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Enhanced chemical reversibility of redox processes in cyanine dye rotaxanes

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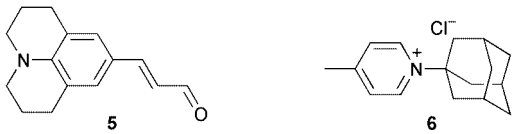
When a cyanine dye is encapsulated inside the cavity of α-cyclodextrin, by rotaxane formation, its one-electron oxidation and reduction become reversible, due to a thousand-fold increase in the kinetic chemical stability of the oxidised and reduced forms of the chromophore.

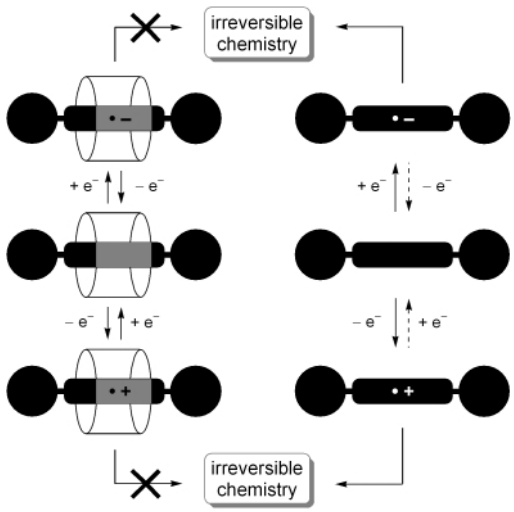
Encapsulation of redox-active guests inside dendrimers and molecular cages often affects the kinetics and thermodynamics of electron transfer, just as the proteins which wrap round biological redox centres control electron transfer in Nature.[1] Conversely, changes in oxidation state can have a dramatic effect on the strength of host–guest interactions.[2] Stoddart and coworkers have used this phenomenon to create rotaxanes[3] which work as molecular machines;[4] oxidation or reduction of the dumbbell component changes the preferred location of the macrocycle, resulting in translational motion. Here we report a redox-active rotaxane which demonstrates a different effect: the macrocycle acts as a protective sheath, preventing the oxidised and reduced forms of the dumbbell from undergoing further chemistry, making both redox processes reversible, whereas in the absence of the threaded macrocycle, the oxidised and reduced forms of the dumbbell are rapidly destroyed by subsequent irreversible reactions (Scheme 1). Electrochemical devices generally require repeated redox cycling without side reactions, so this encapsulation effect may be widely beneficial.

The rotaxanes studied here consist of a cyanine dye dumbbell threaded through α-cyclodextrin. The two rotaxane isomers **1a** and **1b**, and the analogous free dye **2**, were prepared from julolidine aldehyde **3**[5] and diphenylpyridinium **4**[6] as summarised in Scheme 2. This reaction gives a 28% yield of a 3:2 mixture of **1a** and **1b**. Although this yield is modest, it represents a ten-fold improvement compared with our previous synthesis of cyanine dye rotaxanes[7] from aldehyde **5** and adamantylpyridinium **6**. We have also prepared rotaxanes from



the combinations **3** + **6** and **4** + **5**, but **3** + **4** gives the highest yield. The longer julolidine aldehyde **3** probably forms a stronger complex with α-cyclodextrin, with the carbonyl group protruding further through the macrocycle. The diphenylpyridinium **4** also reacts with this aldehyde at a lower temperature than **6**, which leads to a higher yield of dye, as these dyes gradually degrade under the reaction conditions. The two stereoisomers **1a** and **1b** were separated by chromatography and structurally characterised using 2D NMR techniques. The pattern of NOEs shows that the predominant isomer **1a** has the narrower 6-rim of the cyclodextrin towards the julolidine end of the dye, whereas **1b** has the opposite orientation. These NOE results show that the cyclodextrin is located round the reactive polymethine region of the π-system, in both isomers.

The highly conjugated structure of cyanine dyes results in small HOMO–LUMO gaps, making them easy to oxidise and reduce. The one-electron oxidation and reduction potentials ($E_{1/2}^{Ox}$ and $E_{1/2}^{Red}$) and peak absorption wavelengths (λ_{max}) of rotaxanes **1a** and **1b** and free dye **2**, in DMSO, are compared in Table 1.† The different environment around the chromophore in the rotaxanes slightly shifts the absorption, but there is remarkably little variation in the redox potentials. The inclusion of a redox-active guest inside a cyclodextrin often hinders its electrochemical oxidation or reduction,[1] but this effect is not observed in rotaxanes **1a** and **1b**. However, encapsulation has an amazing effect on the electrochemical reversibility of both redox processes, as seen from the cyclic voltammograms of **1b** and **2**, both at a scan rate of 0.2 V s^{-1}, in Fig. 1. The oxidation and reduction of the free dye **2** are chemically irreversible, as shown by the missing peaks in the reverse sweep and by the appearance of a product signal associated with the reduction process at 0.20 V *vs.* Ag. The cyclic voltammogram of the rotaxane **1b** shows that the oxidation and the reduction are now both fully reversible; both processes are well-defined, diffusion controlled, and remain reversible even when the scan rate is reduced to 0.02 V s^{-1}. Identical behaviour is observed for the other rotaxane isomer **1a**. We have tried increasing the scan rate with the free dye **2** in an attempt to achieve reversible



Scheme 1 Rotaxane-encapsulation stabilises the oxidised and reduced forms of the dumbbell, making its electrochemistry reversible.

Table 1 Redox potentials (*vs.* Ag) and λ_{max} for **1a**, **1b** and **2** in DMSO†

Compound	$E_{1/2}^{Ox}$/V	$E_{1/2}^{Red}$/V	λ_{max}/nm
1a	0.75	−0.56	579
1b	0.75	−0.58	590
2	0.74	−0.56	571

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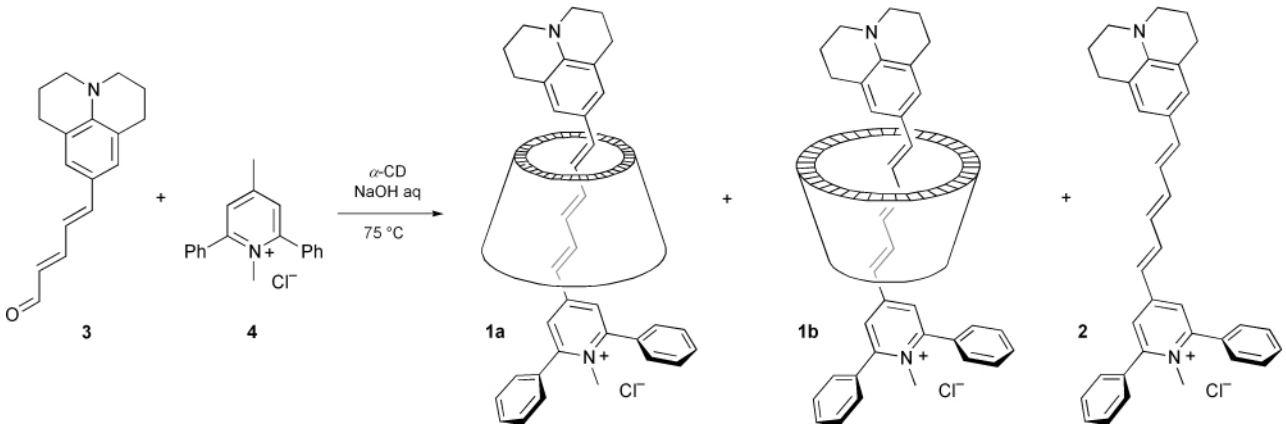

Scheme 2 The cyclodextrin is drawn as a truncated cone with a narrow rim defined by the 6-OH groups and a wide rim defined by the 2,3-OH groups.

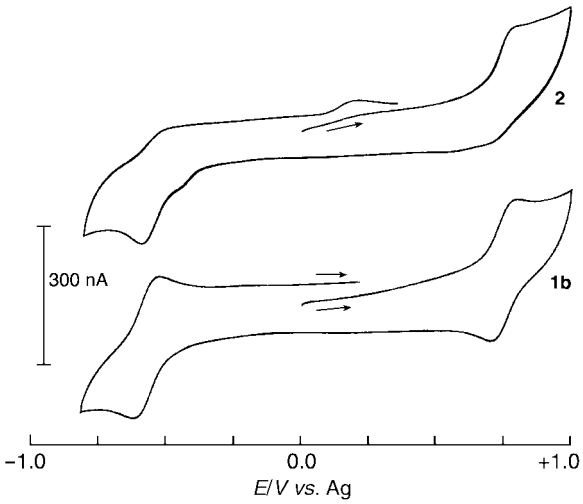

Fig. 1 Cyclic voltammograms for oxidation and reduction of **1b** and **2** DMSO (0.1 M Bu_4NPF_6) with a scan rate of 0.20 V s^{-1}.†

behaviour, and both responses (oxidation and reduction) do indeed become reversible when the scan rate exceeds 20 V s^{-1}. This demonstrates that the shielding effect of the cyclodextrin macrocycle reduces the rate of follow-on reactions of the radical dication and neutral radical forms of the dye by at least three orders of magnitude. The separation between the forward and reverse current peaks (ΔE_p) for both redox processes in both rotaxanes is 78 mV, which is larger than expected for a simple reversible electron transfer process ($\Delta E_p \approx 56$ mV at 298 K). However the peak-to-peak separation does not increase with increasing scan rate, so that there is no evidence that the cyclodextrin retards electron transfer from the electrode surface to the cyanine. These electrochemical measurements were carried out in DMSO (with 0.1 M Bu_4NPF_6) because it is the best solvent for all three compounds. Similar behaviour is also observed in water and in acetonitrile. The rotaxanes **1a** and **1b** are highly soluble in water and give well defined reversible oxidation and reduction signals in this solvent (with 0.1 M KCl electrolyte) whereas the free dye **2** is sparingly soluble in water and exhibits similar irreversible redox processes to those observed in DMSO, complicated by accumulation of material on the electrode surface. In acetonitrile (0.1 M Bu_4NPF_6) the free dye **2** is much more soluble, but its redox processes are still irreversible at 0.2 V s^{-1} scan rate; the rotaxanes are less soluble and tend to adsorb onto the electrode, but both their redox processes remain fully chemically reversible. The electrochemistry of cyanine dyes has been extensively studied because of its relevance to the use of these dyes as photographic silver halide sensitisers.[8] The irreversible oxidation and reduction of **2** is typical for dyes of this type, and fast scan potentiodynamic and AC techniques have been developed to overcome this problem. The irreversiblility of these redox processes is generally attributed to dimerisation of the electrochemically generated radicals, and in a few cases dimeric products have been isolated and characterised.[9]

Previously we have shown that rotaxane formation can enhance the photostability of cyanine dyes. This effect is also observed with these rotaxanes and both compounds fade slower than the free dye **2** when irradiated with visible light in air-saturated aqueous solution (relative rates of fading for **1a**, **1b** and **2** are 0.031 : 0.044 : 1.00 respectively). It is possible that the photo-bleaching of **2** involves photo-induced electron transfer, leading to a direct link between the enhanced photostability and enhanced redox reversibility of these rotaxanes. The mechanisms of these reactions remain to be elucidated but it is significant that rotaxane encapsulation protects the chromophore in both its excited state and in its oxidised and reduced forms. The kinetic stabilisation of the radical dication and neutral radical forms of the dye inside the cyclodextrin cavity is analogous to the stabilisation of radical intermediates by enzymes.[10]

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Notes and references

† The redox potential measurements in Table 1 and Fig. 1 were carried out in DMSO (0.1 M Bu_4NPF_6) by cyclic voltammetry using a conventional three-electrode system with a 0.5 mm diameter Pt disc working electrode, a Pt wire counter electrode and a Ag wire pseudo-reference electrode, under argon at 20 °C. The concentration of **1a**, **1b** and **2** was *ca*. 1 mM. The scan rate was 0.20 V s^{-1} in all cases except for the measurements on **2** in Table 1, where a 20 V s^{-1} scan rate was used to achieve reversibility. $E_{1/2}$ values were estimated from the midpoint of the forward and reverse current peak for each redox process, and were calibrated with internal ferrocene ($E_{1/2}^{Ox}$ = 0.78 *vs*. Ag).

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