Simple molecular-level machines. Interchange between different threads in pseudorotaxanes

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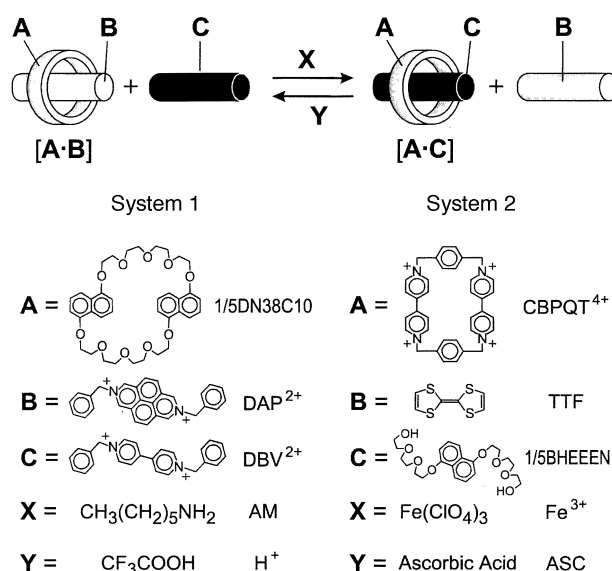[b] School of Chemistry, University of Birmingham, Edgbaston, Birmingham, UK B15 2TT

In suitably designed supramolecular systems, composed of a macrocycle and two different thread-like compounds, it is possible to choose, by means of chemical inputs, which thread enters the macrocycle's cavity, and it is also possible to cause reversible interchange between the two threads. Two such systems are described. In one of them, the macrocyclic component is 1,5-dinaphtho-38-crown-10, the potential threads are 1,1'-dibenzyl-4,4'-bipyridinium and 2,7-dibenzyldiazapyrenium dications, and the chemical input used is amine/acid. In the other system, the macrocyclic component is the tetracationic cyclophane, cyclobis(paraquat-p-phenylene), the potential threads are tetrathiafulvalene and a 1,5-dioxynaphthalene derivative, and the input is reduction/oxidation. These systems are examples of chemically driven molecular-level mechanical machines.

In the last few years, it has been demonstrated that it is possible to design and construct molecular-level systems where the component parts can display changes in their relative positions as a result of some external stimulus, i.e. these systems behave like molecular-level mechanical machines.[1] It has also been shown that, just as in the case of macroscopic machines, three fundamental types of energy can be used to make molecular-level machines work: chemical energy, electrical energy, and light.[1] Pseudorotaxanes,[2] composed of a macrocycle threaded by a thread-like component, are models for simple molecular-level machines since they can undergo threading/dethreading processes that are reminiscent of the acts of threading and dethreading a needle. In previous papers, we have reported the photochemically driven[3] dethreading and the chemically[4] and electrochemically driven[5] cyclic dethreading/rethreading of several pseudorotaxanes. We show here that, in suitably designed systems composed of a macrocycle and two different threads, reversible interchange between the two threads can be achieved (Fig. 1) under the action of an acid/amine or a reduction/oxidation stimulus. Related work on metal ion[4a] and acid[6] control of the threading of two different guests in the cyclobis(paraquat-p-phenylene) cyclophane, and the electrochemical control of host selection in recognition processes[7] have been described.

Results and Discussion

The molecular components which were used in this research are shown in Fig. 1. In system 1, the macrocyclic component (A in Fig. 1) is 1,5-dinaphtho-38-crown-10 (hereafter called 1/5DN38C10) which contains two electron-donor units, and the potential threads, B and C, are the electron acceptors, 2,7-dibenzyldiazapyrenium (DAP^{2+}) and 1,1'-dibenzyl-4,4'-bipyridinium (DBV^{2+}) dications. In system 2, the macrocyclic component A is the tetracationic cyclophane, cyclobis(paraquat-p-phenylene) (CBPQT^{4+}), which contains two electron-acceptor units, and the potential threads B and C are the electron donors tetrathiafulvalene (TTF) and 1,5-bis{2-[2-(2-hydroxy-ethoxy)ethoxy]ethoxy}naphthalene (1/5BHEEEN). In both systems, an important contribution to the formation of pseudorotaxane superstructures comes from $[\pi \cdots \pi]$ stacking interactions between the complementary aromatic units. It is the charge-transfer (CT) interaction associated with the $[\pi \cdots \pi]$ stacking that is responsible[8] for the differences between the photophysical properties of a pseudorotaxane and those of its free molecular components. In particular, pseudorotaxanes (i) show a new, broad absorption band in the visible region, and (ii) do not exhibit the characteristic fluorescence of some of their molecular components (namely, 1/5BHEEEN, 1/5DN38C10, and DAP^{2+}).

Fig. 1 Schematic representation of the reversible interchange between two threads in a pseudorotaxane superstructure along with keys of the molecular components and their abbreviations
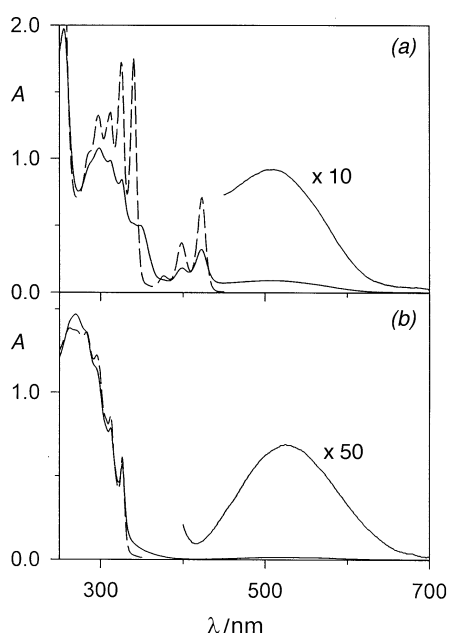
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System 1

Fig. 2(a) shows the absorption spectrum of a CH_2Cl_2/MeCN (9 : 1, v/v) solution 5×10^{-5} M with respect to 1/5DN38C10 and DAP^{2+} compared with the sum of the spectra of the separated components. A new absorption band ($\lambda_{max} = 510$ nm, $\varepsilon_{max} \approx 2000$ M^{-1} cm^{-1}) is present in the solution containing both components as a result of the CT interaction. Similarly, when equimolar (5×10^{-5} M) quantities of 1/5DN38C10 and DBV^{2+} are mixed together in CH_2Cl_2/MeCN (9 : 1, v/v), a new band with a maximum at 525 nm ($\varepsilon_{max} = 650$ M^{-1} cm^{-1}) appears [Fig. 2(b)]. In both cases, the degree of association between the two molecular components to give the pseudorotaxane superstructure[4b,8b,9] [Fig. 3(a), 3(b) process I] can be estimated from the quenching of the intensity associated with the strong fluorescence band of 1/5DN38C10 ($\lambda_{max} = 346$ nm).[10] The values obtained for the stability constant of the adduct were about 2×10^6 M^{-1} for $[1/5DN38C10 \cdot DAP]^{2+}$ and 2×10^4 M^{-1} for
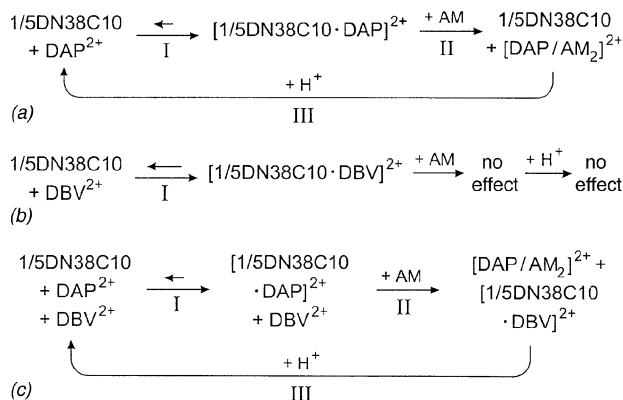
$[1/5DN38C10 \cdot DBV]^{2+}$. Under the experimental conditions used, the fraction of pseudorotaxane superstructure is 90% in the case of DAP^{2+} and 38% for DBV^{2+}.

In a previous investigation,[4b,4e] we found that DAP^{2+} forms strong adducts with aliphatic amines. This affinity was used to promote the chemically induced dethreading of pseudorotaxanes containing the DAP^{2+} unit. When hexylamine at a concentration of 5×10^{-3} M is added to the solution containing the pseudorotaxane $[1/5DN38C10 \cdot DAP]^{2+}$, formation of the adduct between DAP^{2+} and the amine occurs and 100% dethreading of the pseudorotaxane is achieved [Fig. 3(a), process II], as indicated by the appearance of the very intense absorption spectrum ($\lambda_{max} = 595$ nm, $\varepsilon_{max} \approx 7000$ M^{-1} cm^{-1})[4b] of the adduct between DAP^{2+} and the amine and by the total recovery of the luminescence arising from free 1/5DN38C10. This process can be reversed quantitatively by the addition of a stoichiometric amount (with respect to the added amine) of trifluoroacetic acid since protonation of the amine disrupts the interaction with DAP^{2+}, which is then free to thread again with 1/5DN38C10 [Fig 3(a), processes III + I].

Despite its structural similarity with DAP^{2+}, DBV^{2+} does not interact with amines. Addition of hexylamine (5×10^{-3} M) to a solution containing 5×10^{-5} M 1/5DN38C10 and DBV^{2+} does not produce any substantial change in the absorption and emission spectra, except for evidence of the formation of a small amount of DBV^+. The small spectral change observed upon subsequent addition of 5×10^{-3} M trifluoroacetic acid can be attributed to the decomposition in an acid medium of the previously formed DBV^+ species.

The particular behavior of DAP^{2+} with amines has been exploited to construct a machine-like system in which the thread component of a pseudorotaxane is replaced by a different thread under the action of a chemical stimulus. Mixing together 5×10^{-5} M 1/5DN38C10, DAP^{2+} and DBV^{2+} in CH_2Cl_2–MeCN (9 : 1, v/v) causes changes in the absorption and fluorescence spectra identical to those observed for the solution containing only 1/5DN38C10 and DAP^{2+}. Upon addition of hexylamine (5×10^{-3} M), strong spectral changes occur, indicating quantitative formation of the adduct between DAP^{2+} and the amine. The luminescence intensity of 1/5DN38C10 increases, but complete recovery is not achieved; rather, it reaches a level that is the same (within experimental error) of that observed for the solution containing only DBV^{2+} and 1/5DN38C10. These observations indicate that only 84% of the 1/5DN38C10 species initially associated with DAP^{2+} are liberated. The lack of total recovery of the luminescence characteristic of free 1/5DN38C10 can be explained by the fact that, once DAP^{2+} has been engaged quantitatively with the amine, DBV^{2+} can self-assemble with 1/5DN38C10 to give the pseudorotaxane $[1/5DN38C10 \cdot DBV]^{2+}$. The value of the luminescence intensity of 1/5DN38C10 after addition of a 100-fold excess of hexylamine is very similar to that which corresponds to the formation of the pseudorotaxane $[1/5DN38C10 \cdot DBV]^{2+}$ from DBV^{2+} and 1/5DN38C10 under the same experimental conditions. Therefore, the net result is that, in about 16% of the initially formed $[1/5DN38C10 \cdot DAP]^{2+}$ pseudorotaxane species, the DAP^{2+} component is replaced by DBV^{2+} in the cavity of the macrocycle [Fig. 3(c), process II]. The changes in the absorption and fluorescence spectra can be fully reversed by the addition of a stoichiometric amount, with respect to the amine, of trifluoroacetic acid.

In principle, thread exchange could also be monitored by following the disappearance of the CT absorption band of $[1/5DN38C10 \cdot DAP]^{2+}$ ($\lambda_{max} = 510$ nm) and the appearance of a band for $[1/5DN38C10 \cdot DBV]^{2+}$ ($\lambda_{max} = 525$ nm). In practice, this is not possible because the visible spectral region is completely dominated by the absorption bands of the adduct between DAP^{2+} and hexylamine.

Fig. 2 Absorption spectra of CH_2Cl_2–MeCN (9 : 1, v/v) solutions containing (a) 5×10^{-5} M 1/5DN38C10 and DAP^{2+} (full line) compared with the sum of the spectra of the separated components (dashed line), and (b) 5×10^{-5} M 1/5DN38C10 and DBV^{2+} (full line) compared with the sum of the spectra of the separated components (dashed line)

Fig. 3 Schematic representation of the threading/dethreading processes in the systems: (a) 1/5DN38C10 and DAP^{2+}; (b) 1/5DN38C10 and DBV^{2+}; (c) 1/5DN38C10, DAP^{2+} and DBV^{2+}

System 2

Fig. 4 shows the absorption spectrum of a 1×10^{-4} M MeCN solution of TTF and $CBPQT^{4+}$ compared with the sum of the spectra of the separated components. A new absorption band with a maximum in the near IR region ($\lambda_{max} = 855$ nm) is evident in the solution containing both components, on account of the CT interaction present in the pseudorotaxane.[11] Since, in this system, none of the molecular components exhibits fluorescence, the values of ε_{max} for the near IR CT band (ca. 3000 M^{-1} cm^{-1}) and of the stability constant (ca. 1×10^4 M^{-1}) were estimated by fitting the equation corresponding to the equilibrium constant, as a function of the two unknown parameters, to the absorbance values obtained on changing the concentrations of TTF and $CBPQT^{4+}$ from 1×10^{-5} M to 1×10^{-3} M.

Because of the electron donor/acceptor character of the driving force for the self-assembly of the complex $[CBPQT\cdot TTF]^{4+}$ [Fig. 5(a), process I] and the tetracationic nature of the cyclophane component, we anticipated that dethreading could be achieved, as a result of the lack of CT interaction and the presence of electrostatic repulsion, by oxidation of TTF to the radical cation $TTF^{\cdot +}$. Therefore, we have first of all studied the oxidation of TTF by Fe^{3+}. We have found that the absorption spectrum of a 7×10^{-5} M MeCN solution of TTF undergoes strong spectral changes on addition of $Fe(ClO_4)_3$. Two isosbestic points were observed at 331 and 359 nm for addition of less than 1 equiv. of Fe^{3+} with respect to the amount of TTF [Fig. 6(a)]. Between 1 and 2 equivalents of Fe^{3+} another family of curves was obtained, with an isosbestic point at 390 nm [Fig. 6(b)]. We can safely assume that the first set of spectra corresponds to the oxida-
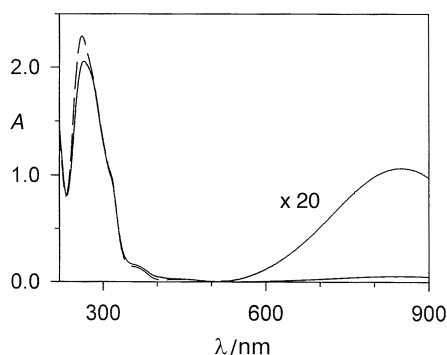

Fig. 6 Spectral changes observed for a 7×10^{-5} M MeCN solution of TTF upon addition of $Fe(ClO_4)_3$: (a) up to 1 equiv.; (b) from 1 to 2 equiv.

tion of TTF to $TTF^{\cdot +}$ and the second one to oxidation of $TTF^{\cdot +}$ to TTF^{2+}.[12,13] Since Fe^{2+} shows negligible absorption bands in the spectral region examined, the spectra obtained after addition of 1 and 2 equiv. of Fe^{2+} can be taken as the spectra of the monocationic $TTF^{\cdot +}$ and dicationic TTF^{2+}, respectively. For $TTF^{\cdot +}$: $\lambda_{max} = 434$ nm ($\varepsilon_{max} = 15000$ M^{-1} cm^{-1}), 577 nm (4000 M^{-1} cm^{-1}); for TTF^{2+}: $\lambda_{max} = 348$ nm ($\varepsilon_{max} = 9000$ M^{-1} cm^{-1}). The values obtained for TTF^{2+} agree with those previously reported,[12] whereas our ε_{max} for $TTF^{\cdot +}$ is about 25% lower than the literature value.[13]

The spectral changes caused by addition of 1 equiv. of $Fe(ClO_4)_3$ to a MeCN solution containing 7×10^{-5} M TTF and 7×10^{-5} M $CBPQT^{4+}$ are shown in Fig. 7. It may be noted that the increase in absorbance in the region of the $TTF^{\cdot +}$ bands is accompanied by a decrease in the region of the CT band, which disappears when all TTF has been oxidized to the monocationic form. At this stage, dethreading of the pseudorotaxane superstructure [Fig. 5(a), process II] has certainly occurred (although direct proof cannot be obtained because the free species do not exhibit any characteristic signal) as a result of the disruption of the CT interaction and presence of an electrostatic repulsion between $TTF^{\cdot +}$ and $CBPQT^{4+}$. Addition of ascorbic acid in aqueous solution

Fig. 4 Absorption spectrum of a 1×10^{-4} M MeCN solution of TTF and $CBPQT^{4+}$ (full line) compared with the sum of the spectra of the separated components (dashed line)
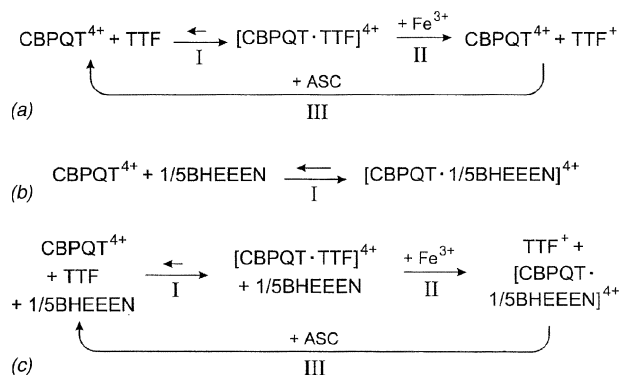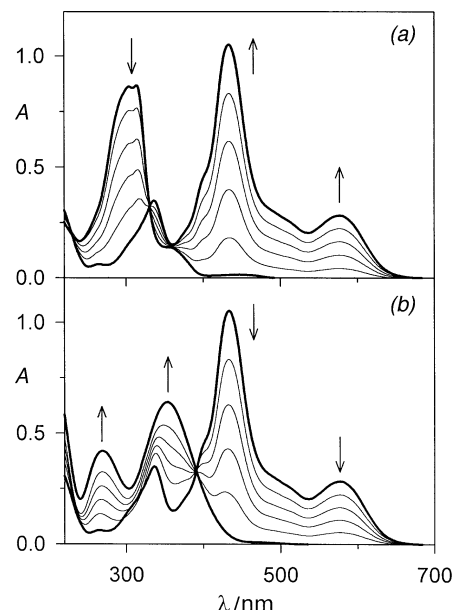

Fig. 5 Schematic representation of the threading/dethreading processes in the systems: (a) $CBPQT^{4+}$ and TTF; (b) $CBPQT^{4+}$ and 1/5BHEEEN; (c) $CBPQT^{4+}$, TTF and 1/5BHEEEN
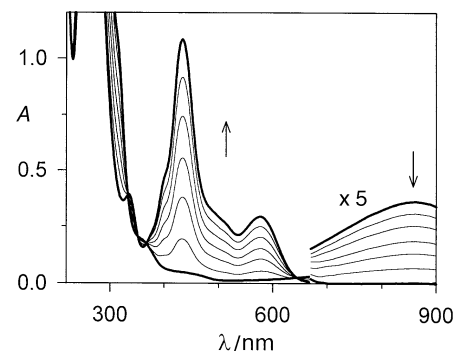

Fig. 7 Spectral changes caused by addition of up to 1 equiv. of $Fe(ClO_4)_3$ to an MeCN solution containing 7×10^{-5} M TTF and 7×10^{-5} M $CBPQT^{4+}$

reverses the spectral changes, indicating that the original pseudorotaxane superstructure is recovered [Fig. 5(a), processes III + I].

The absorption spectrum of an aqueous solution containing 1×10^{-4} M 1/5BHEEEN and $CBPQT^{4+}$ shows a weak broad CT band with $\lambda_{max} = 520$ nm, which is not observed for the separate components. This observation is consistent with the formation of a pseudorotaxane superstructure [Fig. 5(b), process I].[3a,3b] Since quenching of the fluorescence of the 1/5BHEEEN component is also observed, the concentration of free 1/5BHEEEN can be calculated from the residual fluorescence intensity. The ε_{max} of the CT band and the stability constant of the pseudorotaxane species can then be obtained ($\varepsilon_{max} = 550$ M^{-1} cm^{-1} both in H_2O and MeCN; stability constant 8×10^4 M^{-1} in MeCN and 1×10^5 M^{-1} in H_2O). Addition of $Fe(ClO_4)_3$ does not cause any spectral changes.

On the basis of the above results, the combination of $CBPQT^{4+}$ with TTF and 1/5BHEEEN, under appropriate experimental conditions, should lead to the possibility of being able to drive the interchange of the two threads by reduction/oxidation stimulation [Fig. 5(c)]. A necessary condition is, of course, that the stability constant for $[CBPQT \cdot TTF]^{4+}$ formation be higher than that of the $[CBPQT \cdot 1/5BHEEEN]^{4+}$ complex. Since this condition is not satisfied in MeCN, we decided to use H_2O as a solvent. Firstly, we prepared $[CBPQT \cdot TTF]^{4+}$ by stirring 5 mmol of solid TTF in 10 ml of a 5×10^{-5} M solution of $CBPQT^{4+}$ in H_2O. The absorption spectrum obtained after filtration (Fig. 8, curve *a*) is that expected for a 5×10^{-5} M solution of $[CBPQT \cdot TTF]^{4+}$. On addition of $Fe(ClO_4)_3$, spectral changes were observed identical to those previously observed (Fig. 8, curve *b*) for the same system in MeCN. The system can also be driven back to its initial state by reduction of $TTF^{\cdot+}$ with ascorbic acid (Fig. 8, curve *c*).

Addition of 1/5BHEEEN (up to 5×10^{-5} M) to a 5×10^{-5} M aqueous solution of $[CBPQT \cdot TTF]^{4+}$ does not cause any change in the CT absorption band of the pseudorotaxane (Fig. 9, curve *a*). Furthermore, the fluorescence spectrum of 1/5BHEEEN is substantially unaffected. These results indicate that 1/5BHEEEN does not replace TTF in the macrocyclic cavity. On addition of $Fe(ClO_4)_3$ to the above solution, the bands of $TTF^{\cdot+}$ are formed and the CT band of $[CBPQT \cdot TTF]^{4+}$ disappears (Fig. 9, curve *b*), while the fluorescence band of 1/5BHEEEN is substantially quenched (Fig. 9, inset, curve *b*). From a quantitative viewpoint, upon 100% oxidation of TTF, 80% of the fluorescence of 1/5BHEEEN (compared to the fluorescence of free 1/5BHEEEN) is quenched. These results show that oxidation causes dethreading of $TTF^{\cdot+}$ from the $CBPQT^{4+}$ cavity and its replacement by 1/5BHEEEN [as schematically sketched in Fig. 5(c), process II] to a degree that is consistent with the stability constant of $[CBPQT \cdot 1/5BHEEEN]^{4+}$. On subsequent addi-
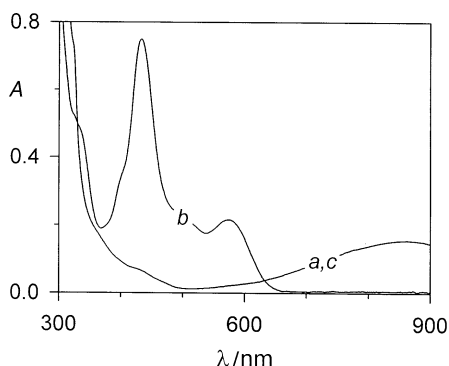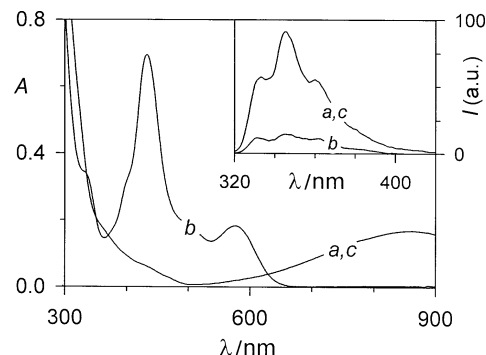
Fig. 9 Absorption and (inset) fluorescence ($\lambda_{exc} = 295$ nm) spectra of: *a*, 5×10^{-5} M aqueous solution of $[CBPQT \cdot TTF]^{4+}$ and 1/5BHEEEN; *b*, the same solution, after addition of 1 equiv. of $Fe(ClO_4)_3$; *c*, solution *b* after addition of 1 equiv. of ascorbic acid

tion of ascorbic acid, the system goes back to its initial conditions [Fig. 9, curve *c*; Fig. 5(c), processes III + I].
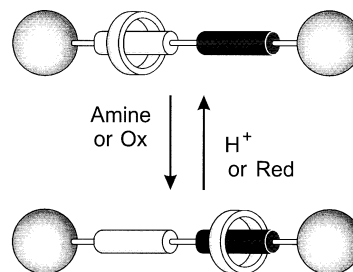
Conclusions

We have shown that in the case of systems constituted by a macrocycle and two potential thread-like components, it is possible to choose, by means of a chemical input, which thread enters the ring's cavity. Since interchanging the thread causes strong spectral changes, the systems behave as chromophoric and/or luminescent molecular switches. The results reported in this paper open the way to the construction of new rotaxanes where the position of the macroring component can be controlled by acid/amine or reduction/oxidation inputs, *i.e.*, chemically driven molecular shuttles[14] (Fig. 10) can be foreseen. While it is difficult to foresee what the practical applications (if any) of these kinds of molecular-level machines might be, we find ourselves able to relate to the conclusion reached by Richard Feynman in his famous address[15] to the American Society of Physics in 1959: *"What would be the utility of such [molecular-level] machines? Who knows? . . . I cannot see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things we can do"*.

Experimental

Chemicals

Merck Uvasol MeCN and CH_2Cl_2 were used as received. Tetrathiafulvalene, hexylamine, trifluoroacetic acid, iron(III) perchlorate, and ascorbic acid were of the best purity

Fig. 8 Absorption spectra of: *a*, 5×10^{-5} M aqueous solution of $[CBPQT \cdot TTF]^{4+}$; *b*, the same solution, after addition of 1 equiv. of $Fe(ClO_4)_3$; *c*, solution *b* after addition of 1 equiv. of ascorbic acid

Fig. 10 Schematic representation of a chemically driven molecular shuttle

commercially available. 1,5-Dinaphtho-38-crown-10,[9b,16] 2,7-dibenzyldiazapyrenium[4b] and 1,1'-dibenzyl-4,4'-bipyridinium[8b] dications (PF_6^- salts), cyclobis(paraquat-*p*-phenylene) tetracation (PF_6^- salt),[3b] and 1,5-bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}naphthalene[3b,8b] were previously prepared and characterized.

Equipment and procedures

Absorption and luminescence spectra were recorded with a Perkin-Elmer λ6 spectrophotometer and an LS50 spectrofluorimeter, respectively. Luminescence lifetimes were measured with an Edinburgh single-photon counting apparatus (D_2 lamp, 300 nm). Correction of the luminescence intensity for inner filter effects was performed when necessary.[10] Experimental errors: absorption and emission maxima, ± 2 nm; extinction coefficients, and luminescence intensities and lifetimes, $\pm 10\%$. All the experiments were carried out on air equilibrated solutions at room temperature.

Acknowledgements

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