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Electrochemically Induced Intermolecular Anion Transfer

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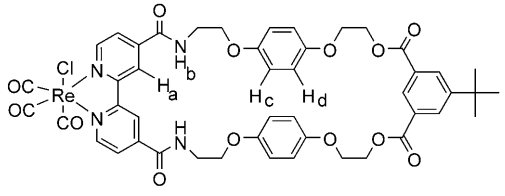
Control over molecular motion still represents a challenge for supramolecular chemists. Although great advances have been reported during the last two decades,[1] the application of molecular machines into real devices is still to come. Supramolecular interlocked structures are among the most studied systems to test molecular motion since they facilitate the detection of relative displacement between their components due to their topological restrictions. Very imaginative examples of chemical,[2] photochemical[3] and electrochemically-driven[4] devices have been described in the literature.

Although the field of anion-coordination chemistry has expanded greatly in recent years,[5] the application of negatively charged species to the area of molecular machines has not been exploited to any great extent. Of the rare examples reported to date the majority focus on rotaxane systems, where competition between axle and macrocycle for anion recognition chemically switches movement between the interlocked components.[6]

Redox-switched systems have mainly been restricted to shuttling in interlocked structures by influencing donor–acceptor electronic interactions[7] and coordination geometry change.[8] For example, Fabbrizzi and co-workers have reported the redox-driven intramolecular nitrate anion translocation between a copper metal centre and a bis-imidazolium anion-recognition site.[9] In this regard, with a few exceptions,[10] ferrocene has not been commonly utilized in molecular machinery, despite its well known electrochemical behavior in supramolecular receptors.[11] This context motivated us to design a supramolecular system which could involve the displacement of an anionic component, electrochemically regulated by the oxidation state of a ferrocene unit.

Herein we report a novel approach to the control of intermolecular motion between two receptors where the location of an anion can be regulated by the redox-controlled relative strength of non-covalent interactions between two recognition sites. Initially, the anion is bound solely by hydrogen bonds. Upon electrochemical oxidation, the anion relocates to be complexed by hydrogen bonds and by favourable electrostatic attractive interactions.

In the design of our system we intended to incorporate a luminescent signalling unit as well as an electrochemically active unit, into two macrocyclic receptors, in order to define a bistable arrangement. In the search for such components, photo-active Re^{I}–2,2′-bipyridine-4,4′-diamide, and redox-active ferrocene-1,1′-dithiourea motifs, were chosen (see below). These fragments are known to be efficient anion recognition agents[12] and will enable spectroelectrochemical techniques to be used in the monitoring of intermolecular anion transfer and switching of the device. Macrocycles **1** and **2** were prepared via multistep synthetic pathways and characterized as described in the Supporting Information.



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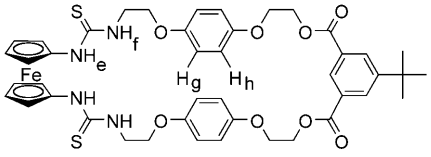

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Preliminary anion-titration experiments were independently carried out with **1** and **2**, by both absorption and emission spectroscopy in acetone solution.[13] Receptors **1** and **2** revealed their ability to bind different anions, as could be quantified by the determination of their stability constants (Table 1).[14] All titrations fitted well a 1:1 stoichiometry model, with most of the anions forming stronger complexes with **1**.

Table 1. Anion-binding constants ($\log K_{ass}$)[a] of **1** and **2**.

	$PhCO_2^-$	AcO^-	HSO_4^-	Br^-
1	6.1	5.3	5.2	4.7
2	4.1	3.9	3.8	5

[a] K_{ass} [M^{-1}] determined by UV/Vis spectroscopy with an error $<10\%$, at 25 °C. [**1**] $=5\times10^{-5}$ M, [**2**] $=10^{-4}$ M in acetone. Association constants, for **1**, have been further confirmed by emission spectroscopy at 25 °C, $\lambda_{exc}=$ 420 nm and [**1**] $=5\times10^{-5}$ M.

Since the initial condition of our dynamic system demanded an unbalanced distribution of the complexed anion between both macrocycles, we focused our study on the benzoate anion, which showed the larger binding constant ratio between **1** and **2**.

Although the low solubility of compounds **1** and **2** in deuterated acetone thwarted any possibility of quantifying binding constants by ^{1}H NMR analysis, a qualitative study could be indeed carried out (Figure 1).[15] It is worth highlighting how the solubility of both receptors is remarkably improved when one equivalent of benzoate is added to the suspension in the NMR tube. This can be interpreted as an initial evidence of the host–guest interaction. Furthermore, a downfield shift is detected for the signals corresponding to the protons more directly involved in the complexation of the anion, in both macrocycles **1** and **2**, as commonly results from the hydrogen bonding interaction between the receptor and the complexed anion (Figure 1).

Interestingly, an upfield shift of the protons, which are complexing the anion in **1**, could be detected after the addition of one molar equivalent of **2** to a 1:1 mixture of receptor **1** and benzoate. Simultaneously, a downfield shift of the thiourea protons is observed in the ^{1}H NMR spectra of the ternary mixture **1**/benzoate/**2**. The structural information, which can be drawn from this experiment, indicates that competitive anion complexation equilibria are established between both macrocycles.

Control experiments carried out by emission spectroscopy also confirmed this result (Figure 2). An important enhancement of the MLCT emission intensity was initially observed when benzoate was added to a solution of **1**. Subsequently, the luminescence intensity of the anion complex was partially quenched after the addition of **2**. In agreement with what has been discussed for the ^{1}H NMR experiments, the decrease in the luminescence can be related to the removal of part of the complexed anion from **1**.[16]

The anion distribution can be determined from the values of the binding constants. Initially, when one equivalent of benzoate is added to a solution of **1** (5×10^{-5} M in acetone) 88% of the anion is bound by the macrocyclic receptor. However, when **1**, **2** and TBA-benzoate are dissolved together, at the same concentration, the ratio of anion complexed by receptor **1** drops to 85%.[17]

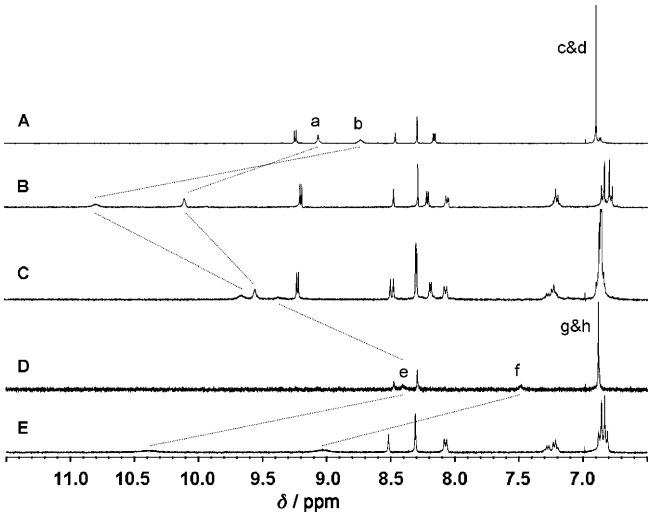

Figure 1. ^{1}H NMR spectra of A) **1**; B) **1**/benzoate 1:1; C) **1**/**2**/benzoate 1:1:1; D) **2**; E) **2**/benzoate 1:1 in deuterated acetone.

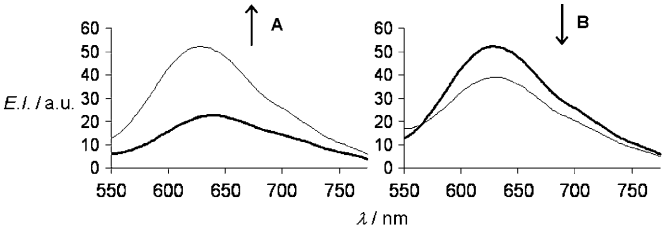

Figure 2. Emission spectra ($\lambda_{exc}=420$ nm) of (A) **1** (5×10^{-5} M) in acetone (——), **1**/benzoate 1:1 (——) and B) **1**/benzoate 1:1 (——), **1**/**2**/benzoate 1:1:1 (——).

The most important condition to be fulfilled by our system in order to achieve an efficient intermolecular anion transfer is that the affinities towards anionic guests can be reversed. In our case, this will be done by a controlled electrochemical potential. A square wave voltammetry titration (Figure 3) of compound **2** with TBA-benzoate showed a double wave behaviour with a cathodic shift in the oxidation potential ($\Delta E_p=0.218$ V). This double wave observation is the usual response to strong anion binding with slow kinetic decomplexation on the voltammetric timescale. According to the square Scheme applied to the equilibria of redox switchable host–guest systems, a binding enhancement factor of 4860 could be estimated for the complexation of benzoate by **2** in its oxidized state.[18] Thus, the resulting binding constant for the oxidized receptor would be approximately $\log K_{ass}=7.8$, which is significantly larger than the binding constant determined for **1**, $\log K_{ass}=6.1$ (Table 1). This promising result may mean that, when **1** and **2** are dis-

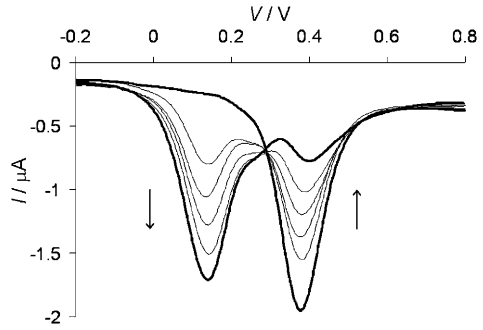

Figure 3. Square wave voltammetry of **2** ($E_p = 0.41$ V) upon addition of benzoate (0–1 equivalents). Scan rate $100\,mV\,s^{-1}$, $[Host] = 5\times10^{-4}$ M in acetone. Supporting electrolyte: $TBAPF_6$ (0.05 M). Potentials are referred to decamethylferrocene (0 V).

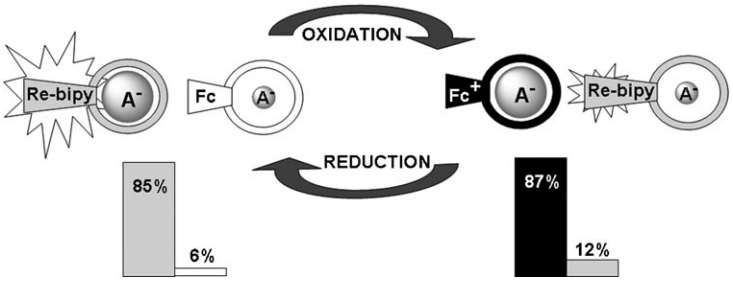

Figure 4. Cartoon representation of the electrochemically driven anion transfer between macrocycles **1** and **2**, accompanied by a variation in the emission intensity of receptor **1**. The size of the encircled anion is related to the percentage of complexed anion by macrocycles **1** and **2**, which is depicted as a column plot.

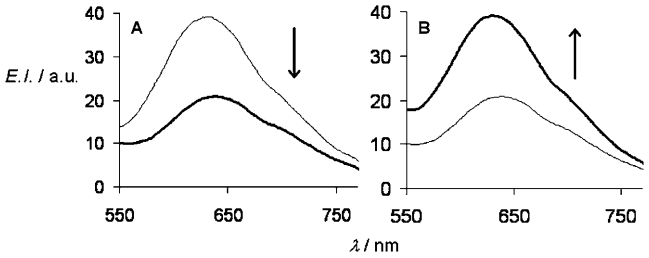

Figure 5. Evolution of the emission intensity ($\lambda_{exc} = 420$ nm, 5×10^{-5} M, $T = 25$ °C) of the mixture **1**/benzoate/**2**/$TBAPF_6$ 1:1:1:200. A) Emission quenching upon oxidation of **2**; B) emission enhancement upon reduction of $\mathbf{2}^+$.

solved together, an anion initially bound to receptor **1** upon oxidation could be transferred to receptor **2**.

Spectroelectrochemical experiments were carried out for a mixture which contained receptors **1**, **2** and benzoate in equimolar concentration (5×10^{-5} M) in acetone. Initially, blank experiments were recorded in order to confirm that no side effects interfered with the experimental requirements of the spectroelectrochemical analysis, such as common ion effect from the supporting electrolyte or emission quenching caused by the presence of $\mathbf{2}^+$ (see the Supporting Information for experimental details).

Interestingly, a noticeable decrease of the luminescence of the **1**/**2**/benzoate/$TBAPF_6$ (1:1:1:200) mixture could be detected when controlled oxidation of the macrocyclic ferrocenophane **2** was carried out by electrolysis at 0.38 V. This emission decrease can be accounted for by the relocation of the benzoate anion from receptor **1** to the oxidized ferrocenium containing receptor $\mathbf{2}^+$. The ferrocenium's positive charge makes a favourable and significant electrostatic contribution to the overall anion-recognition process. Moreover, the positively charged ferrocenium group will also increase the relative acidity of the appended thiourea hydrogen-bond donor groups.[19] Therefore, the combination of stronger hydrogen bonding and electrostatic attraction enhances the anion-binding affinity which facilitates the benzoate anion transferring from receptor **1** to oxidized receptor $\mathbf{2}^+$. Although the emission does not decrease exactly to the level of the free macrocycle **1**, which may indicate that not all the anion is transferred, calculation of the anion distribution shows that the extent of anion transfer is quite significant, with only 12% of the benzoate being now complexed by the Re^I–bipyridinediamide macrocyle (Figure 4).[20]

The reversibility of the anion transfer could be demonstrated (Figure 5). Hence, electrochemical reduction of ferrocenium to ferrocene at −0.2 V was simultaneously accompanied by an enhancement of the emission intensity. Once the receptor **2** recovers charge neutrality, the anion goes back to macrocycle **1** restoring the original anion load distribution.

In conclusion, we have designed and synthesized two macrocyclic anion receptors with the appropriate signaling units to control intermolecular anion transfer by means of an electrochemical stimulus. We have also described a new approach to the control of molecular motion based on hydrogen bonding versus hydrogen bonding plus electrostatic interaction. Currently we are investigating the possibility of integrating these preliminary results, about a forward and back mass transfer, into more elaborated devices.

Experimental Section

See Supporting Information for experimental details.

Acknowledgements

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Keywords: luminescence · macrocycles · molecular devices · molecular recognition · voltammetry

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[13] We decided to use a solvent with a moderate dielectric constant, such as acetone, in order to minimize the effect of the ion-pair dissociation equilibria, but without reaching a highly competitive solvation which would hinder the host–guest interaction. J. W. Jones, H-W. Gibson, *J. Am.Chem. Soc.* **2003**, *125*, 7001. The use of anions as their tetrabutylammonium (TBA) salts also makes possible to assume that this bulky countercation will not form very tight ion pairs.

[14] Binding constants were calculated by non-linear regression of the titration isotherm using the SPECFIT/32 software.

[15] Solubility problems came up when working at the concentration range of the NMR technique (10^{-3} M). Conversely, the solubility of **1** and **2** was good enough when working at more dilute concentration (10^{-4}–10^{-5} M).

[16] Blank experiments revealed that the emission of **1** was not affected by the presence of **2** under our experimental conditions ([**1**]=[**2**]=5×10^{-5} M in acetone; λ_{exc}=400 nm). Thus, we consider that the major cause for the above mentioned emission quenching process would be the removal of the anion from **1**. See the Supporting Information.

[17] For a ternary mixture of **1**, **2** and TBAbenzoate (A^-) in equimolar concentration (5×10^{-5} M) in acetone, having assumed a total dissociation of the TBAbenzoate ion pair (ref. [13]), the two equilibria to be studied are: **1**+A^- ⇄ **1**A^- (K_{1A}) and **2**+A^- ⇄ **2**A^- (K_{2A}). Using

the equations of binding constants and mass balances of all the species in solution, we can calculate the concentration of free anion by solving: $K_{1A}K_{2A}[A^-]^3+(K_{1A}+K_{2A}+K_{1A}K_{2A}[\mathbf{1}]_{tot})[A^-]^2+[A^-]-[A^-]_{tot}=0$. See the Supporting Information. There seems to be a mismatch between the predicted anion distribution and the spectroscopic results which might be due to a secondary process occurring in solution. This is currently under study and it will reported in due course.

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[20] We assume that compound **2** has been completely oxidised to $\mathbf{2}^+$. Therefore, the later and **1** are the two receptors taking part in the anion binding equilibria.

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