Supporting Information for:
Synthesis and Characterization of a Doubly Spin-Labelled Electrochemical Driven Molecular Shuttle

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General procedures .............................................................. S2
Preparation of compound 2 ................................................. S3
Preparation of compound 3 .................................................. S3
Preparation of Axle Az3 ...................................................... S4
Preparation of Dumbbell Dumb3’ and Rotaxane Rot32+4+ .... S5
Preparation of Dumbbell Dumb4’ .......................................... S6
Preparation of Rotaxane Rot42+4+ ........................................ S7
Preparation of compound 4 .................................................. S8
Preparation of compound 5 .................................................. S9
Preparation of compound 6 .................................................. S9
Preparation of compound 7 .................................................. S10
Preparation of compound 9 .................................................. S11
Preparation of compound 10 ............................................... S11
Preparation of compound 11 ............................................... S12
Preparation of compound 12 ............................................... S13
Preparation of Axle Az1 ...................................................... S13
Preparation of Dumbbell Dumb1’ and Rotaxane Rot12+4+ .... S14
Preparation of compound 13 ............................................... S15
Preparation of Axle Az2 ...................................................... S16
Preparation of Dumbbell Dumb2 and Rotaxane Rot2’4+ ...... S17
EPR spectrum of Dumb4’ ..................................................... S19
References ........................................................................ S20
General procedures

$^1H$ NMR spectra were recorded at 298 K on Varian Inova and on Varian Mercury spectrometers operating at 600 and 400 MHz, respectively in CD$_3$CN and in CD$_3$COCD$_3$ solutions using the solvent peak as internal standard (1.94 and 2.05 ppm, respectively). Chemical shifts are reported in parts per million ($\delta$ scale).

EPR spectra has been recorded on a Bruker ELEXYS instrument by using the following instrument settings: microwave power 0.79 mW, modulation amplitude 0.04 mT, modulation frequency 100 kHz, scan time 180 s, 2K data points. Digitised EPR spectra were transferred to a personal computer for analysis using digital simulations carried out with a program developed in our laboratory and based on a Monte Carlo procedure.

The electrochemical cell was home-made and consisted of an EPR flat cell (Wilmad WG-810) equipped with a 25×5×0.2 mm platinum gauze (anode), a platinum wire (cathode). The current was supplied and controlled by an AMEL 2051 general-purpose potentiostat. In a typical experiment, the cell was filled with an acetonitrile solution of rotaxane (ca. 1 mM) containing tetrabutylammonium hexafluorophosphate (ca. 0.1 M) as supporting electrolyte. After thoroughly purging the solution with N$_2$, spectra were recorded at positive settings corresponding to the first one electron oxidation processes of TTF unit. After the formation of TTF radical cation was complete the current was reversed to give the reduction of the radical-cation back to neutral TTF.

ESI-MS spectra were recorded with Micromass ZMD spectrometer by using the following instrumental settings: positive ions; desolvation gas (N$_2$) 230 L/h; cone gas (skimmer): 50 L/h; desolvation temp. 120° C; capillary voltage: 3.2 kV; cone voltage: 40 and 100 V; hexapole extractor: 3 V.

Elemental analysis of the rotaxanes and the dumbbells were performed on a Thermo Flash 2000 CHNS/O analyzer.

All reagents were commercially available and were used without further purification.

Compounds II, III, IV, S$_1$, S$_2$, S$_3$, axle Az4, S$_4$ and CBPQTNO•4PF$_6$ were synthesized according to literature procedures.
Synthesis of compound 2

Compound 2 was prepared following the synthetic procedure reported in ref. [S8a]. A solution of compound 1 (0.04 g, 0.058 mmol), 2,6-diisopropylphenol (0.020 g, 0.116 mmol, 20 μL), K₂CO₃ (0.08 g, 0.58 mmol), 18-crown-6 (0.002 g, catalytic amount), and LiBr (0.0008 g, catalytic amount) in DMF (4.6 mL) was heated under nitrogen atmosphere at 80°C for 48 h. After cooling down to room temperature, the reaction mixture was concentrated in vacuo, treated with water, extracted with dichloromethane, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed (SiO₂, cyclohexane/ethyl acetate 65:35). Fractions containing the product were concentrated in vacuo to give 2 in 99%.

¹H NMR (600 MHz, CD₃CN): δ 1.19 (d, J = 7.2 Hz, 12H), 2.68 (t, J = 6.0 Hz, 2H), 2.94 (t, J = 6.0 Hz, 2H), 2.96 (t, J = 6.0 Hz, 2H), 3.39 (sept, J = 7.2 Hz, 2H), 3.48 (d, J = 4.5 Hz, 2H), 3.55-3.59 (m, 6H), 3.62-3.70 (m, 8H), 3.76-3.79 (m, 2H), 3.85-3.87 (m, 2H), 6.55, 6.56, 6.57 (3 x s, 2H), 7.06-7.13 (m, 3H). ESI-MS: m/z 716.0 (M+Na)⁺.

Synthesis of compound 3

Compound 3 was prepared following the synthetic procedure reported in ref. [S3b]. TsCl (0.024 g, 0.125 mmol) dissolved in anhydrous CH₂Cl₂ (1 mL) was added dropwise over a period of 5 min to an ice-cooled solution of 2 (0.040 g, 0.057 mmol), Et₃N (0.0127 g, 0.125 mmol, 20 μL) and DMAP (0.008 g, cat.) in anhydrous CH₂Cl₂ (2 mL). The reaction mixture was stirred overnight (0°C to rt), whereupon it was washed with saturated NaHCO₃ solution, brine, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed over silica gel column eluting with cyclohexane/ethyl acetate 7:3 and then 1:1. The desired product was collected and concentrated to give 0.013 g (27% yield) of 3.

¹H NMR (600 MHz, CD₃CN): δ 1.18 (d, J = 6.6 Hz, 12H), 2.44 (s, 3H), 2.90 (t, J = 6.0 Hz, 2H), 2.96 (t, J = 6.3 Hz, 2H), 3.39 (sept, J = 6.6 Hz, 2H), 3.47 (s, 4H), 3.56-3.69 (m, 10H), 3.76-3.79
(m, 2H), 3.85-3.87 (m, 2H), 4.09-4.12 (m, 2H), 6.51, 6.52, 6.56, 6.57 (4 x s, 2H), 7.06-7.13 (m, 3H), 7.43 (d, \( J = 8.0 \text{ Hz} \), 2H), 7.78 (d, \( J = 8.0 \text{ Hz} \), 2H). ESI-MS: \( m/z \) 870.5 (M+Na).  

**Synthesis of Axle Az3**

![Synthesis Diagram]

Compound Az3 was prepared following the synthetic procedure reported in ref. [S11]. Compound 3 (0.013 g, 0.015 mmol) and sodium azide (0.005 g, 0.075 mmol) were dissolved in DMF (1 mL) and heated to 80° C for 20 h. After removal of the solvent in vacuo the crude was partitioned between 10 mL of water and CH₂Cl₂, and the aqueous phase was washed with CH₂Cl₂ (3×10 mL). The combined organic extracts were washed with brine, dried (MgSO₄), and the solvent evaporated to give 0.011 g (quantitative yield) of Az3.

\(^1\)H NMR (600 MHz, CD₃CN): \( \delta \) 1.19 (d, \( J = 6.6 \text{ Hz} \), 12H), 2.93, 2.94, 2.97, 2.98 (4 x t, \( J = 6.3 \text{ Hz} \), 4H), 3.35 (t, \( J = 5.1 \text{ Hz} \), 2H), 3.39 (septet, \( J = 6.6 \text{ Hz} \), 2H), 3.55-3.59 (m, 4H), 3.61-3.70 (m, 10H), 3.76-3.79 (m, 2H), 3.85-3.87 (m, 2H), 6.53, 6.54, 6.57 (3 x s, 2H), 7.06-7.13 (m, 3H). ESI-MS: \( m/z \) 741.5 (M+Na).
**Synthesis of Dumbbell Dumb3\(^{\ast}\) and Rotaxane Rot3\(^{2-\ 4+}\)**

![Chemical structure diagram]

\textbf{Rot3}\(^{2-\ 4+}\) was prepared following the synthetic procedure reported in ref. [S4]. Axle \textbf{Az3} (0.014 g, 0.0195 mmol), \textbf{CBPQTNO'4PF}_6 (0.025 g, 0.019 mmol) and stopper \textbf{S-1} (0.0056 g, 0.0195 mmol) were dissolved in DMF (0.15 mL) at -10 °C under N\(_2\) atmosphere and stirred for 10 min. TBTA (0.001 g, 0.0019 mmol) and Cu(CH\(_3\)CN)\(_4\)PF\(_6\) (0.0007 g, 0.0019 mmol) were added to the solution and the resulting mixture was stirred at room temperature for 48 h, at which time the solvent was evaporated. The crude solid was purified twice by column chromatography (SiO\(_2\): Me\(_2\)CO and then 1\% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO, i.d. 15 mm, h 15 cm). The fraction in 1\% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO were collected and concentrated to a minimum volume, and rotaxane \textbf{Rot3}\(^{2-\ 4+}\) was precipitated from this solution through the addition of an excess of cold water. The resulting solid was collected by filtration, washed with water to remove the excess of NH\(_4\)PF\(_6\), and dried by vacuum pump to afford the desired rotaxane as a green powder (0.010 g, 22\% yield).
The fractions in Me$_2$CO containing the dumbbell **Dumb3** were collected, concentrated and again purified on silica gel column eluting with Me$_2$CO:cyclohexane:ethyl acetate 1:0.5:0.5 to give **Dumb3** (yield non calculated).

**Dumb3**: $^1$H NMR (600 MHz, CD$_3$COCD$_3$): δ 1.20 (d, $J = 6.6$ Hz, 12H), 3.00-3.14 (m, 4H), 3.45 (septet, $J = 6.6$ Hz, 2H), 3.56-3.98 (m, 18H), 4.68-4.73 (m, 2H), 6.74-6.78 (m, 2H), 7.03-7.14 (m, 3H).

Anal. Calcd for C$_{48}$H$_{72}$N$_5$O$_6$S$_6$: C, 57.22; H, 7.20; N, 6.95; S, 19.09. Found: C, 57.45; H, 7.01; N, 6.89; S 18.92.

EPR (ACN): $a_N$=15.41 G, $g$ = 2.0061.

ESI-MS: m/z 1006.9 (M+H)$^+$. 

**Rot3**$^{2+4+}$: $^1$H NMR (600 MHz, CD$_3$COCD$_3$): δ 1.18 (d, $J = 6.6$ Hz, 12H), 3.20-3.32 (m, 4H), 3.40 (septet, $J = 6.6$ Hz, 2H), 3.58-4.04 (m, 18H), 4.60-4.70 (m, 2H), 5.68 (br s, 2H), 6.07-6.40 (m, 10H), 7.05-7.13 (m, 3H), 7.97-8.20 (m), 8.47-8.61 (m), 9.40-9.65 (m).

Anal. Calcd for C$_{95}$H$_{122}$F$_{24}$N$_{10}$O$_9$P$_4$S$_6$: C, 49.18; H, 5.30; N, 6.04; S 8.29. Found: C, 48.95; H, 5.38; N, 5.89; S 8.50.

ESI-MS: m/z 2173.6 (M-PF$_6$)$^+$. 

**Synthesis of Dumbbell Dumb4**

Axle **Az4**$^{86}$ (0.0205 g, 0.0336 mmol), and stopper **S-1** (0.0117 g, 0.041 mmol) were dissolved in DMF (0.2 mL) under N$_2$ atmosphere. TBTA (0.0025 g, 0.0047 mmol) and Cu(CH$_3$CN)$_4$PF$_6$ (0.0025 g, 0.0067 mmol) were added to the solution and the resulting mixture was stirred at room temperature for 72 h, at which time the solvent was evaporated. The crude solid was purified by
column chromatography (SiO₂, i.d. 15 mm, h 20 cm). The fractions in Me₂CO containing the dumbbell \textbf{Dumb4} were collected and concentrated (0.020 g, 66% yield).

\textbf{Dumbbell Dumb4}:

\[ ^1\text{H NMR} \ (600 \text{ MHz, CD}_3\text{CN}): \delta \ 1.16 \ (d, \ J = 6.6 \ Hz, 12H), \ 3.39 \ (\text{septet, } J = 6.6 \ Hz, 2H), \ 3.59-4.00 \ (m, 20H), \ 4.24-4.31 \ (m, 4H), \ 4.48-4.52 \ (m, 2H), \ 6.93-6.97 \ (m, 2H), \ 7.05-7.13 \ (m, 3H), \ 7.33-7.40 \ (m, 2H), \ 7.76-7.83 \ (m, 2H), \ 8.00 \ (br \ s, 1H). \]


EPR (ACN): \( a_N = 15.40 \ G, \ g = 2.0061. \)

ESI-MS: \( m/z \ 899.5 \ (\text{M+H}^+) \).

\textit{Synthesis of Rotaxane Rot4^{2-4+}}

\textbf{Rot4}^{2-4+} was prepared following the synthetic procedure reported in ref. [S4]. Axle \textbf{Az4}^{86} (0.020 g, 0.0328 mmol), \textbf{CBPQTNO}\textsuperscript{4}PF\textsubscript{6} (0.040 g, 0.0305 mmol) and stopper \textbf{S-1} (0.009 g, 0.031 mmol) were dissolved in DMF (0.15 mL) at -10 °C under N\textsubscript{2} atmosphere. TBTA (0.0022 g, 0.004 mmol) and Cu(CH\textsubscript{3}CN)\textsubscript{4}PF\textsubscript{6} (0.002 g, 0.0054 mmol) were added to the solution and the resulting mixture was stirred at room temperature for 72 h, at which time the solvent was evaporated. The crude solid was purified by column chromatography (SiO₂: Me₂CO and then 1% w/v NH₄PF₆ solution in
Me₂CO, i.d. 15 mm, h 17 cm). The fractions in Me₂CO containing the dumbbell Dumb⁴⁺ were collected and concentrated. The fraction in 1% w/v NH₄PF₆ solution in Me₂CO were collected and concentrated to a minimum volume, and rotaxane Rot⁴²⁻⁴⁺ was precipitated from this solution through the addition of an excess of cold water. The resulting solid was collected by filtration, washed with water to remove the excess of NH₄PF₆, and dried by vacuum pump to afford the desired rotaxane as a purple powder (0.019 g, 26% yield).

Rotaxane Rot⁴²⁻⁴⁺: ¹H NMR (600 MHz, CD₃CN): δ 1.10 (d, J = 6.6 Hz, 12H), 2.40-2.55 (m, 2H), 3.24-3.31 (m, 2H), 3.60-3.68 (m, 26H), 3.76-3.87 (m, 26H), 4.10-4.13 (m, 2H), 4.22-4.33 (m, 26H), 5.50-6.04 (m, 12H), 6.20-6.33 (m, 2H), 7.04-7.12 (m, 3H), 7.15-7.48 (m, 8H), 7.88-8.22 (m, 8H), 8.50-9.17 (m, 8H). ESI-MS: m/z 2173.6 (M+PF₆)⁺.

Anal. Calcd for C₉₉H₁₂₆F₂₄N₁₀O₁₁P₄: C, 53.76; H, 5.74; N, 6.33. Found: C, 53.38; H, 5.88; N, 6.45. ESI-MS: m/z 2173.6 (M+PF₆)⁺

**Synthesis of Compound 4**

![Diagram of compounds IV and 4](image)

Compound 4 was prepared following the synthetic procedure reported in ref. [S3b,c]. TsCl (0.034 g, 0.18 mmol) dissolved in anhydrous CH₂Cl₂ (1.5 mL) was added dropwise over a period of 5 min to an ice-cooled solution of IV (0.107 g, 0.2 mmol), Et₃N (0.045 g, 0.44 mmol, 62 μL) and DMAP (0.008 g, cat.) in anhydrous CH₂Cl₂ (1 mL). The reaction mixture was stirred overnight (0°C to rt), whereupon it was washed with saturated NaHCO₃ solution, brine, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed over silica gel column (h 11.5 cm, i.d. 20 mm) eluting with ethyl acetate. The second band containing the desired product was collected and concentrated to give 0.059 g of compound 4 (43% yield).

¹H NMR (400 MHz, CD₃CN): δ 2.44 (s, 3H), 2.70 (t, J = 6.0 Hz, 1H), 3.47-3.58 (m, 20H), 3.58-3.62 (m, 2H), 4.10-4.13 (m, 2H), 4.22-4.33 (m, 4H), 6.39 (br s, 2H), 7.41-7.45 (m, 2H), 7.76-7.80 (m, 2H). ESI-MS: m/z 705.8 (M+Na)⁺.
Synthesis of compound 5

Compound 5 was prepared following the synthetic procedure reported in ref. [S8a]. A solution of compound 4 (0.06 g, 0.092 mmol), 2,6-diisopropylphenol (0.033 g, 0.183 mmol, 34 µL), K₂CO₃ (0.127 g, 0.92 mmol), 18-crown-6 (0.002 g, catalytic amount), and LiBr (0.0008 g, catalytic amount) in DMF (7 mL) was heated under nitrogen atmosphere at 80°C for 48 h. After cooling down to room temperature, the reaction mixture was concentrated in vacuo, treated with water, extracted with dichloromethane, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed (SiO₂, h 9 cm, i.d. 25 mm, cyclohexane/ethyl acetate 35:65 until 20:80). Fractions containing the product were concentrated in vacuo to give 5 in 71% yield. The yield was not optimized.

¹H NMR (400 MHz, CD₃CN): δ 1.19 (d, J = 7.2 Hz, 12H), 2.70 (t, J = 6.0 Hz, 1H), 3.39 (septet, J = 7.2 Hz, 2H), 3.47-3.50 (m, 2H), 3.55-3.68 (m, 18H), 3.76-3.80 (m, 2H), 3.84-3.88 (m, 2H), 4.26 (t, J = 1.6 Hz, 2H), 4.28 (t, J = 1.2 Hz, 2H), 6.37, 6.39 (2 x t, J = 1.2 Hz, 2H), 7.05-7.14 (m, 3H). ESI-MS: m/z 688.1 (M+H)⁺, 711.2 (M+Na)⁺, 727.1 (M+K)⁺.

Synthesis of compound 6

Compound 6 was prepared following the synthetic procedure reported in ref. [S3b]. TsCl (0.053 g, 0.279 mmol) dissolved in anhydrous CH₂Cl₂ (1.5 mL) was added dropwise over a period of 5 min to an ice-cooled solution of 5 (0.064 g, 0.093 mmol), Et₃N (0.037 g, 0.37 mmol, 52 µL) and DMAP (0.002 g, 0.019 mmol) in anhydrous CH₂Cl₂ (1 mL). The reaction mixture was stirred for 24 h (0°C
to rt), whereupon it was washed with saturated NaHCO$_3$ solution, brine, dried (MgSO$_4$), and the solvent evaporated. The crude product was chromatographed over silica gel column eluting with cyclohexane/ethyl acetate 7:3. The desired product was collected and concentrated to give 0.063 g of compound 6 (80% yield).

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 1.18 (d, $J = 6.8$ Hz, 12H), 2.44 (s, 3H), 3.39 (septet, $J = 6.8$ Hz, 2H), 3.48 (d, $J = 1.6$ Hz, 4H), 3.53 (d, $J = 1.6$ Hz, 4H), 3.55-3.68 (m, 10H), 3.76-3.79 (m, 2H), 3.85-3.88 (m, 4H), 4.25 (t, $J = 1.2$ Hz, 2H), 4.28 (d, $J = 1.0$ Hz, 2H), 6.35, 6.37, 6.39, 6.42 (4 x t, $J = 1.2$ Hz, 2H), 7.05-7.14 (m, 3H), 7.41-7.45 (m, 2H), 7.76-7.80 (m, 2H). ESI-MS: $m/z$ 866.1 (M+Na)$^+$. 

**Synthesis of 2-(2-(2-(2-iodoethoxy)ethoxy)ethoxy)tetrahydro-2H-pyran (7)**

$\begin{align*}
\text{Compound 7 was prepared following the synthetic procedure reported in ref. [S8b,c]. To an ice-cold (0 °C) solution of 2-(2-(2-iodoethoxy)ethoxy)ethan-1-ol}^{S9}(3 \text{ g, 11.53 mmol) and 2,3-dihydro-2H-pyran (1.06 g, 1.16 mL, 12.69 mmol) in CH}_2\text{Cl}_2 (150 mL) was added p-toluenesulfonic acid monohydrate (0.44 g, 2.31 mmol). The mixture was stirred for 10 min and then warmed gradually to room temperature and stirred overnight. Distilled water was then added to the mixture and the solution extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried over MgSO$_4$, filtered, and concentrated under vacuum. The remaining oil was purified by column chromatography eluting with cyclohexane/ethyl acetate 8:2. The desired product was collected and concentrated to give 2 g of compound 7 (51% yield).}
\end{align*}$

$^1$H NMR (400 MHz, CD$_3$CN): $\delta$ 1.44-1.57 (m, 4H), 1.62-1.71 (m, 1H), 1.72-1.82 (m, 1H), 3.30 (t, $J = 6.4$ Hz, 2H), 3.42-3.49 (m, 1H), 3.49-3.54 (m, 1H), 3.57-3.61 (m, 6H), 3.71 (t, $J = 6.4$ Hz, 2H), 3.74-3.85 (m, 2H), 4.56-4.60 (m, 1H). ESI-MS: $m/z$ 367.1 (M+Na)$^+$. 

S10
Synthesis of 5-(2-(2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethoxy)ethoxy)ethoxy)naphthalen-1-ol (9)

To a stirred suspension of 1,5-dihydroxynapthalene (8) (0.2 g, 1.25 mmol), K₂CO₃ (0.48 g, 3.5 mmol), and 18-crown-6 (catalytic amount) in anhydrous acetonitrile (ACN) (30 mL) a solution of compound 7 (0.43 g, 1.25 mmol) in ACN (8 mL) was added dropwise and the mixture stirred under reflux for 6 h. After cooling down to room temperature, the reaction mixture was filtered and the organic filtrate was concentrated. The residue was subjected to column chromatography (SiO₂, h 18 cm, i.d. 20 mm, cyclohexane/ethyl acetate 1:1). The third spot resulted compound 9 (0.08 g, 17%).

¹H NMR (400 MHz, CD₃CN): δ 1.42-1.53 (m, 4H), 1.58-1.67 (m, 1H), 1.68-1.79 (m, 1H), 3.38-3.45 (m, 1H), 3.46-3.53 (m, 1H), 3.56-3.64 (m, 4H), 3.69-3.82 (m, 4H), 3.91-3.95 (m, 2H), 4.24-4.29 (m, 2H), 4.53-4.56 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.45 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H).

ESI-MS: m/z 399.1 (M+Na)⁺.

Synthesis of compound 10

Compound 10 was prepared following the synthetic procedure reported in ref. [S10]. A solution of 6 (0.015 g, 0.018 mmol), 5-monosubstituted-1-hydroxynaphtalene (9) (0.007 g, 0.018 mmol), K₂CO₃ (0.01 g, 0.072 mmol), 18-crown-6 (0.001 g, catalytic amount), and LiBr (0.001 g, catalytic amount) in ACN (3 mL) was heated under nitrogen atmosphere at reflux for 48 h. After cooling down to room temperature, the reaction mixture was filtered and the solid was washed with ACN.
(10 mL) and the combined organic filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (20 mL), washed with brine (2x10 mL), dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed (SiO₂, h 10 cm, i.d. 10 mm cyclohexane/ethyl acetate 1:1) to give 0.018 g of 10 (quantitative yield) as a yellow-green oil.

^1H NMR (400 MHz, CD₃CN): δ 1.18 (d, J = 6.8 Hz, 12H), 1.41-1.52 (m, 4H), 1.58-1.67 (m, 1H), 1.68-1.78 (m, 1H), 3.32-3.44 (m, 4H), 3.46-3.80 (m, 28H), 3.83-3.87 (m, 2H), 3.91-3.95 (m, 4H), 4.25-4.29 (m, 4H), 4.53-4.56 (m, 1H), 6.30, 6.32, 6.34, 6.38 (4 x t, J = 1.2 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 7.04-7.13 (m, 3H), 7.38 (t, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H). ESI-MS: m/z 1069.5 (M+Na)^+. 

**Synthesis of compound 11**

![Synthesis of compound 11](image)

Compound 11 was prepared following the synthetic procedure reported in ref. [S3b,S10]. To a solution of 10 (0.046 g, 0.043 mmol) in CH₂Cl₂ (5 mL), 12 M HCl (1 mL) was added and the reaction mixture was stirred for 5 h at room temperature. A solution of NaOH 1M was then added until neutral pH. The reaction mixture was extracted with CH₂Cl₂, the combined organic extracts washed with brine, dried over MgSO₄ and concentrated under vacuum. The crude light yellow oil was purified by column chromatography eluting with cyclohexane/ethyl acetate 55:45. The desired product was collected and concentrated to give 0.023 g of compound 11 (55% yield). The yield was not optimized.

^1H NMR (400 MHz, CD₃CN): δ 1.18 (d, J = 6.8 Hz, 12H), 3.32-3.44 (m, 4H), 3.46-3.80 (m, 26H), 3.83-3.87 (m, 2H), 3.91-3.95 (m, 4H), 4.25-4.29 (m, 4H), 6.35 (s, 2H), 6.94 (d, J = 8.0 Hz, 2H), 7.04-7.13 (m, 3H), 7.38 (t, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H). ESI-MS: m/z 986.3 (M+Na)^+. 

S12
Synthesis of compound 12

11

TsCl/Et3N/DMAP

12

Compound 12 was prepared following the synthetic procedure reported in ref. [S3b]. TsCl (0.014 g, 0.072 mmol) dissolved in anhydrous CH₂Cl₂ (1 mL) was added dropwise over a period of 5 min to an ice-cooled solution of 11 (0.023 g, 0.024 mmol), Et₃N (0.01 g, 0.095 mmol, 15 μL) and DMAP (0.008 g, cat.) in anhydrous CH₂Cl₂ (1 mL). The reaction mixture was stirred overnight (0°C to rt), whereupon it was washed with saturated NaHCO₃ solution, brine, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed over silica gel column (h 10 cm, i.d. 10 mm) eluting with cyclohexane/ethyl acetate 1:1. The first band containing the desired product was collected and concentrated to give 0.013 g of compound 12 (48% yield).

¹H NMR (400 MHz, CD₂CN): δ 1.18 (2 x d, J = 6.8 Hz, 12H), 2.38 (s, 3H), 3.38 (2 x septet J = 6.8 Hz, 2H), 3.50-3.67 (m, 20H), 3.69-3.73 (m, 2H), 3.74-3.78 (m, 2H), 3.83-3.95 (m, 6H), 4.06-4.09 (m, 4H), 4.20-4.29 (m, 6H), 6.30, 6.31, 6.33, 6.37 (4 x t, J = 1.2 Hz, 2H), 6.93 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 7.04-7.13 (m, 3H), 7.34-7.41 (m, 4H), 7.73-7.82 (m, 4H). ESI-MS: m/z 1139.8 (M+Na)⁺, 1155.8 (M+K)⁺.

Synthesis of Axle Az1

12

NaN₃

Az1

S13
Az1 was prepared following the synthetic procedure reported in ref. [S11]. A solution of tosylate 12 (0.013 g, 0.0116 mmol), and NaN₃ (0.004, 0.058 mmol) in dry DMF (1 mL) was heated at 80 °C for 1 d. After removal of the solvent, the residue was dissolved in CH₂Cl₂ (10 mL) and distilled water (10 mL) and extracted with CH₂Cl₂. The combined organic extracts washed with brine and dried over MgSO₄ were concentrated under vacuum. The crude product, was purified by column chromatography (SiO₂: cyclohexane/ethyl acetate 1:1) to give the azide Az1 in quantitative yield as a yellow oil.

¹H NMR (400 MHz, CD₃CN): δ 1.18 (d, J = 6.8 Hz, 12H), 3.32-3.42 (m, 2H), 3.50-3.68 (m, 18H), 3.68-3.74 (m, 4H), 3.74-3.79 (m, 2H), 3.83-3.88 (m, 2H), 3.91-3.95 (m, 4H), 4.22 (s, 2H), 4.24-4.29 (m, 6H), 6.30, 6.32, 6.34, 6.37 (4 x br s, 2H), 6.94 (d, J = 8.0 Hz, 2H), 7.04-7.13 (m, 3H), 7.38 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H). ESI-MS: m/z 987.6 (M+H)+, 1010.5 (M+Na)+.

**Synthesis of Dumbbell Dumb1⁻ and Rotaxane Rot1²⁻⁴⁺**

![Chemical structure diagrams of Az1, CBPQTNO 4PF₆, S-1, Dumb1⁻, Rot1²⁻⁴⁺](image_url)
Rotaxane Rot1\(^{2+}\) was prepared following the synthetic procedure reported in ref. [S4]. Axle Az1 (0.0185 g, 0.0187 mmol), CBPQTNO\(^{4}\)PF\(_6\) (0.032 g, 0.024 mmol) and stopper S-1 (0.0067 g, 0.0234 mmol) were dissolved in DMF (0.15 mL) at -10 °C under N\(_2\) atmosphere, forming a brown solution. TBTA (0.0017 g, 0.0032 mmol) and Cu(CH\(_3\)CN)\(_4\)PF\(_6\) (0.0012 g, 0.0032 mmol) were added to the solution and the resulting mixture was stirred at room temperature for 72 h, at which time the solvent was evaporated. The crude solid was purified by column chromatography (SiO\(_2\): Me\(_2\)CO and then 1% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO, i.d. 10 mm, h 17 cm). The fractions in Me\(_2\)CO containing the dumbbell Dumb1\(^{-}\) were collected and concentrated. The fraction in 1% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO were collected and concentrated to a minimum volume, and rotaxane Rotaxane Rot1\(^{2+}\) was precipitated from this solution through the addition of an excess of cold water. The resulting solid was collected by filtration, washed with water to remove the excess of NH\(_4\)PF\(_6\), and dried by vacuum pump to afford the desired rotaxane as a green powder (yield non calculated).

Dumbbell Dumb1\(^{-}\): \(^1\)H NMR (600 MHz, CD\(_3\)CN): \(\delta\) 1.17 (d, \(J = 6.4\) Hz, 12H), 3.35-3.41 (m, 2H), 3.50-3.96 (m, 30H), 4.18-4.30 (m, 8H), 4.33-4.45 (m, 2H), 4.48 (br s, 2H), 6.20-6.40 (br s, 2H), 6.82-7.01 (m, 2H), 7.03-7.16 (m, 3H), 7.25-7.46 (m, 2H), 7.69-7.87 (m, 3H).

Anal. Calcd for C\(_{66}\)H\(_{94}\)N\(_5\)O\(_{12}\)S\(_4\): C, 62.04; H, 7.42; N, 5.48; S 10.04. Found: C, 62.29; H, 7.32; N, 5.41; S 10.25

EPR (ACN): \(a_N=15.40\) G, \(g = 2.0061\).

ESI-MS: \(m/z\) 1277.8 (M+H)\(^+\).

Rotaxane Rotaxane Rot1\(^{2+}\): \(^1\)H NMR (600 MHz, CD\(_3\)CN): \(\delta\) 1.17 (d, \(J = 6.4\) Hz, 12H), 3.35-3.41 (m, 2H), 3.50-3.96 (m, 32H), 4.21-4.29 (m, 6H), 4.44-4.56 (m, 2H), 5.32-5.42 (m, 2H), 5.60-5.91 (m, 10H), 6.84-6.97 (m, 2H), 7.04-7.13 (m, 3H), 7.18-7.83 (m) 8.64-9.10 (m).

Anal. Calcd for C\(_{113}\)H\(_{144}\)F\(_24\)N\(_{10}\)O\(_{15}\)P\(_4\)S\(_4\): C, 52.39; H, 5.60; N, 5.41; S 4.95. Found: C, 53.05; H, 5.55; N, 5.30; S 4.88.

ESI-MS: \(m/z\) 2446.1 (M-PF\(_6\))\(^+\).

Synthesis of compound 13
Compound 13 was prepared following the synthetic procedure reported in ref. [S3b]. TsCl (0.161 g, 0.85 mmol) dissolved in anhydrous DCM (5 mL) was added dropwise over a period of 5 min to an ice-cooled solution of IV (0.090 g, 0.170 mmol), TEA (0.038 g, 0.375 mmol, 53 μL) and DMAP (0.008 g, cat.) in anhydrous DCM (2 mL). The reaction mixture was stirred overnight (0°C to r.t.), whereupon it was washed with saturated NaHCO₃ solution, brine, dried (MgSO₄), and the solvent evaporated. The crude product was chromatographed over silica gel column (h 10 cm, i.d. 25 mm) eluting with EtOAc. The second band containing the desired product was collected and concentrated to give 0.102 g of compound 13 (85% yield).

\[ ^1\text{H NMR (400 MHz, CD₃CN): } \delta 2.44 (s, 6H), 3.49 (s, 8H), 3.53 (s, 8H), 3.61 (t, J = 4.4 Hz, 4H), 4.11 (t, J = 4.4 Hz, 4H), 4.26 (s, 4H), 6.38 (br s, 2H), 7.43 (d, J = 8 Hz, 4H), 7.78 (d, J = 8 Hz, 4H). \]

ESI-MS: \( m/z \) 860.2 (M+Na)⁺.

**Synthesis of compound Az2**

![Chemical structure](image)

Az2 was prepared following the synthetic procedure reported in ref. [S11]. A solution of ditosylate 13 (0.100 g, 0.119 mmol), and NaN₃ (0.077, 1.19 mmol) in dry DMF (10 mL) was heated at 80 °C for 2 d. After removal of the solvent, the residue was dissolved in DCM and distilled H₂O and extracted with DCM. The combined organic extracts washed with brine and dried over MgSO₄ were concentrated under vacuum to give the azide Az2 in quantitative yield as a yellow oil (Rf=0.25 in Cy/EtOAc 1/1).

\[ ^1\text{H NMR (400 MHz, CD₃CN): } \delta 3.37 (t, J = 4.8 Hz, 4H), 3.52-3.61 (m, 18H), 3.63 (t, J = 4.8 Hz, 4H), 4.27 (s, 4H), 6.39 (br s, 2H). \]

ESI-MS: \( m/z \) 601.1 (M+Na)⁺.
Synthesis of Dumbbell Dumb2 and Rotaxane Rot2\(^{4+}\)

Rot2\(^{4+}\) was prepared following the synthetic procedure reported in ref. [S13]. Axle Az2 (0.015 g, 0.026 mmol), CBPQTNO•4PF\(_6\) (0.034 g, 0.026 mmol) and di-tert-butyl acetylenedicarboxylate (0.015 g, 0.065 mmol) were dissolved in CH\(_3\)CN (0.13 mL) at 0 °C under N\(_2\) atmosphere and the resulting mixture was stirred at room temperature for 72 h, at which time the solvent was evaporated. The crude solid was purified by column chromatography (SiO\(_2\): Me\(_2\)CO and then 1% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO, i.d. 10 mm, h 17 cm). The fractions in Me\(_2\)CO containing the dumbbell Dumb2 were collected and concentrated. The fraction in 1% w/v NH\(_4\)PF\(_6\) solution in Me\(_2\)CO were collected and concentrated to a minimum volume, and rotaxane Rot2\(^{4+}\) was precipitated from this solution through the addition of an excess of cold H\(_2\)O. The resulting solid was collected by filtration, washed with water to remove the excess of NH\(_4\)PF\(_6\), and dried by vacuum pump to afford the desired rotaxane as a green powder in 30% yield.

Dumbbell Dumb2: \(^1\)H NMR (600 MHz, CD\(_3\)CN): \(\delta\) 1.56 (s, 18H), 1.58 (s, 18H), 3.44-3.52 (m, 20H), 3.84 (t, \(J = 5.2\) Hz, 4H), 4.22-4.33 (m, 4H), 4.70 (t, \(J = 5.2\) Hz, 4H), 6.39 (br s, 2H).
ESI-MS: $m/z$ 1032.2 (M+H)$^+$.  
Anal. Calcd for C$_{44}$H$_{66}$N$_6$O$_{14}$S$_4$: C, 51.25; H, 6.45; N, 8.15, S, 12.44. Found: C, 51.03; H, 6.55; N, 8.04, S 12.35.

Rotaxane Rot2$^{4+}$: $^1$H NMR (600 MHz, CD$_3$CN): δ 1.55-1.61 (m, 36H), 3.30-3.80 (m, 20H), 4.22-4.40 (m, 4H), 4.50-4.70 (m, 4H), 5.22-5.40 (m, 2H), 5.60-5.95 (m, 10H), 7.40-7.70 (m, 7H), 7.80-8.20 (m, 4H), 8.25-8.50 (m, 4H), 8.70-9.15 (m, 8H).  
Anal. Calcd for C$_{91}$H$_{116}$F$_{24}$N$_{11}$O$_{17}$P$_4$S$_4$: C, 46.63; H, 4.99; N, 6.57, S, 5.47. Found: C, 46.99; H, 5.05; N, 6.38, S 5.38.  
EPR (ACN): $a_N=14.84$ G, $g = 2.0061$.  
ESI-MS: $m/z$ 2197.2 (M-PF$_6$)$^+$. 
EPR spectrum of Dumb4' recorded in ACN at 328 K.
References


We prepared compound **I** in 80% yield starting from 1,5-dihydroxynaphthalene and 2-(2-(2-iodoethoxy)ethoxy)ethanol.


