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Redox induced translocation of a guest molecule between viologen–resorcinarene and β-cyclodextrin

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Abstract

Here we report the design of a three-component supramolecular system in which a guest molecule reversibly translocates between two macrocyclic hosts.

Keywords: Water-soluble calixarenes; Viologen; Host–guest complexes; Molecular machines

The design of various artificial molecular machines has become a scientific area of growing interest during the last decade. Their basic principle is carrying out a machine-like movement under external stimuli.[1] One of the interesting topics of molecular machines chemistry is the design of supramolecular systems in which redox conversions involve molecular movement of one part of the system.[2] Different species are used as redox active parts in molecular machines, for example, metal complexes, quinones, fullerene, tetrathiafulvalenes and viologens.[3] Viologens are well-known electrochromic compounds, which are used widely in molecular machines design because of their ability to undergo two successive reversible one-electron reductions and their dicationic form is an electron-deficient species capable of forming charge-transfer (CT) complexes with electron-donating molecules.[4]

Generally, the stability of viologen CT complexes is not high in solution and only their incorporation into well-organised supramolecular assemblies results in stabilization of the CT structure.[5] For example, attaching viologen units onto a resorcinarene platform leads to the appearance of strong complexation ability towards aromatic compounds due to CT complex formation between viologen units and aromatic guests.[6] The stability of viologen CT complexes can also be controlled electrochemically: the reduction of viologen usually results in destabilization of the CT.[7] This interesting observation prompted us to design a new type of electrochemically controllable molecular machine based on resorcinarene with four viologen units ($\mathbf{1}^{8+}$).[8] The molecular machine consists of two macrocycles ($\mathbf{1}^{8+}$ and β-cyclodextrin (β-CD)) and a guest (1,5-diaminonaphthalene (**2**)). The feature of the molecular machine is reversible translocation of the guest between two macrocycles, depending on the oxidation state of macrocycle $\mathbf{1}^{8+}$. β-CD was chosen as a second macrocycle because its structure is appropriate for the inclusion of **2** inside its cavity and also the hydrophobic interaction between the β-CD cavity and **2** must be weaker than the CT complex between **2** and $\mathbf{1}^{8+}$. One of the most intriguing examples of molecular machine chemistry is the redox driven movement of electroactive cobaltocene between two electroinactive hosts (β-cyclodextrin and *p*-sulfonatocalix[6]arene).[9] In our reported system, the redox inactive guest **2** reversibly translocates between one active and another inactive macrocyclic host, depending on the oxidation state of one of the macrocycles (Scheme 1).

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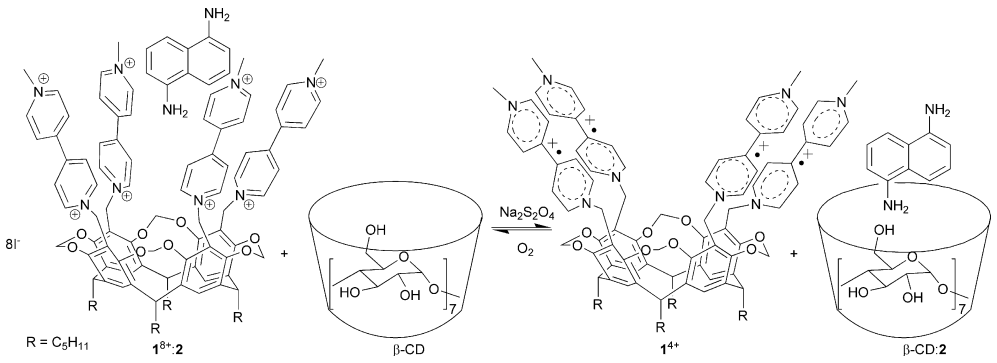

Scheme 1.

It has been found that the water-soluble viologen-resorcinarene $\mathbf{1}^{8+}$ forms stable complexes with **2** in the presence of β-CD. In the ^{1}H NMR spectra, the addition of $\mathbf{1}^{8+}$ to a D_2O solution of **2** leads to a significant upfield shift of the proton signals of **2** showing inclusion complex formation between $\mathbf{1}^{8+}$ and **2** (Fig. 1). The addition of β-CD to a D_2O solution of $\mathbf{1}^{8+}$:**2** does not noticeably shift the proton signals of $\mathbf{1}^{8+}$ and **2** indicating the absence of any interaction between β-CD and complex $\mathbf{1}^{8+}$:**2**. A 2D DOSY experiment confirmed the lack of β-CD influence on the $\mathbf{1}^{8+}$:**2** complex stability: the addition of β-CD to a $\mathbf{1}^{8+}$:**2** solution did not change the diffusion coefficients of the proton signals of $\mathbf{1}^{8+}$ and **2** (Table 1). The reason for the preferable location of **2** on resorcinarene instead of the β-CD cavity is the formation of a charge-transfer complex between the viologen fragments of $\mathbf{1}^{8+}$ and guest **2** which is much stronger ($\lg K_a = 4.6$)[6] than the hydrophobic interaction between **2** and β-CD ($\lg K_a = 2.0$, Supplementary data). K_a can be estimated[†] from DOSY data: $\lg K_a = 1.7 \pm 0.1$ for β-CD + **2** and $\lg K_a = 4.6 \pm 0.1$ for $\mathbf{1}^{8+} + \mathbf{2}$. Both constants are in good agreement with those calculated from the UV-spectroscopy titration data.

Table 1
Diffusion coefficients for **1**, **2** and β-CD and their combinations (D_2O, $c = 5$ mM, $T = 298$ K), $\times 10^{-10}$ m^2 s^{-1}

	D_1 (m^2 s^{-1})	D_2 (m^2 s^{-1})	$D_{\beta\text{-CD}}$ (m^2 s^{-1})
Free compounds	1.5	7.3	2.8
$\mathbf{1}^{8+} + \mathbf{2}$	1.3	1.7	—
β-CD + **2**	—	6.6	2.8
$\mathbf{1}^{4+} + \mathbf{2}$	—	7.2	—
2 + $Na_2S_2O_4$	—	7.4	—
$\mathbf{1}^{8+} + \mathbf{2}$ + β-CD	1.2	1.6	2.7
$\mathbf{1}^{4+} + \mathbf{2}$ + β-CD	—	6.5	2.7

The reported results are the mean value of multiple data points and the standard deviations are less than 0.1×10^{-10} m^2 s^{-1} in all cases.

Treatment of a mixture of $\mathbf{1}^{8+}$:**2** and β-CD with a reducing agent such as sodium dithionite ($Na_2S_2O_4$) results in the appearance of new absorbance bands in the UV–visible spectrum at 350, 520 and 880 nm, these are characteristic features of a viologen cation radical dimer[11] (Fig. 2). This evidence suggests that $Na_2S_2O_4$ reduces the viologen moieties of $\mathbf{1}^{8+}$ with the formation of $\mathbf{1}^{4+}$ where the viologen cation radicals are dimerised on the calixarene platform. The dimerisation of viologen radical cations leads to the destruction of the CT complex between $\mathbf{1}^{4+}$ and **2** with **2** leaving the calixarene cavity: in the ^{1}H NMR spectrum, the addition of $Na_2S_2O_4$ causes the disappearance of the proton signals of resorcinarene due to the paramagnetic nature of $\mathbf{1}^{4+}$ and to a down-field shift of the proton signals of **2** owing to the dissociation of $\mathbf{1}^{4+}$:**2**. Diffusivity data

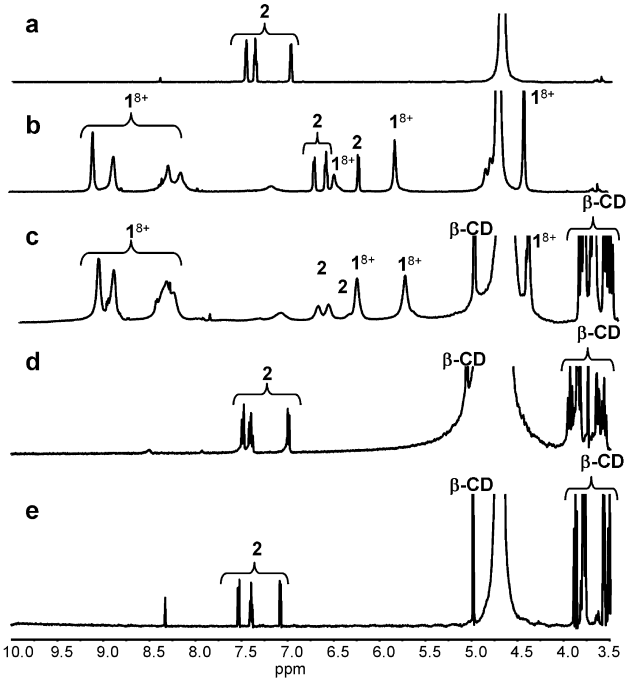

Fig. 1. Fragments of ^{1}H NMR spectra (600 MHz) in D_2O (5 mM) of (a) free guest **2**, (b) $\mathbf{1}^{8+} + \mathbf{2}$, (c) $\mathbf{1}^{8+} + \mathbf{2}$ + β-CD, (d) $\mathbf{1}^{4+} + \mathbf{2}$ + β-CD and (e) **2** + β-CD.

[†] The diffusion coefficient of **2** in the β-CD + **2** system (Table 1) is larger than D of β-CD but less than for free **2**. This is due to fast exchange on the NMR time scale, so the weighted average D is observed for the guest-molecules which are present in two distinct states in solution: monomeric and associated.[10]

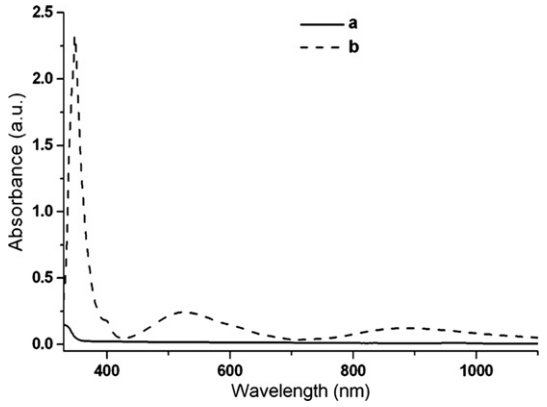

Fig. 2. UV–visible spectra in H_2O (0.01 mM) (1 cm cell) of $\mathbf{1}^{8+} + \mathbf{2} + \beta$-CD before (a) and after (b) addition of $Na_2S_2O_4$.

fully support the above conclusion. Namely, the diffusion coefficient of **2** becomes much larger after the generation of $\mathbf{1}^{4+}$ proving the destruction of the $\mathbf{1}^{4+}$:**2** complex. Moreover, its value is less than for free **2** and indicates the formation of a β-CD:**2** complex due to the interaction of **2** with β-CD (Table 1) with approximately the same K_a as for the pure β-CD:**2** system.

Thus, it seems that the reduction of $\mathbf{1}^{8+}$ results in **2** leaving the $\mathbf{1}^{4+}$:**2** complex by translocation into the β-CD cavity leading to free resorcinarene $\mathbf{1}^{4+}$ and the molecular complex β-CD:**2** ($\mathbf{1}^{4+}$ + β-CD:**2**). Exposure of the reduced ($\mathbf{1}^{4+}$ + β-CD:**2**) system to oxygen reverses the spectral changes and the initial UV–visible and NMR spectra are restored, thus indicating regeneration of the molecular system where **2** is complexed with $\mathbf{1}^{8+}$ and β-CD is free.

In conclusion, we have described a three-molecule system in which reversible translocation of a guest molecule between two macrocycles can be controlled by reduction/oxidation of one of the macrocycles. The obtained results have potential for the construction of redox-controlled nanodevices on surfaces for applications in molecular electronics. We are currently working along this line.

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Supplementary data

The supplementary data include the UV–visible titration profiles of **2** with β-CD and 2D DOSY experimental data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.098.

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