Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 5637

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COMMUNICATION

Redox-driven sulfate ion transfer between two tripodal tris(urea) receptors†

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Received 26th April 2011, Accepted 15th June 2011
DOI: 10.1039/c1ob05651d

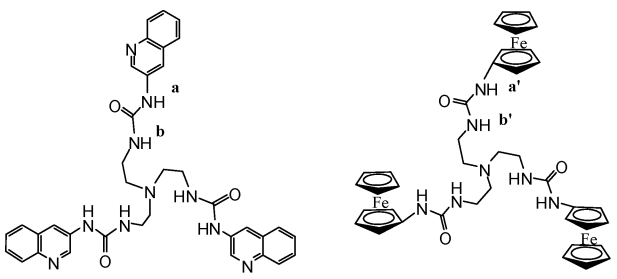
Two anion receptors with the same tripodal scaffold but different signaling groups are employed to control intermolecular anion transfer *via* an electrochemical stimulus, which is detected by the change of the fluorescence intensity before and after electrochemical oxidation of the ferrocenyl units.

A molecular-level machine can be defined as an assembly of a discrete number of molecular components designed to perform mechanical-like movements (outputs) as a consequence of appropriate external stimuli (inputs).[1] In such processes energy inputs, such as chemical energy, electrical energy (redox systems), or light, have to be supplied to make the machine work.[2] Great progress has been achieved in this field during the last decades;[3] however, most of the involved components focus on cations (metal ions and H^+) and organic molecules,[4] whereas research on anions in the area of molecular machines has been relatively limited.[5]

Anion coordination has become an area of significant importance because anions exist extensively in nature and play ubiquitous roles in environmental, life and medical sciences.[6] In recent years, anion-directed assembly of different supramolecular structures has attracted much attention. Beer *et al.*[7] reported the first example of anion templated pseudorotaxane in 2001, which was formed between a macrocycle and ion pair threads through both first- and second-sphere coordination of the chloride ion. The same group also illustrated the sulfate ion templated synthesis of a mechanically bonded triply interlocked capsule.[8]

Redox systems have the ability to adjust host–guest interactions upon electrochemical switching.[9] The ferrocene group has been widely used as an electron probe due to its special properties like reversible electron transfer, thermal stability, aromaticity *etc.*,[10] but such groups have not been commonly utilized in molecular machinery.[11] Recently, two macrocyclic anion receptors with the photo-active Re^{I}-2,2′-bipyridine-4,4′-diamide and redox-active ferrocene-1,1′-dithiourea motifs as signaling units were designed to control intermolecular transfer of the benzoate anion by means of an electrochemical stimulus.[5a] The displacement of a benzoate ion is electrochemically regulated by the oxidation state of the ferrocene unit.

We have been interested in anion recognition and anion coordination, and have synthesized a series of urea-based receptors.[12] Previous work has shown that selective encapsulation of sulfate ion can be achieved by a tripodal tris-urea backbone with different substituents.[12,13] It is known that selective binding of sulfate represents a challenge due to its large hydration energy.[14] In this work, we have chosen two tripodal tris(urea) receptors as candidates for anion motion. The fluorescence (quinolinyl) and electrochemical (ferrocenyl) signaling units were installed to the tripodal backbone to yield the receptors L^1 and L^2 (Scheme 1). These functional groups enable the intermolecular motion of sulfate ion modulated by the redox-controlled non-covalent interactions. The anion is initially complexed only by hydrogen bonds in the neutral state, and after electrochemical oxidation it is bound by both hydrogen bonds and electrostatic attractions.[5] The same tripodal tris(urea) anion-binding backbone was employed to ensure a direct comparison of the binding affinities, and the monitoring of the anion motion is realized by fluorescence measurements. The tripodal tris(urea) receptors L^1 and L^2 were designed and synthesized previously by our group and their detailed anion binding properties were reported elsewhere.[12f,15]



L^1 L^2

Scheme 1 The structure of the receptors L^1 and L^2.

According to previous studies on the anion binding behavior of the two receptors,[12f,15] both L^1 and L^2 showed the largest affinity for SO_4^{2-}, forming the 1 : 1 (host/guest) complexes with association constants of log $K(L^1)$ = 6.21 and log $K(L^2)$ = 5.78 (see also Fig. S3, ESI†) as determined by UV-vis spectroscopy in DMSO solution. Thus, the sulfate binding properties of the two ligands meet the requirement for an unbalanced distribution of the

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† Electronic supplementary information (ESI) available: Experimental procedures, ^{1}H NMR spectra, UV-vis spectra, and cyclic voltammetry (CV) data. See DOI: 10.1039/c1ob05651d

complexed anion between both receptors, and should be suitable for intermolecular anion transfer.

The competitive anion binding of ligands L^1 and L^2 was studied by the ^1H NMR technique in DMSO-d_6 (Fig. 1). After 1 equivalent of SO_4^{2-} was added independently to the solution of L^1 or L^2, the urea NH protons of both receptors showed very large downfield shifts ($\Delta\delta_{NHa}$ 1.68 and $\Delta\delta_{NHa'}$ 1.84 ppm; $\Delta\delta_{NHb}$ 2.15 and $\Delta\delta_{NHb'}$ 2.12 ppm; Fig. 1, A/B and D/E) due to the hydrogen bonding interactions between the receptor and anion. However, when L^1, L^2 and SO_4^{2-} (1 : 1 : 1) were mixed together, slight back shifts ($\Delta\delta_{NHa}$ 1.13 ppm; $\Delta\delta_{NHb}$ 1.59 ppm; Fig. 1C) of the NH protons in L^1 were observed compared to the complex [$L^1 \cdot SO_4^{2-}$]. Noticeably, the urea protons in L^2 recovered remarkably in the ternary mixture $L^1/SO_4^{2-}/L^2$, with chemical shifts close to those of the free ligand L^2 (Fig. 1C). These results indicate that competitive anion complexation equilibria were established between the two receptors, and L^1 showed a much larger binding affinity to sulfate than L^2 in solution. The percentage of [$L^1 \cdot SO_4^{2-}$] existing in the ternary mixture was estimated to be about 83–88% based on the shifts of urea protons, which was consistent with the $K(L^1)$ and $K(L^2)$ obtained from UV-vis titrations (see details in the ESI†).

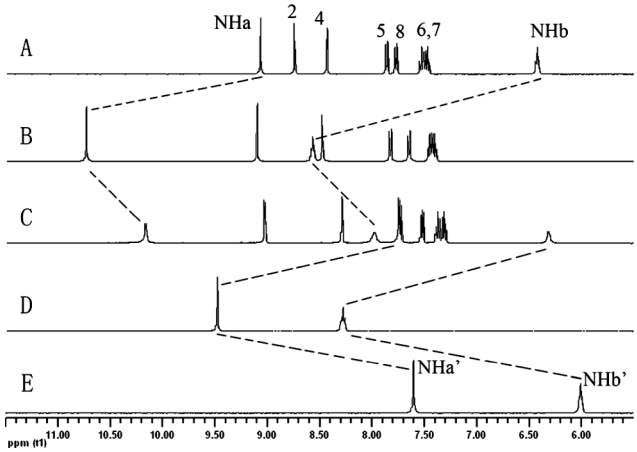

Fig. 1 ^1H NMR spectra of (A) L^1; (B) L^1/SO_4^{2-} 1 : 1; (C) $L^1/L^2/SO_4^{2-}$ 1 : 1 : 1; (D) L^2/SO_4^{2-} 1 : 1; (E) L^2 in DMSO-d_6 (5 mM).

Fluorescence studies of the competitive experiments for L^1 and the neutral state of L^2 were also carried out (Fig. 2). A distinct

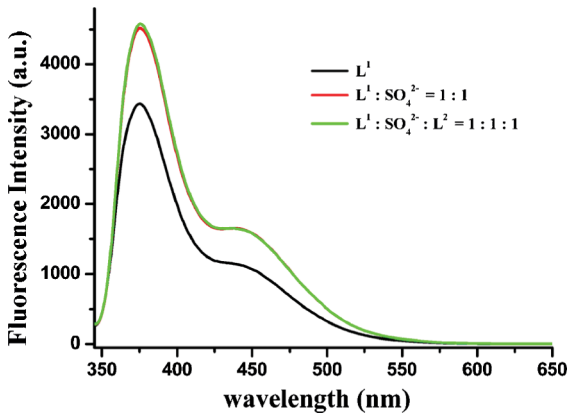

Fig. 2 Emission spectra (λ_{ex} = 335 nm) in DMSO of L^1 (1×10^{-5} M) (black), L^1/SO_4^{2-} 1 : 1 (red) and $L^1/L^2/SO_4^{2-}$ 1 : 1 : 1 (green).

enhancement of the emission intensity was initially detected when sulfate was added to a solution of L^1 due to an increase of the rigidity of L^1 induced by conformational reorganization upon anion binding.[15,16] However, in contrast to the perturbation of L^2 observed in the NMR experiments, the addition of one equivalent of L^2 to the solution of L^1/SO_4^{2-} (1 : 1) induced negligible changes of the fluorescence intensity. This is also different from the Re–bipy system,[6a] wherein some quenching of the fluorescence by the ferrocene-based receptor was observed before oxidation. The different response in the fluorescence (compared to NMR results) of this work might be due to the smaller concentrations used in the fluorescence experiments, in which the faint competition could not be detected. Nevertheless, this property may be beneficial for the detection of the anion motion after oxidation.

In order to achieve efficient intermolecular anion transfer, a critical condition is that the affinities towards anionic guests can be reversed between the two receptors. In the present work, the binding affinities are potentially reversible upon a controlled electrochemical treatment. Firstly, to exclude the interference of the quinolinyl-functionalized receptor L^1 in the electrochemical experiment, L^1 should be electrochemically inactive within the range of potentials to be used for the electrochemistry. This was confirmed by the CV curve of L^1 which showed no electrochemical response in the potential window (Fig. S4, ESI†).

A cyclic voltammetry titration (Fig. S5, ESI†) of compound L^2 with $(TBA)_2SO_4$ revealed an obvious cathodic shift of the ferrocene/ferrocenium reduction peak (ΔE_{pc} = 0.127 V) with a decrease of peak current, indicating strong anion binding. A binding enhancement factor of 140 in DMSO solution could be estimated for the complexation of sulfate with $(L^2)^{3+}$ according to the equation applied to the equilibria of redox switchable host–guest systems.[10] Thus, at the oxidized state, the binding constant would be approximately log $K((L^2)^{3+})$ = 7.93, which is obviously larger than the binding constant of L^1 (6.21).

Since the electrostatic force between the oxidized state of L^2 and anion would enhance the binding affinity which then would switch the competition of the two ligands toward sulfate, a hypothesis could be established that when L^1 and L^2 are dissolved together, an anion initially bound to receptor L^1 may be transferred to receptor L^2 after oxidation. To prove this hypothesis, spectroelectrochemical experiments were carried out for a mixture containing the two receptors and sulfate in equimolar concentration (1×10^{-5} M) in DMSO.

Here again, the side effects that would interfere with the spectroelectrochemical experiment, such as the common ion effect from the supporting electrolyte or emission quenching caused by the presence of L^2 and $(L^2)^{3+}$, should be excluded. Therefore, we carried out a blank experiment (Fig. S6, ESI†): the emission spectra of L^1 and L^1/SO_4^{2-} (1 : 1) were recorded after adding the supporting electrolyte ($TBAPF_6$, 1 mM) to confirm that the presence of hexafluorophosphate anion in 100-fold excess has no effect on the fluorescence results. Fortunately, the emission intensity of a solution containing receptors L^1 and L^2 was indeed not affected by the presence of the supporting electrolyte. Moreover, the emission spectrum of a mixture of $L^1/L^2/TBAPF_6$, *i.e.* in the absence of SO_4^{2-} anion, did not show obvious changes in the emission intensity after the oxidation of L^2 to $(L^2)^{3+}$ (Fig. S6b, ESI†).

As anticipated, a remarkable decrease of the intensity of fluorescence of the $L^1/(L^2)^{3+}/SO_4^{2-}/TBAPF_6$ (1 : 1 : 1 : 100) mixture

(Fig. 3a) was detected when controlled oxidation of the ferrocenyl receptor L^2 was carried out by electrolysis at 0.02 V. This emission quenching can be attributed to the relocation of the sulfate anion from receptor L^1 to the oxidized receptor $(L^2)^{3+}$. The positive charges of the oxidation state of $(L^2)^{3+}$ cause significant electrostatic force which contributes to the anion-recognition process. Furthermore, the positively charged ferrocenium group will also increase the relative acidity of the urea groups.[17] Therefore, the sulfate ion moved from receptor L^1 to the oxidized receptor $(L^2)^{3+}$ because the stronger hydrogen bonding and extra electrostatic attractions result in closer binding between sulfate and $(L^2)^{3+}$. Nevertheless, the emission did not decrease to the level of the free receptor L^1, which may indicate that not all of the sulfate ions were transferred (Fig. 3a). Moreover, electrochemical reduction of ferrocenium to ferrocene at –0.23 V was carried out, which resulted in an enhancement of the emission to the original intensity, suggesting that when the receptor L^2 was recovered to the neutral state, the anion went back to L^1 (Fig. 3b). The reversibility of the anion transfer is demonstrated in Fig. 4.

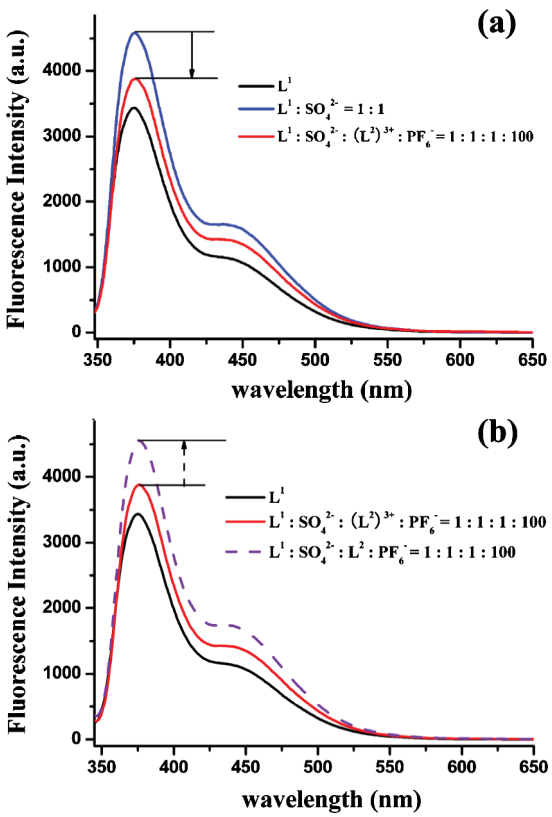

Fig. 3 Evolution of the emission intensity (λ_{ex} = 335 nm, 1×10^{-5} M) of the mixture $L^1/SO_4^{2-}/L^2/TBAPF_6$ (1 : 1 : 1 : 100). (a) Emission quenching upon oxidation of L^2; (b) emission recovery upon reduction of $(L^2)^{3+}$.

A further cycle was attempted, but the oxidized state of L^2 could not capture the sulfate ion from L^1 again as indicated by the fluorescence measurements. This may be due to the receptor L^2 being unstable under the experimental conditions and can partially decompose or deposit on the electrode during the redox processes, which was supported by the NMR spectrum of a solution of $L^1/L^2/SO_4^{2-}/TBAPF_6$ (1 : 1 : 1 : 2, DMSO-d_6, 5 mM) after one

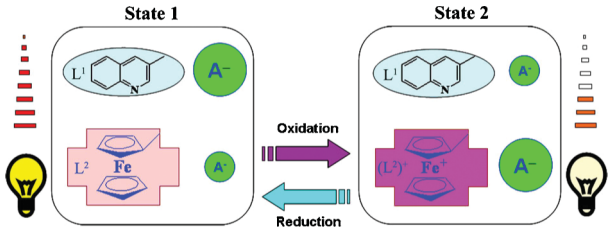

Fig. 4 Cartoon representation of the electrochemically driven anion transfer between L^1 and L^2 (the size of the A^- spheres indicates their relative binding strength to L^1 or L^2).

redox cycle (see ESI for details†) and the observation of deposition of some dark material on the surface of the counter Pt electrode.

In conclusion, we have employed two tripodal tris(urea) anion receptors with similar structure but different signaling units to control and detect intermolecular anion transfer *via* an electrolytic stimulus. This molecular motion is based on hydrogen bonding *versus* hydrogen bonding plus electrostatic interactions. The similar backbone of the two receptors may exclude the interference of different structures, and the results demonstrate that redox-switchable ferrocene groups may be attractive candidates in molecular motion devices.

This work was supported by the National Natural Science Foundation of China (Grant No. 20872149).

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