CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

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Introducing negative charges into bis-*p*-phenylene crown ethers: a study of bipyridinium-based [2]pseudorotaxanes and [2]rotaxanes

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1. The formation of outer sphere [2]pseudorotaxane salt

The interaction of the viologen moiety of the dumbbell-shaped "axle" **20** with the negatively charged crown ether **3** was studied. In this system the crown ether is "locked out" since the bulky stoppers prevent threading. The dumbbell-shaped **20** and the carboxylate **3** were dissolved in a mixture of deuterated acetonitrile and methanol 80/20 v/v and the proton NMR spectra were recorded (Figure S1). In neat acetonitrile this system can not be studied due to immediate decomposition caused, possibly, by high basicity of the carboxylate **3** in acetonitrile.[1]

Clearly, the interaction leads to a significant up-field shift of the aromatic protons (6.9 and 6.7 ppm) of the crown ether **3**. However, this relatively minor shift, 0.05-0.15 ppm, is smaller than the shifts typically observed (Figure 4, main text) for the related [2]pseudorotaxane salt **15** (0.5-0.6 ppm).

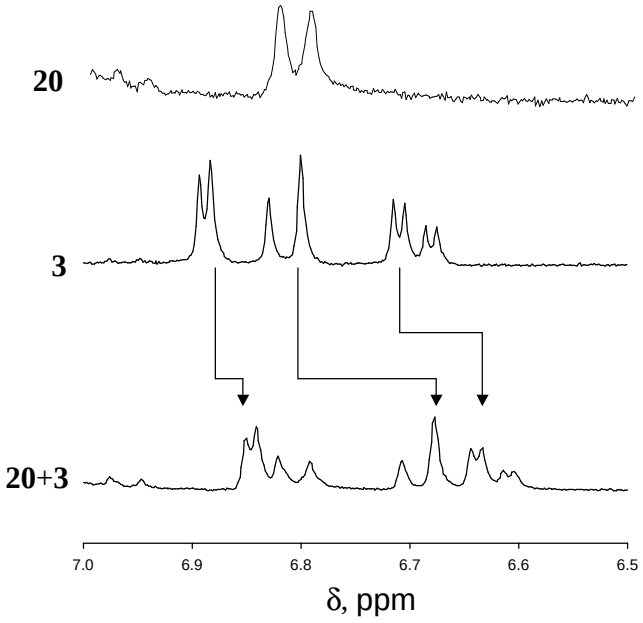
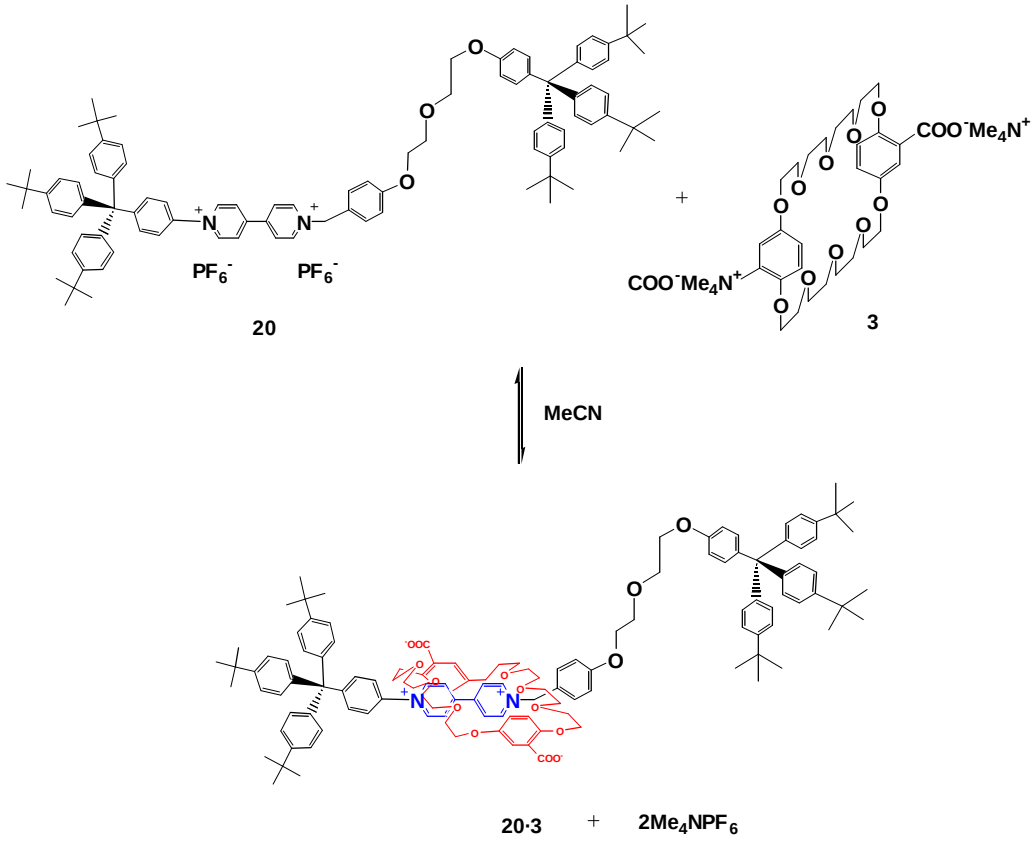


Figure S1. Partial H NMR spectra of the dumbbell-shaped viologen **20**, the crown ether **3** and their mixture in acetonitrile/methanol 80/20.

It is concluded, therefore, that the interaction of the carboxylate crown ether **3** with the viologen moiety of **20** involves an "outer sphere" wrapping of the crown ether around the viologen moiety as shown in Scheme S1. This mechanism would suggest a diamagnetic shielding due to the proximity of the aromatic systems. A further investigation of this mechanism is impeded by the rapid decomposition of the adduct **20**·**3** *via* reduction of the viologen moiety and cleavage of the stopper group.



Scheme S1. Proposed interaction of the dumbbell-shaped viologen **20** with the anionic crown ether **3**

2. Determination of equilibrium constants

Association constants K_a were measured using previously described dilution method monitored by UV-visible spectroscopy at 25 °C in water and aqueous mixtures.[2] Typically, 10.0±0.2 micromoles of the 1:1 mixture of a viologen (**5-8**) and crown ether (**1-4**) were dissolved in an aliquot (3.00±0.03 mL) of solvent so that the concentration relative error was less that 3%. The solution was subsequently diluted accurately with the solvent (aliquots 1.00±0.01 mL) and the UV absorption spectra were recorded at 25±0.1 °C The absorption maxima were measured in the range 0.1-1 with a relative error not exceeding 1%. The values of c/A (c – nominal concentration of [2]pseudorotaxane salt, A – absorbance) were plotted against $(A)^{-1/2}$. The linear regression parameters, the slope **b** and intercept **a**, and their standard errors were routinely calculated. Association constants, K_a = a/b^2, free energies, $?G^o = -RT\ln K$ values and the respective error bars (confidence level 95%) are given in Table S1.

The above dilution method produces reasonably reliable results in the range 10^2-$5\cdot10^5$ $dm^3\cdot mol^{-1}$. As seen from Table S1, the association constants of the [2]rotaxane salts rapidly increase with the addition of an organic solvent to water. Consequently, they could not be reliably measured in neat organic solvent. In order to estimate K_a in neat organic solvents, the constants were measured in aqueous solvent mixtures and the log plot of the equilibrium constant against the molar composition of the solvent was extrapolated to the neat solvent as shown below. The solvent mixtures were prepared by weighing so that the relative error of the solvent molar composition was below 0.2 %. The linear regression parameters, the slope and intercept, and their standard errors were routinely calculated. The extrapolated association constants, K_a, and free energies, $?G^o$, values and the respective error bars (confidence level 95%) are given in Table S1.

For example, shown in Figure S2 is the semi-logarithmic plot of the association constant between the viologen bromide **5** and the carboxylate **3** as a function of the molar fraction of methanol in the solvent system. It can be reasonably anticipated that the linearity would stand and that in neat methanol $K_a = (7.8\pm3)\cdot10^5$ $dm^3\cdot mol^{-1}$. This extrapolation is based on an assumption that the ionising power, *Y*, of a solvent mixture is a linear function of the molar composition of this mixture. For instance, the data presented in Bentley and Llewellyn review[2b] on the ionising power *Y* of the aqueous solvent mixtures, support this assumption.

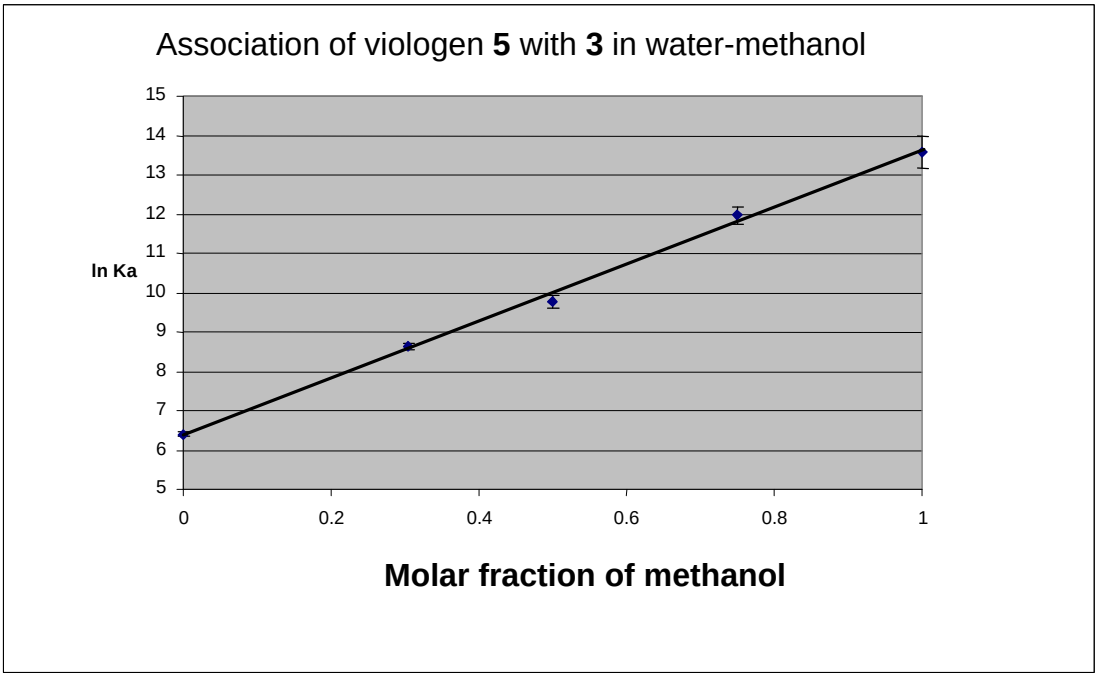


Figure S2. Association constant of the viologen **5** with the crown ether **3** as a function of solvent composition at 25 °C.

Table S1: Association constants of [2]pseudorotaxanes[a]

Viologen	Crown ether	Solvent system	Mol ratio	K_a ($dm^3 \cdot mol^{-1}$)	*?G* ($kJ \cdot mol^{-1}$)
5	**1**	MeOH	-	$(5.1\pm0.2)\cdot10^2$	-15.5±0.1
5	**1**	H_2O	-	insoluble	-
6	**1**	MeCN	-	$(1.2\pm0.1)\cdot10^2$	-11.8±0.4
5	**2**	MeOH	-	$(7.3\pm0.4)\cdot10^2$	-16.3±0.1
5	**3**	H_2O	-	$(6.0\pm0.3)\cdot10^2$	-15.9±0.1
5	**3**	H_2O/MeOH	70/30	$(5.6\pm0.2)\cdot10^3$	-21.4±0.1
5	**3**	H_2O/MeOH	50/50	$(1.7\pm0.3)\cdot10^4$	-24.2±0.4
5	**3**	H_2O/MeOH	25/75	$(1.6\pm0.4)\cdot10^5$	-29.7±0.6
5	**3**	MeOH[b]	-	$(7.8\pm3)\cdot10^5$	-33.6±2
5	**3**	H_2O/MeCN	50/50	$(3.7\pm0.7)\cdot10^4$	-26±0.5
5	**3**	H_2O/MeCN	25/75	$(4.7\pm1.2)\cdot10^5$	-32.3±0.7
5	**3**	MeCN	-	$(3.6\pm1.6)\cdot10^6$	-37.4±1.6

6	**3**	H_2O/MeCN	67/33	$(3.5\pm0.2)\cdot10^{3}$	-20.2±0.2
6	**3**	H_2O/MeCN	50/50	$(2.1\pm0.1)\cdot10^{4}$	-24.6±0.2
6	**3**	H_2O/MeCN	25/75	$(5.5\pm1.6)\cdot10^{5}$	-32.7±0.7
6	**3**	MeCN	-	$(1.2\pm0.5)\cdot10^{7}$[b]	-40.2±2
5	**4**	H_2O/MeOH	80/20	$(5.1\pm0.5)\cdot10^{4}$	-21.1±0.2
5	**4**	H_2O/MeOH	67/33	$(9.9\pm1.3)\cdot10^{4}$	-22.8±0.3
5	**4**	H_2O/MeOH	50/50	$(3.6\pm0.3)\cdot10^{4}$	-26.0±0.2
5	**4**	H_2O/MeOH	25/75	$(5.8\pm0.6)\cdot10^{5}$	-32.8±0.3
5	**4**	MeOH[b]	-	$(4\pm2)\cdot10^{6}$	-37.7±2
6	**4**	H_2O/MeOH	67/33	$(7.1\pm0.5)\cdot10^{3}$	-21.9±0.2
6	**4**	H_2O/MeOH	50/50	$(4.0\pm0.2)\cdot10^{4}$	-26.2±0.2
6	**4**	H_2O/MeOH	33/67	$(5.6\pm0.5)\cdot10^{5}$	-32.8±0.2
6	**4**	H_2O/MeOH	25/75	$(1.5\pm0.4)\cdot10^{6}$	-35.2±0.6
6	**4**	MeOH[b]	-	$(4\pm2)\cdot 10^{7}$	-43±2
7	**3**	H_2O	-	$(3.4\pm1.5)\cdot10^{2}$	-14.5±1
7	**3**	H_2O/MeOH	50/50	$(3.7\pm0.8)\cdot10^{3}$	-20.3±0.6
7	**3**	H_2O/MeOH	25/75	$(1.05\pm2)\cdot10^{4}$	-23.0±0.5
7	**3**	MeOH[b]	-	$(3.4\pm0.8)\cdot10^{4}$	-25.9±0.7
8	**3**	H_2O/MeCN	50/50	$(5.9\pm1)\cdot10^{2}$	-15.8±0.5
8	**3**	H_2O/MeCN	25/75	$(6.3\pm0.6)\cdot10^{3}$	-21.7±0.3
8	**3**	MeCN[b]	-	$(6.8\pm1)\cdot10^{4}$	-27.6±0.6

[a] Dilution method monitored by UV spectroscopy, 25 °C; [b] Extrapolated values.

3. Calculation of electrostatic association energy increment.

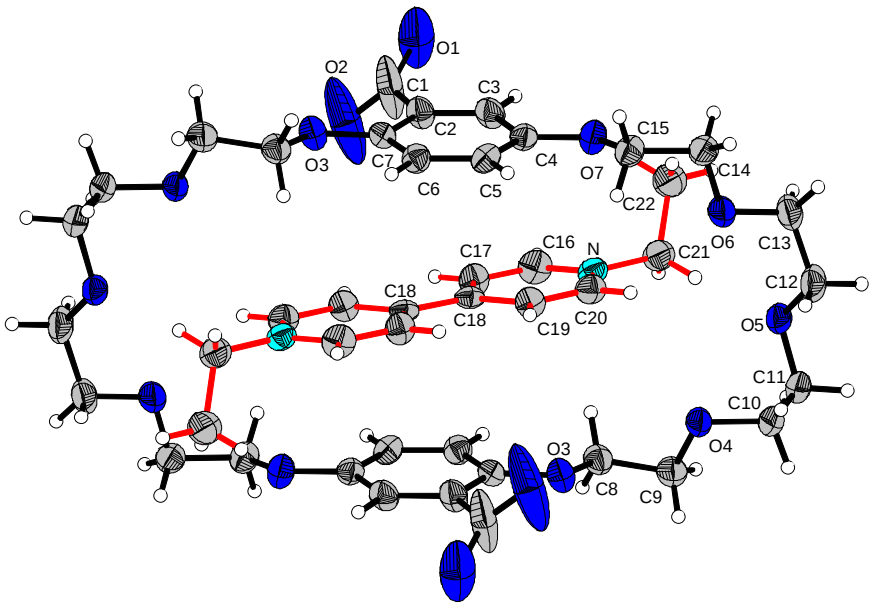


Figure S2. Crystal structure of the [2]pseudorotaxane salt **15**

Let us consider the dissociation of the [2]pseudorotaxane salt **15** into the crown ether anion and the viologen cation (c.f. Scheme 3). We start with the initial configuration identical to that in crystalline **15** and separate the viologen dication and the crown ether dianion to a distance greater than Bjerrum lengths in a solvent with dielectric constant ε. We will neglect the ionic strength in this case.

Table S2. Atom charges and inter atomic distances in [2]pseudorotaxane salt **15**

Atom, i	Charge	Atom, j	Charge	r_{ij} (Å)
N	+1	O1	-0.5	5.77
N	+1	O2	-0.5	5.71
N	+1	O1'	-0.5	7.22
N	+1	O2'	-0.5	5.47

It has been shown that the acetonitrile's dielectric properties may be treated as constant (ε = 36) for distances in excess of 5.5 Å.[3] Hence, the molar electrostatic association energy E can be calculated by multiplying the sum of point-charged atom-atom electrostatic energy contributions by the Avogadro number N_A.

$$E = N_A \sum_{i=1} \sum_{j=1} \frac{z_i z_j}{4\pi\varepsilon\varepsilon_o r_{ij}}$$

where z_i and z_j are the electrostatic point charges assigned to atoms *i* and *j*; *r* - the respective interatomic distances in crystalline **15**. Due to the symmetry of the structure **15** only one type of nitrogen atoms and two types of carboxylate oxygen atoms were taken into account.

In acetonitrile (ε = 36) the resulting value for the [2]pseudorotaxane salt **15** is *E* = -28.7 kJ·mol^{-1}. This is in good agreement with experimentally observed stabilisation of [2]rotaxane salt by about 28.4 kJ·mol^{-1} i.e. the difference in stability between [2]pseudorotaxane **6·1** and [2]pseudorotaxane salt **15** incorporating identical viologen moieties.

In water (ε = 79) calculated electrostatic stabilisation energy *E* = -13.0 kJ·mol^{-1}. This value cannot be compared directly to the experimental results since the [2]pseudorotaxanes of **1** are not formed in neat water. The calculated value exceeds the energy predicted on the basis of generally observed 5 kJ·mol^{-1} increments per 1:1 ion pairs due, possibly, to cooperative interactions.[4,5]

4. Influence of the ionic strength on the equilibrium association constant.

It can be expected, on the basis of the Debye-Huckel correlations, that the apparent K_a of the [2]rotaxane salt **15** is higher at lower ionic strength. Accordingly, the influence of the ionic strength on the apparent K_a was studied. It was suggested that in the case of hexafluorophosphate **6** a lower ionic strength is created by co-formed tetramethylammonium hexafluorophosphate (Scheme 3) than by tetramethylammonium bromide the in case of **5**.

In order to study the effect of the ionic strength, the association constant between viologen and macrocyclic anion was measured in the presence of an added salt. Because the association of [2]rotaxane salts (Scheme 3) is an ion pair formation process the equilibrium is expected to be influenced by the ionic strength of the media.[4,5] Therefore, the observed equilibrium constant K_a should obey a Debye Huckel correlation. At a low ionic strength μ we assume:

$$K_a^{obs} = \frac{[VC]}{[V]*[C]} = \frac{a_{VC}}{a_V a_C} g^2 = K_a g^2 < K_a$$

$$\log g = -Az^2\sqrt{m}$$

$$\log K_a^{obs} / K_a = -2Az^2\sqrt{m}$$

where A is the solvent parameter (0.5 in water, 1.64 in acetonitrile; 1.00 in methanol:water 1:1 at 25 ºC).[8,9]

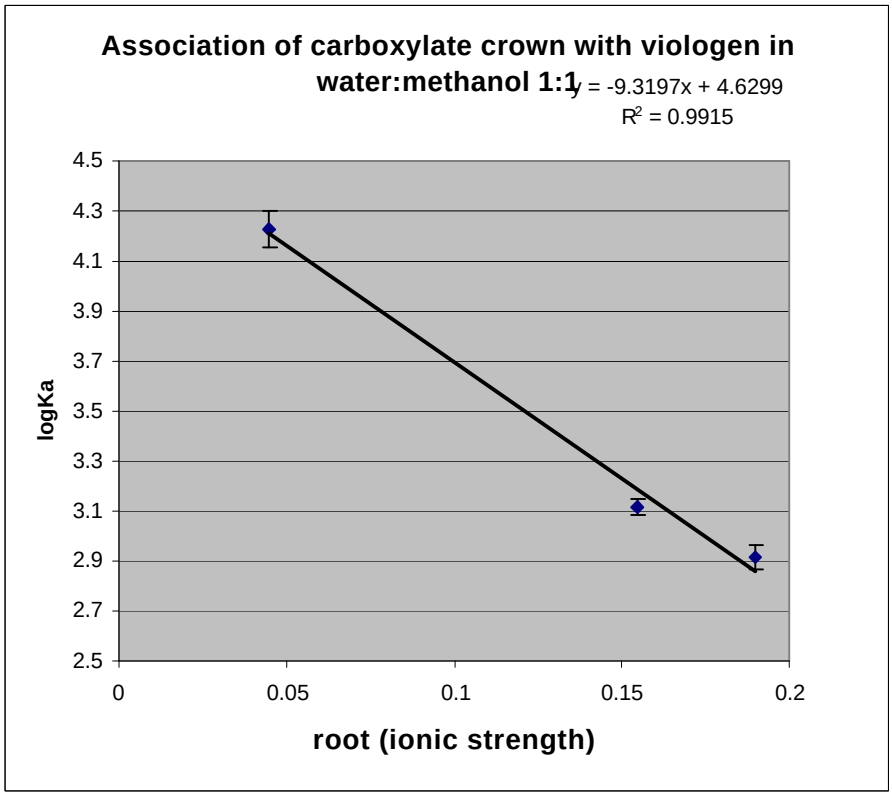
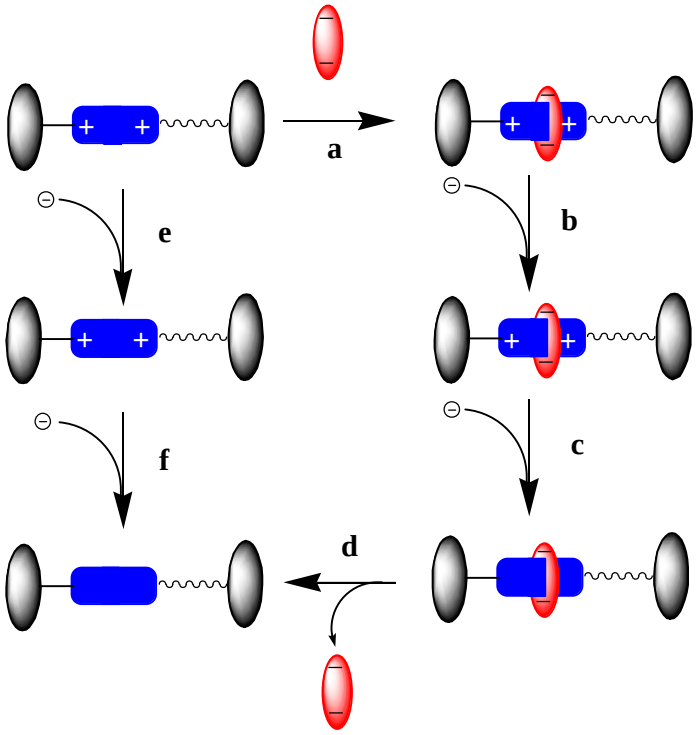


Figure S4. Association constant of **5** with **3** in water:methanol as a function of total ionic strength.

The association constant between the viologen dibromide **5** and the tetramethylammonium crown ether salt **3** was studied in methanol-water 1:1 v:v. This association was studied in the absence of an added electrolyte and following the addition of tetramethylammonium perchlorate to maintain a constant ionic strength. The Debye-Huckel correlation of observed association constant ($\log K_a$) vs. ionic strength $(\mu)^{1/2}$ is shown in Figure S4. As expected, K_a rapidly decreases with the addition of the electrolyte. The slope, –9.3, is in reasonably good agreement with the expected value for a 2:2 electrolyte in water:methanol ($-2Az^2 = -8$).

5. Thermodynamic consideration of the electrochemical shifts and association free energy of [2]rotaxane salt.

In order to estimate the values of the negative electrochemical shift in [2]rotaxane salt **22** quantitatively we consider imaginary electrochemical thermodynamic cycle shown in Scheme S2. The following discussion is not intended to claim numerical accuracy but simply outline a possible first round interpretation.



Scheme S2 Theoretical electrochemical cycle of the [2]rotaxane salt 22.

Apparently

$?G_a - ?G_e - ?G_f + ?G_d + ?G_c + ?G_b = 0$

Therefore,

$?G_a + ?G_d = ?G_e + ?G_f - ?G_c - ?G_b = (?G_e - ?G_b) + (?G_f - ?G_c)$

The terms in parentheses are associated with the respective reduction stages and are characterised by electrochemical reduction potentials shifts $?E$ of the [2]rotaxane salt (steps **b**, **c**) compared to its axle component (steps **e**, **f**). Hence,

$?G_e - ?G_b = ?E_{e/b}*F$ and $?G_f - ?G_c = ?E_{c/f}*F$

Finally,

$(?E_{e/b} + ?E_{c/f})*F = ?G_a + ?G_d$

To find the total electrochemical shift $?E_{e/b} + ?E_{c/f}$ we assume:

1. that the free energy of [2]rotaxane salt formation $?G_a$ in solution (this is a kinetically forbidden process) is equal to that of a similar [2]pseudorotaxane salt, e.g. **15**, $?G_a$ = -40 kJ·mol^{-1} (Table 1).

2. that the interaction of a neutral viologen moiety with a negatively charged crown ether is negligible $?H_d \sim 0$. Indeed, this has been found by electrochemical study of the [2]pseudorotaxane salt **15**. The same argument has been used previously to estimate the interaction energy of fully reduced viologens with crown ethers in solution.[15]

3. that the entropy term of the dissociation of the reduced [2]rotaxane $?S_d$ is about +40 J·K^{-1}·mol^{-1} as expected for a reaction of this type.[5,7]

At 25 °C

$(?E_{e/b} + ?E_{c/f})*F = ?G_a + ?G_d = ?G_a - T?S_d$ = -52 kJ·mol^{-1}

and accordingly

$?E_{e/b} + ?E_{c/f}$ = - 0.54 V

The estimated value of the total electrochemical shift is close to the experimental data on the [2]pseudorotaxane salts **23** (-0.61 V) and **24** (-0.55 V). The relatively large negative electrochemical shift in the case of carboxylate [2]rotaxane salt **22** (total -0.89 V) is discussed in the main text.

6. General experimental procedures

Reagents and solvents were purchased from commercial sources and were used as received. All reactions were performed under an atmosphere of nitrogen. Chromatographic separations were performed using silica (40-63 micron) or alumina (40 micron) in the specified solvent system. Melting points were estimated using a Gallenkamp melting point device and were not corrected. NMR spectra were recorded using a Varian Inova 300 spectrometer at 25.0 °C in the indicated solvent. Mass spectra were run on a Micromass LCT spectrometer. Absorption spectra were recorded at 25.0 °C on a Perkin-Elmer Lambda-45 instrument equipped with a PTP-1 temperature control system.

All cyclic voltammograms were recorded under the following conditions. The working electrode was a platinum wire. The counter electrode was a platinum gauze. The reference electrode was a non-aqueous Ag/Ag^+ electrode with a fill solution consisting of 0.010 $mol \cdot dm^{-3}$ $AgNO_3$ in the electrolyte solution. The electrochemical measurements of the [2]pseudorotaxane salts and of the corresponding viologen moieties have been carried out in an electrolyte solution consisting of 0.010 $mol \cdot dm^{-3}$ tetraethylammonium hexafluorophosphate (Et_4NPF_6) in dry acetonitrile; the measurements of the [2]rotaxanes and [2]rotaxane salts and of their corresponding dumbbell component have been carried out in an electrolyte solution consisting of 0.010 $mol \cdot dm^{-3}$ tetrabutylammonium perchlorate (TBAP). The solutions were degassed by freezing-vacuum-thaw procedure and filled up with nitrogen. All cyclic voltammograms (CV) were recorded on a Solartron SI 1287 potentiostat controlled by a LabView program running on a Machintosh Power PC at a scan rate of 0.100 $V \cdot s^{-1}$ and at the concentration of $2.0 \cdot 10^{-3}$ $mol \cdot dm^{-3}$.

Crystal structure determinations

Crystal data were collected at room temperature using a Bruker SMART APEX CCD area detector diffractometer. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[10a] The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[10b,c] Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. The protons of the solvent water molecules could not be detected. Anisotropic temperature factors were used for all non-hydrogen atoms.

CCDC 633834 - 633836 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. Synthesis and characterisation of materials.

Compound 1, bis-p-phenylene-34-crown-10: This compound was prepared according to the procedure reported.[11]

Compound 9, ethyl 2,5-dihyroxybenzoate: 2,5-Dihydroxybenzoic acid (3.08 g, 20 mmol) was suspended in ethanol (50 cm^3) and sulphuric acid (0.1 cm^3) was added. The mixture was heated under reflux for 6 days after which it was treated with sodium hydrogen carbonate and concentrated under reduced pressure. The residue was extracted with ethyl acetate, the solution was dried with $MgSO_4$ and concentrated under reduced pressure to give 3.4 g of ester (93%) as a white solid: m.p. 78 °C (lit.[12] m.p. 77.5-78); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.40 (s, 1 H), 7.30 (d, *J* = 3 Hz, 1 H), 7.00 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 6.88 (d, *J* = 9 Hz, 1 H), 4.68 (s, 1 H), 4.40 (q, *J* = 7 Hz, 2 H), 1.41 (t, *J* = 7 Hz, 3 H); elemental analysis calcd (%) for $C_9H_{10}O_4$ (182.17): C, 59.34; H, 5.53; found C, 59.19; H, 5.43.

Compound 10, ethyl 5-[2-{2'-{2''-{2'''-bromoethoxy}-ethoxy}-ethoxy}-ethoxy]-2-hydroxybenzoate: Ester **9** (364 mg, 2 mmol) was dissolved in acetonitrile (25 cm^3), dry potassium carbonate (0.42 g, 3 mmol) and 1-bromo-2-{2-[2-(2-bromo-ethoxy)-ethoxy]-ethoxy}-ethane (0.960 g, 3 mmol) were added and the mixture was heated at 60 ^{o}C for 3 days with vigorous stirring. The liquid phase was separated, concentrated under reduced pressure and the residue was separated by chromatography (silica, 20-35% ethyl acetate in cyclohexane) to give **10** (0.26 g, 31%) as a pale liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.40 (s, 1 H), 7.36 (d, *J* = 3 Hz, 1H), 7.10 (dd, *J* = 3 Hz, *J* = 9 Hz, 1H), 6.90 (d, *J* = 9 Hz, 1 H), 4.40 (q, *J* = 7 Hz, 2H), 4.10 (t, *J* = 4.5 Hz, 2 H), 3.8 (m, 12 H), 3.47 (t, *J* = 7 Hz, 2 H), 1.41 (t, *J* = 7 Hz, 3 H); elemental analysis calcd (%) for $C_{17}H_{25}BrO_7$ (421.28): C, 48.47; H, 5.98, Br, 18.97. found C, 48.22; H, 6.03; Br, 19.50.

Compound 2, ethyl bis-p-phenylene-34-crown-10-1^2,15^2-dicarboxylate: **10** (0.42 g, 1 mmol) was taken up in acetonitrile (30 cm^3) and dry potassium carbonate (420 mg, 3 mmol) was added. The mixture was heated with vigorous stirring at 80 ^{o}C for 3 days. The mixture was filtered and the liquid phase was concentrated under reduced pressure after which the residue was separated by column chromatography (alumina, 50% ethyl acetate in cyclohexane) to give **2** (180 mg, 53 %) as an off-white solid: m.p. 68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 3 Hz, 2 H), 6.93 (dd, *J* = 3 Hz, *J* = 9 Hz, 2 H), 6.80 (d, *J* = 9 Hz, 2 H), 4.31 (q, *J* = 7 Hz, 4 H), 4.0 (m, 8H), 3.8 (m, 8H), 3.7 (m, 16 H), 1.35 (t, *J* = 7 Hz, 6 H); MS (ES): m/z 698 [M+H_2O]; elemental analysis calcd (%) for $C_{34}H_{48}O_{14}$ (680.74): C, 59.99; H, 7.11; found C, 59.60; H, 7.00.

Compound 11, bis-p-phenylene-34-crown-10-1^2,15^2-dicarboxylic acid: Diester **2** (38 mg, 0.055 mmol) in ethanol (2 cm^3) was treated with aqueous 10% sodium hydroxide (0.2 cm^3) at 60 °C for 2 h. The mixture was concentrated under reduced pressure, diluted with water (2 cm^3) and carefully acidified with HCl to pH 1. The product was extracted with dichloromethane and concentrated to give acid **11** (35 mg, 100%) as a white solid: m.p. 126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 3 Hz, 2H), 7.01 (dd, *J* = 3 Hz, J = 9 Hz,2H), 6.80 (d, *J* = 9 Hz, 2H), 4.21 (m, 4H), 4.0 (m, 4 H), 3.9 (m, 4 H), 3.8 (m, 4 H), 3.7 (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.4, 153.7, 151.6, 122.2, 118.8, 116.8, 115.0, 71.0, 70.7, 70.6, 70.5, 70.0, 69.4, 68.8, 68.2; MS (ES): m/z 642 [M+H_2O]; elemental analysis calcd (%) for $C_{30}H_{40}O_{14}$ (624.63): C, 57.69; H, 6.45; Found C, 57.20; H, 6.53.

Compound 3, bis(tetramethylammonium) bis-p-phenylene-34-crown-10-1^2,15^2-dicarboxylate: Acid **11** (47 mg, 0.075 mmol) was taken up into methanol (2 cm^3) and tetramethylammonium hydroxide pentahydrate (27 mg, 0.15 mmol) was added. The mixture was stirred for 2 h, concentrated and dried to furnish the salt **3** as a white powder: ^{1}H NMR (300 MHz, CD_3OD) δ = 7.00 (d , *J* = 3 Hz, 2H), 6.91(d , *J* = 9 Hz, 2 H), 6.78 (dd, *J* = 3 Hz, *J* = 9 Hz, 2 H), 4.11 (m, 4H), 4.06 (m, 4 H), 3.8 (m, 8 H), 3.7 (m, 16 H), 3.14 (s, 24H); elemental analysis calcd (%) for $C_{38}H_{62}N_2O_{14}$ (770.90): C, 59.20; H, 8.11; N, 3.63; found C, 58.22; H, 8.01; N, 3.51.

Compound 12, bis-p-phenylene-34-crown-10-1^2,15^2-disulphonic acid (*anti*-**12**) and bis-p-phenylene-34-crown-10 -1^2,15^3-disulphonic acid (*syn*-**12**): Chlorosulphonic acid (1 cm^3) was added to the crown ether **1** (116 mg, 0.216

mmol) at 0 °C. The mixture was kept cold for 1 h after which it was poured on ice. The product was extracted with CH_2Cl_2 and concentrated to a give mixture of *syn*- and *anti*-**12** (118 mg, 78 %) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (d+d, *J* = 3 Hz, 2H), 7.1 (dd+dd, *J* = 3 Hz, *J* = 9 Hz, 2H), 7.03 (d+d, *J* = 9 Hz, 2H), 4.23 (m, 4H), 4.08 (m, 4 H), 3.93 (m, 4 H), 3.84 (m, 4 H), 3.7 (m, 16 H); MS (ES) m/z 697 [M+H]; elemental analysis calcd (%) for $C_{28}H_{40}O_{16}S_2$ (696.74): C, 48.27; H, 5.79; S, 9.20; found C, 48.10; H, 5.99; S, 9.16.

Compound 4, bis-tetrabutylammonium bis-p-phenylene-34-crown-10-1^2,15^2-disulfonate (*anti*-**4**) and bis-tetrabutylammonium bis-p-phenylene-34-crown-10-1^2,15^3-disulfonate (*syn*-**4**): Tetrabutylammonium hydroxide (0.29 cm^3 of 1.0 mol dm^{-3} solution) was added to the acid **12** (100 mg, 0.144 mmol). The mixture was stirred for 2 h and was evaporated to give the mixture of salts **4** (168 mg, 100 %) as a glassy solid: ^{1}H NMR (300 MHz, CD_3CN) δ = 7.4 (m, 2H), 6.9 (m, 2H), 6.80 (m, 2H), 4.1 (m, 4H), 4.0 (m, 4 H), 3.8 (m, 8 H), 3.6 (m, 16 H), 3.1 (t, *J* = 8 Hz, 16 H), 1.6 (m, 16 H), 1.35 (tq, *J* = 7.5 Hz, 16 H), 0.99 (t, *J* = 7 Hz, 24 H); elemental analysis calcd (%) for $C_{60}H_{110}N_2O_{16}S_2$ (1179.65): C, 61.09; H, 9.40; N, 2.37, S, 5.44; found C, 60.96; H, 9.24; N, 2.39; S, 5.32.

Compound 5, 1,1'-diethyl-4,4'-bipyridinium bromide: A bright yellow solid: m.p. 232 °C; ^{1}H NMR (300 MHz , D_2O) δ = 9.06 (d, *J* = 6 Hz, 4 H), 8.47 (d, *J* = 6 Hz, 4 H), 4.80 (m, 4H), 1.64 (t, *J* = 7 Hz, 6H); MS (ES): m/z 214 [M$^+$]; elemental analysis calcd (%) for $C_{14}H_{18}N_2Br_2$: C, 44.95; H, 4.85; N, 7.49; Br, 42.73; found: C, 45.12; H, 4.76; N, 7.21; Br, 42.50.[13]

Compound 6, 1,1'-diethyl-4,4'-bipyridinium bis-hexafluorophosphate: A white powder: m.p. 242-244 °C; ^{1}H NMR (300 MHz, CD_3CN) δ = 8.96 (d, *J* = 7 Hz, 4 H), 8.44 (s, 4H), 4.73 (q, *J* = 7 Hz, 4H), 1.71 (t, 4H); MS (ES): m/z 214 [M$^+$]; elemental analysis calcd (%) for $C_{14}H_{18}N_2P_2F_{12}$: C, 33.35; H, 3.60; N, 5.55; P, 12.29; F, 45.21; found: C, 34.09; H, 3.45; N, 5.36.

Compound 7, 3,3'-dimethyl-1,1'-diethyl-4,4'-bipyridinium dibromide, and **8,** 3,3'-dimethyl-1,1'-diethyl-4,4'-bipyridinium bis- hexafluorophosphate: 3,3'-Dimethyl-4,4'-bipyridine (40 mg, 0.22 mmol) and ethyl bromide (1.0 cm^3, 15 mmol) were heated at 50 °C in acetonitrile (2.5 cm^3) for 3 days. The precipitate dibromide **7** (60 mg, 66%) was collected and dried as an off-white solid: mp >260 °C (dec.); ^{1}H NMR (300 MHz, CD_3OD) δ = 9.24 (s, 2H), 9.10 (d, *J* = 7 Hz, 2 H), 8.12 (d, *J* = 7 Hz, 2 H), 4.80 (q, *J* = 7 Hz, 4 H), 2.41 (s, 6H), 1.78 (t, *J* = 7Hz, 6 H). The salt was dissolved in water (5 cm^3) and was treated with aqueous potassium hexafluorophosphate to precipitate the product **8** as a white solid: m.p. >200 °C (dec.); ^{1}H NMR (300 MHz, CD_3CN) δ = 8.80 (s, 2H), 8.72 (d, *J* = 7 Hz, 2 H), 7.82 (d, *J* = 7 Hz, 2 H), 4.64 (q, *J* = 7 Hz, 4 H), 2.28 (s, 6H), 1.68 (t, *J* = 7Hz, 6 H); MS (ES) m/z 242 [M$^+$]; elemental analysis calcd (%) for $C_{16}H_{22}F_{12}N_2P_2$ (532.4): C, 36.10; H, 4.17; N, 5.26; found C, 36.40; H, 4.12; N, 5.42.

Compound 14, tetramethylammonium 2,5-dimethoxybenzoate: 2,5-Dimethoxybenzoic acid (**13**) was added to the solution of tetramethylammonium hydroxide pentahydrate in methanol. The mixture was sonicated for 30 minutes and the resulting solution was concentrated and dried to yield the product **14** as a glassy solid: ^{1}H NMR (300 MHz, CD_3OD) δ = 6.98 (d, *J* = 3 Hz, 1H), 6.91(dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 6.85 (d, *J* = 3 Hz, 1 H), 3.81 (s, 3H), 3.75 (s, 3H), 3.18 (s, 12 H); MS (ES) m/z (%) 256.2 (70) [M$^+$+H]; elemental analysis calcd (%) for $C_{13}H_{21}NO_4$ (255.3): C, 61.16; H, 8.29; N, 5.49. found C, 60.72; H, 8.12; N, 5.32.

Compound 15, 1,1'-diethyl-[4,4']-bipyridinium bis-p-phenylene-34-crown-10-1^2,15^2-dicarboxylate dodecahydrate: Viologen **6** (6 mg, 0.012 mmol) was dissolved in methanol (1 cm^3) and a solution of the macrocycle **3** (8 mg, 0.012 mmol) in methanol-water (1 cm^3) was added. The precipitate of tetramethylammoniun hexafluorophosphate was filtered off and the mother liquor was left to evaporate furnishing deep-red crystals of **15***12H_2O (8 mg, 80%): elemental analysis calcd (%) for $C_{44}H_{80}N_2O_{26}$: C, 50.18; H, 7.66; N, 2.66; found C, 50.52; H, 6,74; N, 2.70; the compound **15** was characterised by X-ray crystallography.

Compound 16, 1,1'-diethyl-[4,4']-bipyridinium bis-p-phenylene-34-crown-10-1^2,15^2-disulphonate dihydrate sesquiethanolate: Viologen **6** (6 mg, 0.012 mmol) was dissolved in ethanol (1cm^3) and a solution of **4** (10 mg

mixture of isomers *syn* and *anti*, 0.006 mmol of each) in methanol (1 cm^3) was added. The precipitate of tetrabutylammoniun hexafluorophosphate was filtered off and the mother liquor was left to evaporate furnishing orange crystals of *anti*-**16** (3 mg, 50%) $[C_{14}H_{18}N_2]^{2+}[C_{28}H_{38}O_{16}S_2]^{2-}$ *$2H_2O$*$1.5C_2H_6O$ as demonstrated by X-ray crystallography data; ^{1}H NMR (400 MHz, CD_3OD, ethanol omitted) δ = 9.05 (d, *J* = 6.8 Hz, 4H), 8.10 (d, *J* = 6.8 Hz, 4H), 6.83 (d, *J* = 2.8 Hz, 2 H), 6.36 (dd, *J* = 2.8 Hz, J = 9.2 Hz, 2H), 6.28 (d, 3.81 (s, *J* = 9.2 Hz,2H), 4.85 (q, *J* = 7.2 Hz, 4H), 3.75 (m, 24H), 3.68 (m, 8H), 1.78 (t, J = 7.2 Hz, 6H); no satisfactory microanalysis was obtained due to the loss of various amounts of ethanol and water.

Compounds 18•PF_6, 1-{4-[tris(4-t-butylphenyl)-methyl]-phenyl}-4,4'-bipyridinium hexafluorophosphate, **19,** 4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)- ethoxy)-benzylbromide, **20,** 1-{4-[tris(4-t-butylphenyl)-methyl]-phenyl}-(4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)- ethoxy)-benzyl)-[4,4']-bipyridinium) bis-hexafluorophosfate: These were prepared as described elsewhere.[14]

Compound 21, 1-{4-[tris(4-t-butylphenyl)methyl]phenyl}-1'-(4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)-ethoxy)-benzyl)-[4,4']-bipyridinium) bis-p-phenylene-34-crown-10-1^2,15^2–dicarboxylic acid bis(hexafluorophosfate): Monocation **18** (10 mg, 0.012 mmol), bromide **19** (12 mg, 0.015 mmol), acid **11** (10 mg, 0.015 mmol), chlorobenzene (0.12 cm^3) and benzonitrile (0.05 cm^3) were mixed at room temperature. After 10 days the residue was purified by column chromatography (ethyl acetate then acetone/MeOH/$MeNO_2$/aqueous KPF_6 75/17/5/3 v/v) to give the axle **20** (10 mg, 40%) and the rotaxane **21** (13.5 mg, 50%) as an orange glassy solid: ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ = 9.50 (d, *J* = 7 Hz, 2 H), 9.21 (d , *J* = 7 Hz, 2 H), 8.51 (d , *J* = 7 Hz,2 H), 8.40 (d, *J* = 7 Hz, 2 H), 8.03 (d, *J* = 8 Hz, 2 H), 7.80 (d, *J* = 8 Hz, 2 H), 7.74 (d, *J* = 8 Hz, 2 H), 7.41 (d, *J* = 9 Hz, 6 H), 7.31 (m, 12 H), 7.20 (d, *J* = 8 Hz, 2 H), 7.10 (d, *J* = 8 Hz, 6 H), 7.08 (d, *J* = 9 Hz, 2 H), 6.83 (d, *J* = 9 Hz, 2 H), 6.77 (d, *J* = 3 Hz, 2 H), 6.70, (d, *J* = 9 Hz, 2 H), 6.40 (dd, *J* = 3 Hz, *J* = 9 Hz, 2 H), 6.12 (d, *J* = 14 Hz, 2 H), 5.96 (d, *J* = 14 Hz, 2 H), 4.22 (m, 4H), 4.11 (m, 4H), 3.9-3.5 (m, 36H), 1.33 (s, 27), 1.3 (s, 27H); MS (ES): m/z (%): 1948.7 (5), 1949.7 (6), 1950.7 (5) [M-2HPF_6], 145 (100) [PF_6^-]; elemental analysis calcd (%) for $C_{125}H_{148}F_{12}N_2O_{17}P_2$ (2240.44): C, 67.01; H, 6.66; N, 1.25; found C, 66.40; H, 6.56; N, 1.42.

Compound 22, 1-{4-[tris(4-t-butylphenyl)-methyl]-phenyl}-1'-(4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)-ethoxy)-benzyl)-[4,4']-bipyridinium) bis-p-phenylene-34-crown-10-1^2,15^2-dicarboxylate: Acid **21** (13.5 mg, 6 mcmol) was dissolved in dichloromethane (2 cm^3) and was treated with aqueous sodium bicarbonate solution. The organic layer was concentrated under reduced pressure and purified by column chromatography (ethyl acetate then acetone/methanol/nitomethane 50/40/10 v/v) to give the rotaxane **22** (83%) as a red glassy solid: ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ = 8.25 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8 Hz, 2H), 7.3 (d, *J* = 9 Hz, 6 H), 7.16 (m, 18 H), 6.8 (d, *J* = 9 Hz, 2H), 6.2-5.8 (6 H), 4.2 (m, 4H), 4.15 (m, 4H), 3.9-3.6 (m, 36H), 1 .3 (s, 27), 1.2 (s, 27H); MS (ES): m/z (%): 1948.5 (2), 1949.5 (3), 1950.5 (2) [M^+], 145 [PF_6^-] not found; elemental analysis calcd (%) for $C_{125}H_{146}N_2O_{17}$ (1948.5): C, 77.05; H, 7.55; N, 1.44; found: C, 76.11; H, 7.66; N, 1.20.

Compounds 23 and 24, 1-{4-[tris(4-t-butylphenyl)methyl]phenyl}-1'-(4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)-ethoxy)-benzyl)-[4,4']-bipyridinium) bis-p-phenylene-34-crown-10-1^2,15^2-disulphonate), and **24**, 1-{4-[tris(4-t-butylphenyl)methyl]phenyl}-(4-(2-(2-(4-[tris-{4-t-butylphenyl}-methyl]-phenoxy)-ethoxy)-ethoxy)-benzyl)-[4,4']-bipyridinium) bis-p-phenylene-34-crown-10-1^2,15^3-disulphonate): Monocation **18** (24 mg, 0.030 mmol), bromide **19** (25 mg, 0.032 mmol) and **4** (38 mg, 0.032 mmol) were dissolved in acetonitrile (0.15 cm^3) and were left at room temperature for 6 days. The residue was purified by column chromatography (ethyl acetate, acetone, acetone/methanol 50/50 v/v) to give the *anti*-[2]rotaxane salt **23** (30 mg, 50%) as a red glassy solid: ^{1}H NMR (300 MHz, $(CD_3)_2CO$): d = 9.27 (d, *J* = 7 Hz, 2 H), 9.25 (d, *J* = 7 Hz, 2 H), 8.34 (d+d, *J* = 7 Hz, 4 H), 8.14 (d, *J* = 9 Hz, 2H), 7.83 (d, *J* = 9 Hz, 2H), 7.66 (d, *J* = 9 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 6 H), 7.29 (d, *J* = 9 Hz, 6 H), 7.27 (d, *J* = 8.5 Hz, 6 H), 7.1 (m, 10H), 6.81 (d, *J* = 9 Hz, 2 H), 6.71 (d, *J* = 3 Hz, 2 H), 6.30 (d, *J* = 9 Hz, 2 H), 6.23 (dd, *J* = 3 Hz, *J* = 9 Hz, 2H), 6.06 (d, *J* = 14 Hz, 2 H), 6.00 (d, *J* = 14 Hz, 2 H),

4.20 (m, 2H), 4.10 (m, 2H), 3.88 (m, 4H), 3.6-3.7 (m, 32 H), 1.30 (s, 27 H), 1.27 (s, 27 H); MS (ES): m/z (%): 2043.9 (21) [M+Na^+]; elemental analysis calcd (%) for $C_{123}H_{146}N_2O_{19}S_2$: C, 73.11; H, 7.28; N, 1.39; S, 3.17; found: C, 72.91; H, 7.28; N, 1.30; S, 3.32; *syn*-[2]rotaxane salt **24** (30 mg, 50%) as a red glassy solid: ^{1}H NMR (300 MHz, $(CD_3)_2CO$): d = 9.24 (d, *J* = 7 Hz, 2 H), 9.01 (d, *J* = 7 Hz, 2 H), 8.49 (d, *J* =7 Hz, 2 H), 8.24 (d, *J* =7 Hz, 2 H), 8.08 (d, *J* = 9 Hz, 2H), 7.76 (d, *J* = 9 Hz, 2H), 7.68 (d, *J* = 9 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 6H), 7.26 (d, *J* = 9 Hz, 12H), 7.27 (d, *J* = 8.5 Hz, 6H), 7.1 (m, 10H), 6.80 (d, *J* = 9 Hz, 2H), 6.53 (d, *J* = 3 Hz, 2H), 6.40 (d, *J* = 9 Hz, 2H), 6.09 (dd, *J* = 3 Hz, *J* = 9 Hz, 2H), 6.00 (s, 2 H), 4.20 (m, 2H), 4.10 (m, 2H), 3.9 (m, 4H), 3.6-3.7 (m, 32H), 1.29 (s, 27H), 1.26 (s, 27H); MS (ES): m/z (%): 2043.9 [M+Na^+]; elemental analysis calcd (%) for $C_{123}H_{146}N_2O_{19}S_2$: C, 73.11; H, 7.28; N, 1.39; S, 3.17; found C, 72.88; H, 6.98; N, 1.20; S, 3.55.

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