Controlled dethreading/rethreading of a scorpion-like pseudorotaxane and a related macrobicyclic self-complexing system

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A scorpion-like pseudorotaxane ($1 \cdot H^{2+}$), composed of a macrocyclic polyether containing a 1,5-dioxynaphthalene (1,5-DON) and a 1,3-dioxybenzene (1,3-DOB) electron-donor unit, the latter bearing a 4,4'-bipyridinium electron-acceptor tail, underwent threading/dethreading motions under control of (i) solvent polarity and (ii) solution acidity. Furthermore, the complexation of $1 \cdot H^{2+}$ with the *trans*-1,2-bis(1-benzyl-4-pyridinio)ethylene electron acceptor can be acid/base controlled. The spectroscopic properties of a related macrobicyclic compound 2^{4+} (comprised of an electron-donor and an electron-acceptor macrocycle that share a benzene ring) have also been investigated. The results obtained for 2^{4+} are consistent with the presence of intramolecular self-complexed species where the electron-donor macrocycle is threaded through the electron-acceptor one. Electrochemical experiments confirm the self-complexing structures of $1 \cdot H^{2+}$ and 2^{4+}. It seems likely that both compounds undergo decomplexation upon electrochemical stimulation.

Introduction

Much attention is currently being devoted to molecular-level systems in which the relative positions of the component parts can change as a result of some external stimulus.[1,2] Such systems could find applications for information processing at the molecular level[3] and can also be viewed as the forerunners of nanoscopic machines.[1g] Appealing examples of chemical compounds where controlled mechanical movements can take place are suitably designed pseudorotaxanes, rotaxanes, and catenanes.[4] It has been shown that, in these systems, the relative displacements of the component parts (i) can be induced by chemical energy, electrical energy and light, and (ii) can be monitored by a variety of techniques including NMR, absorption and emission spectroscopy, and electrochemistry.[1a–c,e–g,2c–f]

Conventional pseudorotaxanes[4] are made of two covalently disconnected components, namely a macrocycle and a thread (Fig. 1a), which contain complementary recognition sites. The threading and dethreading motions can be controlled by an external stimulus capable of switching on/off one of the recognition sites.[5] In the dethreaded state each of the two components, the macrocycle and the thread, are free to move independently in solution. Such a "disordered" situation can nevertheless lead to well defined properties for the supramolecular system, e.g. all the free threads are luminescent whereas the threaded ones are not.[5,6] Therefore, the threading/dethreading process can exhibit binary logic behavior. It has indeed been shown that suitably designed pseudorotaxanes can perform as molecular-level logic gates.[6]

From the machine-like viewpoint, however, the molecular level structure and the movement of the component parts should be spatially well defined. For pseudorotaxane-type systems this goal can be reached in a molecular context by connecting[7] (Fig. 1b) the macrocycle and the thread by a covalent tether. The result is a self-complementary molecule.[8]

Several examples of compounds consisting of a macrocyclic head and a tail that contain complementary recognition sites have recently been studied.[7,9–11] In this paper we report the results of an investigation on the dethreading/rethreading motions of compound $1 \cdot H^{2+}$ and on the self-complexation of the related macrobicyclic compound 2^{4+}, which is comprised of electron-donor and electron-acceptor macrocycles sharing a benzene ring (Fig. 2).

Experimental

Materials

The synthesis and characterization of compounds $1 \cdot H^{2+}$[9b] and 2^{4+}[9a] (Fig. 2) as their PF_6^- salts have been reported previously. The *trans*-1,2-bis(1-benzyl-4-pyridinio)ethylene
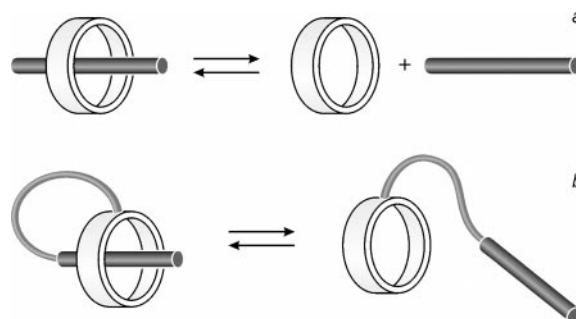

Fig. 1 Schematic representations of (a) a conventional pseudorotaxane and (b) a self-complexing molecule in which a macrocycle is linked by a covalent tether to a tail containing a recognition unit.
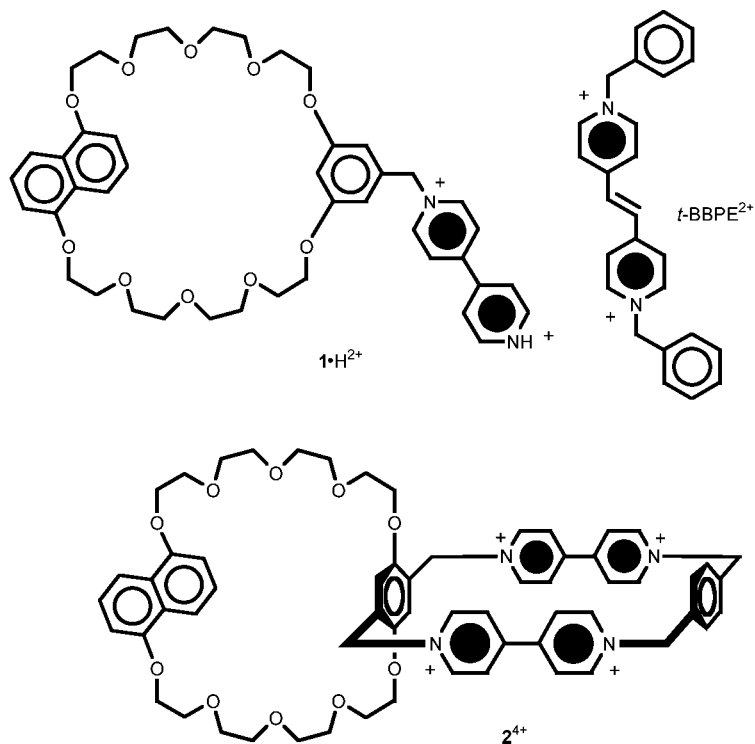
Fig. 2 Structural formulae of the investigated compounds $1 \cdot H^{2+}$ and 2^{4+}, as well as of the t-BBPE^{2+} species that has been used in the experiment described in Fig. 8.

dication[12] (t-BBPE^{2+}, Fig. 2), and model compounds 1,5-dimethoxynaphthalene (1,5-DMN),[13] $3 \cdot 2PF_6$,[14] 4,[12] $5 \cdot 4PF_6$[14] and $6 \cdot 4PF_6$[13] (Fig. 3) were all available from previous investigations. 2,6-Lutidine (2,6-dimethylpyridine), tributylamine (n-Bu$_3$N) and trifluoroacetic acid were of the highest commercial purity used without further purification.

Spectroscopic measurements

Absorption and luminescence measurements were carried out at room temperature in MeCN or CH$_2$Cl$_2$ (Merck Uvasol^{TM})

Fig. 3 Structural formulas of the model compounds $3 \cdot H_2^{4+}$, 4, 5^{4+} and 6^{4+} for the electroactive units of compounds $1 \cdot H^{2+}$ and 2^{4+}.

solutions, or in mixtures of such solvents, with concentrations ranging from 2×10^{-3} to 3×10^{-5} mol L^{-1}. UV-Vis absorption spectra were recorded with a Perkin-Elmer λ16 spectrophotometer, using quartz cells with pathlength 0.2, 0.5, 1.0 or 5.0 cm. Luminescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube, on air-equilibrated solutions. Right-angle excitation with 1 cm × 1 cm square quartz cuvettes and front-face excitation with triangular quartz cells were employed for luminescence experiments carried out on dilute and concentrated solutions, respectively. 1,5-DMN ($\Phi = 0.38$, $\tau = 7.5$ ns in aerated MeCN)[13] was used as a luminescence standard in relative quenching experiments. In these experiments excitation was performed at an isosbestic wavelength for the sample and the standard; when this approach was not possible, corrections for differences in the excitation conditions were applied.[15] Luminescence spectra at 77 K were recorded on a CH$_2$Cl$_2$–MeOH 1 : 1 v/v rigid matrix contained in a quartz tube which, in turn, was immersed in a quartz Dewar, filled with liquid nitrogen. Luminescence lifetimes were measured by time-correlated single-photon counting with Edinburgh Instruments DS199 equipment (D$_2$ lamp, $\lambda_{ex} = 300$ nm). Experimental errors: wavelengths, ± 1 nm; molar absorption coefficients, and luminescence intensities and lifetimes, 15%.

Electrochemical experiments

Conventional electrochemical experiments were carried out in argon-purged CH$_2$Cl$_2$ or MeCN (Romil Hi-Dry^{TM}) solutions at room temperature or at 228 K (by employing a liquid N$_2$/EtOH low-temperature bath) with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments the working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with a 0.05 μm alumina–water slurry on a felt surface, immediately prior to use. In all cases the counter electrode was a platinum spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode (QRE). The potentials reported are
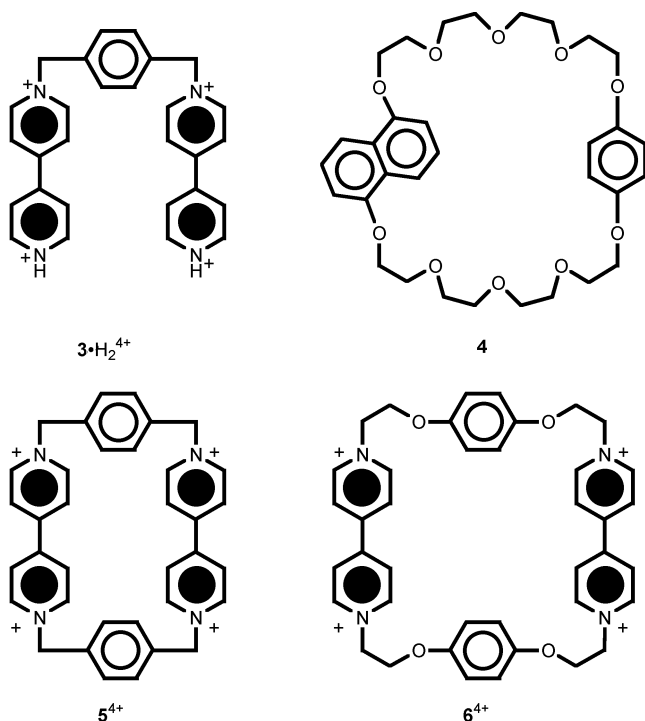
referred to the SCE by measuring the AgQRE potential with respect to ferrocene. The concentration of the compounds examined was of the order of 5×10^{-4} mol L^{-1}; 0.1 mol L^{-1} tetraethylammonium hexafluorophosphate (TEAPF$_6$) and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were added to MeCN and CH$_2$Cl$_2$ solutions, respectively, as supporting electrolytes. Cyclic voltammograms were obtained with scan rates in the range 0.05–10 V s^{-1}; DPV experiments were performed with a scan rate of 0.02 V s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. The number of electrons exchanged in each process was estimated by comparing the current intensity of the corresponding CV wave with that observed for the monoelectronic oxidation of ferrocene, after correction for differences in the diffusion coefficients.[16] The experimental error on the potential values was estimated to be ±10 mV.

Results and discussion

Solvent-driven dethreading/rethreading of compound 1·H^{2+}

Compound 1·H^{2+} (Fig. 2) is composed of a macrocyclic polyether containing a 1,5-dioxynaphthalene (1,5-DON) and a 1,3-dioxybenzene (1,3-DOB) electron-rich unit, the latter bearing a covalently linked 4,4'-bipyridinium electron-deficient tail. As its PF$_6^-$ salt, 1·H^{2+} is highly soluble in MeCN, moderately soluble in CH$_2$Cl$_2$ (at least up to 2×10^{-3} mol L^{-1}), and is thermally stable in both solvents.

In very dilute solutions (3×10^{-5} mol L^{-1}) the absorption spectrum of compound 1·H^{2+} in MeCN at 298 K (Fig. 4, curve a) shows only a very weak tail ($\varepsilon < 70$ L mol^{-1} cm^{-1}) in the visible region and it is very similar to the sum of the spectra of its chromophoric units, namely 1,5-DON, 1,3-DOB, and 4,4'-bipyridinium. On increasing concentration, however, the structure of the 1,5-DON band is lost, the intensity of the tail in the visible spectral region increases and the solution becomes colored. For a 2×10^{-3} mol L^{-1} solution a band with maximum at 480 nm ($\varepsilon = 150$ L mol^{-1} cm^{-1}) can be observed (Fig. 4, curve b).

The absorption spectrum of compound 1·H^{2+} in CH$_2$Cl$_2$ solution is similar, but not identical, to that observed in concentrated MeCN solution (Fig. 4, curve c). In this case, however, the spectrum does not depend on the concentration. The most important feature is the presence of an absorption band in the visible region ($\lambda_{max} = 510$ nm, $\varepsilon = 300$ L mol^{-1} cm^{-1}), responsible for the pink color of the solution.

The different results obtained for MeCN and CH$_2$Cl$_2$ solutions can be accounted for as follows. The absorption bands observed in the visible region are typical[5c,7a,12] of the charge-transfer (CT) interaction between bipyridinium dications and 1,5-DON. In CH$_2$Cl$_2$ the dicationic bipyridinium unit is self-complexed with the macrocyclic part of the molecule, whose
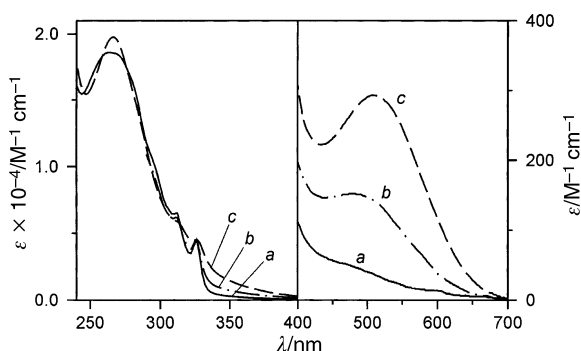
oxygen atoms offer a much more favorable environment than the non-polar solvent molecules (1,1'-dimethyl-4,4'-bipyridinium is highly insoluble in CH$_2$Cl$_2$). Although intermolecular complexation is possible, evidence for intramolecular complexation is given by the fact that the absorption spectrum does not change with concentration.[17] Inspection of CPK (Corey-Pauling-Koltun) space-filling molecular models shows that the bipyridinium tail can easily be accommodated inside the macrocycle. A threaded structure (Fig. 5a) seems therefore more likely than a side-on one (Fig. 5b) because the former facilitates formation of additional [C–H···O] hydrogen bonds between the α bipyridinium hydrogen atoms and some of the polyether oxygen atoms.[18]

In MeCN the dicationic bipyridinium moiety is well solvated by the polar solvent molecules, so that, in dilute solutions, the more stable isomer of compound 1·H^{2+} is the decomplexed one (Fig. 5c). This suggestion is supported by the low values of association constants between aromatic crown ethers and 1,1'-dimethyl-4,4'-bipyridinium in MeCN solution.[19] The weak absorption tail in the visible region observed under such conditions (Fig. 4, curve a) can be assigned to a through-bond CT interaction between the 1,3-DOB moiety of the macrocycle and the appended bipyridinium unit. As the concentration increases, however, intermolecular complexation takes place and a CT band arising from the interaction between the 1,5-DON and bipyridinium units appears.

Evidence for the presence of decomplexed species in dilute MeCN and self-complexed ones in CH$_2$Cl$_2$ is also provided by the fluorescence measurements. Although the intense fluorescence band characteristic of the 1,5-DON unit ($\lambda_{max} = 328$ nm, $\tau = 7.5$ ns in aerated MeCN)[13] is strongly quenched,[20,21] in both solvents, in CH$_2$Cl$_2$ solution the fluorescence intensity quenching is ten times larger than that observed in dilute MeCN solution. This observation suggests that, in CH$_2$Cl$_2$ solution, compound 1·H^{2+} adopts a conformation that maximizes the quenching of the potentially luminescent 1,5-DON unit, as would be the case when the bipyridinium tail is threaded (Fig. 5a) in the crown ether ring.[22] Addition of MeCN to a 5×10^{-5} mol L^{-1} CH$_2$Cl$_2$ solution of 1·H^{2+} causes the disappearance of the visible absorption band and an increase in the fluorescence intensity (Fig. 6), showing that the larger fluorescence quenching observed in CH$_2$Cl$_2$ solution is indeed related to the conformation which is responsible for the presence of the CT absorption band in the visible region. Concentrated (1×10^{-3} mol L^{-1}) MeCN solutions of 1·H^{2+} show a much stronger fluorescence quenching[20] than dilute (2×10^{-5} mol L^{-1}) ones, as expected because of the intermolecular complexation (see above).

In conclusion, the conformation of compound 1·H^{2+} is solvent dependent:[23] the dethreaded conformation is the more abundant one in very dilute solutions of the polar solvent MeCN and the self-threaded[18] one is preferred in the non-polar solvent CH$_2$Cl$_2$. Since the conformational change is accompanied by a visible color change and by a change in the fluorescence intensity, 1·H^{2+} can be viewed as an optical sensor for solvent polarity.

Base/acid-driven dethreading/rethreading of compound 1·H^{2+}

We have shown above that, in CH$_2$Cl$_2$ solution, 1·H^{2+} is present in a self-complexed (threaded)[18] conformation (Fig. 5a). On addition of tributylamine (1 equivalent) or 2,6-lutidine

Fig. 4 Absorption spectrum at 298 K of compound 1·H^{2+} in: (a) 3×10^{-5} mol L^{-1} MeCN solution; (b) 2×10^{-3} mol L^{-1} MeCN solution; (c) 3×10^{-5} mol L^{-1} CH$_2$Cl$_2$ solution.
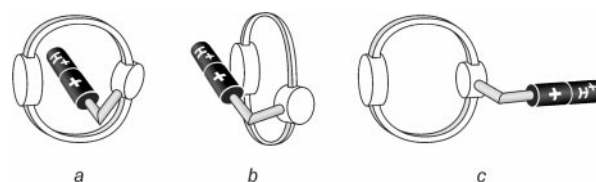
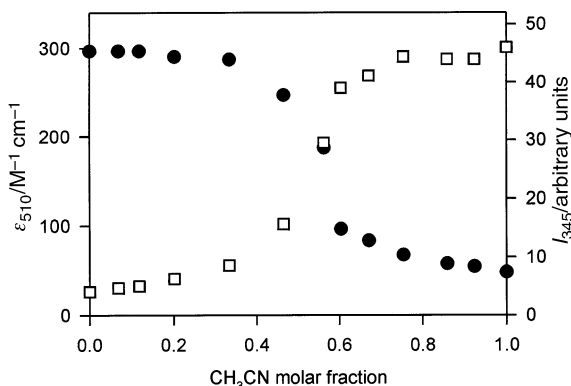**Fig. 5** Cartoons representing the threaded (a), side-on (b) and dethreaded (c) conformations of compound 1·H^{2+}.

Fig. 6 Changes in the absorbance at 510 nm (●) and in the fluorescence intensity at 345 nm (λ_{ex} = 295 nm) (□) upon addition of MeCN to a 5×10^{-5} mol L^{-1} CH$_2$Cl$_2$ solution of compound $1 \cdot H^{2+}$ at 298 K.

(*ca.* 4 equivalents) the CT band at 510 nm completely disappears and the structured bands at 311 and 326 nm, characteristic of the uncomplexed 1,5-DON unit, are recovered. Furthermore, the fluorescence intensity of the 1,5-DON unit partially revives (*ca.* 2.5 times enhancement). Identical titration curves are obtained by plotting the decrease in absorbance of the CT band and the increase in the fluorescence intensity of the 1,5-DON unit *vs.* amine equivalents. This process can be reversed quantitatively by adding an excess of trifluoroacetic acid (*ca.* 6 equivalents with respect to the added amine).

These results can be accounted for as shown in Fig. 7. Upon addition of a base the terminal pyridinium ring of compound $1 \cdot H^{2+}$ undergoes deprotonation, so that the tail becomes a monocationic 4-pyridyl(4-pyridinium) unit. Since a pyridyl unit is not a good electron acceptor, while a pyridinium unit is, this tail is a much poorer electron acceptor than the protonated tail, so that the original CT interaction with the electron donor macrocycle is disabled. At the same time deprotonation makes the tail much more soluble in the non-polar CH$_2$Cl$_2$ solvent. As a consequence, deprotonation causes dethreading, while addition of acid directs the system back to the threaded conformation.[18,24]

Base/acid control of the complexation of an external guest by compound $1 \cdot H^{2+}$

The base/acid driven dethreading/rethreading cycle (see above) has been used to trigger the complexation of an external guest, namely the *trans*-1,2-bis(1-benzyl-4-pyridinio)ethylene electron acceptor (t-BBPE^{2+}, Fig. 2), into the macrocyclic cavity of compound 1^+. In CH$_2$Cl$_2$ solution t-BBPE^{2+} forms a stable (K_{stab} *ca.* 6.5×10^4 L mol^{-1}, as determined from fluorescence titrations) CT adduct with the crown ether 1,5-dinaphtho-38-crown-10 (1,5DN38C10), which contains the same 1,5-DON donor unit that is present in $1 \cdot H^{2+}$. By analogy with many other similar systems,[4a,5c,6a,12,19] this adduct has most likely a pseudorotaxane-type structure. The formation of the adduct can be evidenced by (*i*) the modification of the absorption spectrum with respect to the sum of the spectra of the components, and (*ii*) the quenching of the fluorescence characteristic of 1,5DN38C10.
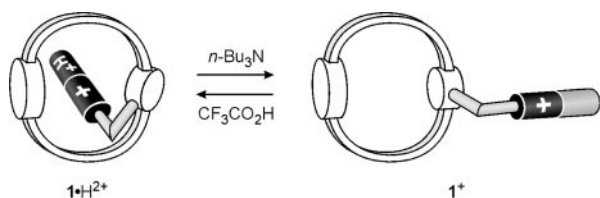
The absorption spectrum of a CH$_2$Cl$_2$ solution containing 3.2×10^{-4} mol L^{-1} compound $1 \cdot H^{2+}$ and 9×10^{-6} mol L^{-1} t-BBPE^{2+} (whose solubility in CH$_2$Cl$_2$ is very low) matches exactly the sum of the spectra of the isolated components in the same concentration. After addition of 6.4×10^{-4} mol L^{-1} tributylamine the absorption spectrum becomes different from the sum of the spectra of the components; in particular, a decrease in the intensity of the absorption bands characteristic of the 1,5-DON unit (311 and 326 nm) and of t-BBPE^{2+} (340–350 nm), and the appearance of an absorption tail in the 350–380 nm region, are observed. These changes are the same as those observed in the absorption spectrum of the solution containing 1,5DN38C10 and t-BBPE^{2+}. Owing to the lack of suitable luminescence signals,[25] it is difficult to assess the amount of t-BBPE^{2+} threaded through 1^+. A rough calculation done on the basis of the absorption tail intensity at 370 nm, compared with that of the 1,5DN38C10/t-BBPE^{2+} system, suggests that t-BBPE^{2+} is quantitatively engaged by 1^+. Evidence of strong complexation comes also from a comparison of low-temperature emission spectra. At 77 K, t-BBPE^{2+} shows an intense and structured fluorescence band that can no longer be seen in frozen solutions which also contain, besides 9×10^{-6} mol L^{-1} t-BBPE^{2+}, 3.2×10^{-4} mol L^{-1} $1 \cdot H^{2+}$ and 6.4×10^{-4} mol L^{-1} tributylamine. This behavior can be explained by the fact that the fluorescence is quenched by low-lying CT levels when t-BBPE^{2+} is encapsulated within the macrocyclic crown ether. Although it is difficult to push this comparison to a fully quantitative level, there is evidence that a large amount of t-BBPE^{2+} is complexed by 1^+.

The results can be rationalized as schematized in Fig. 8. t-BBPE^{2+} is a poorer electron acceptor than the 4,4′-bipyridinium unit;[12] moreover, the latter is entropically advantaged, as it is covalently linked to the host crown ether. Thus, t-BBPE^{2+} cannot dethread compound $1 \cdot H^{2+}$. When tributylamine is added $1 \cdot H^{2+}$ undergoes deprotonation and then dethreading (see above) so that the external guest can enter the open macrocyclic cavity. This process can be reversed by addition of 2.5×10^{-3} mol L^{-1} CF$_3$CO$_2$H: the terminal pyridine unit of 1^+ is protonated and the $1 \cdot H^{2+}$ species undergoes self-threading, pushing t-BBPE^{2+} out of the macrocycle cavity. In conclusion, amines can open and protons can close the 'door' of the macrocyclic cavity of $1 \cdot H^{2+}$, thereby allowing or preventing the threading of an external guest.

Electrochemical behavior of compound $1 \cdot H^{2+}$

The electrochemical behavior of compound $1 \cdot H^{2+}$ was investigated by cyclic and differential pulse voltammetry in MeCN and CH$_2$Cl$_2$. The potentials of the various processes are gath-
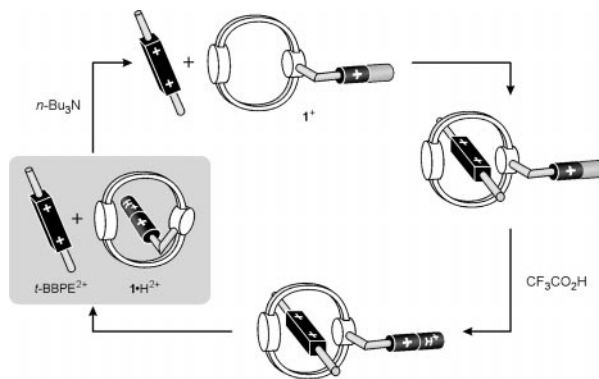

Fig. 7 Base/acid-driven dethreading/rethreading of compound $1 \cdot H^{2+}$.

Fig. 8 Base/acid control of the complexation of t-BBPE^{2+} by compound 1^+.

Table 1 Electrochemical data for compound $1 \cdot H^{2+}$ and its deprotonated form 1^+, and for some model compounds (298 K; working electrode, glassy carbon)

Compound	Solvent	E/V vs. SCE[a]		
$1 \cdot H^{2+}$	CH_2Cl_2	$+1.45^{b,c}$	-0.40	-0.82
$1^{+\,d}$	CH_2Cl_2	$+1.28^{b,c}$	-0.67^b	-0.82
$1 \cdot H^{2+\,e}$	CH_2Cl_2	$+1.51^{b,c}$	-0.42	-0.72
$1 \cdot H^{2+}$	MeCN	$+1.31^{c,f}$	-0.42	-0.80
$1^{+\,d}$	MeCN	$+1.28^{c,f}$	-0.86^c	
$1 \cdot H^{2+\,e}$	MeCN	$+1.30^{c,f}$	-0.44	-0.78
$3 \cdot H_2^{4+}$	MeCN		-0.43^c	-0.79^c
$3^{2+\,d}$	MeCN		-0.82^g	
$3 \cdot H_2^{4+\,e}$	MeCN		-0.47^c	-0.80^c
4	CH_2Cl_2	$+1.48^b$	$+1.28^b$	
4	MeCN	$+1.32^b$	$+1.16^b$	

[a] Halfwave potential values ($E_{1/2}$), unless otherwise noted. [b] Chemically irreversible process; E_p value at scan rate of 0.2 V s^{-1}. [c] Two-electron transfer process. [d] After addition of tributylamine in a stoichiometric amount with respect to the number of protonated 4-pyridyl groups. [e] After addition of tributylamine and subsequent treatment with trifluoroacetic acid in a stoichiometric amount with respect to the previously added amine. [f] At scan rates higher than 1 V s^{-1} this process gains reversibility ($E_{1/2}$ = +1.20 V). [g] Four-electron transfer process.

ered in Table 1, where the values of some reference compounds (Fig. 3) are also reported for comparison purposes.

Under the experimental conditions used (6.0 × 10^{-4} mol L^{-1}), the $1 \cdot H^{2+}$ species adopts a self-threaded conformation in CH_2Cl_2, while in MeCN most of the molecules are involved in intermolecular complexes, as evidenced by the spectroscopic investigation at different $1 \cdot H^{2+}$ concentrations (see above). In both solvents the experimental cyclic voltammetries show two reversible one-electron reduction processes, and a chemically irreversible two-electron oxidation process which becomes reversible only at scan rates higher than 1 V s^{-1} in MeCN solution.
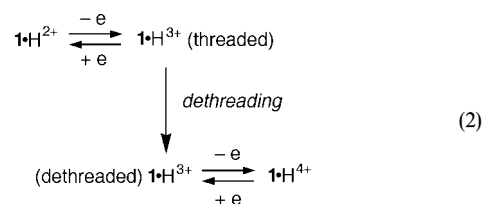
By comparison with model compound $3 \cdot H_2^{4+}$ (Fig. 3, Table 1), which is soluble only in MeCN, we can assign the two reduction processes of $1 \cdot H^{2+}$ to the two successive reductions of the bipyridinium unit. After addition of a stoichiometric amount of tributylamine, the reduction potential is shifted toward more negative potentials, as expected for the pyridyl(pyridinium) unit of the deprotonated form 1^+ (Table 1). It should be noted that, in MeCN solution, after the addition of the amine, both 1^+ and the model compound 3^{2+} show only one peak, which corresponds to the transfer of two electrons. This behavior can be explained tentatively by an ECE (electrochemical–chemical–electrochemical) mechanism, as illustrated in eqn. (1) for 1^+. The monoreduced pyridyl(pyridinium) unit of 1 is protonated by the tributylammonium cation, leading to a $1 \cdot H^+$ species with a standard potential less negative than that of 1^+. Addition of trifluoroacetic acid restores the initial electrochemical pattern, confirming the reversibility of the deprotonation process and the resistance of the system to base/acid stimulation, as observed in the spectroscopic studies.

$$1^+ \underset{-e}{\overset{+e}{\rightleftarrows}} 1$$
$$\updownarrow + H^+$$
$$1 \cdot H^+ \underset{-e}{\overset{+e}{\rightleftarrows}} 1 \cdot H \qquad (1)$$
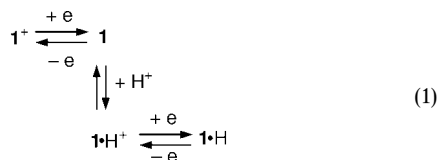
The two-electron oxidation process of compound $1 \cdot H^{2+}$ is likely to involve both the 1,5-DON and 1,3-DOB units. Crown ether 4 (Fig. 3, Table 1) is a satisfactory model for the 1,5-DON, but not for the 1,3-DOB, unit of $1 \cdot H^{2+}$ since (i) 1,3-dimethoxybenzene is oxidized at more positive potentials than 1,4-dimethoxybenzene,[26] and (ii) the 1,3-DOB unit of

$1 \cdot H^{2+}$ bears a 4,4′-bipyridinium substituent. The results show that the oxidation of the 1,5-DON unit of $1 \cdot H^{2+}$ occurs at more positive potentials than in the case of compound 4. This observation is fully consistent with the engagement of the 1,5-DON unit in CT interactions with the 4,4′-bipyridinium unit, and is consistent with the spectroscopic results (see above).

In CH_2Cl_2 solution it might be expected (eqn. 2) that the one-electron oxidized form $1 \cdot H^{3+}$ undergoes dethreading because of electronic repulsions and the disruption of CT interactions. Oxidation of the 1,3-DOB unit should therefore take place in the dethreaded structure, but the lack of suitable model compounds does not allow us to discuss this possibility.

$$1 \cdot H^{2+} \underset{+e}{\overset{-e}{\rightleftarrows}} 1 \cdot H^{3+} \text{ (threaded)}$$
$$\downarrow \text{ dethreading} \qquad\qquad (2)$$
$$\text{(dethreaded) } 1 \cdot H^{3+} \underset{+e}{\overset{-e}{\rightleftarrows}} 1 \cdot H^{4+}$$

Spectroscopic properties of compound 2^{4+}

Compound 2^{4+} (Fig. 2) is composed of two macrocycles sharing a benzene ring. As expected, this tetracationic species exhibits a very poor solubility in CH_2Cl_2 (<5 × 10^{-5} mol L^{-1}). The spectroscopic properties are the same in CH_2Cl_2 and MeCN solutions.

Inspection of CPK space-filling molecular models show that compound 2^{4+} can undergo self-complexation, as indicated in Fig. 9. In the solid state, the 1,5-DON unit is indeed sandwiched between the two bipyridinium units, a structure which is stabilized by π–π stacking interactions and by [C–H···O] hydrogen bonds.[9a] NMR Spectroscopic analysis indicated that such a self-complexed structure is maintained in CD$_3$CN solution at 233 K, and that a high temperature (309 K) rotation can occur about the –CH$_2$–C$_6$H$_2$R$_2$–CH$_2$– axis of the disubstituted p-xylyl group.[9a] The absorption spectrum of 2^{4+} in MeCN solution is shown in Fig. 10, together with the sum of the spectra of its chromophoric component units, taken as 1,1′-dibenzyl-4,4′-bipyridinium, 1,4-dimethoxybenzene and 1,5-dimethoxynaphthalene. The rather intense tail in the 320–400 nm region (ε = 2500 L mol^{-1} cm^{-1} at 350 nm) can be assigned to a through-bond CT interaction between the 1,4-DOB and 4,4′-bipyridinium units, whereas the much weaker and broad absorption band with a maximum at 560 nm compares well with the CT band found for pseudorotaxanes comprised of a 1,5-DON unit threaded through a tetracationic macrocycle containing two 4,4′-bipyridinium units.[5c,7a] These results confirm that the stable conformation of compound 2^{4+} is the self-complexed one (Fig. 9a).

In compound 2^{4+} the fluorescence of the 1,5-DON unit is strongly quenched (>200 times), with a residual emission that, by evaluation of its lifetime, can be assigned to small amounts of 1,5-dimethoxynaphthalene-type impurities.
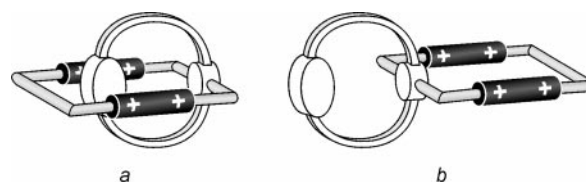

Fig. 9 Cartoon representation of the two possible conformations of compound 2^{4+}.
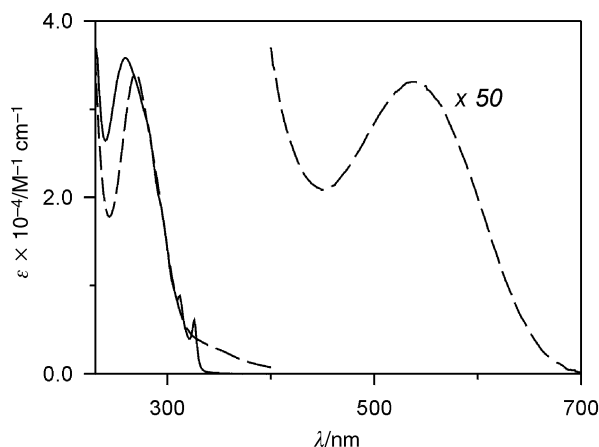
Fig. 10 Absorption spectrum of compound 2^{4+} (dashed line), and sum of the spectra of its chromophoric units, 4,4′-bipyridinium, 1,4-DOB and 1,5-DON (full line) in MeCN at 298 K.

Electrochemical control of the self-complexation process of compound 2^{4+}

The electrochemical behavior of compound 2^{4+} could only be investigated by cyclic and differential pulse voltammetry in MeCN since this compound is not sufficiently soluble in CH_2Cl_2. By comparison with the behavior of compounds 5^{4+} and 6^{4+} (Fig. 3, Table 2), the two reversible reduction peaks of 2^{4+} can be ascribed to successive reduction of the bipyridinium units. Each reduction involves the transfer of two electrons, thus evidencing that the two bipyridinium units of 2^{4+} are electrochemically equivalent. The negative shift of the reduction processes of 2^{4+}, with respect to 5^{4+}, demonstrates the involvement of the bipyridinium units in CT interactions with the electron-donating 1,5-DON and 1,4-DOB groups, as

Table 2 Electrochemical data for compound 2^{4+} and model compounds 4, 5^{4+} and 6^{4+} (MeCN solution, 298 K; working electrode, glassy carbon)

Compound	E/V vs. SCE[a]			
2^{4+}	$+1.62^b$	$+1.50^b$	$-0.40^{c,d}$	-0.80^c
4	$+1.32^b$	$+1.16^b$		
$5^{4+\ e}$			-0.29^c	-0.71^c
$6^{4+\ f}$		$+1.51^{b,c}$	-0.35^c	-0.80^c

[a] Halfwave potential values $(E_{1/2})$, unless otherwise noted. [b] Chemically irreversible process; E_{pa} value at scan rate of 0.2 V s^{-1}. [c] Two-electron transfer process. [d] At 228 K a splitting of this process is observed. [e] Data from ref. 12. [f] Data from ref. 13.

evidenced by the spectroscopic investigations. The occurrence of these kinds of interactions between the bipyridinium and 1,4-DOB units of 2^{4+} is also suggested by comparison with the behavior[13] of macrocycle 6^{4+}. Although the lack of a good model compound for the tetracationic part of the molecule prevents us from entering into a detailed discussion of the results, it is reasonable[6b,7a] to assume that the injection of two electrons into 2^{4+} weakens the CT interaction responsible for self-complexation, thus leading to escape of the 1,5-DON unit from the macrocyclic cavity. Therefore, the successive two-electron reduction should occur on the uncomplexed species (Fig. 11a). An investigation of the cathodic region at 228 K reveals splitting of the first reduction peak. This result is consistent with the presence of two redox couples (complexed and decomplexed $2^{4+/2+}$) that can be interconverted according to a square scheme.[27]

In the anodic region compound 2^{4+} shows two distinct one-electron chemically irreversible oxidation processes that have to involve the 1,5-DON and 1,4-DOB units. Although 4 is a good model for the 1,5-DON unit of 2^{4+}, it is not so good for the 1,4-DOB unit, which carries, in 2^{4+}, strong electron-acceptor substituents.[28] The results show (Table 2) that oxidation of the 1,5-DON unit of 2^{4+} occurs at much more positive potentials than in the case of compound 4. This observation is fully consistent with a self-complexed conformation (Fig. 9a), as suggested by the spectroscopic results (see above). The second oxidation process of 2^{4+} can be assigned to its 1,4-DOB unit. The lack of good model compounds does not allow us to establish whether such an oxidation occurs in the original self-complexed conformation or in the decomplexed one. Clearly, in the one-electron oxidized form 2^{5+}, the presence of electrostatic repulsion and the disappearance of the CT interaction that stabilizes the self-complexed conformation of 2^{4+} are expected to cause escape of the positively charged 1,5-DON unit from the cavity of the tetracationic macrocycle (Fig. 11b).

Conclusion

We have investigated the spectroscopic and electrochemical properties of the scorpion-like compound $1 \cdot H^{2+}$ and of the related macrobicyclic compound 2^{4+}, which is composed of two macrocycles sharing a benzene ring. Both compounds contain electron-donor and electron-acceptor units that promote CT interactions capable of stabilizing self-complexed structures (Figs. 5 and 9). We have shown that $1 \cdot H^{2+}$ can be dethreaded (*i*) by increasing the solvent polarity and (*ii*) by addition of a base. Both $1 \cdot H^{2+}$ and 2^{4+} are also likely to undergo decomplexation/recomplexation upon electrochemical stimulation.
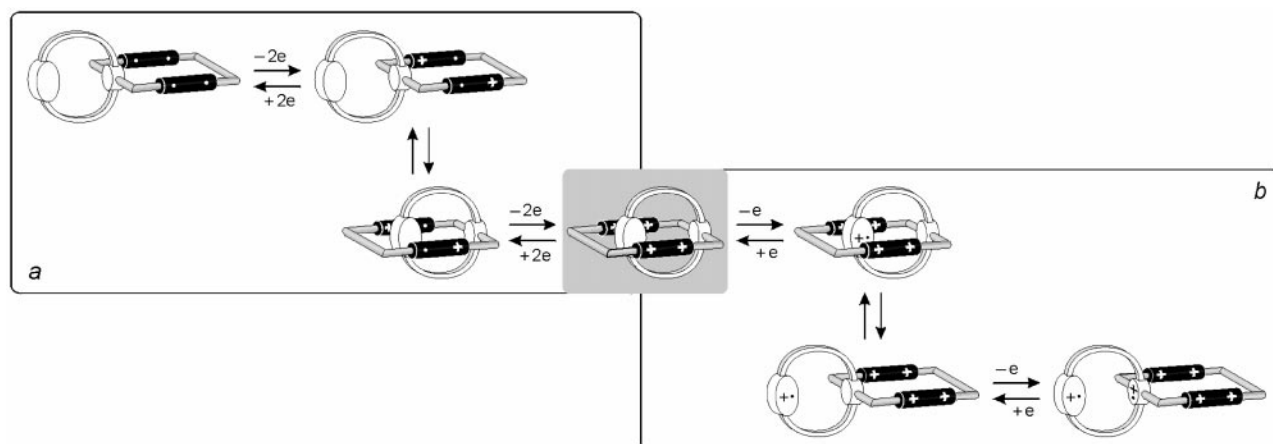

Fig. 11 Scheme of the electrochemically controlled mechanical movements that can take place in compound 2^{4+}.

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