Supplementary Material (ESI) for Chemical Communications
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SUPPLEMENTARY INFORMATION

Anion templated surface assembly of a redox-active sensory rotaxane

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Experimental

Unless otherwise specified chemicals were purchased from Avocado or Sigma Aldrich and used as received. Dimethyl 5-hydroxyisophthalate (**3**)[1], trimethyl(ferrocenylmethyl)-ammonium iodide,[2] **6**•HCl,[3] and 1'-formyl-1,2,3,4,5-pentaphenyl ferrocene[4] were prepared according to literature procedures. ^{1}H NMR spectra were recorded on a Varian Mercury spectrometer operating at 300MHz, Mass Spectrometry was performed in the Inorganic Chemistry Department at the University of Oxford.

1. Ashton, P. R.; Anderson, D. W.; Brown, C. L.; Shipway, A. N.; Stoddart, J. F.; Tolley, M. S. *Chem., Eur. J.* **1998**, *4*, 781-795.
2. Lednicer, D.; Hauser, C. R. *Org. Synth.* **1960**, *40*, 31.
3. Sambrook, M. R.; Beer, P. D.; Wisner, J. A.; Paul, R. L.; Cowley, A. R. *J. Am. Chem. Soc.* **2004**, *126*, 15364-15365.
4. Butler, D. C. D.; Richards, C. J. **2002**, *Organometallics*, *21*, 5433-5436.

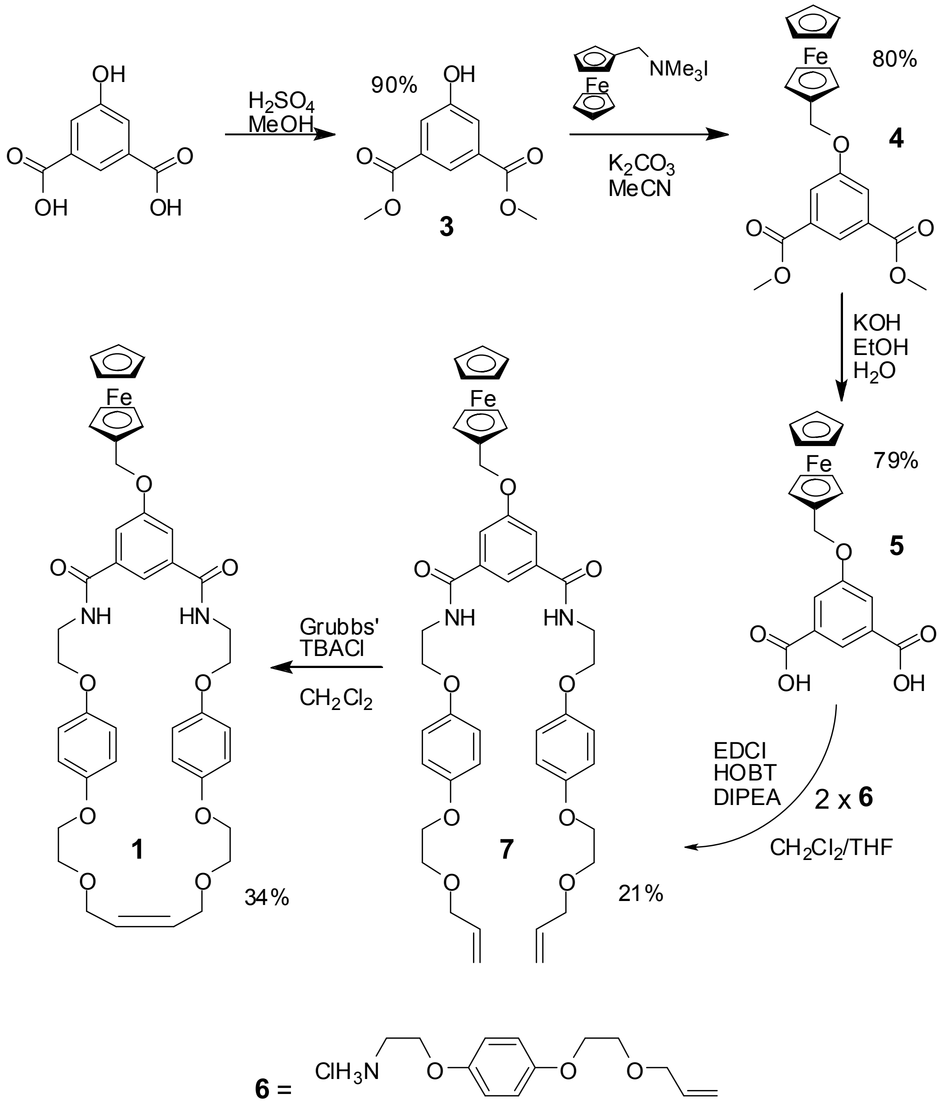
Synthesis of 1'-Hydroxymethyl-1,2,3,4,5-pentaphenyl ferrocene

1'-Formyl-1,2,3,4,5-pentaphenyl ferrocene (270 mg, 0.45 mmol) was dissolved in dry THF (20 ml) under N_2. $LiAlH_4$ (70 mg, 1.8 mmol) was added and the mixture stirred for 45 mins at room temp. 10% $HCl_{(aq)}$ (ca. 8 ml) was added cautiously, causing vigorous effervescence. The resulting brown suspension was extracted with diethyl ether (3 x 10 ml), the combined organic layers dried ($MgSO_4$) and evaporated to give the product as a bright orange solid (265 mg, 0.45 mmol, 98%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ = 7.15-6.84 (many H, m, Ar*H*), 4.14 (4H, br s, Cp*H*), 3.97 (2H, br s, C*H₂*). ^{13}C NMR (75MHz, $CDCl_3$, TMS) 135.61 (*Ar*), 132.30 (*Ar*), 127.07 (*Ar*), 126.10 (*Ar*), 87.46 (*Cp*Ar), 85.45 (*Cp*CH_2), 75.79 (*Cp*H), 74.27 (*Cp*H) 67.06 (*C*H_2). Solid Probe EI HRMS *m/z* observed: 594.1649, 580.1813; calc for $[C_{41}H_{30}FeO]^+$: 594.1646, $[C_{41}H_{32}Fe]^+$ 580.1853. Single spot by TLC (CH_2Cl_2/silica).

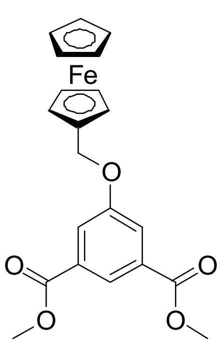
1'-Bromomethyl-1,2,3,4,5-pentaphenyl ferrocene

A solution of PBr_3 (0.55 ml, 1.58 g, 5.85 mmol) in dry benzene was added dropwise to a stirred solution of 1'-hydroxymethyl-1,2,3,4,5-pentaphenyl ferrocene (0.49 g, 0.82 mmol) in dry benzene (15 ml) under N_2. The orange solution was stirred at room temp. for 20 mins and then heated to reflux for 30 mins. Crushed ice (ca. 30 ml) was added to produce an orange morass. This was extracted with diethyl ether (3 x 15 ml), the combined organic layers dried ($MgSO_4$) and evaporated to give the product as an orange solid which was purified by column chromatography (CH_2Cl_2/silica) (0.40 g, 0.61 mmol, 74%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ = 7.18-6.96 (many H, m, Ar*H*), 4.30 (2H, m, Cp*H*), 4.27 (4H, s, Cp*H* and C*H₂*). Solid Probe EI MS *m/z* observed: 658.15, 580.20; calc for $[C_{41}H_{31}BrFe]^+$: 658.10, $[C_{41}H_{32}Fe]^+$:580.19.

Synthesis of Macrocycle 1

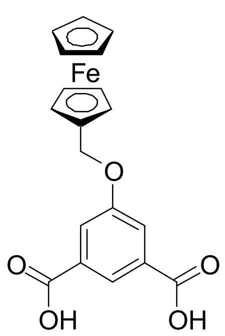


4 Dimethyl 5-(ferrocenylmethoxy)isophthalate



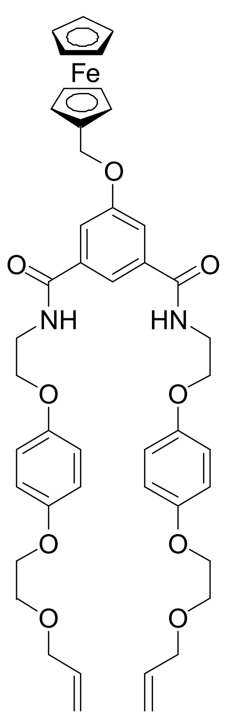
Dimethyl 5-hydroxyisophthalate (150 mg, 0.71 mmol), trimethyl(ferrocenylmethyl)-ammonium iodide (300 mg, 0.78 mmol), potassium carbonate (110 mg, 0.78 mmol) and 18-crown-6 (30 mg, catalytic) were dissolved in MeCN (25 ml) and heated to reflux for 6 hrs. The solvent was removed *in vacuo* and the residue partitioned between water (15 ml) and CH_2Cl_2 (15 ml). The aqueous layer was extracted with further CH_2Cl_2 (2 x 15 ml) and the combined organic fractions dried ($MgSO_4$), filtered through a plug of silica, and evaporated to provide the product as an orange solid (230 mg, 0.58 mmol, 80%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ = 8.26 (1H, br s, Ar*H*), 7.78 (2H, br s, Ar*H*), 4.87 (2H, s, Cp*H*), 4.31 (2H, s, Cp*H*), 4.19 (7H, br s, Cp*H* and C*H*$_2$), 3.92 (6H, m, C*H*$_3$). ESI HRMS *m/z* observed: 431.0554, calc for $[C_{21}H_{20}FeO_5 + Na]^+$: 431.0558.

5 5-(Ferrocenylmethoxy)isophthalic acid



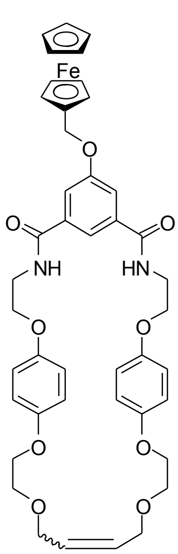
4 (0.50 g, 1.2 mmol) was suspended in EtOH (50 ml). A solution of KOH (0.21 g, 3.7 mmol) in water (5 ml) was added and the mixture heated to reflux for 18 hrs. The resulting orange solution was reduced to half the volume *in vacuo* and aqueous citric acid (1M, 8 ml) to achieved pH 5. Water (50 ml) was then added to generate a precipitate, which was collected by filtration, washed with water and dried under vacuum to give the product as an orange powder. ^{1}H NMR (300MHz, acetone-d^6, TMS) δ = 8.28 (1H, br s, Ar*H*), 7.76 (2H, br s, Ar*H*), 4.87 (2H, s, Cp*H*), 4.28 (2H, s, Cp*H*), 4.19 (2H, s, C*H*$_2$), 4.14 (5H, s, Cp*H*). ESI HRMS (negative ion) *m/z* observed: 379.0383, calc for $[C_{19}H_{16}FeO_5 - H]^-$: 379.0269.

7 *N*^{1},*N*^{3}-Bis(2-(4-(2-(allyloxy)ethoxy)phenoxy)ethyl)-5-(ferrocenylmethoxy)isophthalamide



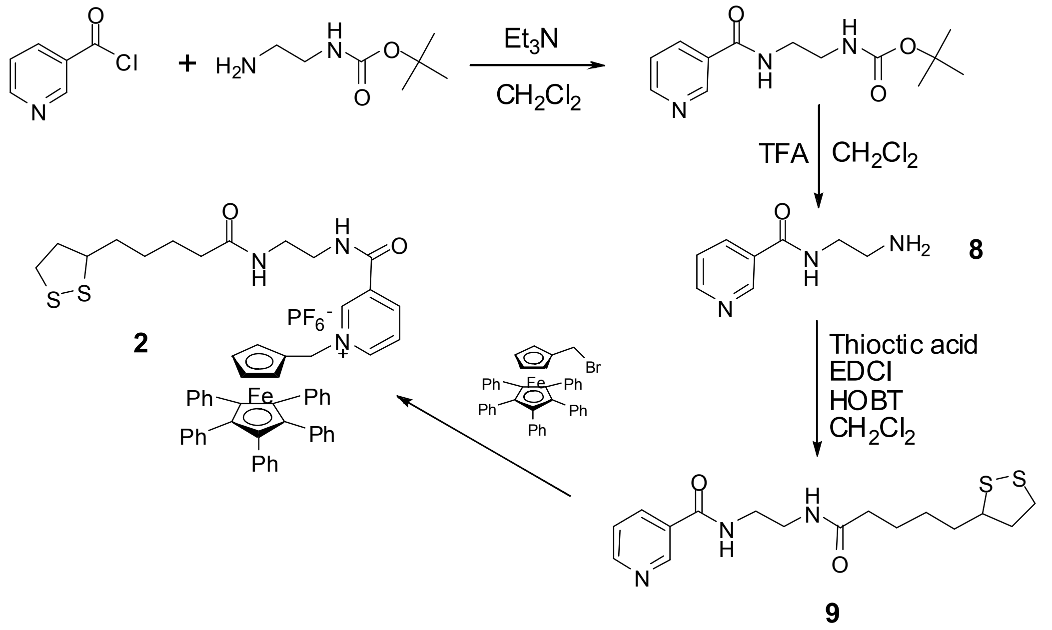
HOBT (180 mg, 1.3 mmol), **5** (230 mg, 0.60 mmol) and **6**•HCl (330 mg, 1.2 mmol) were dispersed in dry CH_2Cl_2 (15 ml) and THF (15 ml) under N_2. Diisopropylethylamine (0.60 ml, 450 mg, 3.5 mmol) and EDCI (320 mg, 1.7 mmol) were added and the mixture stirred for 64 hrs at room temp. The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2. The solution was washed with water (20 ml), $NH_4Cl_{(aq)}$ (1M, 20 ml) and sat. $NaHCO_{3(aq)}$(20 ml). It was then dried ($MgSO_4$) and evaporated to give an orange solid which was purified by column chromatography (silica, CH_2Cl_2:MeOH 100:2) to give the product (210 mg, 0.25 mmol, 42%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ = 7.71 (1H, br s, Ar*H*), 7.48 (2H, br s, Ar*H*), 6.81 (10H, br s, N*H* and Ar*H* quinone), 5.99-5.84 (2H, m, C*H*=CH_2), 5.28 (2H, d, *J* = 17.4 Hz, CH=CH_2), 5.18 (2H, d, *J* = 10.1 Hz, CH=CH_2), 4.85 (2H, s, Cp*H*), 4.28 (2H, s, Cp*H*), 4.17 and 4.16 (7H, s, CpCH_2 and Cp*H*), 4.08-4.01 (12H, m, CH_2CH=CH_2 and CH_2OArOCH_2), 3.82-3.72 (8H, m, NHCH_2 and ArOCH_2CH_2O).

Macrocycle 1

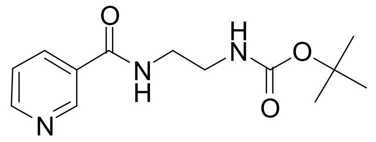


Precursor **7** (170 mg, 0.21 mmol) TBACl (89 mg, 0.32 mmol) and Grubbs' catalyst (17 mg, 10 wt%) were stirred together in dry CH_2Cl_2 (100 ml) under N_2 for 64 hrs. The solvent was removed *in vacuo* and the resulting residue purified by column chromatography (silica, ethyl acetate:hexane 7:3) to afford the product as an orange solid (56 mg, 0.071 mmol, 34%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) δ = 7.55 (1H, br s, Ar*H*), 7.53 (2H, br s, Ar*H*), 6.91 (2H, br s, N*H*), 6.76-6.69 (8H, m, Ar*H* quinone), 5.83 (1.6H, br s, C*H*=C*H cis*), 5.75 (0.4H, br s, C*H*=C*H trans*), 4.82 (2H, s, Cp*H*), 4.29 (2H, s, Cp*H*), 4.16 (7H, br s, CpCH_2 and Cp*H*), 4.08-3.98 (12H, m, CH_2CH=CH_2 and CH_2OArOCH_2), 3.80-3.72 (8H, m, NHCH_2 and ArOCH_2CH_2O). ESI HRMS *m/z* observed: 813.2599, calc for $[C_{43}H_{46}N_2O_9 + Na]^+$: 813.2541.

Synthesis of Thread 2

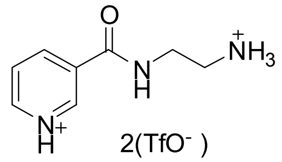


tert-Butyl 2-(nicotinamido)ethylcarbamate



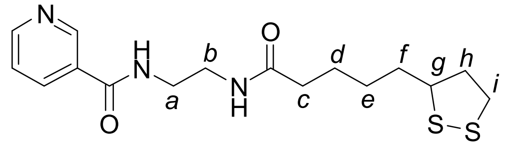
Nicotinic acid (1.5 g, 12 mmol) was stirred in thionyl chloride (25 ml) for 2 hrs. The thionyl chloride was removed *in vacuo* and the residue dissolved in dry CH_2Cl_2 (30 ml). This solution was cooled to 0°C and to it was added slowly a solution of *tert*-butyl 2-aminoethylcarbamate (1.95 g, 12 mmol) and triethylamine (5 ml) in CH_2Cl_2 (30 ml). The mixture was stirred overnight at room temp. It was then washed with water (2 x 20 ml), dried ($MgSO_4$) and evaporated to produce the product as a white solid (2.6 g, 9.8 mmol, 82%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) $\delta = 9.01$ (1H, d, $J = 1.4$ Hz, Ar*H*), 8.65 (1H, dd, $J = 4.9$, 1.8 Hz, Ar*H*), 8.11 (1H, dt, $J = 8.0$, 1.8 Hz, ArH), 7.77 (1H, br s, N*H*), 7.32 (1H, dd, $J = 7.9$, 5.0, Ar*H*) 5.28 (1H, br, N*H*), 3.53 (2H, m, C*H*$_2$), 3.37 (2H, m, C*H*$_2$), 1.37 (9H, s, *t*-Bu*H*). ESI HRMS *m/z* observed: 266.1503, calc for $[C_{13}H_{19}N_3O_3 + H]^+$: 266.1505.

8•2TfOH N-(2-Aminoethyl)nicotinamide bis(hydrotrifluoroacetate)



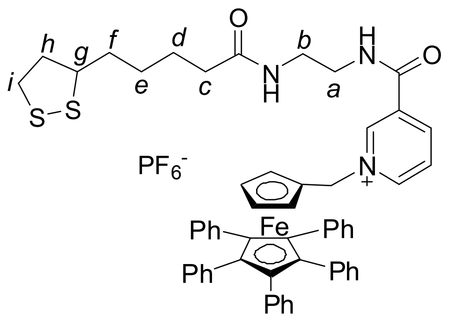
tert-butyl 2-(nicotinamido)ethylcarbamate (1.0 g, 3.8 mmol) was dissolved in CH_2Cl_2 (30 ml) and cooled to 0°C. Trifluoroacetic acid (2 ml) was added and the mixture stirred for 2 hrs. The solvent was removed *in vacuo* to give the product as a brown solid (1.42 g, 3.6 mmol, 96%) which was used crude in the next step. ^{1}H NMR (300MHz, $CDCl_3/CD_3OD$, TMS) $\delta = 9.14$ (1H, s, Ar*H*), 8.78 (1H, d, $J = 5.0$ Hz, Ar*H*), 8.61 (1H, dt, $J = 8.2, 1.8$ Hz, Ar*H*), 7.77 (1H, dd, $J = 7.8, 5.2$ Hz, Ar*H*), 3.68 (2H, t, $J = 5.8$ Hz, CH_2), 3.16 (2H, t, $J = 5.7$ Hz, CH_2).

9 N-(2-(5-(1,2-Dithiolan-3-yl)pentanamido)ethyl)nicotinamide



Thioctic acid (0.52 g, 2.5 mmol), HOBT (0.36 g, 2.7 mmol) and EDCI (0.58 g, 3.0 mmol) were stirred together in dry CH_2Cl_2 (50 ml) under N_2 for 5 min. To this solution was added a solution of **7** (1.0 g, 2.5 mmol) and triethylamine (0.51 g, 5.0 mmol) and stirring continued for 16 hrs. The mixture was washed with water (3 x 50 ml), dried ($MgSO_4$) and evaporated to afford a pale yellow solid (0.81 g, 2.3 mmol, 90%). ^{1}H NMR (300MHz, $CDCl_3$, TMS) $\delta = 9.05$ (1H, d, $J = 1.4$ Hz, Py*H*), 8.69 (1H, dd, $J = 4.9, 1.8$ Hz, Py*H*), 8.12 (1H, dt, $J = 8.0, 1.8$ Hz, Py*H*), 7.84 (1H, br s, N*H*), 7.36 (1H, dd, $J = 7.9, 4.8$ Hz, Py*H*) 6.44 (1H, br s, N*H*) 3.62-3.41 (5H, m, H_a, H_b and H_g), 3.17-3.01 (2H, m, H_i), 2.38 (1H, m, H_{h1}), 2.20 (2H, t, $J = 7.4$ Hz, H_c), 1.82 (1H, m, H_{h2}), 1.68-1.55 (4H, m, H_d and H_f), 1.46-1.32 (2H, m, H_e). ESI HRMS *m/z* observed: 354.1315, calc for $[C_{16}H_{23}N_3O_2S_2 + H]^+$: 354.1310.

Thread **2** PF_6 salt 3-(2-(5-(1,2-dithiolan-3-yl)pentanamido)ethylcarbamoyl)-1-(1,2,3,4,5-pentaphenylferrocen-1'-yl)pyridinium hexafluorophosphate



1’-Bromomethyl-1,2,3,4,5-pentaphenyl ferrocene (50 mg, 76 µmol) and **9** (27 mg, 76 µmol) were heated to reflux in a mixture of MeCN (20 ml) and $CHCl_3$ (3 ml) under N_2 for 16 hrs. The solvent was removed *in vacuo*, the orange residue redissolved in acetone (5 ml) and filtered. To the filtrate was added $NH_4PF_{6(aq)}$ (2 M, ca. 2 ml) and water (5 ml) to generate a precipitate. This was collected by filtration, washed with water and dried under vacuum to give the product as an orange powder (33 mg, 31 µmol, 40%). ^1H NMR (300MHz, $CDCl_3$, TMS) δ = 8.95 (1H, s, Py*H*), 8.82 (1H, d, *J* = 6.8 Hz, Py*H*), 8.37 (1H, d, *J* = 5.7 Hz, Py*H*), 8.00-7.87 (2H, m, N*H* and Py*H*), 7.23-6.87 (many H, m, Ar*H*) 6.48 (1H, br s, N*H*), 5.36 (2H, s, NCH_2Cp) 4,47 (1H, s, Cp*H*), 4.41 (1H, s, Cp*H*), 3.62-3.41 (5H, m, H_a, H_b and H_g), 3.13-2.97 (2H, m, H_i), 2.39 (1H, m, H_{h1}), 2.21 (2H, t, *J* = 7.2 Hz, H_c), 1.89-1.28 (many H, m, H_{h2}, H_d, H_f and H_e). ESI MS *m/z* observed: 932.34, calc for $[C_{57}H_{54}N_3FeO_2S_2]^+$: 932.30.

Salt metathesis – conversion of Thread $\mathbf{2}^+$ PF_6^- salt to Thread $\mathbf{2}^+$ Cl^- salt.

A solution of $\mathbf{2}^+$ PF_6^- salt (33 mg, 31µmol) in CH_2Cl_2 (5 ml) was washed four times with 10 ml portions of aqueous NH_4Cl solution (2 M). The organic phase was dried ($MgSO_4$) and the solvent removed *in vacuo* to give the product as an orange powder.

Electrochemistry

All electrochemistry was carried out using an Autolab PGSTAT 12 potentiostat with a 3 electrode cell. A Ag/$AgNO_3$ reference electrode (BAS) was used for all measurements, with a platinum mesh counter electrode. 100mM TBA PF_6 in acetonitrile was used as the electrolyte for all experiments. For diffusive electrochemical measurements, a graphite working electrode (BAS) was employed. For measurements involving thread and rotaxane SAMs, the SAMs were formed on gold working electrodes (BAS, diameter 1.6 mm). Electrodes were cleaned beforehand by treatment with piranha solution (3:1 by volume conc. H_2SO_4:H_2O_2) followed by mechanical polishing with an aqueous suspension of alumina microparticles (0.05 μ, Buehler). *Caution! Piranha solution reacts violently with organic material and should be handled with extreme caution!*

Diffusive electrochemical titrations

The electrochemical sensing characteristics of macrocycle **1** dissolved at a concentration of 0.1mM in an electrolyte solution of 100mM TBA PF_6 in acetonitrile were investigated by cyclic voltammetry, using a graphite working electrode (BAS); scans were recorded with a scan rate of 100 mV s^{-1}. Aliquots of anion solutions were added to the electrochemical cell with a Hamilton syringe.

Thread SAM formation

SAMs of the thread $\mathbf{2^+PF_6^-}$ were formed on gold working electrodes (BAS, diameter 1.6 mm) by immersing the electrode in a 1mM solution of the compound in $CHCl_3$ for > 12 hrs. The penta-phenyl ferrocene-capped nicotinamide axle $\mathbf{2^+PF_6^-}$ could be assembled on gold electrodes with molecular coverages (0.6 (±0.09) x 10^{-10} molecules cm^{-2}) which reflect the combined steric and electrostatic repulsions expected between neighbouring threads. These adlayers displayed well-behaved quasi-reversible electrochemical characteristics (see table).

Rotaxane SAM formation

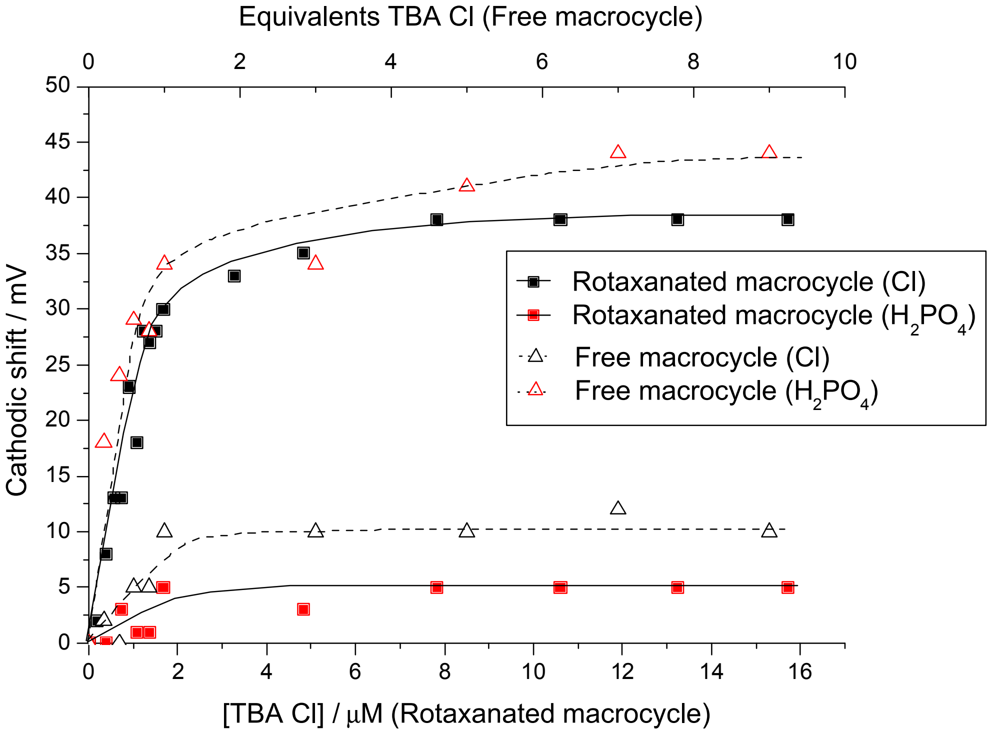
Rotaxane monolayers were formed on gold working electrodes (BAS, diameter 1.6 mm) by immersing the electrode in a 10:1 mixture of macrocycle **1** and thread **2^+Cl^-** (3 mM: 0.3 mM) in $CHCl_3$ for >12hrs, followed by sonication in $CHCl_3$ to remove any non-chemisorbed compound. The trapping of the macrocycle at the electrode surface in this way was monitored by the observation of both macrocycle and thread oxidation peaks by square wave voltammetry. The macrocycle: axle peak charge ratios, which reflect the degree of axle threading, vary from 1:1.1 to 1:3.

As a control, electrodes were immersed in a solution of macrocycle **1** in the absence of thread **2^+Cl^-,** which resulted in no redox peaks in the SWV indicating that macrocycle **1** does not adsorb non-specifically to the gold electrode.

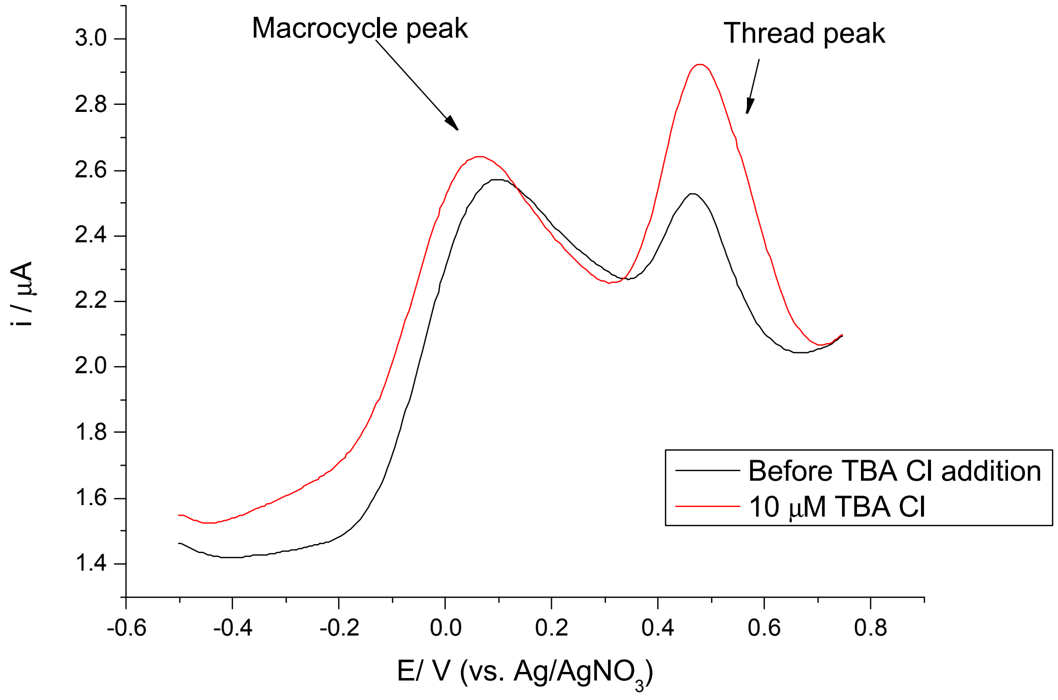
Table S1. Electrochemical data for macrocycle 1 and thread 2^+ (obtained using an electrolyte solution of 100 mM TBA PF_6 in acetonitrile, all potentials vs. $Ag/AgNO_3$)

	$E_{1/2}$ (CV)	ΔE_p (CV)	E_p (SWV)	Γ / mol cm^{-2}
Diffusive macrocycle **1**	151 mV	68 mV	155 mV	N/A
Diffusive thread $\mathbf{2^+PF_6^-}$	454 mV	90 mV	453 mV	N/A
Thread $\mathbf{2^+PF_6^-}$ SAM	460 mV	23 mV	463 mV	0.5×10^{-10}
Rotaxane SAM ($\mathbf{2}^+$ signal)	458 mV	38 mV	477 mV	0.21×10^{-10}
Rotaxane SAM (**1** signal)	146 mV	41 mV	155 mV	0.07×10^{-10}

In estimating the lateral dimensions of the macrocycle from CaCHE software and assuming a conformation where the molecular axis lies parallel to the underlying surface, the molecular footprint is estimated to be ~195 Å^2. Integration of the macrocycle Faradaic wave gives a surface coverage of 4.2 – 5.8 x 10-4 molecules Å^2), or 9.5 ± 1.5 % of the maximum.



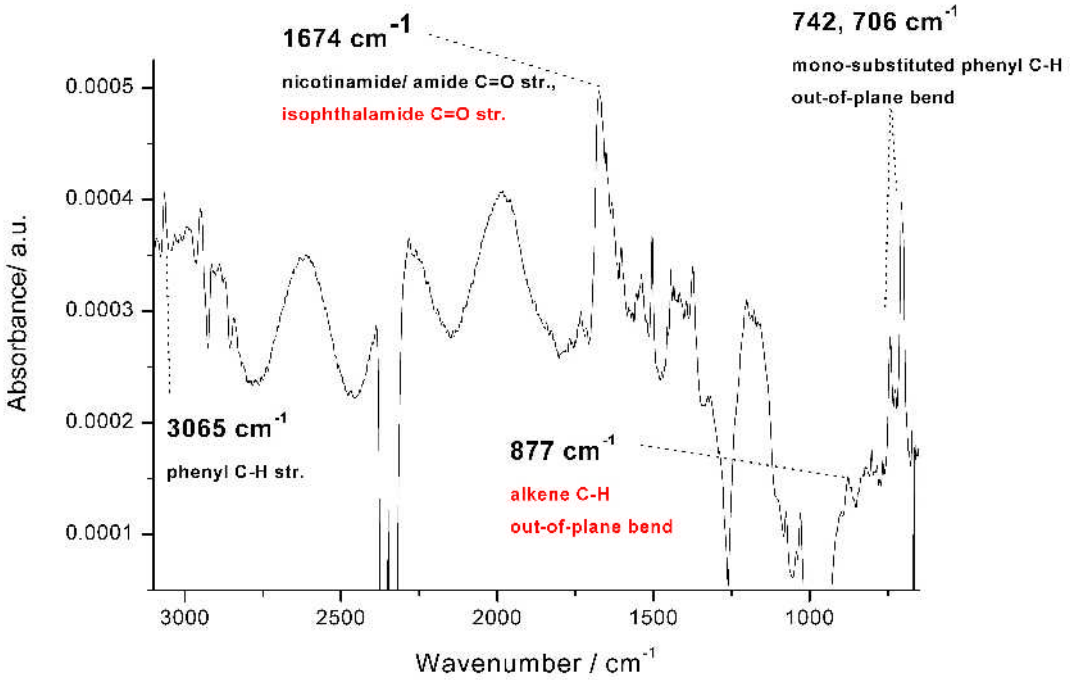
The comparative voltammetric responses of the macrocycle appended ferrocenyl moeties (1) to chloride and dihydrogen phosphate when free in solution and when threaded onto the stoppered surface assembled thread (2).



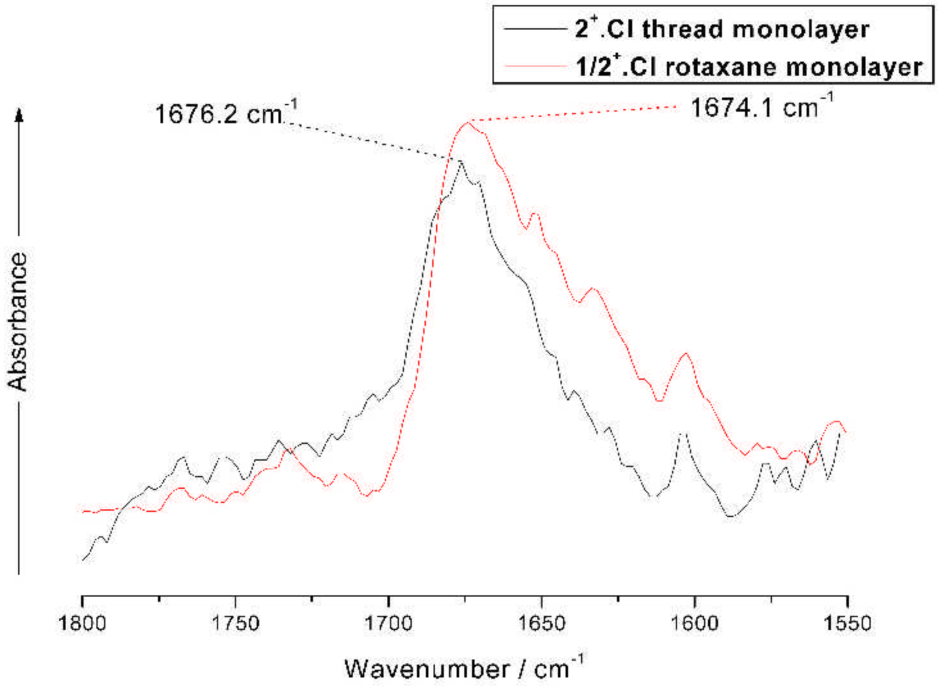
SWV response of rotaxane SAM to chloride addition in acetonitrile.

FTIR

Monolayers of the **2^+Cl^-** thread and **$1/2^+$ Cl^-** rotaxane were additionally characterised by FTIR reflectance spectroscopy. The FTIR spectrum of the **2^+Cl^-** monolayer showed strong absorbances at 706 cm^{-1} and 743 cm^{-1}, characteristic of out-of plane bending of the phenyl C-H bonds, a strong signal at 1676 cm^{-1}, characteristic of the amide carbonyl group stretch associated with the nicotinamide and amide groups (unresolved under a broad band, fwhm 44 cm^{-1}), and a signal at 3065 cm^{-1}, which can be assigned to phenyl C-H stretches. The spectrum of the **$1/2^+$ Cl^-** rotaxane monolayer (figure 1) also showed phenyl C-H out-of plane bending signals (at 706 cm^{-1} and 742 cm^{-1}), a phenyl C-H stretching signal at 3065 cm^{-1}, and a band associated with amide carbonyl stretches (for the isophthalamide, nicotinamide and amide groups) centred at 1674 cm^{-1}, indicating the presence of the thread. Evidence for the presence of macrocycle **1** in the monolayer comes from a signal at 877 cm^{-1} (also observed in the solid state spectrum of **1,** but not observed in the spectrum of the **2^+ Cl^-** monolayer), associated with the out-of-plane bending of the alkene C-H bonds of the macrocycle. Further evidence of the presence of **1** comes from the shifting of the carbonyl stretch centre towards lower wavenumbers and a broadening of the band from fwhm = 30 cm^{-1} to 44 cm^{-1}, which is likely to be a result of the superimposition of the isophthlamide carbonyl stretches of **1** with the amide signals of compound **2^+ Cl^-.**



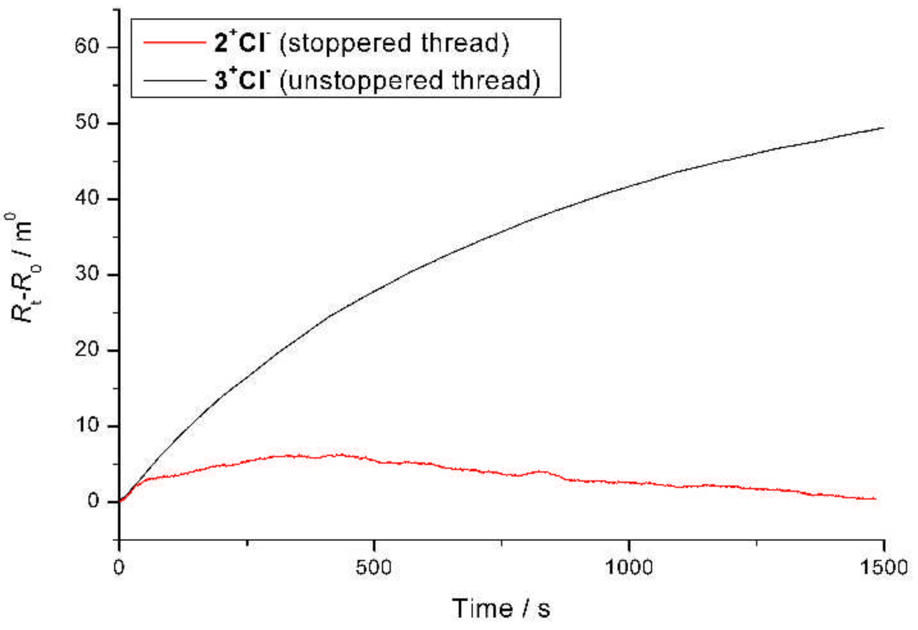
FTIR reflectance spectrum of a $1/2^+$ Cl^- monolayer on gold. Signals associated with the thread 2^+ Cl^- are highlighted in black; signals associated with the macrocycle are highlighted in red.



Comparison of the amide C=0 stretch signal observed by FTIR spectroscopy for monolayers of thread 2^+ and rotaxane $1/2^+$.Cl.

SPR.

An Autolab ESPRIT SPR spectrometer with 50 nm gold on quartz SPR chips (Autolab) were used for all experiments. In addition to the solution phase ^{1}H NMR studies, evidence that macrocycle **1** forms a rotaxane with a pyridinium-nicotinamide chloride containing thread comes from SPR spectroscopy. Addition of a 0.8 mM solution of **1** in acetonitrile to a gold SPR chip modified with a monolayer of **3$^+$ Cl$^-$** (an unstoppered analogue of thread **3$^+$ Cl$^-$**) led to a significant SPR response indicative of binding of the macrocycle at the surface (*i.e.* pseudorotaxane formation). No SPR response was observed for addition of macrocycle **1** to SPR chips modified with dodecanethiol monolayers or **2$^+$ Cl$^-$** monolayers, which indicates that there is no non-specific binding of **1** at the surface, and that the penta-phenyl-ferrocene group of **2$^+$ Cl$^-$** does effectively act as a stopper, preventing the annulus of macrocycle **1** from passing over it.



Comparative SPR responses of 2^+Cl^- (stoppered thread) and 3^+Cl^- (unstoppered thread) modified SPR substrates to addition of macrocycle 1. The reponse of the 3^+Cl^- modified surface is indicative of pseudorotaxane formation.

ELLIPSOMETRY

Ellipsometry studies of the **$1/2^+$ Cl^-** rotaxane monolayer indicated that the thickness of the monolayer was 1.02 ± 0.30 nm, a figure broadly consistent with CACHE modelling.