (m, 3H, H_a & H_j), 3.87 (dd, $J = 7.9$

Hz and $J = 5.9$ Hz, 2H, H_b), 3.17 (q, $J = 6.7$ Hz, 2H, H_g), 2.39 (s, 4H, H_d & H_e), 1.71 (quint., $J = 7.5$ Hz, H_i), 1.47-1.25 (m, 18H, H_h & alkyl CH_2); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.2$ (succinamide CO), 172.0 (succinamide CO), 162.78 (imide CO), 162.77 (imide CO), 141.8 (phenyl ArC_q), 141.2 (phenyl ArC_q), 130.9 (naphthalene ArCH), 130.8 (naphthalene ArCH), 128.7 (phenyl ArCH), 128.41 (phenyl ArCH), 128.37 (phenyl ArCH), 128.0 (phenyl ArCH), 126.8 ($2 \times$ phenyl ArCH), 126.62 (naphthalene ArC_q), 126.58 (naphthalene ArC_q), 126.5 (naphthalene ArC_q), 126.2 (naphthalene ArC_q), 50.5 (CH_a), 48.6 (CH_n), 44.8 ($\text{CH}_{2(m)}$), 43.8 ($\text{CH}_{2(b)}$), 40.9 ($\text{CH}_{2(j)}$), 39.6 ($\text{CH}_{2(g)}$), 31.8 ($\text{CH}_{2(d \text{ or } e)}$), 31.7 ($\text{CH}_{2(d \text{ or } e)}$), 29.7, 29.6, 29.5, 29.3, 28.0, 27.0, 26.9 ($10 \times \text{CH}_2$); FAB-MS (3-NOBA matrix): $m/z = 909$ [$(\text{M}+\text{H})^+$] (anal. calcd for $\text{C}_{58}\text{H}_{60}\text{N}_4\text{O}_6 + \text{H}^+$: $m/z = 909$).

[2]-(1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-[N-(2,2-diphenylethyl)-N'-(12-{[4-(2,2-diphenylethylamino)-4-oxobutanoyl]amino}dodecyl)-naphthalene-1,4,5,8-tetracarboxylic diimide]-rotaxane (2a)

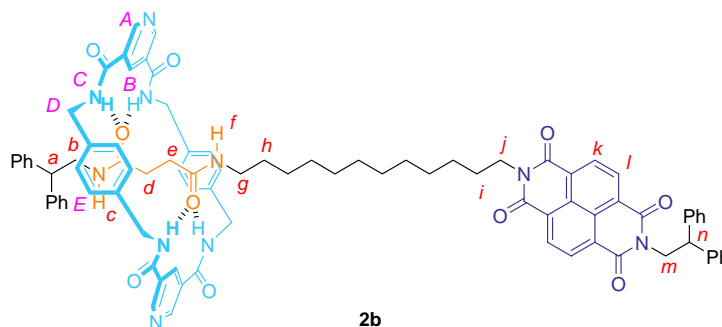


Solutions of isophthaloyl dichloride (354 mg, 1.74 mmol) in chloroform (10 mL) and *p*-xylylenediamine (237 mg, 1.74 mmol) with triethylamine (489 μL , 3.49 mmol) in chloroform (10 mL) were simultaneously added using motor-driven syringe pumps over 4 h to a solution of thread **3** (198 mg, 0.218 mmol) in chloroform (20 mL). Following addition, the mixture was allowed to stir for a further 2 h before removal of the off-white precipitate by filtration. The resulting filtrate was diluted with chloroform (40 mL) and

washed with hydrochloric acid (1N, 3 × 80 mL), sodium hydrogen carbonate (sat. aq., 3 × 100 mL) and brine (sat., 100 mL). The organics were then dried (MgSO₄) and evaporated to give a pale brown residue. This material was purified by flash chromatography (SiO₂; methanol/chloroform, 1:99), then the product-containing material was washed repeatedly in hot toluene to remove all traces of the thread starting material, affording the [2]rotaxane **2a** as a pale yellow solid (88.0 mg, 28%); mp > 100 °C (decomp.); ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, *J* = 7.6 Hz, 2H, H_k or H_l), 8.64 (d, *J* = 7.6 Hz, 2H, H_k or H_l), 8.39 (s, 2H, H_C), 8.18 (dd, *J* = 7.8 Hz and *J* = 1.2 Hz, 4H, H_B), 7.60 (t, *J* = 7.7 Hz, 2H, H_A), 7.55 (t, *J* = 5.0 Hz, 4H, H_D), 7.35-7.13 (m, 20H, PhH), 7.01 (s, 8H, H_F), 5.90-5.86 (m, 2H, H_c & H_j), 4.88 (d, *J* = 8.0 Hz, 2H, H_m), 4.78 (t, *J* = 7.8 Hz, 1H, H_n), 4.48 (d, *J* = 5.1 Hz, 8H, H_E), 4.14 (t, *J* = 7.6 Hz, 2H, H_j), 4.06 (t, *J* = 7.8 Hz, 1H, H_a), 3.71 (dd, *J* = 7.6 Hz and *J* = 5.8 Hz, 2H, H_b), 3.02 (q, *J* = 6.7 Hz, 2H, H_g), 1.73-1.64 (m, 2H, H_i), 1.41-1.36 (m, 2H, H_h), 1.34-1.22 (m, 16H, alkyl CH₂), 0.96 (s, 4H, H_d & H_e); ¹³C NMR (100 MHz, CDCl₃): δ = 173.0 (succinamide C=O), 172.8 (succinamide C=O), 166.4 (macrocycle C=O), 162.8 (2 × imide C=O), 141.4 (phenyl ArC_q), 141.2 (phenyl ArC_q), 137.7 (xylyl ArC_q), 133.8 (isophthaloyl ArC_q), 131.5 (ArCH_B), 130.9 (naphthalene ArCH), 130.8 (naphthalene ArCH), 129.14 (ArCH_A), 129.10 (ArCH_F), 128.9 (phenyl ArCH), 128.41 (phenyl ArCH), 128.37 (phenyl ArCH), 127.8 (phenyl ArCH), 127.2 (phenyl ArCH), 126.8 (phenyl ArCH), 126.57 (naphthalene ArC_q), 126.56 (naphthalene ArC_q), 126.5 (naphthalene ArC_q), 126.2 (naphthalene ArC_q), 123.9 (ArCH_C), 50.5 (CH_a), 48.6 (CH_n), 44.8 (CH_{2(m)}), 44.2 (CH_{2(b)}), 43.9 (CH_{2(E)}), 40.9 (CH_{2(I)}), 39.8 (CH_{2(g)}), 29.6, 29.54, 29.49, 29.43, 29.40, 29.3, 29.2, 28.0, 27.0, 26.9 (12 × CH₂); HRMS (FAB, 3-

NOBA matrix): $m/z = 1441.6759 [(M+H)^+]$ (anal. calcd for $^{12}C_{89}^{13}CH_{89}N_8O_{10}^+$: $m/z = 1442.6735$).

[2]-(1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-9,12,22,25-dibenzo-3,5,16,18-di[5-pyridyl]cyclohexacosane)-[N-(2,2-diphenylethyl)-N'-(12-{[4-(2,2-diphenylethylamino)-4-oxobutanoyl]amino}dodecyl)-naphthalene-1,4,5,8-tetracarboxylic diimide]-rotaxane (2b)



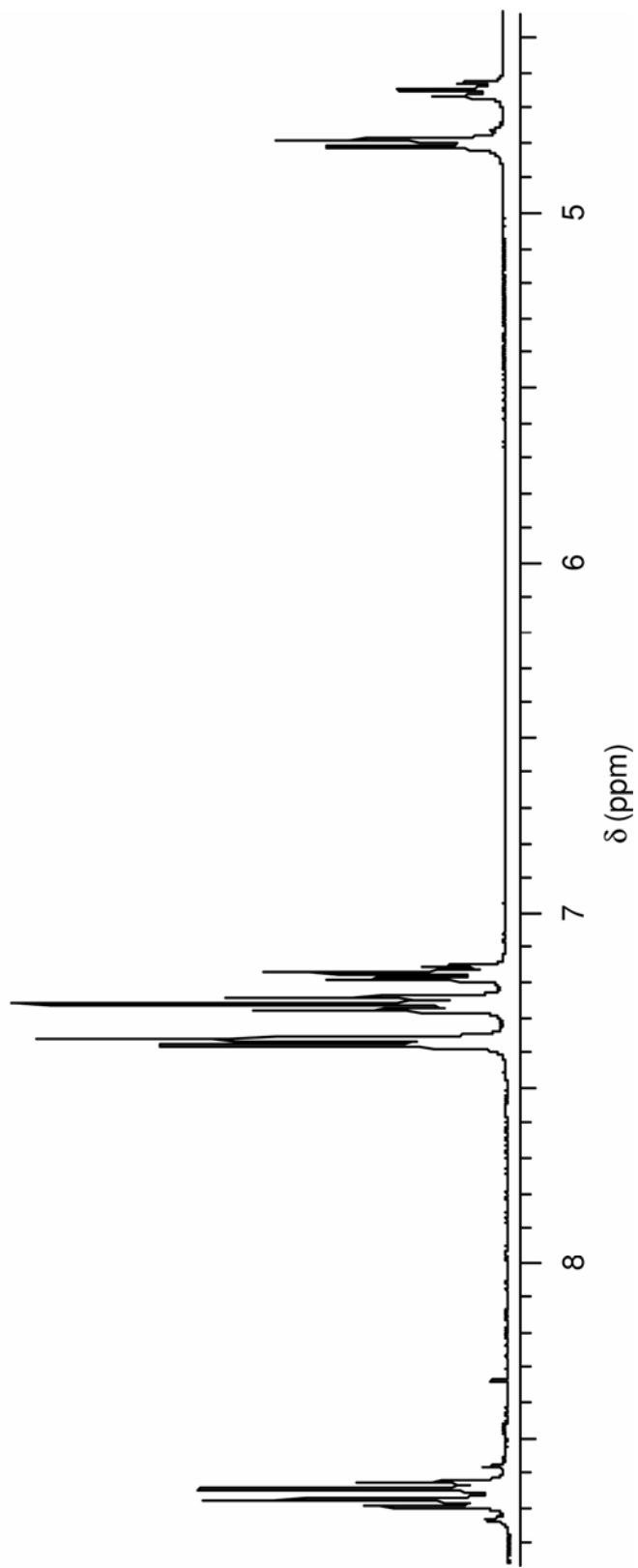
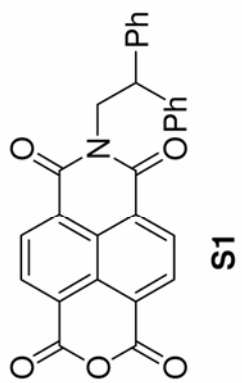
Solutions of freshly prepared pyridine-3,5-dicarbonyl dichloride (303 mg, 1.49 mmol) in chloroform (8 mL) and *p*-xylylenediamine (202 mg, 1.49 mmol) with triethylamine (417 μ L, 2.98 mmol) in chloroform (8 mL) were simultaneously added using motor-driven syringe pumps over 4 h to a solution of thread **3** (169 mg, 0.186 mmol) in chloroform (20 mL). Following addition, the mixture was allowed to stir for a further 16 h before removal of the off-white precipitate by filtration. The resulting filtrate was diluted with chloroform (40 mL) and washed with hydrochloric acid (1N, 3 \times 80 mL), sodium hydrogen carbonate (sat. aq., 3 \times 100 mL) and brine (sat., 100 mL). The organics were then dried ($MgSO_4$) and evaporated to give a pale brown residue. This material was purified by flash chromatography (SiO_2 ; methanol/chloroform, 1:99 to 3:97), then the product-containing material was washed repeatedly in cold toluene to remove all traces of the thread starting material, affording the [2]rotaxane **2b** as a pale brown solid (93.0 mg, 35%); mp 143-146 $^{\circ}C$; 1H NMR (400 MHz, $CDCl_3$): $\delta = 9.11$ (s, 4H, H_A), 8.67-8.61 (m, 6H, H_B & H_k & H_l), 8.09 (s, 1H, H_c), 7.92 (s, 1H, H_j), 7.57 (s, 4H, H_C), 7.31-7.12 (m,

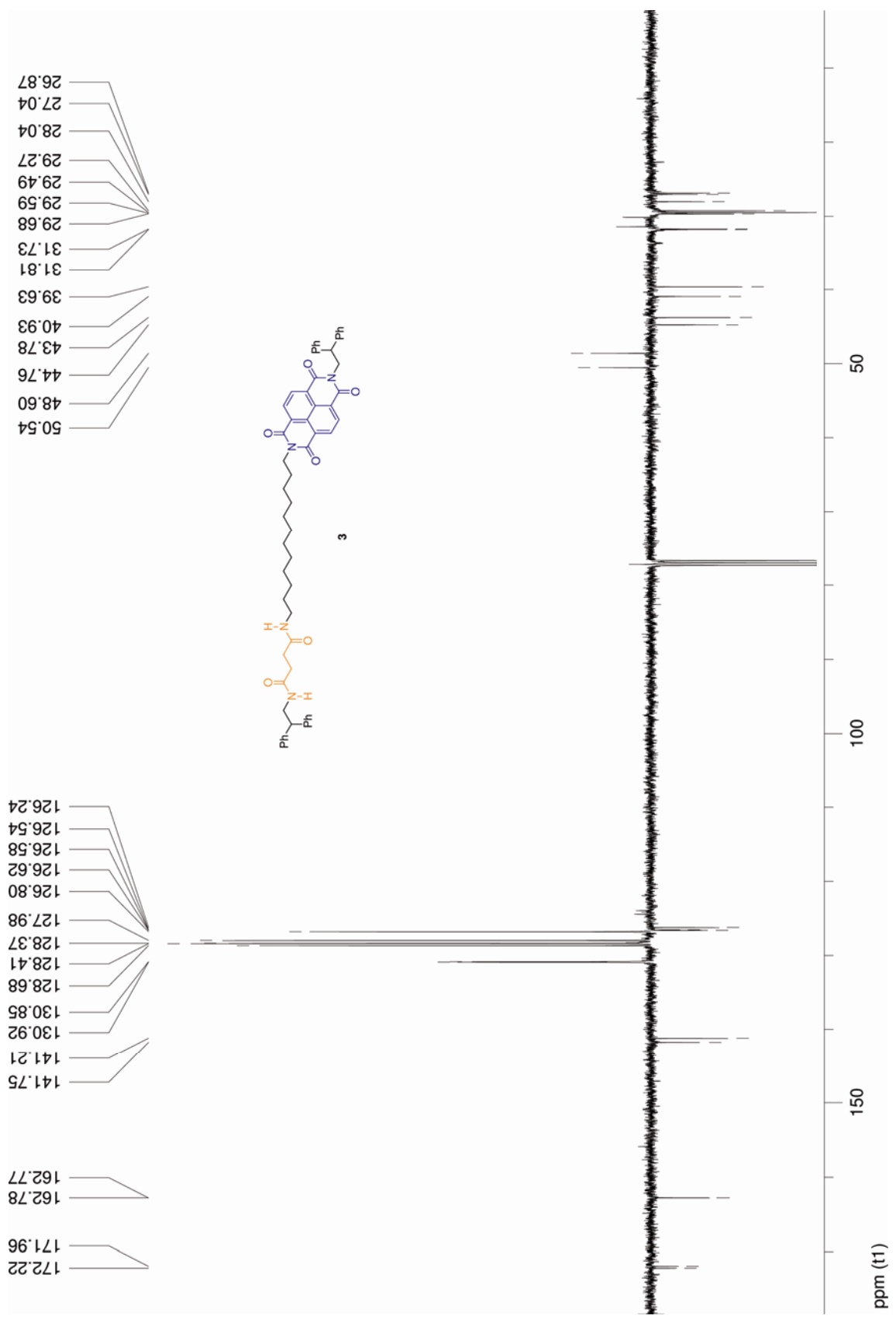
28H, H_E & H_{Ph}), 4.86 (d, *J* = 8.0 Hz, 2H, H_m), 4.77 (t, *J* = 7.5 Hz, 1H, H_n), 4.56 (s, 8H, H_D), 4.14-4.10 (m, 3H, H_a & H_j), 3.83 (br t, 2H, H_b), 3.11 (d, *J* = 4.5 Hz, 2H, H_g), 1.71 (br s, 2H, H_i), 1.44-1.43 (m, 2H, H_h), 1.41-1.22 (m, 16H, alkyl CH₂), 1.02 (s, 4H, H_d & H_e); ¹³C NMR (100 MHz, CDCl₃): δ = 173.6 (succinamide C=O), 173.2 (succinamide C=O), 163.7 (macrocycle C=O), 162.7 (2 × imide C=O), 151.4 (ArCH_A), 141.5 (phenyl ArC_q), 141.2 (phenyl ArC_q), 137.4 (xylyl ArC_q), 131.6 (ArCH_B), 130.9 (naphthalene ArCH), 130.8 (naphthalene ArCH), 129.6 (ArCH_E), 128.9 (phenyl ArCH), 128.5 (pyridyl ArC_q), 128.41 (phenyl ArCH), 128.37 (phenyl ArCH), 127.8 (phenyl ArCH), 127.2 (phenyl ArCH), 126.8 (phenyl ArCH), 126.6 (2 × naphthalene ArC_q), 126.5 (naphthalene ArC_q), 126.2 (naphthalene ArC_q), 50.6 (CH_a), 48.6 (CH_n), 44.8 (CH_{2(m)}), 44.4 (CH_{2(b)}), 44.1 (CH_{2(D)}), 40.9 (CH_{2(j)}), 39.8 (CH_{2(g)}), 29.52, 29.49, 29.31, 29.26, 28.0, 27.1 (12 × CH₂); HRMS (FAB, 3-NOBA matrix): *m/z* = 1444.6687 [(M+H)⁺] (anal. calcd for ¹²C₈₇¹³CH₈₇N₁₀O₁₆⁺: *m/z* = 1444.6640).

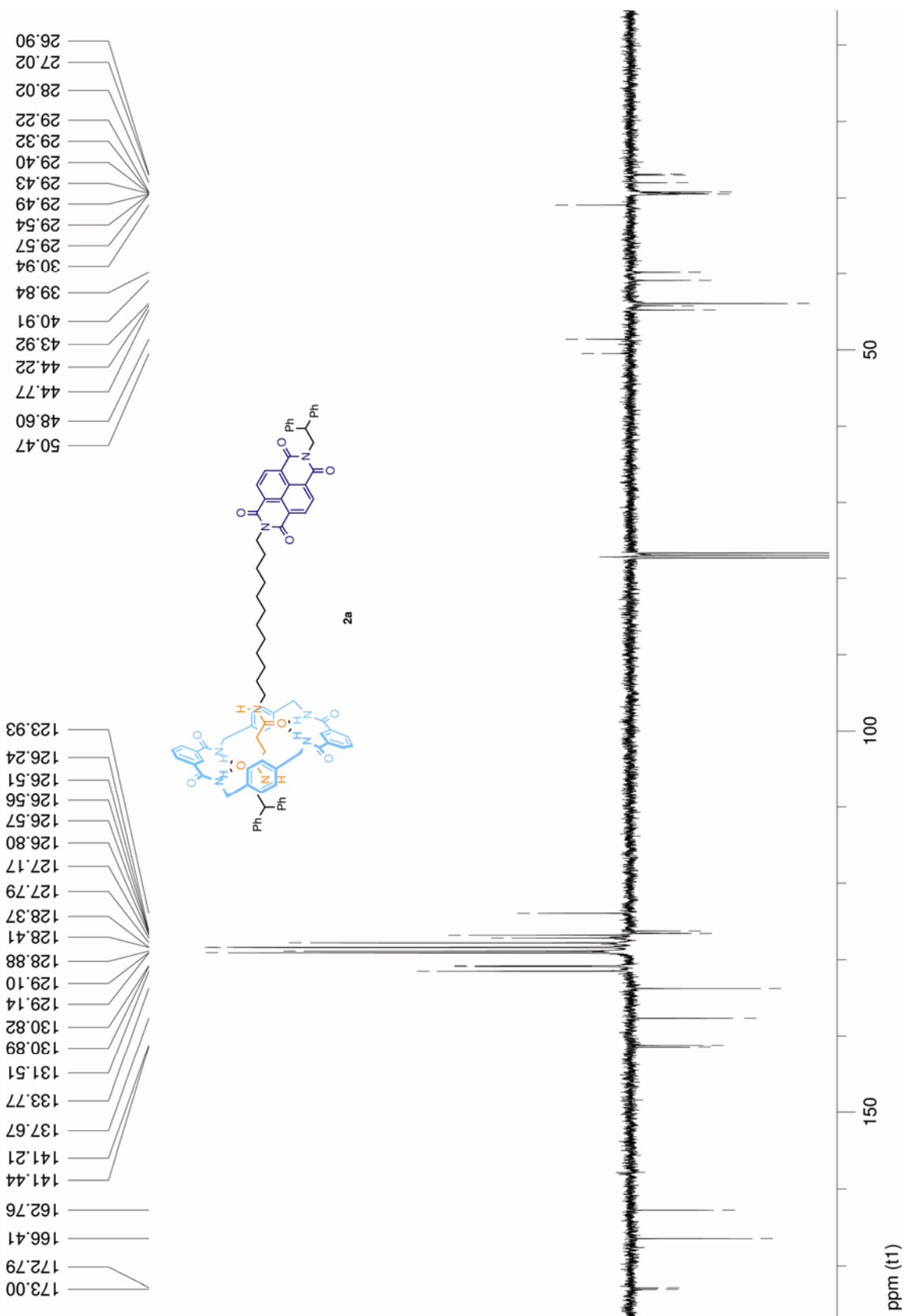
¹H and ¹³C NMR spectra of new compounds

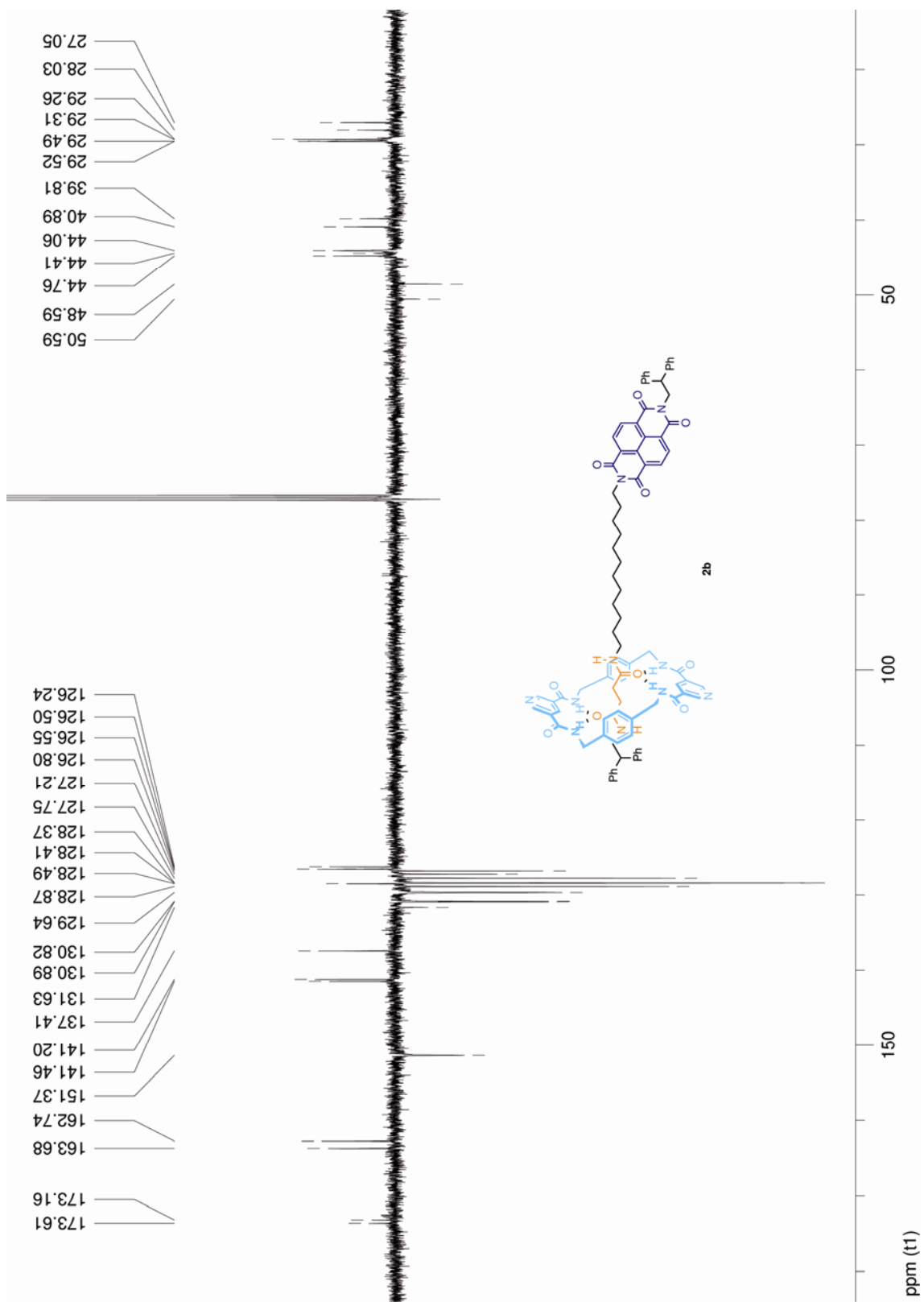
For ¹H NMR spectra of thread **3** and rotaxanes **2a** and **2b**, see Figures 1 and S2.

The spectra of **S1** was recorded in (CD₃)₂SO; all other spectra CDCl₃. All spectra recorded at 298 K.









2. AM1 calculations of imide and diimide charge densities on oxygen

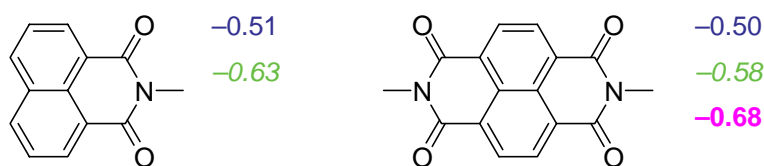


Figure S1. Charges on the oxygen atoms in 1,8-naphthalimide and naphthalene-1,4,5,8-diimide (AM1 calculations): plain blue – neutral state; italic green– radical anion; bold pink – dianion.

3. Supplementary partial ^1H NMR spectra to show position of the macrocycle in rotaxane **2b** in CDCl_3 .

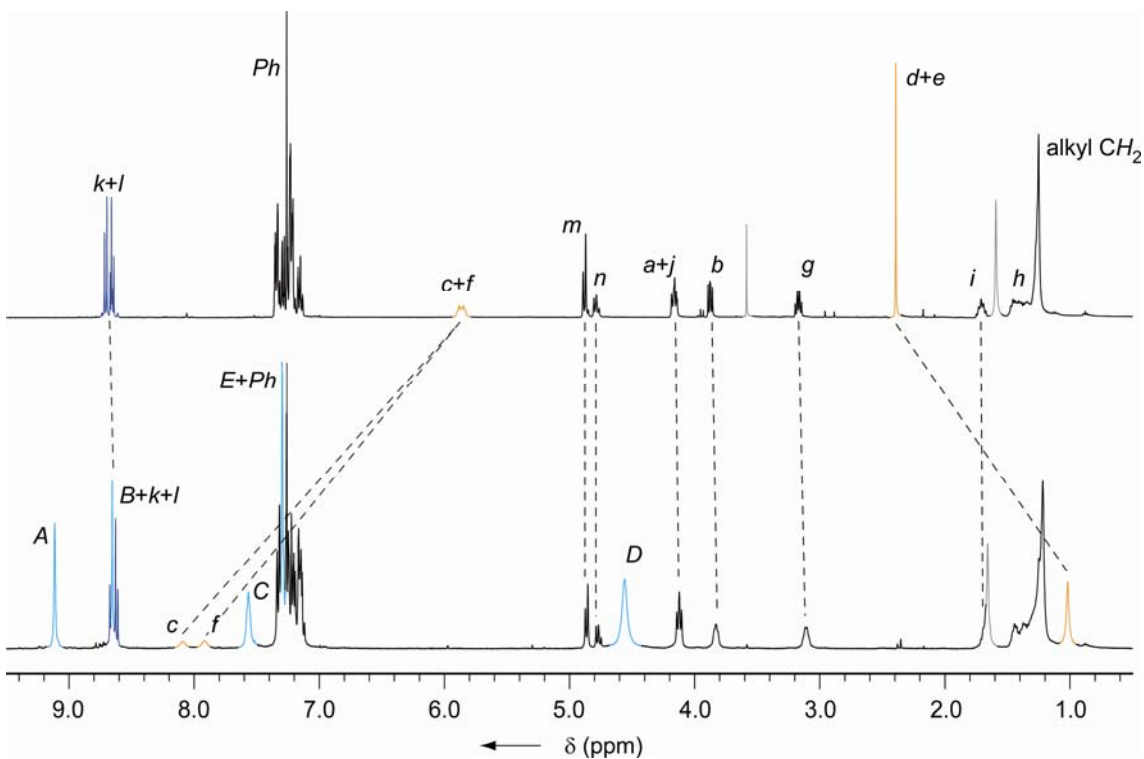


Figure S2. ^1H NMR spectra (400 MHz, CDCl_3 , 298 K) of thread **3** (upper) and rotaxane **2b** (lower). The ^1H NMR assignments and coloring correspond to the labeling shown in the characterization of **2b** and **3** in Section 1 of the Supporting Information. Residual water peaks are shown in grey

4. Electrochemistry

Materials

All chemicals used were reagent grade. Tetrabutylammonium hexafluorophosphate (TBAH, Fluka) was used as supporting electrolyte as received. Tetrahydrofuran (LiChrosolv) was treated according to a procedure described elsewhere.² For the voltammetric experiments, the solvent was distilled into the electrochemical cell, prior to use, by a trap-to-trap procedure. Electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) experiments were carried out in aqueous (Millipore) solutions with 0.1 M KCl as supporting electrolyte.

Instrumentation and Measurements

In the voltammetric experiments, a one-compartment electrochemical cell of airtight design was used, with high-vacuum glass stopcocks fitted with Viton (DuPont) O-rings to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenk flask containing the solvent were made by spherical joints fitted with Viton O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically $1.0\text{--}2.0 \times 10^{-5}$ mbar. The working electrode consisted of platinum disk ultramicroelectrodes (with radii from 5 to 62.5 μm) also 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 reference electrodes were separated from the working electrode by ~ 0.5 cm. Potentials were measured with the ferrocene or decamethylferrocene standards and are always referred to saturated calomel electrode (SCE). $E_{1/2}$ values correspond to $(E_{\text{pc}} + E_{\text{pa}})/2$ from CV. Ferrocene (or

decamethylferrocene) was also used as an internal standard for checking the electrochemical reversibility of a redox couple. The temperature dependence of the relevant internal standard redox couple potential was measured with respect to SCE by a nonisothermal arrangement.³ Voltammograms were recorded with an AMEL Model 552 potentiostat or a custom-made fast potentiostat controlled by either an AMEL Model 568 function generator or an ELCHEMA Model FG-206F. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda thermostat. The minimization of ohmic drop was achieved through the positive feedback circuit implemented in the potentiostat.

ESI and CA experiments were performed using a two-compartment electrochemical cell also fitted with a saturated calomel electrode (SCE) and a platinum spiral as counter electrode with an Autolab Model PGSTAT 30 (ECO CHEMIE).

Digital simulation of electrochemical experiments

The simulations of the electrochemical experiments were carried out by the DigiSim 3.0 software by Bioanalytical Systems Inc. All the fitting parameters were chosen so as to obtain a visual best fit over a 10^2 – 10^3 -fold range of scan rates.

Wide potential range CV scans of rotaxane 2a illustrating the effect of irreversible reduction of the macrocycle on shuttling

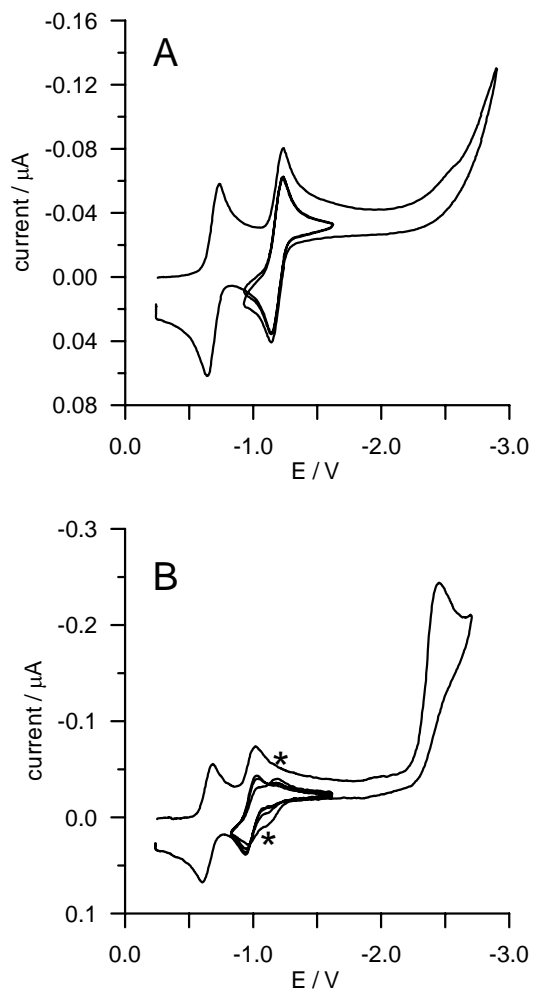


Figure S3. CV curves of a 0.5 mM solutions of (A) **3** or (B) **2a** in THF (supporting electrolyte: 0.05 M tetrabutylammonium tetrafluoroborate). Working electrode: platinum disc (125 μm diameter). $\nu = 1 \text{ V s}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$. Asterisks denote redox peaks associated with the co-conformer *succ-2a*.

Solution-phase CV curve for [2]rotaxane **2b**

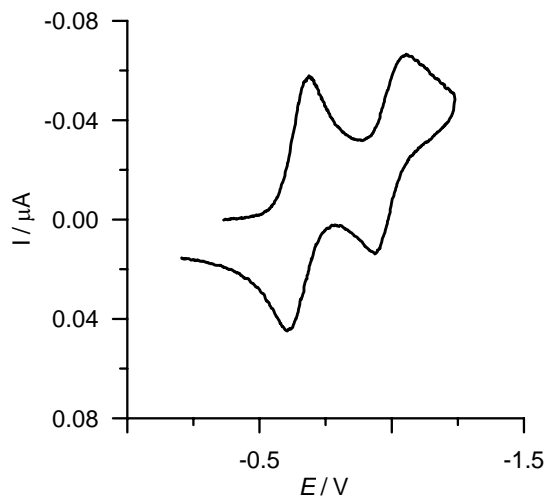


Figure S4. CV curve of a 0.5 mM solution of **2b** in THF (supporting electrolyte: 0.05 M tetrabutyl ammonium tetrafluoroborate). Working electrode: platinum disc (125 μm diameter). $\nu = 1 \text{ V s}^{-1}$; $T = 25 \text{ }^\circ\text{C}$.

Simulation and fitting of CV curves for [2]rotaxanes **2a** and **2b** and thread **3**

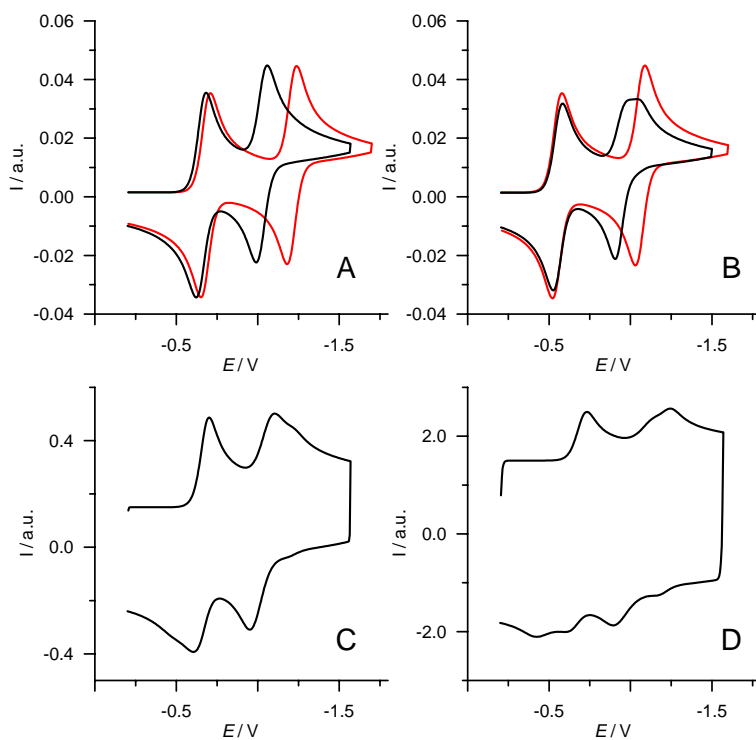


Figure S5. Digitally-simulated CV curves of **2a** (black lines) or **3** (red lines) calculated according to the mechanism depicted in Scheme 1 under the conditions of Figures 2 A–D.

Table S1. Calculated equilibrium and rate constants of rotaxanes **2a** and **2b** by simulation of the experimental voltammograms using DigiSim[®].^a

Equilibrium	$K_{\text{eq}}^b [k_f/k_b]$ (at 298 K) Solution (THF)	$K_{\text{eq}}^c [k_f/k_b]$ (at 218 K) Solution (THF)
<i>succ-2</i> \Leftrightarrow <i>ndi-2</i>	$(5.0 \pm 1) \times 10^{-3}$ [[$(10 \pm 2) \times 10^3$ / $(2.0 \pm 0.3) \times 10^6$]	$(5.0 \pm 1) \times 10^{-3}$ [[$(1.0 \pm 0.2) \times 10^2$ / $(2.0 \pm 0.3) \times 10^4$]
<i>succ-2⁻</i> \Leftrightarrow <i>ndi-2⁻</i>	2.0 ± 0.4 [[$(10 \pm 2) \times 10^3$ / $(5.0 \pm 0.8) \times 10^3$]	0.30 ± 0.06 [[$(1.0 \pm 0.2) \times 10^2$ / $(3.0 \pm 0.5) \times 10^2$]
<i>succ-2²⁻</i> \Leftrightarrow <i>ndi-2²⁻</i>	$(4.0 \pm 0.8) \times 10^3$ [[$(10 \pm 2) \times 10^3$ / (2.5 ± 0.4)]	$(1.0 \pm 0.2) \times 10^2$ [[$(1.0 \pm 0.2) \times 10^2$ / (1.0 ± 0.2)]

^a For rotaxane **2a** or **2b** in THF solution: $k_h^\circ = 10^2 \text{ cm s}^{-1}$ (i.e., Nernstian heterogeneous ET), diffusion coefficient = $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

^b Equilibrium constants were determined with 20% accuracy.

^c Values not optimized.

Electrochemical impedance spectra of 2b·11-MUA·Au(111) surfaces

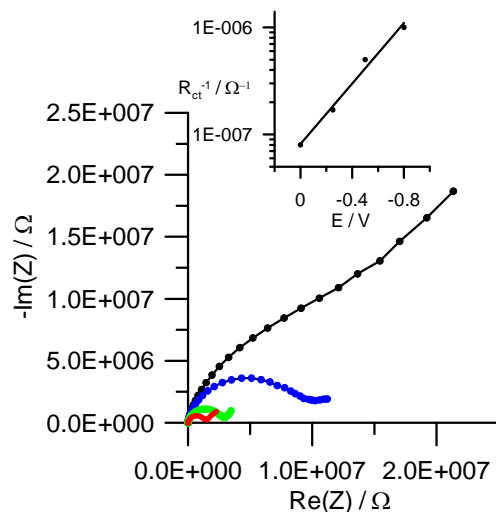


Figure S6. EIS spectra, at different potentials, of **2b**·11-MUA·Au(111). Solution: aqueous 0.1 M KCl. $T = 25$ °C. The out-of-phase component of the impedance, $-Z''$, plotted vs. the in-phase one, Z' – Z'' and Z' being parametric functions of the frequency (Nyquist plot) – is shown. Spectra were taken at various potentials in the range from 0 to -0.9 V vs. SCE, i.e., in the same potential region where the first reduction of **2b** may take place. Investigation of the second reduction of *ndi* remained instead precluded by the instability of SAMs at $E \leq -1.0$ V.⁴ The electrical response of the interface was described in terms of the equivalent circuit shown in Figure S7, below. R_{Ω} represents the solution resistance, C_{dl} the double-layer capacitance, R_{ct} the charge-transfer resistance (related to the exchange current i_0 and clearly omitted in the case of data obtained in the case of bare 11-MUA films). The Warburg element, associated with mass transport phenomena, was omitted in the present case since the rotaxane was assumed to remain confined during the experiment at the SAM surface. The electrical parameters were evaluated by fitting procedures, using the CNLS method described by Boukamp.⁵ Inset: The log of reciprocal of the charge transfer resistance scales linearly with potential as expected, since the heterogeneous ET rate constant is related to

R_{ct} by the following relationship: $k_{ET} = \left(\frac{RT}{n^2 F^2 A C_0} \right) \times \left(\frac{1}{R_{ct}} \right)$.⁶

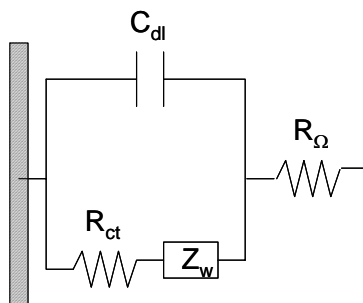


Figure S7. Randles equivalent circuit describing the electrical response of the electrochemical interface. In the circuit, R_{Ω} represents the solution resistance, C_{dl} the double layer capacitance, R_{ct} the charge transfer resistance (related to the exchange current i_0 and standard rate constant) and Z_w the Warburg element, describing the time (frequency) dependence of mass transport.

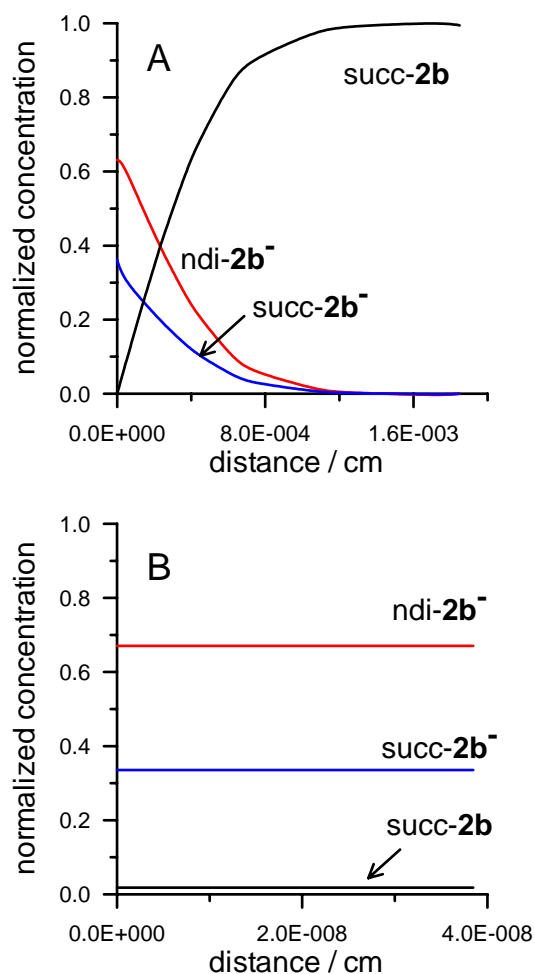


Figure S8. Surface concentration profiles of pristine *succ-2b* (black lines), *succ-2b⁻* (blue lines) and *ndi-2b⁻* (red lines) co-conformations following a 10 ms potential step at -0.9 V. Concentrations were calculated according to the square mechanism in Scheme 1 and assuming either (A) semi-infinite diffusion of all species or (B) species constrained to a monolayer at the electrode surface. Simulation shuttling parameters were those obtained from solution-phase CV experiments, reported in Table S1. In the simulation of film behavior (B), the heterogeneous ET rate constant was assumed to be 4×10^{-5} cm s $^{-1}$, on the basis of EIS results indicating a standard rate constant for ET of $\sim 10^3$ s $^{-1}$ and assuming that ET occurs through a thickness of $\sim 4 \times 10^{-8}$ cm. The slow ET step should be the rate-determining process in this case and will dominate any lowering of shuttling kinetics as a result of surface confinement. It can be seen that equilibrium concentrations are still attained within 10 ms.

5. Surface preparation and characterization

Sample preparation

Samples consist of [2]rotaxane **2b** grafted onto 11-mercaptoundecanoic acid (11-MUA) self-assembled monolayer (SAM) on Au(111) *via* interactions between pyridine groups of the rotaxane macrocycle and the carboxylic acid group of 11-MUA. They were prepared in two steps: first, 150 nm thick Au(111) films supported by mica substrates (prepared in a custom-made vacuum deposition system as described in ref. 6) were immersed into a 1 mM chloroform solution of 11-MUA for 1 day, rinsed with solvent and dried under an argon flow to obtain a compact and ordered 11-MUA SAM.⁷ In a second step, the 11-MUA SAM was immersed in a 0.5 mM dichloromethane solution of rotaxane **2b** for 5 days, rinsed copiously with solvent and dried under argon.⁸ Rotaxane films used as a reference for XPS were prepared by placing a drop of rotaxane solution directly on gold. The samples were measured after the solvent had evaporated completely.

X-ray photoemission spectroscopy (XPS)

XPS measurements were performed with a SSX-100 (Surface Science Instruments) photoelectron spectrometer with a monochromatic Al K_α X-ray source ($h\nu = 1486.6$ eV) and base pressure of 10^{-10} Torr. The energy resolution – full width at half-maximum (FWHM) measured on gold Au(4f_{7/2}) – was set to 1.0 eV to analyze rotaxane films directly deposited on Au(111) and 1.2 eV to analyze the rotaxane monolayers in order to minimize data acquisition time and simultaneously maximize the signal intensity. The photoelectron take-off angle was 37°. Binding energies were referenced to the substrate signal Au(4f_{7/2}) at 84.0 eV. Spectral analysis included background subtraction and peak separation using mixed Gaussian-Lorentzian functions, in a least squares curve-fitting

program Winspec, which was developed in the LISE laboratory of the Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium.

Quantification of the surface coverage

Table S2. Estimation of surface coverage of rotaxane **2b** grafted on 11-MUA SAM. Calculated values of elemental composition (in atomic percentages) and ratios for 2, 6 and 10% coverage taking into account the stoichiometry of the molecules and experimental results.

	Expected compositions at different coverages			Experimental
	2% coverage	6% coverage	10% coverage	
C (at%)	79.0	79.5	79.9	78 ± 2
O (at%)	13.6	12.7	12.1	15 ± 2
N (at%)	1.2	2.9	4.0	2.8 ± 0.6
S (at%)	6.2	4.9	4.0	4.4 ± 0.9
C/N	63.8	27.1	19.8	27 ± 2
S/N	5.0	1.7	1.0	1.6 ± 0.2

6. References

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