

Introducing Negative Charges into Bis-*p*-phenylene Crown Ethers: A Study of Bipyridinium-Based [2]Pseudorotaxanes and [2]Rotaxanes

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Abstract: This paper describes novel host–guest systems comprising viologen cations (guests) and the derivatives of bis-*para*-phenylene-34-crown-10 (hosts) with anionic groups COO[−] or SO₃[−]. The structure of the resulting charge-compensated host–guest complexes, their association constants and their electrochemical behaviour have been studied. In the solid state, the viologen cations thread the negatively charged crown ethers forming electroneutral zwitterion-like [2]pseudorotaxane salts; in solution this threaded geometry is preserved. The association constants of [2]pseudorotaxane salts incorporating the 1,1'-diethylviologen moiety in solu-

tion are significantly higher than those of previously reported analogues. The extrapolated association free energies in non-aqueous media exceed $-40 \text{ kJ} \cdot \text{mol}^{-1}$ at 25 °C. This significant increase of the interaction free energy makes these compounds stable even in aqueous solutions. The association constants of [2]pseudorotaxane salts incorporating sterically more hindered 1,1'-diethyl-3,3'-dimethylviologen moieties

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are significantly lower. Structurally related [2]rotaxane salts, in which the oppositely charged ionic components are mechanically interlocked, have been prepared in good yields. It has been shown that [2]rotaxane salts incorporating *anti*-isomers of bisfunctionalised crown ethers are cycloenantiomeric. In both [2]pseudorotaxane and [2]rotaxane salts, the electrostatic interactions between the viologen moieties and the negatively charged crown ethers lead to very significant negative shifts of viologen reduction potentials up to 450 mV. The findings of the present study are valuable for the design of nanoscale molecular electronic devices.

Introduction

Molecular electronics and artificial molecular machinery are undergoing a breakthrough in recent years.^[1] The progress in these fields relies on the ability of the molecular components to perform their function consistently. Supramolecular chemistry, surface chemistry and nanoparticle chemistry offer a range of applications in material science, biomedical monitoring and analysis.^[2] Therefore, intelligent and robust components are required for nanoscale molecular and supramolecular architectures to function as intended in solution or at the surface.

Particularly interesting are electronically addressable and switchable molecules and interlocked molecular systems,

such as [2]rotaxanes. Recently, for example, electron transfer processes at the surface have been studied in systems incorporating orientation-specific tripodal linkers connecting electroactive moieties.^[3] The topology of [2]rotaxanes allows, in principle, the macrocyclic component of a [2]rotaxane to undergo a reversible internal translational motion (RITM), thus working as a molecular shuttle or switch.^[4] Despite the rapid growth in this area and various approaches to study RITM in switchable [2]rotaxanes, little was known until recently about their detailed conformation and methods to elucidate and control their conformations.^[5] While in many cases the RITM can be achieved by applying an appropriate stimulus, it is noted that the most remarkable results were obtained both in solution and on surfaces when strong electrostatic interactions were used to control the RITM of macrocyclic components of the interlocked molecules.^[1,6]

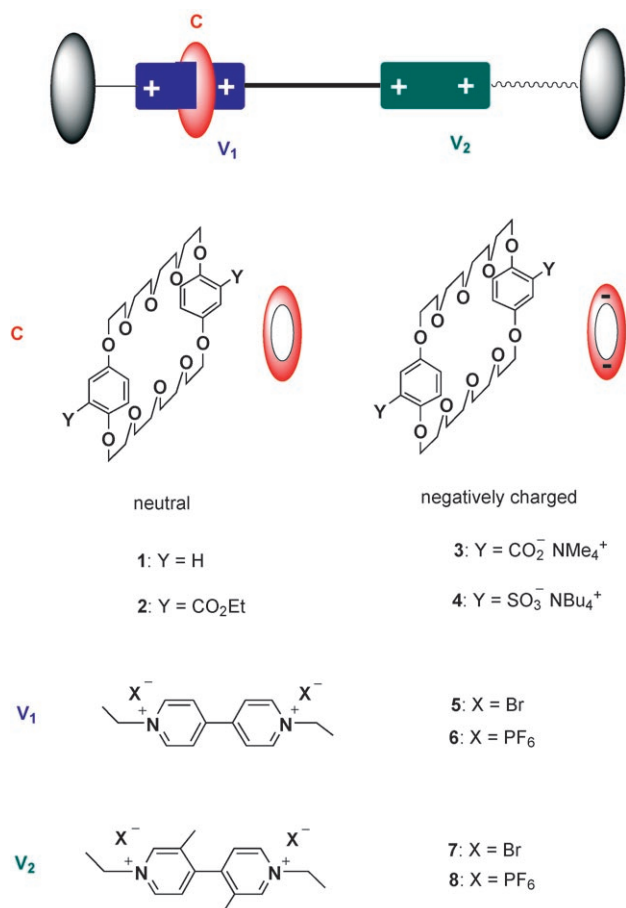
It has recently been demonstrated that electrostatic *repulsion* forces can be modulated to control the shuttling and/or circumrotation movements in interlocked molecular systems.^[6a,b] However, electrostatic attraction forces have not been used in this capacity. It is surprising as the electrostatic at-

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traction is the most common intercomponent interaction found in salts, ion pairs and supramolecular and biomolecular systems.^[6c-k] It was shown recently that electrostatic attraction can direct ionic self-assembly.^[6l]

A switchable [2]rotaxane is represented in Scheme 1. This interlocked molecular system comprises the crown ether **C** threaded by the dumbbell-shaped component (“axle”), in-



Scheme 1. Bistable [2]rotaxane (top) incorporating a crown ether (e.g. **1–4**) and two viologen stations (e.g. **5–8**).

corporating two positively charged and, therefore, electrochemically active viologen sites V₁ and V₂. Assuming that V₁ represents the “strong” viologen recognition site, an electrically neutral crown ether, such as **1** or **2**, which is initially localised at V₁, can be switched to the “weak” site V₂ by means of electrochemical or photochemical reduction of V₁.^[3b,4b,c,5] Let us consider how a negative charge on the crown ether may influence its RITM in [2]rotaxane. In this case, a strong electrostatic attraction additionally stabilises both translational isomers (co-conformations) of the [2]rotaxane when the crown ether, for example, **3**, is localised at viologen site V₁ or V₂. The electrostatics will create deeper energy wells for **3** at both viologen sites in this interlocked system. It is important to find out whether the electrochemically controlled switching is still feasible in this case. This

will be determined by the chemical structure, stability and electrochemical behaviour of [2]rotaxanes and [2]pseudorotaxanes incorporating model viologens **5–8** and charged crown ethers **3** and **4**.

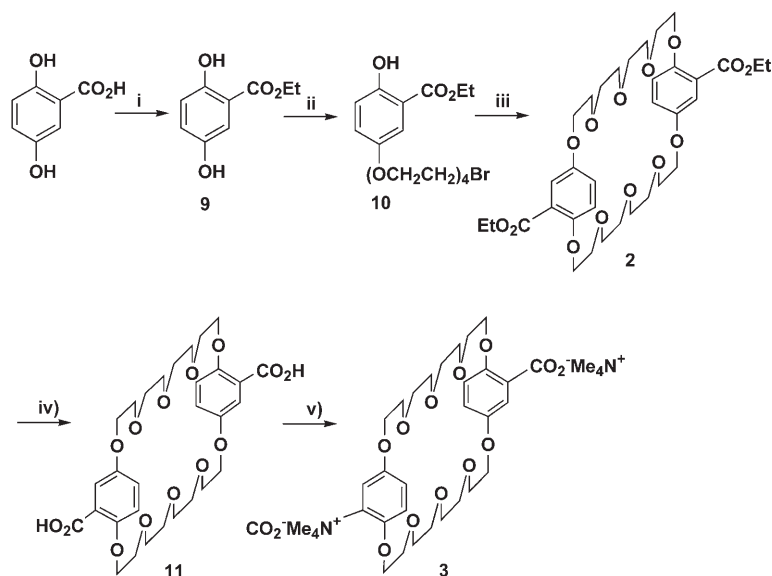
In the present paper, we report the discovery of a novel type of [2]pseudorotaxanes and related [2]rotaxanes in which the molecular components are oppositely electrically charged. Consequently, the mutual molecular recognition is significantly enhanced by the resulting intercomponent electrostatic attraction forces. In these compounds, termed here [2]pseudorotaxane and [2]rotaxane salts, respectively, the positive and negative charges are internally compensated. The findings reported allow us to predict that electrostatic attraction interactions of components will help control shuttling-type RITM in interlocked molecular systems. Further work on the preparation and application of interlocked systems of even greater complexity is under way.

Results and Discussion

Preparation of anionic crown ethers: The prototype *bis-p*-phenylene-34-crown ether **1**, its carbalkoxy derivatives as well as derivatives of other crown ethers have been previously prepared and their association with cations has been studied.^[7] It has been found that association with viologens increases with the addition of the ester groups to the backbone of **1**.^[7b] However, no attempts have been made to prepare anionic bis-*p*-phenylene crown ethers and to test their complexation with viologens. It is worth noting that strong binding of metal cations to anionic aliphatic crown ethers^[7c,d] as well as strong binding of lysine to an anionic cylinder-shaped artificial molecular receptor have been described.^[7f] It was demonstrated that the addition of carboxylates to the crown-ether backbone gives a mean log*K* increment 2.6 for divalent cations.^[7d]

In the present work, we studied novel anionic crown ethers **3** and **4** and compared them to the neutral crown ethers **1** and **2** (Scheme 1). It was expected that the negatively charged **3** and **4** would interact strongly with the positively charged viologens **5–8** and the resulting electroneutral [2]pseudorotaxane salts would include one doubly negatively charged macrocycle and one doubly positively charged viologen moiety. It should be noted, that the model viologens **5** and **6** incorporate a more electron deficient and less sterically hindered viologen moiety, V₁, than the viologens **7** and **8** (V₂).^[3b,4b,c] As a consequence, the V₁ moiety possesses a higher affinity for crown ethers and can be reduced at less negative potentials than V₂.

The synthesis of the carboxylate crown ether **3** was carried out from an aromatic building block, **9**, and a glycol chain building block, via the ester **2** and acid **11** (Scheme 2). Firstly, **9** was alkylated at the more accessible 5-hydroxyl by using an excess of the dibromide at 60 °C. This was possible due to the intramolecular hydrogen bonding between the 2-hydroxyl group and the ethoxycarbonyl group in the ester **9**. The cyclisation of the resulting bromide **10** at a slightly



Scheme 2. Preparation of the macrocyclic carboxylate **3**. Reaction conditions (room temperature unless otherwise stated): i) ethanol, H_2SO_4 , reflux, 6 d, 93%; ii) $\text{Br}-(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{Br}$, K_2CO_3 , acetonitrile, 60°C , 3 d, 31%; iii) K_2CO_3 , acetonitrile, 80°C , 3 d, 53%; iv) a) NaOH , ethanol, 60°C , 2 h; b) HCl , 100%; v) tetramethylammonium hydroxide, methanol, 100%.

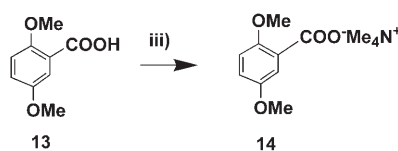
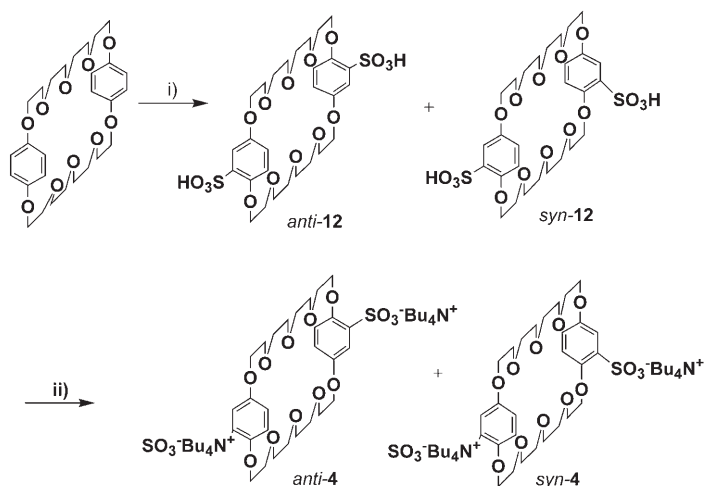
higher temperature, 80°C , furnished the crown ester **2** in good yield. The ester groups of **2** were saponified and the acid **11** was isolated as a colourless monoclinic crystalline material. The tetramethylammonium salt **3** was prepared and used in the present study as it has the advantage of being soluble in water, methanol, acetonitrile and other solvents.

The molecular structure of the acid **11** was confirmed by X-ray diffractometry (Figure 1). Clearly, the two carboxylic groups of **11** are attached to the bis-*p*-phenylene-34-crown-10 backbone in the *anti*-position and point in opposite directions. The distances between the oxygen atoms of the two different carboxylate groups (7.2–8.0 Å) are similar to the typical distances between positively charged nitrogen atoms in viologen guests (7.0 Å), providing a good geometric fit.^[5d,e]

The synthesis of the crown ether **4** was carried out by the direct sulphonation of the crown ether **1** with chlorosul-

phonic acid (Scheme 3). The product is a mixture of two isomeric disulphonic acids *syn*-**12** and *anti*-**12** in equimolar quantities. As attempts to isolate individual isomers of **12** failed, the two acids were converted into a mixture of tetrabutylammonium salts **4**. This material was used for the measurements and for subsequent synthetic steps.

For the purposes of comparative study of the anionic crown ethers, a model aromatic carboxylate **14** was prepared as shown in Scheme 3. This compound incorporates a *p*-dialkoxycaromatic ring and a negatively charged carboxylate group thus representing the aromatic unit of macrocyclic **3**.



Scheme 3. Top: preparation of macrocyclic sulphonate **4**; bottom: preparation of acyclic carboxylate **14**. Reaction conditions (room temperature unless otherwise stated): i) HSO_3Cl , 0°C , 1 h, 78%; ii) tetrabutylammonium hydroxide, methanol, 100%; iii) tetramethylammonium hydroxide, methanol, 100%.

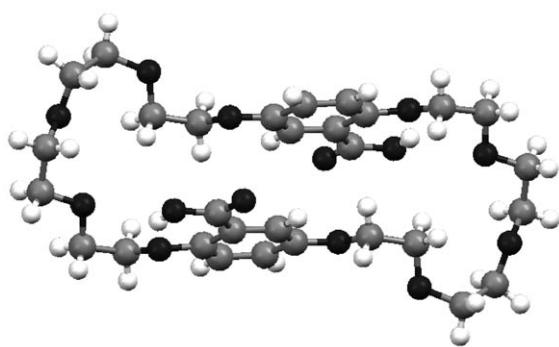


Figure 1. X-ray crystal structure of the macrocyclic acid **11**.

Structure of [2]pseudorotaxane salts: The [2]pseudorotaxane salts **15** and **16** were prepared by ion-exchange reac-

tions between the viologen hexafluorophosphate **6** and the macrocyclic salts **3** and **4** in aqueous alcohol (Scheme 4). These reactions yield deeply coloured solutions of the highly polar [2]pseudorotaxane salts, while the insoluble tetraalkylammonium salts precipitate and can be filtered off.

The crystal structures of hydrated [2]pseudorotaxane salts **15** and **16** are shown in Figure 2a and b, respectively. In both structures, the viologen moiety threads the anionic macrocycle. This important finding demonstrates that in the solid state the threaded species, **15** and **16**, are more favourable than other possible ion-paired species. It should be noted that the position, orientation and internal dihedral angle of the viologen moiety in **15** and **16** are similar to those in common [2]pseudorotaxanes containing the neutral crown ether **1**.^[5d,e] However, there are a few surprising features. For example, in the [2]pseudorotaxane salt **15** the distance between the anionic carboxylate groups of the crown ether moiety (around 10 Å) is considerably greater than in the structure of the acid **11** (7.2 Å) due, possibly, to electrostatic repulsion. As a result, in the solid [2]pseudorotaxane salt **15**, the cationic nitrogen of the viologen moiety and the anionic carboxylates are rather far from each other (the closest contact is 5.5 Å) and the carboxylates point away from the viologen moiety into layers of hydrating water molecules. The hydration shell of water molecules (twelve molecules per each [2]rotaxane salt unit) form layers separating adjacent [2]pseudorotaxane salt units from each other. This type of hydration prevents direct contacts between the carboxylate groups and the positively charged nitrogen atoms. As all attempts to fully dehydrate the [2]pseudorotaxane salt **15** led to irreversible decomposition, the constitutional water is likely to be an additional stabilisation factor of the [2]pseudorotaxane salt in the solid state. It is also noted that as the viologen moieties are commonly extremely sensitive to bases, the presence of excess base or excess carboxylate

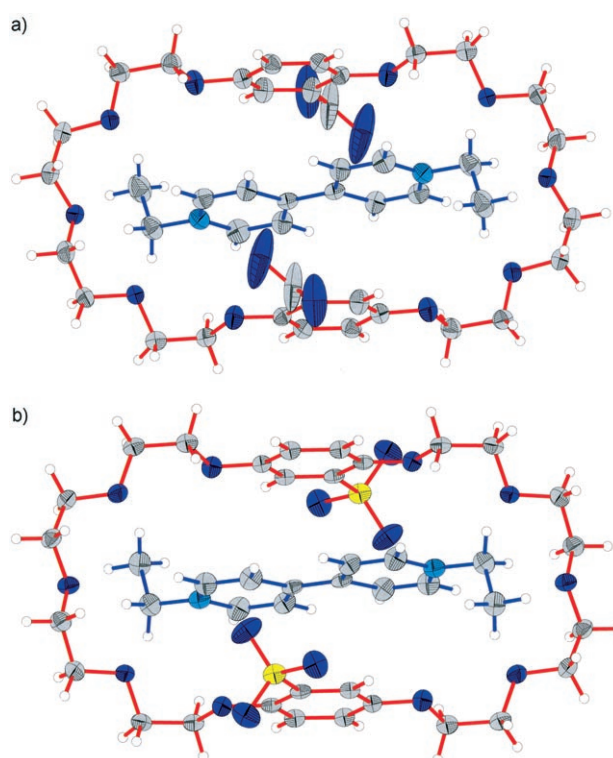
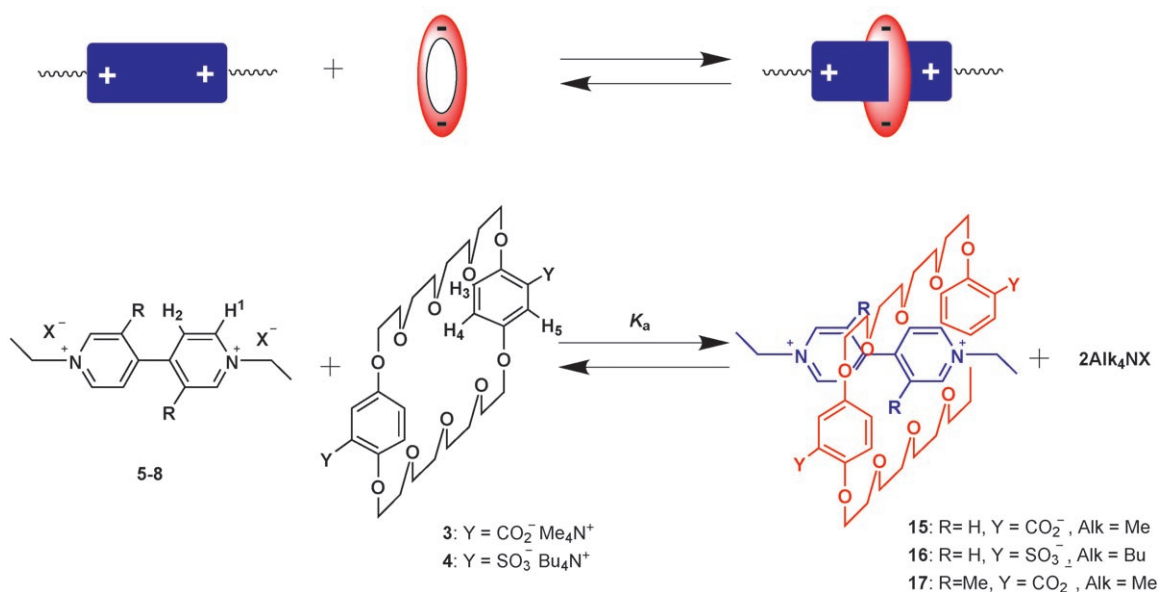


Figure 2. a) X-ray crystal structure of the [2]pseudorotaxane salt **15**. b) X-ray crystal structure of the [2]pseudorotaxane salt **16**.

should be strictly avoided when preparing [2]pseudorotaxane salt **15**. By comparison, in the solid [2]rotaxane salt **16**, the distance between the anionic sulphonate groups of the crown ether moiety (8.9–10 Å) and their closest contacts with viologen nitrogens (5.2 Å) are slightly shorter than in the structure **15**. Additionally, the number of the hydrating water molecules (only two per each [2]pseudorotaxane salt



Scheme 4. Formation of [2]pseudorotaxane salts in solution

unit) is substantially lower than in **15**. As a result, in the solid [2]pseudorotaxane salt **16**, the cationic nitrogen of the viologen moiety and the anionic sulphonates are not separated from each other by layers of water molecules. It can be concluded, that the sulphonate groups provide better charge delocalisation than the carboxylate groups and improve the stability of [2]pseudorotaxane salts.

While the key finding of the above crystallographic study is that the positively charged viologen moieties form stable threaded [2]pseudorotaxane salts with negatively charged crown ethers in the solid state, the question which arises is whether the threaded structure remains preserved in solution. To answer this question, the study of the [2]pseudorotaxane salts and related species in solution was carried out by NMR spectroscopy.

The proton NMR spectra of the individual viologen bromide **5**, tetramethylammonium carboxylate **3** and their equimolar mixture were recorded in methanol at 25 °C (Figure 3a). Given the high value of association constant K_a under the specified conditions (vide infra), the association equilibrium is fully shifted towards the formation of [2]pseudorotaxane salt **15** (Scheme 4: R=H, X=Br). The interactions between the viologen moiety and the negatively charged crown ether in **15** are accompanied by significant

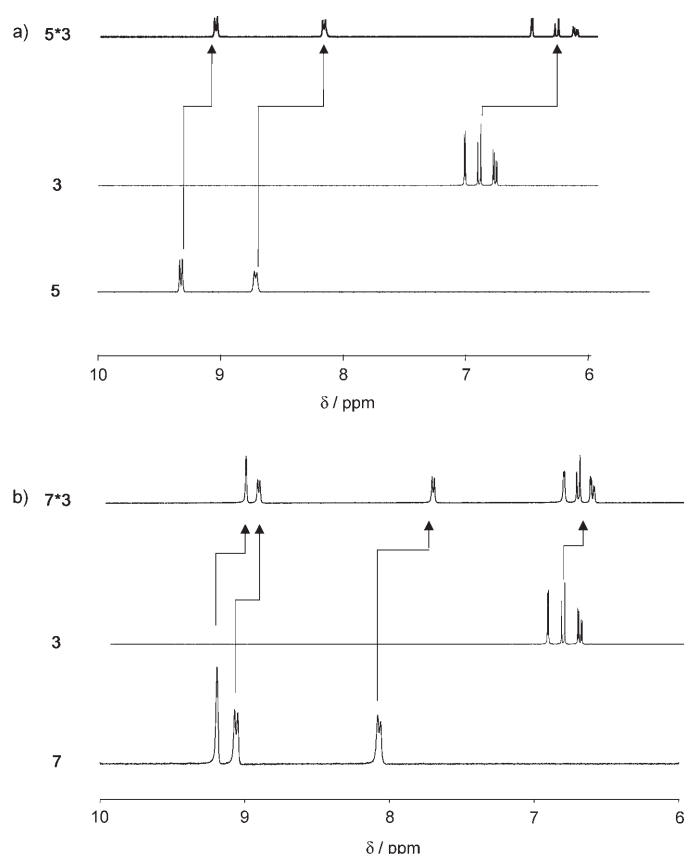


Figure 3. a) Partial ¹H NMR spectra of viologen **5**, crown ether **3** and their equimolar mixture in CD₃OD at 25 °C; b) partial ¹H NMR spectra of viologen **7**, crown ether **3** and their equimolar mixture in CD₃OD at 25 °C (concentration 1.00 × 10⁻² mol dm⁻³).

upfield shifts of the resonances in the region of δ=8.0–9.5 ppm (H₁ and H₂ of the viologen moiety, Scheme 4) and in the region of δ=6.0–7.3 ppm. (H₃–H₅ of the crown ether). These shifts in the case of the [2]pseudorotaxane salt **15** are attributed to mutual strong diamagnetic shielding due to the π-stacking of viologen and crown ether aromatic systems.^[8] Consequently, it can be concluded that in solution the viologen moiety threads the negatively charged crown ether **3** to form [2]pseudorotaxane salt **15**. A NOESY study of **15** demonstrates that when irradiating the H₂ protons of the viologen (δ=8.1 ppm) strong interactions are observed with the H₁ protons of the viologen at δ=9.1 ppm and with all three aromatic protons H₃, H₄, H₅ (region δ=6.0–6.6 ppm) of the crown ether. Similar experimental observations were made for the interaction of the bromide **5** with the sulphonate **4** in methanol.

The ¹H NMR spectra of the sterically hindered 3,3'-dimethylviologen bromide **7**, the tetramethylammonium salt **3** and their equimolar mixture were also recorded in methanol at 25 °C (Figure 3b). Given the high value of K_a under the specified conditions, the association equilibrium is shifted towards formation of [2]pseudorotaxane salt **17** (Scheme 4: R=Me, X=Br). The interactions between the viologen moiety and the negatively charged crown ether **3** in this case are accompanied by significant upfield shifts of the resonances in the region of δ=8.0–9.2 ppm (H₁ and H₂ of the viologen moiety) and less significant upfield shifts in the region of δ=6.5–7.0 ppm (H₃–H₅ of the crown ether). Similarly to the [2]rotaxane salt **15**, the upfield shifts of H₁ and H₂ of the viologen moiety can be attributed to diamagnetic shielding by the closely approaching aromatic systems of the crown ether. The relatively small values of the observed upfield shifts of the crown ether protons H₃–H₅ probably indicate that the sterically hindered 3,3'-dimethylviologen moiety in [2]pseudorotaxane salt **17** cannot adopt a fully planar conformation. This steric barrier prevents the formation of a “sandwiched” three-decked [2]pseudorotaxane structure and diminishes the diamagnetic shielding effect. A NOESY study of the [2]pseudorotaxane salt **17** demonstrates that when irradiating the H₂ protons of the viologen, strong interactions are observed with the H₁ protons of the viologen and with all three aromatic protons H₃, H₄, and H₅ of the crown ether. It is concluded, that in solution, the viologen moieties of **5** and **7** thread the negatively charged crown ether **3** to form [2]pseudorotaxane salts **15** and **17**.

The interaction of viologen bromide **5** with the non-macrocyclic carboxylate **14** was studied and compared to the macrocyclic anions **3** and **4**. Although the interaction of **5** with carboxylate **14** can be observed visually (orange colour of a 1:2 mixture of **5** and **14** in methanol), the ¹H NMR spectrum of this mixture at 25 °C (Figure 4) shows no upfield shifts of the resonances. This demonstrates that the observed upfield NMR shifts for [2]pseudorotaxane salts **15** and **17** should be attributed to threading rather than formation of ion pairs or charge-transfer interactions.

Having established that the viologens **5** and **7** thread negatively charged crown ethers in solution, it was interesting

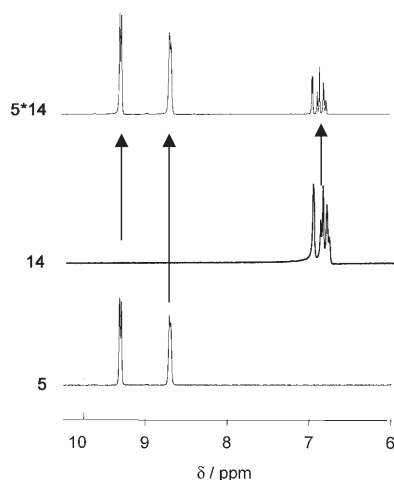


Figure 4. Partial ^1H NMR spectra of viologen **5**, carboxylate **14** and their mixture in CD_3OD at 25°C (concentration of **5** $1.00 \times 10^{-2} \text{ mol dm}^{-3}$).

to study the possibility of an interaction between a sterically stoppered dumbbell-shaped “axle” containing a viologen moiety and a negatively charged crown ether. Additional experiments (see the Supporting Information, part 1) have shown that the electrostatic interactions in this case lead to the formation of ion pairs, possibly by wrapping of the crown ether around the viologen moiety.

On the basis of the above comparative NMR spectroscopic study of the interactions between viologens and carboxylate anions **3** and **14**, it is concluded that in solution, as in the solid state, the viologens thread the anionic crown ethers to form [2]pseudorotaxane salts.

Association constants of [2]pseudorotaxane salts: It is expected that the thermodynamic stability of the [2]pseudorotaxane salts incorporating negatively charged crown ethers **3** and **4** and viologens would be substantially higher than that of the [2]pseudorotaxanes incorporating neutral crown ethers **1** and **2**. The equilibrium association constants K_a between viologens **5–8** and crown ethers **1–4** (Scheme 4) were measured by using a dilution method.^[9] The equilibrium was monitored by UV/visible spectroscopy at 25°C in water/methanol mixtures for bromides **5** and **7** and in water/acetonitrile mixtures for hexafluorophosphates **6** and **8**. The results are given in Table 1.

The association of the viologen **5** with the neutral crown ethers **1** and **2** is not observed in water (due to sparing solubility of the crown ether) and is moderately strong in methanol (Table 1). On the contrary, the association of **5** with the anionic crown ether **3** is sufficiently strong to be measured even in neat water. The K_a in

this case increases rapidly with the addition of methanol or acetonitrile due, possibly, to the decrease of ionising power of the solvent media.^[10,11] Consequently, the association constant K_a cannot be directly measured in neat methanol or acetonitrile due to poor linearity of the acquired data.

To estimate association constants K_a in neat organic solvents, the respective measurements were carried out in aqueous mixtures and the results were extrapolated. This was done on the basis of an assumption that the ionizing power Y of a solvent mixture can be approximated by a linear function of the composition of this mixture (see the Supporting Information, part 2).^[10]

Clearly, the association constants of 1,1'-diethylviologens **5** and **6** with the negatively charged crown ethers **3** and **4** are generally 4–5 orders of magnitude higher than the association constants with neutral crown ethers **1** and **2** in the same solvent (Table 1). The association constants of [2]pseudorotaxane salts incorporating 3,3'-dimethyl-1,1'-diethylviologens **7** and **8** and negatively charged crown ethers **3** and **4** are, as expected, 1–2 orders of magnitude lower than the association constants of 1,1'-diethylviologens **5** and **6** (Table 1). Apparently, the steric hindrance within the 3,3'-dimethyl-1,1'-diethylviologen moiety decreases its predilection for complexation with crown ethers.^[3b,4b] In short, the observed affinity of the disubstituted crown ethers CY_2 (cf Scheme 1) towards viologens decreases in the following order: $-\text{SO}_3^- > -\text{COO}^- \gg -\text{COOEt} > -\text{H}$.

The crystal structure data on [2]pseudorotaxane salts can be used to estimate the electrostatic energy contribution to their stability in solution. For example, considering the association free energy, ΔG° , of the viologen **6** with the neutral crown ether **1** ($-11.8 \text{ kJ mol}^{-1}$ in acetonitrile, Table 1) and with the charged crown ether **3** ($-40.2 \text{ kJ mol}^{-1}$ in acetonitrile) one can conclude that the estimated electrostatic contribution to the ΔG° value in the case of **3** is $\Delta(\Delta G^\circ) = -28.4 \text{ kJ mol}^{-1}$. Assuming that the viologen **6** threads the charged crown ether **3** in solution forming [2]rotaxane salt **15** (Scheme 4), the electrostatic energy contribution to this process is equal to the electrostatic interaction energy, E_e , between the viologen dication and the crown ether dianion in solution. E_e can be estimated (see the Supporting Infor-

Table 1. Association constants of [2]pseudorotaxanes and [2]pseudorotaxane salts.^[a]

Viologen	Host	Complex	Solvent	K_a [$\text{dm}^3 \text{ mol}^{-1}$]	ΔG° [kJ mol^{-1}]
5	1	5·1	MeOH	$(5.1 \pm 0.2) \times 10^2$	-15.5 ± 0.1
6	1	6·1	MeCN	$(1.2 \pm 0.1) \times 10^2$	-11.8 ± 0.4
5	2	5·2	MeOH	$(7.3 \pm 0.4) \times 10^2$	-16.3 ± 0.1
5	3	15	H_2O	$(6.0 \pm 0.3) \times 10^2$	-15.9 ± 0.1
5	3	15	MeOH ^[b]	$(7.8 \pm 3) \times 10^2$	-33.6 ± 2.0
5	3	15	MeCN ^[b]	$(3.6 \pm 1.6) \times 10^6$	-37.4 ± 1.6
6	3	15	MeCN ^[b]	$(1.2 \pm 0.5) \times 10^7$	-40.2 ± 2.0
5	4	16	MeOH ^[b]	$(4 \pm 2) \times 10^6$	-37.7 ± 2.0
6	4	16	MeOH ^[b]	$(4 \pm 2) \times 10^7$	-43.0 ± 2.0
7	3	17	MeOH ^[b]	$(3.4 \pm 0.8) \times 10^4$	-25.9 ± 0.7
8	3	17	MeCN ^[b]	$(6.8 \pm 1) \times 10^4$	-27.6 ± 0.6
5	14	--	MeOH	$(1.5 \pm 0.2) \times 10^2$	-12.3 ± 0.3

[a] Dilution method monitored by UV spectroscopy at 25°C . [b] Extrapolated value (see Supporting Information, part 2 for details).

mation, part 3) on the basis of the atom charges, interatomic distances and the dielectric constant of the solvent. The estimated value $E_c = -28.7 \text{ kJ mol}^{-1}$ is in good agreement with the observed $\Delta(\Delta G^\circ)$. It also is in a reasonable agreement with the recent findings on the electrostatic interaction in a molecular system comprising a quadruply positively charged ring component and a doubly positively charged axle component.^[12] The electrostatic repulsion interaction energy in that case was $+37.7 \text{ kJ mol}^{-1}$.

Association of the viologen **5** with the non-macrocyclic carboxylate **14** (Table 1) was also studied in neat methanol. As expected, the association ($K_a = 1.5 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$) is significantly weaker than that of the preorganised macrocyclic doubly-charged crown ethers **3** and **4**. It is concluded, therefore, that multiple electrostatic interactions as well as complementary dimensions of anionic crown ethers and viologens lead to the strong association of viologens with anionic crown ethers.

Interestingly, the association constant between the viologen bromide **5** and the carboxylate crown ether **3** is 4.6 times higher in acetonitrile (Table 1, $K_a = 3.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$) than in methanol ($K_a = 7.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$). This difference can reasonably be explained by a higher degree of solvation for the carboxylate anions in methanol when compared to acetonitrile.^[11] The association constant in neat acetonitrile is 3.3 times higher when using hexafluorophosphate **6** (Table 1, $K_a = 1.2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1}$) compared to the bromide **5**. As shown in the Supporting Information (part 4), this effect can be explained by a possible difference in the ionic strength created by the coformed tetramethylammonium salt Alk_4NX (cf. Scheme 4).

It can be concluded that the viologen cations as guests thread anionic crown ethers and form stable [2]pseudorotaxane salts. The association constants of [2]pseudorotaxane salts in non-aqueous solvents exceed $10^7 \text{ dm}^3 \text{ mol}^{-1}$. The association of the highly polar [2]pseudorotaxane salts decreases in polar media and in the presence of added ions.

Electrochemistry of [2]pseudorotaxane salts: As discussed above, the RITM function of a switchable [2]rotaxane (Scheme 1) involves the electrochemical reduction of the viologen moiety V_1 followed by the shuttling of the macrocyclic

component C to V_2 . Earlier, it has been demonstrated that the complexation of crown ethers with viologens shifts the peak reduction potentials E_p of the viologen to more negative values.^[3b,4b,7b] It can be expected that due to strong electrostatic interactions, the negative electrochemical shifts in [2]pseudorotaxane salts will be far more pronounced than in [2]pseudorotaxanes incorporating neutral crown ethers.

The cyclic voltammograms of the viologen hexafluorophosphate **6**, in the absence and in the presence of carboxylate crown ether **3**, were recorded in acetonitrile containing Et_4NPF_6 as supporting electrolyte (Figure 5). As expected, the peak reduction potentials of the viologen moiety in the resulting [2]pseudorotaxane salt **15** are significantly shifted towards more negative values both for the first and second reduction stages (Table 2). It can be noted, that while the negative shifts observed for [2]pseudorotaxane salts reach exceptional values, up to -235 mV , no shift is observed for the first stage of the reverse oxidation process (Table 2).

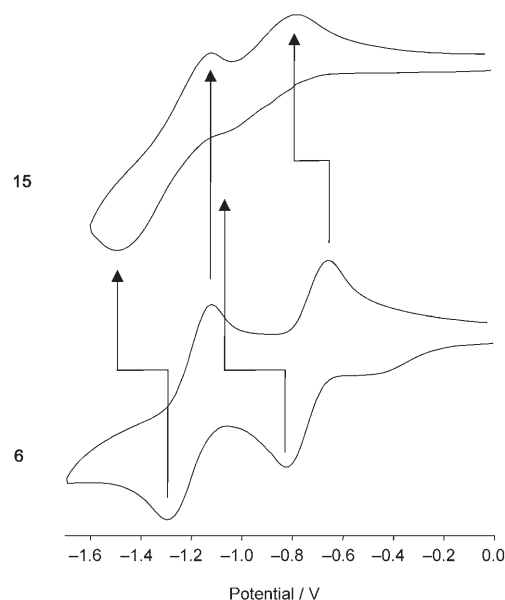


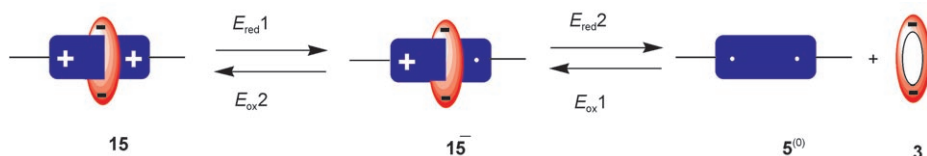
Figure 5. Cyclic voltammograms of viologen **6** ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) and [2]pseudorotaxane salt **15** ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) recorded at 100 mV s^{-1} in acetonitrile containing Et_4NPF_6 ($0.010 \text{ mol dm}^{-3}$) at 25°C .

Table 2. Peak reduction and oxidation potentials^[a] of [2]rotaxane and [2]pseudorotaxane salts.^[b]

Viologen	Host	Complex	V^{2+}/V^{+} [V]	V^{+}/V^{-} [V]	V^{-}/V^{+} [V]	V^{+}/V^{2+} [V]
6	–	–	–0.839	–1.305	–1.126	–0.667
6	14	–	–0.853	–1.347	–1.098	–0.634
6	3	15	–1.073	–1.484	–1.124	–0.770
6	4	16	–1.122	–1.466	–1.123	–0.735
8	–	–	–1.252	–1.510	–1.266	–1.049
8	3	17	–1.443	–1.686	–1.261	–1.168
20	–	–	–0.676	–1.008	–0.910	–0.550
20	11	21	–0.846	–1.208	–0.913	–0.656
20	3	22	–1.128	–1.440	–1.058	–0.721
20	<i>syn-4</i>	24	–0.894	–1.339	–1.010	–0.797
20	<i>anti-4</i>	23	–0.979	–1.324	–1.097	–0.782

[a] Values have been extracted numerically; accuracy not poorer than 10 mV . [b] Concentration $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ in acetonitrile containing supporting electrolyte Et_4NPF_6 ($0.010 \text{ mol dm}^{-3}$); scan rate 100 mV s^{-1} ; 25°C .

The above findings can be interpreted in terms of reduction and dissociation of the [2]pseudorotaxane salt **15** as shown in Scheme 5. The large negative shifts of reduction



Scheme 5. Electrochemical reduction and dissociation of [2]pseudorotaxane salt **15**.

potentials $E_{\text{red}1}$ and $E_{\text{red}2}$ clearly demonstrate strong electrostatic interaction of the components in the [2]pseudorotaxane salt **15** in its parent oxidised state and in the first reduced state **15**[•]. However, full reduction of the viologen moiety leads to dissociation of the electroneutral thread **5**⁽⁰⁾ and the carboxylate **3**. Consequently, the first oxidation potential of the system $E_{\text{ox}1}$ is not shifted.

The cyclic voltammograms of 3,3'-dimethylviologen **8** in the absence and in the presence of the carboxylate **3** were also recorded under the above conditions. Similarly to the viologen **6** and the corresponding [2]pseudorotaxane salt **15**, the peak reduction potentials of the viologen moiety of [2]pseudorotaxane salt **17** are significantly shifted towards more negative values both for the first and second reduction stages (Table 2). It is noted, however, that due to the steric hindrance, the electrostatic interaction in **17** is weaker and the negative shifts observed (−190 and −175 mV upon first and second reduction, respectively) for **17** are smaller than those observed for the [2]pseudorotaxane salt **15**.

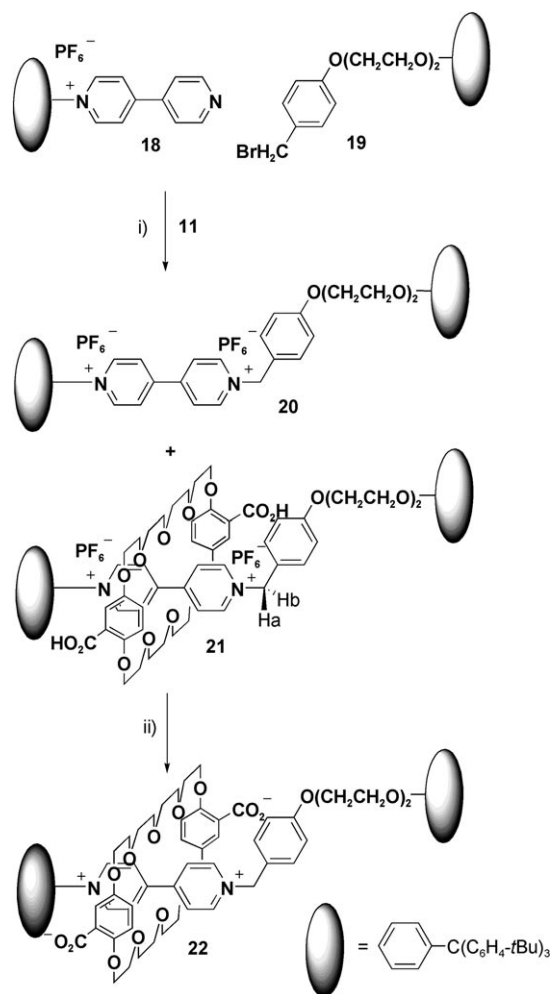
By comparison, cyclic voltammograms of the viologen **6** in the absence and in the presence of the carboxylate **14** were recorded under the above conditions. It was found that the first and second peak reduction potentials of the viologen moiety were shifted towards more negative values by 14 and 43 mV (Table 2) and the respective peak oxidation potentials were shifted towards more positive values by 30 mV. As the resulting average potentials were virtually unaffected, it was reasoned that the electrostatic interaction of the viologen moiety with the acyclic carboxylate **4** was insufficient to maintain stable molecular associates.

Finally, it can be concluded that viologens and negatively charged *p*-phenylene crown ethers form very stable [2]pseudorotaxane salts in solution and in the solid state. These complexes retain the threaded geometry of the [2]pseudorotaxanes formed by neutral crown ethers. Electrostatic non-covalent interaction in these complexes is one of the strongest (up to 40 kJ mol^{−1}) among known intermolecular interactions in solution. The stability of the [2]pseudorotaxane salts is upheld by the cooperative electrostatic attraction and preorganised geometry of the host and guest.

The above findings are valuable for the design of novel [2]ionorotaxanes. For example, on the basis of [2]rotaxane salt stability constants for the viologens **5** and **7** it can be reasonably expected that in a switchable [2]rotaxane salt

(Scheme 1), incorporating two viologen stations V_1 and V_2 , the anionic crown ether will be localised predominantly at the “strong” viologen station V_1 .

[2]Rotaxane salts: The [2]rotaxane salts were prepared by using an efficient three-component self-assembly reaction under high concentration conditions as shown in Scheme 6.^[3a] Typically, the monocation pre-



Scheme 6. Synthesis of [2]rotaxane **21** and its conversion into [2]rotaxane salt **22**. Reaction conditions (room temperature): i) PhCl/PhCN, 10 d, yield of **21**: 50%; ii) sodium bicarbonate, water/nitromethane, 1 min, 83%.

cursor **18**, the crown ether and the stopper component **19** were dissolved in a minimum amount of an aromatic solvent (benzonitrile, chlorobenzene) and were left at ambient conditions until the reaction is complete. Usually, the viologen axle component, **20**, was formed as a side product.^[5d]

The carboxylic diacid [2]rotaxane **21** was prepared from the macrocyclic acid **11** in a mixture of benzonitrile/chlorobenzene as the solvent (Scheme 6). The [2]rotaxane **21** was obtained in reasonably good yield (50%) which was limited by the solubility of the acid **11** in the reaction media.

In the proton NMR spectrum of **21** (Figure 6), the resonances of the methylene protons H_a and H_b (Scheme 6) are represented by two doublets at $\delta = 5.96$ and 6.12 ppm, re-

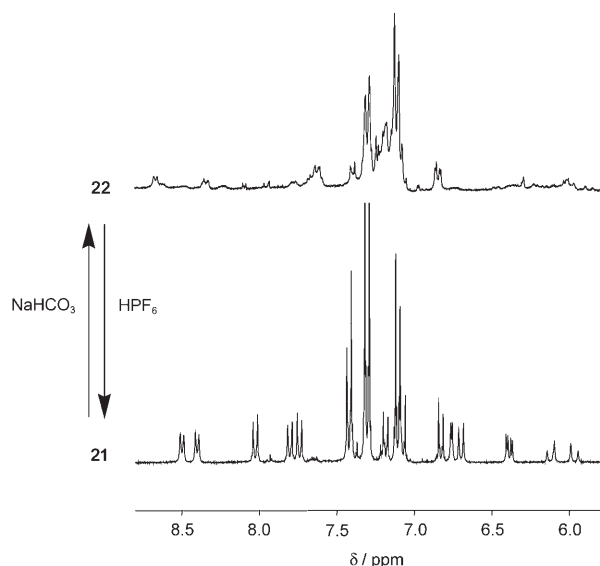


Figure 6. Partial ^1H NMR spectra of [2]rotaxanes **21** and **22** in acetone at 25°C.

spectively, with a proton–proton coupling constant of $J = 14$ Hz. This interesting behaviour can be explained by the cycloenantiomerism^[13] of the [2]rotaxane **21**. Indeed, although the individual components of **21** (the dumbbell-shaped **20** and the crown ether **11**) are not chiral, no symmetry element is present when **20** and **11** are interlocked forming chiral [2]rotaxane **21**. The [2]rotaxane **21** can be deprotonated by sodium bicarbonate and the neutral [2]ionorotaxane **22** can be extracted into nitromethane. Individual **22** is a deep-red glassy solid which, when dissolved, can be easily converted back into **21** by treatment with HPF_6 .^[14]

The proton NMR spectra reveal striking differences between acidic the form of **21** and its conjugated base [2]rotaxane salt **22** (Figure 6). In the proton NMR spectrum of **22** all signals of the viologen moiety, the crown ether aromatic rings and the benzylic protons are significantly broadened. However, the original spectrum of acid **21** can be fully restored simply by addition of HPF_6 .

The electrochemical behaviour of [2]rotaxanes **21** and **22** provides important insights in relation to the nature and strength of the intercomponent interactions in these interlocked molecules. The cyclic voltammograms of axle component **20**, [2]rotaxanes **21** and [2]rotaxane salt **22** in acetonitrile containing tetra(*n*-butyl)ammonium perchlorate (TBAP) are shown in Figure 7; the electrochemical peak potential data are given in Table 2.

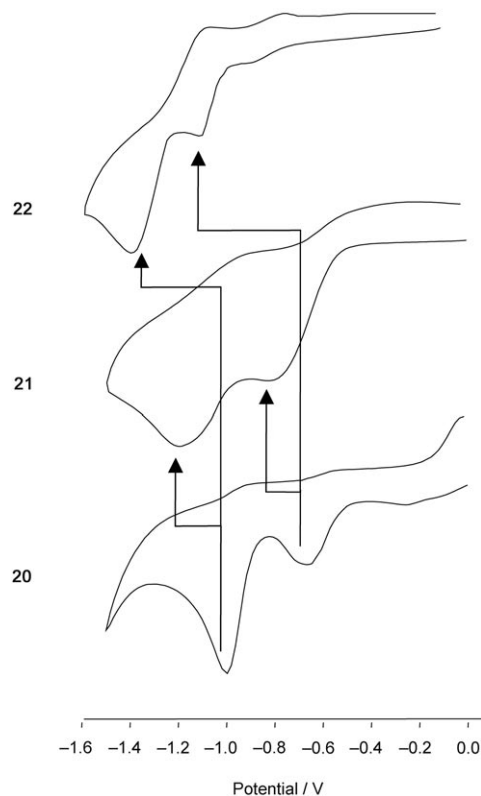
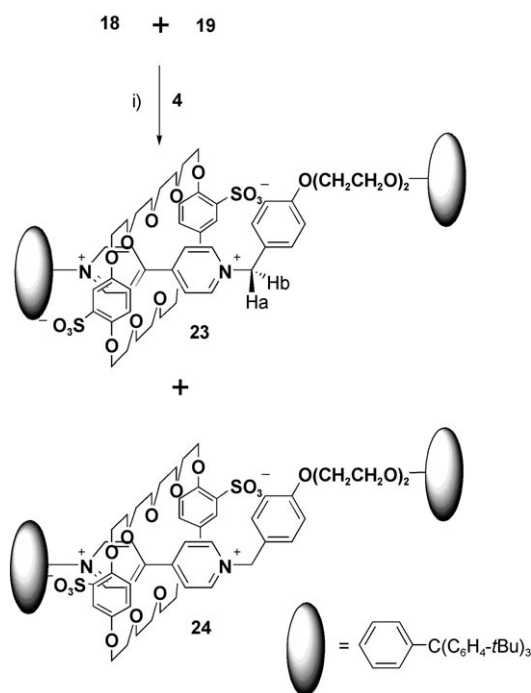


Figure 7. Cyclic voltammograms of **20** ($2 \times 10^{-3} \text{ mol dm}^{-3}$), [2]rotaxane **21** ($2 \times 10^{-3} \text{ mol dm}^{-3}$) and [2]rotaxane salt **22** ($2 \times 10^{-3} \text{ mol dm}^{-3}$) recorded at 100 mV s^{-1} in dry acetonitrile containing TBAP ($0.010 \text{ mol dm}^{-3}$) at 25°C.

The peak reduction potentials of the [2]rotaxane **21**, in comparison to the axle component **20**, are shifted to more negative values by 170–200 mV. In the [2]rotaxane salt **22**, the intercomponent interaction leads to a very significant peak shifts up to -450 mV. The latter figure is considerably greater than the expected electrochemical shift estimated on the basis of the electrostatic interaction in analogous [2]pseudorotaxane salt **15** (see the Supporting Information, part 5). This discrepancy is, possibly, caused by a different spatial position of the carboxylate groups in **22**, permitting closer contacts with the positively charged nitrogen atoms of the viologen moiety.

Neutral sulphonate [2]rotaxane salts **23** and **24** were prepared (Scheme 7) by using a mixture of *syn*- and *anti*- isomers of the crown ether **4**. Each of the isomeric [2]rotaxane salts is formed in 50% yield due to the presence of equal amounts of the *syn*- and the *anti*- isomers of the salt **4** in the mixture. Unexpectedly, unlike the starting **4**, the [2]rotaxane salts **23** and **24** can be separated by column chromatography. Any protonation effects have not been noticed for isomeric sulphonate [2]rotaxane salts **23** and **24**. Consequently, the application of sulphonate anionic crown ethers and sulphonate [2]rotaxane salts is considered to be more promising in a wider range of solvents and under a wider range of conditions.

Detailed examination of the ^1H NMR spectra of the two diastereomeric [2]rotaxane salts **23** and **24** (Figure 8) reveals



Scheme 7. Synthesis of [2]rotaxane salts **23** and **24**. Reaction conditions: i) room temperature, benzonitrile, 6 d.

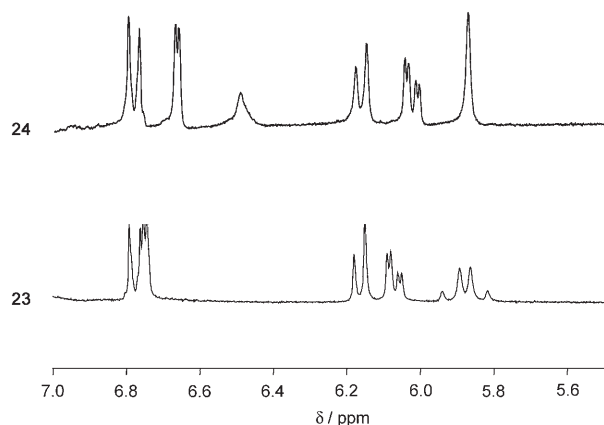


Figure 8. Partial ^1H NMR spectra of the [2]rotaxane salts **23** and **24** in acetone.

that only in one of them, the N-benzylic methylene protons H_a and H_b are diastereotopic due to cycloenantiomerism (proton–proton coupling constant $J_{\text{H-H}} = 14$ Hz). This is in full agreement with the structure of the *anti*-isomer **23** (Scheme 7) in which the protons H_a and H_b are non-equivalent.^[13] As the ^1H NMR spectrum of the [2]rotaxane salt **24** demonstrates no non-equivalence of the benzylic proton resonances, it is concluded that in **24** the sulphonate groups are *syn*- to each other.

The different symmetry characteristics of the two isomeric [2]rotaxane salts **23** and **24** control their chemical behaviour. For example, the reason that **23** and **24** can be separated by

column chromatography is that the [2]rotaxane salt **23** is the one which can be eluted with neat acetone while [2]rotaxane salt **24** (its symmetrical configuration is analogous to a *meso*-form) behaves as a very polar compound and cannot be eluted with neat acetone. Apparently, *anti*-orientation of the sulphonate groups in **23** allows a better electrostatic shielding of the positively charged viologen moiety of **23**. It is believed that the [2]rotaxane salt **24**, unlike **23**, cannot adopt a conformation in which both positive charges of the viologen moiety are shielded by anionic groups and, consequently, it behaves like a more-polar compound.

The electrochemical characterisation of the two isomeric [2]rotaxane salts **23** and **24** provided additional insights into the nature and strength of the intercomponent interactions in these interlocked systems. The cyclic voltammograms of axle dumbbell-shaped component **20** and the two isomeric [2]rotaxane salts **23** and **24** in acetonitrile containing TBAP appear as Figure 9. The respective electrochemical peak po-

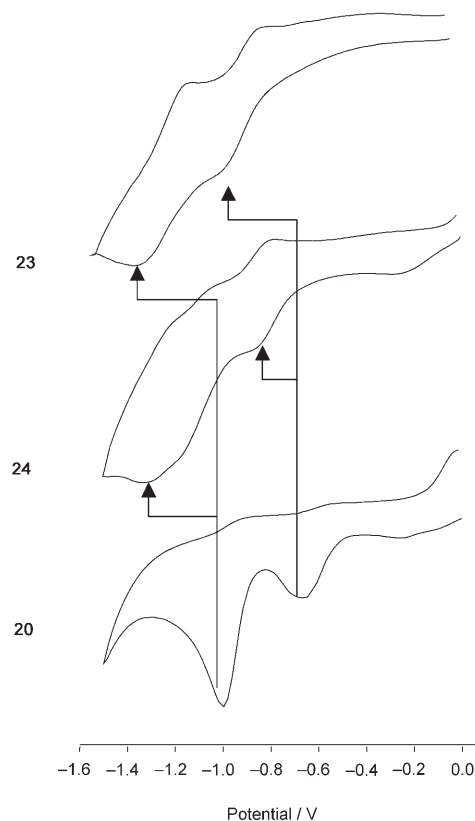


Figure 9. Cyclic voltammograms of **20**, **23** and **24** (each 2.0×10^{-3} mol dm $^{-3}$) recorded at 100 mVs $^{-1}$ in acetonitrile containing TBAP (0.010 mol dm $^{-3}$) at 25°C .

tentials are given in Table 2. The key observation is that both [2]rotaxane salts **23** and **24** demonstrate large negative shifts of the first and second reduction processes (Table 2). This observation is in full agreement with strong electrostatic intercomponent interaction in [2]ionorotaxanes. As discussed above, the less-polar *anti*-isomer **23** has a more effec-

tive shielding of the positively charged viologen dication. Consequently, the first electrochemical reduction peak of the viologen moiety in this rotaxane is shifted by -303 mV. In the more-polar **24**, the same viologen dication is shielded by the negatively charged *syn*-isomer of **4** to a lesser extent. Consequently, the first electrochemical reduction peak in the [2]rotaxane salt **24** is shifted by only -218 mV.

Apart from [2]pseudorotaxane salts (vide supra), in which the first oxidation potentials were not shifted due to dissociation of the reduced species (Scheme 5), the first oxidation potential shifts were observed for both [2]rotaxane salts **23** and **24** (Table 2). As the charged crown ether is secured at the viologen moiety by the bulky stopper groups, the dissociation of the reduced [2]rotaxane salt is precluded. Therefore, the viologen moiety of an [2]rotaxane salt (for example, **23**) experiences the electrostatic effect of the negatively charged ring component even in the fully reduced state, 23^{2-} ; consequently, even the first oxidation potential of this viologen is negatively shifted. A similar, although weaker, effect has been previously observed for a common [2]rotaxane containing the neutral crown ether **1**.^[5d]

It can be concluded that novel [2]rotaxane salts represent an important new class of artificial molecular systems in which the components are not only mechanically interlocked but are also strongly electrostatically attached. Intramolecular electrostatic interactions in [2]rotaxane salts can be controlled by applying external electrical or chemical stimuli. This opens possibilities for the design of controlled reversible molecular switching systems driven by electrostatic attraction forces.

Conclusion

Electrically neutral [2]pseudorotaxane and [2]rotaxane salts have been prepared and characterised for the first time. In these systems, doubly positively charged viologen cations thread doubly negatively charged crown ethers. Due to the strong electrostatic attraction between the host and guest components there are several aspects in which the behaviour of [2]pseudorotaxane salts and [2]rotaxane salts differs from previously known [2]rotaxane systems:

- 1) [2]Pseudorotaxane salts are remarkably stable. Due to strong non-covalent electrostatic interactions between their components, the association free energy in neat organic solvents reaches -40 kJ mol⁻¹ (extrapolated value).
- 2) The electrostatic interactions between mechanically interlocked components of the [2]pseudorotaxane salts and [2]rotaxane salts lead to extraordinarily big negative shifts of their electrochemical reduction potentials.
- 3) Anionic carboxylate groups of [2]rotaxane salts can be reversibly protonated. However, no protonation effects have been observed for an analogous sulphonate [2]rotaxane salt under the same conditions. Therefore, sulphonate [2]rotaxane salts maintain their internal charges in a wider range of acidity of the media.
- 4) [2]Rotaxane salts with *anti*-orientation of the functional groups at the crown ether moiety are cycloenantiomeric unlike their individual interlocked components. It was found that electrochemical behaviour and polarity of the diastereomeric [2]rotaxane salts depend significantly on the orientation of the functional groups.

The use of controlled intramolecular electrostatic interactions already helps to narrow the gap between actual and desirable parameters of functional molecular entities.^[1,6] Although the synthesis of interlocked molecular systems has become a routine among modern chemists, little has been done to redesign the existing [2]rotaxanes and modify them with ionic groups to fully realise their development potential for molecular electronics and nanoscience. The findings of the present study of prototype rotaxane salts indicates that the enhanced stability and electrochemical behaviour of these systems can be useful for a range of exciting potential applications.

Experimental Section

Details on the experimental procedures, calculations, measurements and characterization of the compounds are given in the Supporting Information, parts 1–7. CCDC-633834 and -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

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- [14] The synthesis of the [2]rotaxane salt **22** should be feasible by a direct assembly of the monocation precursor **18**, the anionic crown ether **3** and the stopper component **19**. However, attempts to prepare **22** in this way were unsuccessful, due to fast competitive alkylation of the carboxylate anionic groups of **3** with the stopper component **19**.

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