A supramolecular assembly controlled by anions: threading and unthreading of a pseudorotaxane

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The pseudorotaxane formed in CH_2Cl_2 solution by (9-anthrylmethyl)methylammonium hexafluorophosphate salt and dibenzo-24-crown-8 can be unthreaded by addition of NBu_4Cl through the formation of a strong ammonium chloride ion pair, while pseudorotaxane rethreading can be performed by addition of $NHBu_3PF_6$; all these processes can be followed by pronounced changes in the luminescence spectra, which could allow the use of this system as a fluorescent sensor for chloride ions.

The association between crown ethers and ammonium salts has been widely studied and employed to synthesise self-assembling supramolecular systems.[1–5] In particular, the remarkable capability of the ammonium–crown interaction to be switched on/off through acid–base equilibria has also been exploited to induce mechanical movements in systems such as rotaxanes and pseudorotaxanes.[6–8] In this context, we previously examined the photophysical properties of adducts between fluorescent ammonium ions and aromatic crown ethers, pointing out that the nature of the counteranion of the ammonium cation could influence its association with crown ethers in low polarity solvents where strong ion pairs are formed. Starting from this point, we have conceived a new way, based on anion exchange, of controlling the threading and unthreading of a previously examined pseudorotaxane.[6,8]

All experiments were carried out in CH_2Cl_2 solution at room temperature. The experimental equipment and procedures have been previously described.[6] PF_6^- and Cl^- salts were prepared from commercial (9-anthrylmethyl)methylamine. The other compounds were commercial products. All fluorescence spectra were appropriately corrected.[9]

We have already reported the absorption and fluorescence spectra of (9-anthrylmethyl)methylammonium (**1**H$^+$) hexafluorophosphate and dibenzo-24-crown-8 (**2**), together with the properties of the adduct they origin.[6] Absorption and fluorescence spectra of **1**·HCl present some differences from those of **1**·HPF_6; in particular, the fluorescence intensity is about 35% weaker and the maximum is shifted from 421 to 419 nm. A decrease in the fluorescence lifetime from 8.5 to 5.5 ns is also observed. These findings give clear evidence for the formation of a highly associated ion pair with Cl^-, since the fluorescence of the anthracene moiety is very sensitive to the electronic density on the nearby nitrogen atom, which can be responsible for electron transfer quenching processes.[10] If 1 equiv. NBu_4Cl is added to a 2×10^{-4} M solution of **1**·HPF_6, a decrease in the fluorescence intensity and lifetime is observed as expected for the formation of the **1**H$^+$Cl$^-$ ion pair. On addition of an excess of the $NHBu_3PF_6$ salt, the fluorescence of **1**H$^+$ increases although it does not reach the initial intensity, because of the competition between **1**H$^+$ and $NHBu_3^+$ to form ion pairs with Cl^- [eqn. (1)].

$$\mathbf{1}\mathrm{H}^+\mathrm{Cl}^- + \mathrm{NHBu_3}^+ \overset{K_\mathrm{exc}}{\rightleftharpoons} \mathrm{NHBu_3}^+\mathrm{Cl}^- + \mathbf{1}\mathrm{H}^+ \qquad (1)$$

An even larger effect of the chloride ion on the fluorescence spectra is observed when **2** is present. If equimolar amounts (2×10^{-4} M) of **1**·HPF_6 and **2** are mixed in a CH_2Cl_2 solution, the adduct **1**H**2**$^+$ PF_6^- is formed, where the fluorescence of **2** is completely quenched by an energy transfer process to the anthracene moiety. On the contrary, in a solution of **1**·HCl (2×10^{-4} M) and **2** (2×10^{-4} M) no association is observed, and, as a consequence, no sensitization of the fluorescence of **1**H$^+$ on excitation of **2** is detected. This behaviour in solution can be described on the basis of equilibria (2) and (3)

$$\mathbf{1}\mathrm{H}^+ + \mathrm{A}^- \overset{K_\mathrm{ip}}{\rightleftharpoons} \mathbf{1}\cdot\mathrm{HA} \qquad (2)$$

$$\mathbf{1}\mathrm{H}^+ + \mathbf{2} \overset{K_\mathrm{as}}{\rightleftharpoons} \mathbf{1}\mathrm{H}\mathbf{2}^+ \qquad (3)$$

where A^- is the counteranion. If K_ip is very large, as it is for Cl^-, equilibrium (3) cannot compete with equilibrium (2), and the adduct with **2** cannot be formed, while if it is small (as for PF_6^-) the adduct formation is observed. This set of equilibria, together with the different affinity of the chloride ions for the different ammonium ions ($NH_2R_2^+ > NHR_3^+ >> NR_4^+$) can be used for controlling the threading and unthreading of this pseudorotaxane. In a solution of **1**·HPF_6 (2×10^{-4} M) and **2** (2×10^{-4} M) the fluorescence of **2** is, as already observed, completely quenched while sensitised fluorescence of **1**H$^+$ is observed (Fig. 1). On addition of 1 equiv. NBu_4Cl the fluorescence of **2** is completely recovered and the sensitised fluorescence of anthracene disappears (Fig. 1). Simultaneously

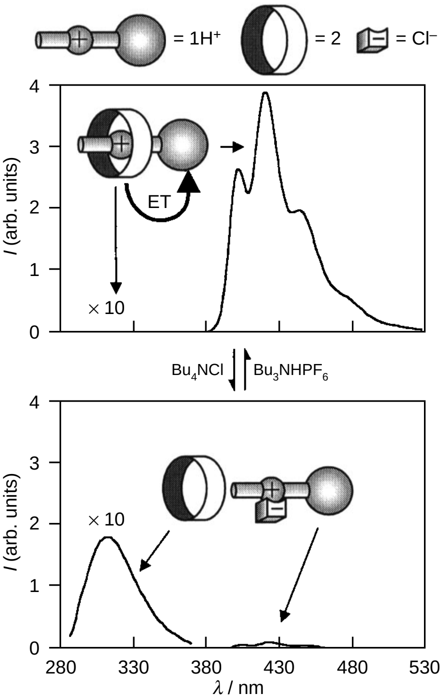

Fig. 1 Changes in the fluorescence spectrum of a CH_2Cl_2 solution of **1**H$^+$ (2×10^{-4} M) and **2** (2×10^{-4} M) upon unthreading and threading of the pseudorotaxane structure caused by addition of NBu_4Cl and $NHBu_3PF_6$, respectively

the anthracene fluorescence (on excitation at λ = 381 nm, where only the anthracene moiety absorbs) decreases to the intensity expected for the **1**H^+Cl^- ion pair formation and the fluorescence lifetime decreases to 5.5 ns. These results indicate that addition of NBu_4Cl leads to the formation of the **1**H^+Cl^- ion pair, preventing the ammonium cation from binding to the crown ether (Fig. 1). Further addition of 1 equiv. $NHBu_3PF_6$ leads again to complete quenching of the fluorescence of **2**, while the **1**H^+ fluorescence intensity and lifetime increase to the initial values, indicating that the pseudorotaxane structure is regenerated. In this case, addition of the $NHBu_3^+$ cation, more strongly bound to Cl^- than to the NBu_4^+ ion, gives rise to equilibrium (1), that, although spontaneously shifted to the left side, can be driven in the presence of **2** to the right side by the occurrence of equilibrium 3, allowing the almost complete formation of the **1**H·**2**$^+$ pseudorotaxane. As can be seen from Fig. 1, dramatic changes in the fluorescence intensities of **1**H^+ and **2** can be observed on every step of the working cycle. This cycle could be repeated several times on the same system, without losing its efficiency, also because tertiary and quaternary ammonium salts cannot compete with **1**H^+ on the association with **2** [equilibrium (3)]. Ion pairing results in a new way of controlling the association of hydrogen bonded supramolecular systems. As a consequence, the pseudorotaxane **1**H**2**$^+$ can be unthreaded and threaded again in three different ways: (i) by adding an acid and then a base, (ii) by adding a base and then an acid or (iii) by adding NBu_4Cl and then $NHBu_3PF_6$. New supramolecular systems could be conceived which, through the combination of these three different modes, would carry out various and complicated logical operations.[11]

Moreover the sensitivity of the ammonium–crown supramolecular systems to the chloride concentration could be usefully employed for the development of new fluorescent chemosensors for chloride ions.[12] Studies in this direction are actually in progress.

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Notes and References

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