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Electrochemically induced dethreading of a 2-pseudorotaxane based on the 1,2-bis(4,4′-pyridinium)ethane/24-crown-8 ether motif

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Abstract—Reversible electrochemical regulation of dethreading and rethreading of a 2-pseudorotaxane complex composed of a dibenzo-24-crown-8 'wheel' noncovalently bound to the ethyl bridge of a bis-viologen 'axle' is demonstrated by cyclic voltammetry.
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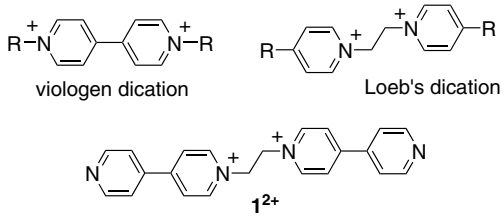
Supramolecular systems that respond to external stimuli by undergoing reversible complexation or translocation events are useful for integration into applications such as molecular logic, information storage and processing or as the active mechanical components in molecular devices and nanoscale functional materials. Rotaxanes, pseudorotaxanes and catenanes have been advertised as some of the best examples of dynamic supramolecular systems because they can act as molecular 'shuttles' and undergo long-range motion along a molecular 'track'.[1–3] Researchers such as Stoddart and co-workers,[4] Sauvage and co-workers,[5] Credi et al.[6] and Brouwer et al.[7] have used chemical, photochemical and electrochemical inputs to trigger changes in the supramolecular makeup of pseudorotaxane and rotaxane systems and have demonstrated the reversible control of threading and translocation processes in these topologically important self-assembled structures.

Threaded systems that are disposed to electrochemical regulation must be constructed from robust redox-active 'wheels' or 'axles' such as those containing the popular dialkylated 4,4′-bipyridinium dication (viologen) substructure. The viologen's role in an 'axle' component typically relies on the electrostatic π–π stacking to electron-rich cyclophanes or hydrogen-bonding and $N^+\cdots O$ interactions to crown ethers. When the viologen dication is electrochemically reduced, the decrease in the noncovalent electrostatic interactions between components results in translocation of the 'wheel' in the case of rotaxanes or dethreading in the case of pseudorotaxanes.



$\mathbf{1}^{2+}$

Loeb and Wisner have described the use of a dicationic axle, in which the nitrogens of the two pyridinium heterocycles are joined together by an ethyl bridge.[8] Unlike their viologen counterparts, threaded systems using this motif are held together by the attraction between the electron deficient *N*-ethyl linker and the electron rich crown ethers. The absence of cation–π interactions is countered by strong $C–H\cdots O$ hydrogen-bonding and $N^+\cdots O$ interactions. Bipyridine analogues such as dication $\mathbf{1}^{2+}$ are instrumental in constructing threaded coordination networks[9] and porphyrin stoppered rotaxanes.[10]

Despite the versatility of systems such as $\mathbf{1}^{2+}$, we are unaware of any reports describing how they respond to electrochemical stimuli. The dication can be easily converted into a redox-active tetracation by alkylating the terminal pyridines of $\mathbf{1}^{2+}$ to produce bis(viologen) $\mathbf{2}^{4+}$, which forms pseudorotaxane **2[DB24C8]**$^{4+}$ when treated with dibenzo-24-crown-8. Here, we report that reduction of a viologen substructure in **2[DB24C8]**$^{4+}$ results in the disassembly of the pseudorotaxane as shown in Scheme 1. This dethreading process is presumably a consequence of weakening the hydrogen bonds

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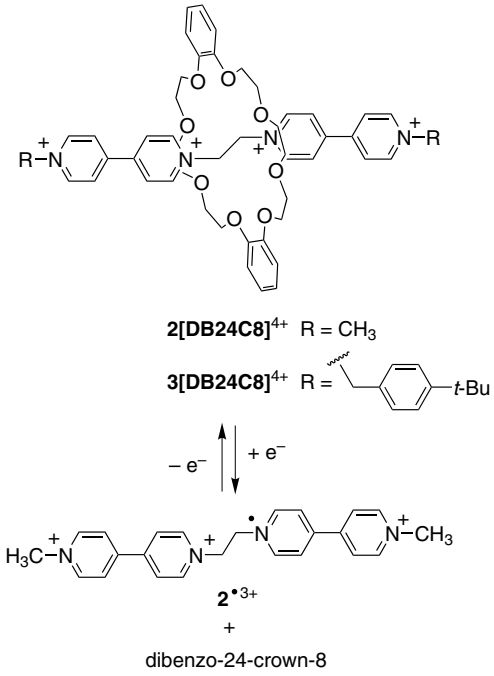

Scheme 1. All counterions are PF_6^-.

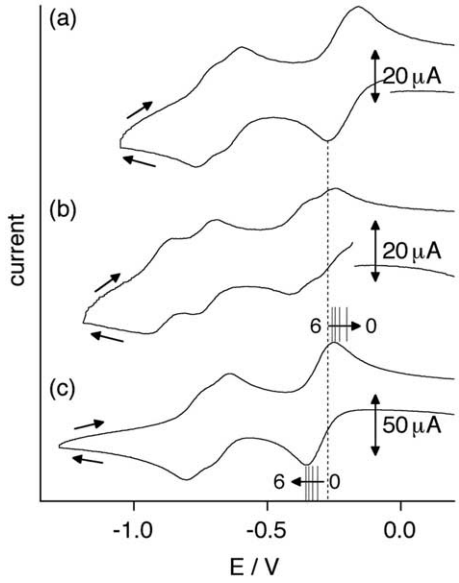

Figure 1. Cyclic voltammograms of CH_3CN solutions of (a) bis(viologen) $\mathbf{3}^{4+}$ (6.0×10^{-4} M), (b) rotaxane **3[DB24C8]**$^{4+}$ (4.5×10^{-4} M) and (c) bis(viologen) $\mathbf{2}^{4+}$ (9.5×10^{-4} M) + 6 equiv 24-crown-8 **DB24C8** at 200 mV/s. The solid vertical lines show the potentials of $\mathbf{2}^{4+}$ alone and with 2, 4 and 6 equiv **DB24C8**.

and the $N^+ \cdots O$ interactions holding the neutral crown ether and the radical trication $\mathbf{2}^{\bullet 3+}$ together.

The formation of **2[DB24C8]**$^{4+}$ is achieved by adding dibenzo-24-crown-8 to a solution of the 'axle' $\mathbf{2}^{4+}$ in acetonitrile. The amount of the pseudorotaxane existing in solution naturally depends upon the quantity of the crown ether added and in the presence of 6 M equiv, all bis(viologen) appears to be threaded as shown by the trends in the ^1H NMR spectra paralleling those already reported by Loeb and co-workers.[8,9] The presence of 100 mM $TBAPF_6$ used as the electrolyte in the electrochemical experiments did not significantly affect the formation of the pseudorotaxane and the ^1H NMR spectrum did not change.

A comparison of the cyclic voltammograms (CVs)[†] of the locked rotaxane **3[DB24C8]**$^{4+}$[11] and pseudorotaxane **2[DB24C8]**$^{4+}$ demonstrates the success of the dethreading process (Fig. 1 and Table 1). Because the sterically encumbering 4-*tert*-butylbenzyl stoppers effectively locks the 'wheel' onto the 'axle' in rotaxane **3[DB24C8]**$^{4+}$, its CV provides an excellent representation of the electrochemical behaviour of pseudorotaxane **2[DB24C8]**$^{4+}$ and serves as a control to determine the effect the crown ether has on the four consecutive reductions of the 'axle'.

The effect of the crown ether is immediately apparent when the CVs of the rotaxane **3[DB24C8]**$^{4+}$ and the 'axle' $\mathbf{3}^{4+}$ alone are compared (Fig. 1a and b). The first reduction potential (−275 mV) of free $\mathbf{3}^{4+}$ corresponds to a two-electron process while a cathodic shift in potential appears for all of the consecutive one-electron reductions in rotaxane **3[DB24C8]**$^{4+}$ presumably due to stabilizing interactions between the components of the complex. It is noteworthy that the current injected for the full reduction of both the free axle and the complexed axle of the rotaxane are comparable (−11.3 C/mol and −10.8 C/mol) and that the presence of the crown ether wheel does not significantly interfere with the heterogeneous electron transfer reaction. Although evidence of direct electron transfer to redox-active components in rotaxanes have been reported before, many systems exhibit a significant decrease in the current intensity and rates of electron transfer as a result of complexation.[12,13] Our result is not surprising as the root of complexation within Loeb's system lies mainly within the ethyl bridge, leaving the redox-active viologens accessible to the electrode.

As expected, the CV of the bis(viologen) $\mathbf{2}^{4+}$ strongly resembles that of $\mathbf{3}^{4+}$. When portions of **DB24C8** are added to the electrochemical cell, there is a systematic cathodic shift of the first reductive and re-oxidative peak potentials. However, the peak does not split into two separate reductions as seen in the CV of the locked rotaxane **3[DB24C8]**$^{4+}$. The shifts of the peak maximize at 45 and 54 mV, respectively, when 6 equiv of the crown are added. The fact that these values are very similar to the difference between the peak potentials between axle $\mathbf{3}^{4+}$ and rotaxane **3[DB24C8]**$^{4+}$ (35 and 85 mV) signifies effective threading between $\mathbf{2}^{4+}$ and **DB24C8**. By combining the fact that the third and fourth reduction potentials and their corresponding oxidations do not shift when the crown ether is added with the observation that the first two-electron reduction is

[†] Electrochemical cyclic voltammetry experiments were performed using a glassy carbon disk working electrode (5 mm diameter), a platinum wire counter electrode, a Ag/AgCl (in a saturated NaCl solution) reference electrode and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. All results were referenced against ferrocene (0.475 V vs SCE).

Table 1. Electrochemical data[a] for compounds $\mathbf{2}^{4+}$, $\mathbf{2}^{4+}$ + **DB24C8** (6 equiv), $\mathbf{3}^{4+}$ and **3[24C8]**$^{4+}$ in CH_3CN

Compound	$E_{red}(1)$	$E_{red}(2)$	$E_{red}(3)$	$E_{red}(4)$	$E_{ox}(1)$	$E_{ox}(2)$	$E_{ox}(3)$	$E_{ox}(4)$
$\mathbf{2}^{4+}$	−311	−311	−732[b]	−802	−724[b]	−639	−194	−194
$\mathbf{2}^{4+}$ + 2 equiv **DB24C8**	−329	−329	−732[b]	−801	−724[b]	−643	−231	−231
$\mathbf{2}^{4+}$ + 4 equiv **DB24C8**	−342	−342	−732[b]	−801	−724[b]	−639	−241	−241
$\mathbf{2}^{4+}$ + 6 equiv **DB24C8**	−356	−356	−732[b]	−801	−724[b]	−640	−248	−248
$\mathbf{3}^{4+}$	−275	−275	−652[b]	−765	−688[b]	−592	−157	−157
3[DB24C8]$^{4+}$	−310[b]	−416	−777	−953	−860	−694	−348[b]	−242

[a] In millivolts referenced against Fc/Fc+.
[b] Shoulder.

cathodically shifted but not split into two distinct peaks, we can conclude that the 'wheel' is decomplexed after the first electron is injected. The cathodic shift of the first electronic reduction, due to the presence of **DB24C8**, promotes the congruency of the second electron reduction of the now free axle component, which is normally reduced at a more positive potential. The labile nature of the mono-reduced form of the complex comes as no surprise since minor alterations to the hydrogen bonding strength of the ethyl bridge, which is strongly dictated by the electron deficiency of the pendant pyridiniums, typically results in relatively large changes in association strengths and rates of association/dissociation processes.[8]

In conclusion, we have demonstrated that complexation within the versatile 1,2-bis(4,4′-pyridinium)ethane/24-crown-8 ether motif can be electronically regulated with the addition and subsequent removal of one electron. Encouraged by the findings that the complex displays limited hindrance to the direct electron transfer reaction, we are now in the process of examining the kinetics for this mode of regulation, which will be reported in due course.

Acknowledgements

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References and notes

1. Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, 2003; pp 348–386.
2. Kaifer, A. E.; Gomez-Kaifer, M. *Supramolecular Electrochemistry*; Wiley-VCH: Weinheim, 1999; pp 142–163.
3. Raymo, F. M.; Stoddart, J. F. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2003; pp 219–248.
4. Badic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1848.
5. Collin, J. P.; Dietrich-Buchecker, C.; Gavina, P.; Molero, M. C. J.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477–487.
6. Credi, A.; Montalti, M.; Balzani, V.; Langford, S. J.; Raymo, F. M.; Stoddart, J. F. *New J. Chem.* **1998**, *22*, 1061–1065.
7. Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. *Science* **2001**, *291*, 2124–2128.
8. Loeb, S.; Wisner, J. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2838–2840.
9. Davidson, G. J. E.; Loeb, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 74–77.
10. Chichak, K.; Walsh, M. C.; Branda, N. R. *Chem. Commun.* **2000**, 847–848.
11. The synthesis and characterization of $\mathbf{3}^{4+}$ and **3[DB24C8]**$^{4+}$ was performed as described in Loeb, S. J.; Wisner, J. A. *Chem. Commun.* **1998**, 2757–2758; The synthesis of $\mathbf{2}^{4+}$ is outlined in: McGeachie, J.; Summers, L. A. *Z. Naturforsch. Teil B* **1986**, *41*, 1255–1259.
12. Kim, H. J.; Jeon, W. S.; Ko, Y. H.; Kim, K. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 5007–5011.
13. Devonport, W.; Blower, M. A.; Bryce, M. R.; Goldenberg, L. M. *J. Org. Chem.* **1997**, *62*, 885–887.