Simple Mechanical Molecular and Supramolecular Machines: Photochemical and Electrochemical Control of Switching Processes**

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Abstract: Photochemical control of a self-assembled supramolecular 1:1 pseudorotaxane (formed between a tetracationic cyclophane, namely the tetrachloride salt of cyclobis(paraquat-*p*-phenylene), and 1,5-bis[2-(2-(2-hydroxy)ethoxy)ethoxy]naphthalene) has been achieved in aqueous solution. The photochemical one-electron reduction of the cyclophane to the radical trication weakens the noncovalent bonding interactions between the cyclophane and the naphthalene guest—π–π interactions between the π-electron-rich and π-electron-poor aromatic systems, and hydrogen-bonding interactions between the acidic α-bipyridinium hydrogen atoms of the cyclophane and the polyether oxygen atoms of the naphthalene derivative—sufficiently to allow the guest to dethread from the cavity; the process can be monitored by the appearance of naphthalene fluorescence. The radical tricationic cyclophane can be oxidized back to the tetracation in the dark by allowing oxygen gas into the system. This reversible process is marked by the disappearance of naphthalene fluorescence as the molecule is recomplexed by the tetracationic cyclophane. This supramolecular system can be chemically modified such that the π-electron-rich unit, either a naphthalene derivative or a hydroquinone ring, and the tetracationic cyclophane are covalently linked. We have demonstrated that the π-electron-rich residue in this system is totally "self-complexed" by the cyclophane to which it is covalently attached. Additionally, the self-complexation can be switched "off" and "on" by electrochemical two-electron reductions and oxidations, respectively, of the tetracationic cyclophane component. Thus, we have achieved the construction of two switches at the nanoscale level, one driven by photons and the other by electrons.

Keywords
luminescence · photochemistry · redox chemistry · self-assembly · self-complexation · template syntheses

Introduction

In everyday life, we make extensive use of macroscopic devices called "machines". They are assemblies of components designed to achieve specific functions. The concept of a machine can be extended to the molecular level.[1–6] The machines of the macroscopic world are designed and constructed by mechanical engineers. Molecular machines, which have dimensions on the nanometer scale, are constructed by molecular engineers, that is, chemists. Molecular machines, like macroscopic machines, need energy to operate. For several reasons, the most convenient forms of energy to make molecular machines work are light and electricity. In this paper, we describe some studies aimed at the construction of simple photochemically and electrochemically driven molecular machines that could play a role in storing and processing information at the molecular level.[7]

The design of molecular machines can take advantage of the concepts of self-assembly,[8] self-organization,[9] and self-replication,[10] which synthetic chemists are adopting as part of their toolbox for chemical manipulation and transformation.[11] Nature uses these concepts, sometimes in conjunction with en-

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zymes, to create her hierarchy of structures and superstructures. Our research efforts have been directed toward developing systems that rely on these concepts and which are totally unnatural in their chemical design. To this end, we have been involved in the self-assembly of the so-called catenanes,[1,2] rotaxanes,[1,3] and pseudorotaxanes.[14] Until recently, the synthesis of such structures was very inefficient, since the syntheses relied upon a statistical approach.[15] However, with the advent of supramolecular chemistry,[16] host–guest chemistry,[17] and template-directed synthesis[18] such compounds and complexes can be self-assembled routinely in the laboratory.[19] The mutual stereoelectronic recognition of the component parts that form the new catenanes and rotaxanes "lives on" in their molecular structures. This memory phenomenon can be observed in these novel compounds by physical techniques like ^{1}H NMR spectroscopy[20] and X-ray crystallography.[21]

The exploitation of noncovalent bonding interactions—namely π–π interactions[22] and hydrogen-bonding interactions[23]—has led to the construction of so-called molecular shuttles and switches.[24] In these molecular devices, the architecture of the catenanes and rotaxanes in solution can be controlled by i) the dielectric constant of the solvent media,[25] ii) photons,[26,27] iii) electrons,[28,29] or iv) protons[28,30]. Figure 1 depicts the structural formulae of a controllable [2]catenane[25] **1**·4PF$_6$ and a controllable [2]rotaxane[28] $\mathbf{2}^{4+}$. Simple mechanical molecular machines based on other types of catenanes have also been reported.[31,32]

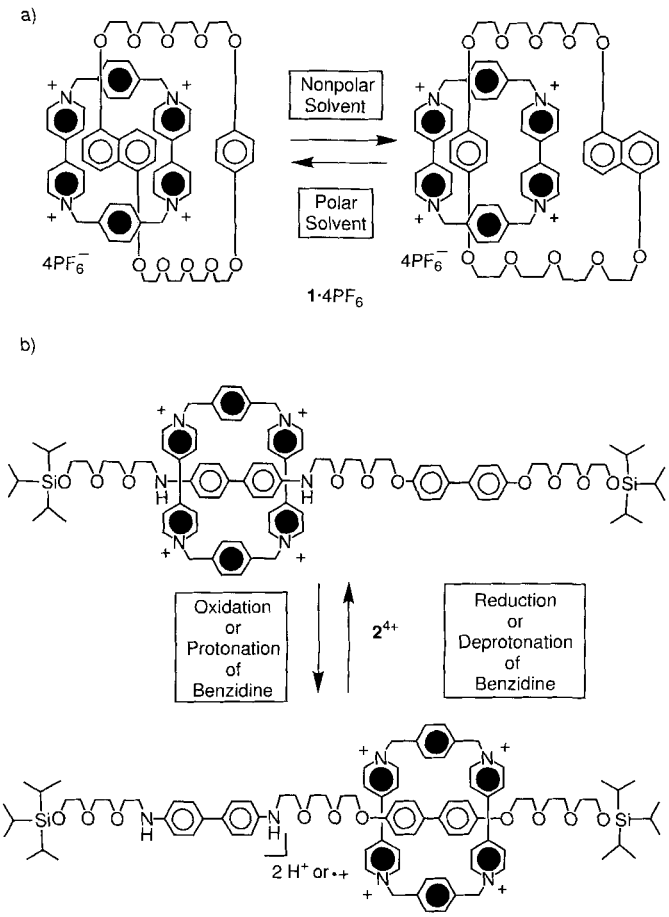


Fig. 1. A [2]catenane **1**·4PF$_6$ and a [2]rotaxane $\mathbf{2}^{4+}$, which have been shown to act as binary molecular switches when affected by an external stimulus, e.g., in the case of a) the [2]catenane **1**·4PF$_6$ by changing of the dielectric constant of the solvent, and b) the [2]rotaxane $\mathbf{2}^{4+}$ by protonation/deprotonation of the secondary amino function associated with the benzidine residue. For the latter compound, switching can also be achieved by benzidine oxidation/reduction.

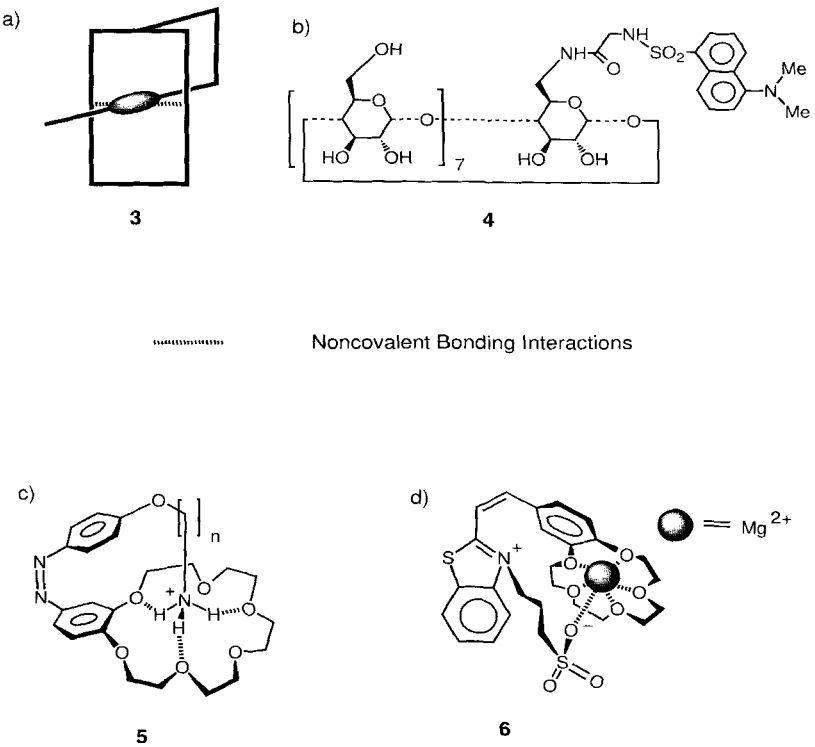
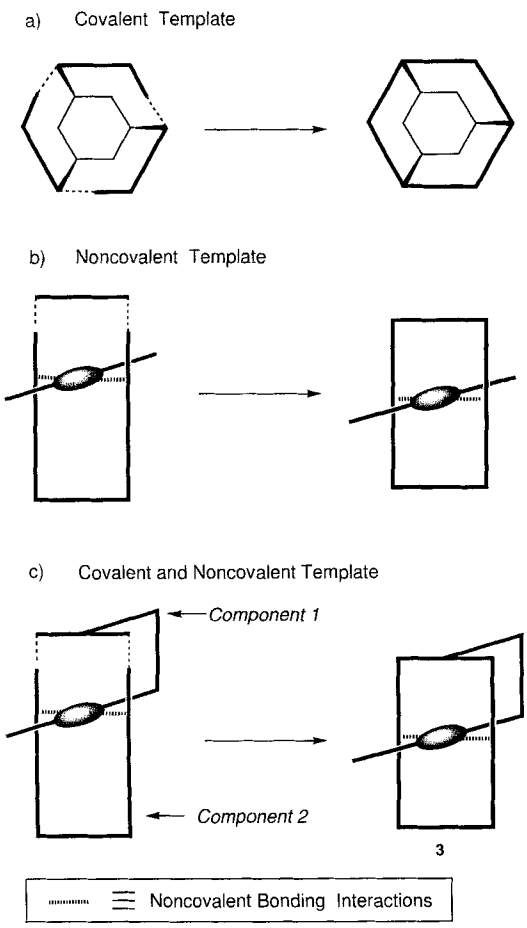


Fig. 2. Representations of chemical systems exhibiting self-complexing geometries. a) Cartoon representation of a self-complexing macrocycle **3** in which the noncovalent bonding interactions are the same as those that bring together the components of catenanes and rotaxanes. b) Self-complexed macrocycle **4**, where the cyclic entity is a β-cyclodextrin and the arm is terminated by a disubstituted naphthalene ring system. c) Self-complexed macrocycle **5**, in which the cyclic component is a crown ether that binds a primary alkylammonium center by (N$^+$–H···O) hydrogen bonding interactions. d) Self-complexed macrocycle **6**, in which the appended arm is linked by electrostatic interactions to a positively charged metal cation.

In this paper, we report the synthesis of self-complexed compounds depicted by the cartoon **3** in Figure 2. Other types of compounds (**4**, **5**, and **6** in Figure 2) that display "self-complexing" properties have already been synthesized. The synthesis of such compounds involves attaching the "arm" component to a preformed macrocycle; the arm then becomes included in the cavity as a result of i) hydrophobic interactions[33] (**4**, Figure 2), ii) hydrogen bonding[34] (**5**, Figure 2), or iii) ionic interactions[35] (**6**, Figure 2). In our case (**3**, Figure 2), the macrocyclic component forms with the aid of noncovalent bonding interactions around a template that is covalently linked to one of the macrocyclic precursors. Thus, the covalent[36] (Scheme 1a) and noncovalent[18,37] (Scheme 1b) template strategies can be combined (Scheme 1c) to form macrocycles of the type **3** with self-complexing topologies. We show that one of the compounds synthesized by the combined covalent and noncovalent strategy behaves as a molecular machine in which the



Scheme 1. Representation of a) a covalent template, b) a noncovalent template, and c) a combination of both templates in operation during the self-assembly of a self-complexing macrocycle.

switching process can be controlled by electrochemical means. Furthermore, we describe in detail the behavior of a photochemically driven supramolecular machine based on a self-assembled [2]pseudorotaxane.[26]

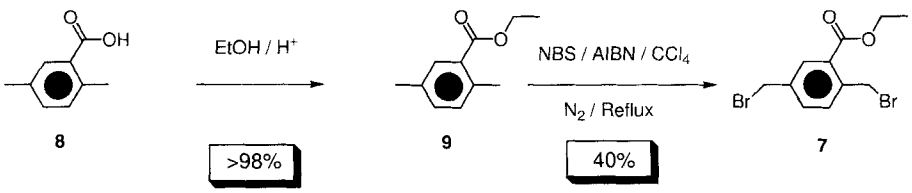
The construction of photochemically and electrochemically driven molecular and supramolecular machines shows the versatility of the self-assembly approach for the fabrication of nanometre-scale systems that could ultimately play a role in storing, processing, and transmitting information at the molecular level and beyond.[1-7]

Results and Discussion

Synthesis of precursors and self-assembly of macrocycles: In order to self-assemble self-complexing macrocycles following the template-directed methodology depicted in Scheme 1c, we must link the template unit covalently to one of the macrocycle precursors. To this end, a model benzylic dibromide **7**[38] derivatized with the ethyl ester functionality (Scheme 2) was synthesized by the acid-catalyzed esterification of 2,5-dimethylbenzoic acid (**8**) with ethanol, affording **9**.[38] The ester **9** was subsequently subjected to an NBS radical bromination with AIBN as the initiator to afford the chemically modified benzylic dibromide **7**.[38]

Having established that this simple ethyl ester functionality could be introduced into one of the precursors of the tetracationic cyclophane component, the dibromide **10** was prepared (Scheme 3), in which the ethyl group is replaced by a long polyether chain containing a π-electron-rich 1,5-dioxynaphthalene unit, which can act as a template for the self-assembly of the tetracationic cyclophane. This dibromide was produced in a convergent manner by coupling the acid chloride **11** and the naphthalene-containing alcohol **12**. The acid chloride **11** was formed in two steps from 2,5-dimethylbenzoic acid **8** by an initial radical bromination, with AIBN as the initiator, to afford the benzylic dibromide **13**. This dibromide was then treated with thionyl chloride, yielding the acid chloride **11**. The alcohol **12** was synthesized in two steps from 1,5-dihydroxynaphthalene **14**. An initial bisalkylation of **14** with 2-(2-chloroethoxy)-ethanol, under basic conditions (K_2CO_3), afforded the diol **15**. This diol was monomethylated with MeI under basic conditions (NaH) to afford the alcohol **12**. Furthermore, a dibromide was also prepared wherein the methoxy group in the dibromide **10** (Scheme 3) was formally replaced by an adamantoyl group. The adamantoyl group is sufficiently large to prevent the unthreading of the 1,5-dioxynaphthalene component from the cavity of the tetracationic cyclophane.[13b,h] The dibromide **16** was synthesized (Scheme 4) by monoesterification of the diol **15** with 1-adamantoyl chloride **17** to afford the ester **18**, which was then esterified once more with the benzoyl chloride **11** to give the dibromide **16**. In addition, it was argued that, if the π-electron-rich 1,5-dioxynaphthalene component was replaced by a smaller and less π-electron-rich hydroquinone unit, it would be possible to construct a macrocycle in which the covalently appended template would be less tightly bound. To this end, the dibromide **19** (Scheme 5) was synthesized with the synthetic strategy previously employed for **10** (Scheme 3). The phenol **20** was treated under basic conditions with 2-(chloroethoxy)ethanol to afford the alcohol **21**.[12g] Esterification of the alcohol **21** with the acid chloride **11** yielded the dibromide **19**. Additionally, to permit covalent incorporation of a photoactive anthracene unit into the tetracationic cyclophane, the bis(pyridylpyridinium) salt **22**·2PF_6 was produced (Scheme 6) by firstly bromomethylating anthracene to afford the dibromide **23**,[39] which was then refluxed with an excess of 4,4'-bipyridine in MeCN, followed by counterion exchange.

The template-directed synthesis of the tetracationic cyclophane **24**·4PF_6 was achieved (Scheme 7) in a yield of 35% by



Scheme 2. The synthesis of the dibromide **7**, a precursor of the modified tetracationic cyclophane **28**·4PF_6.

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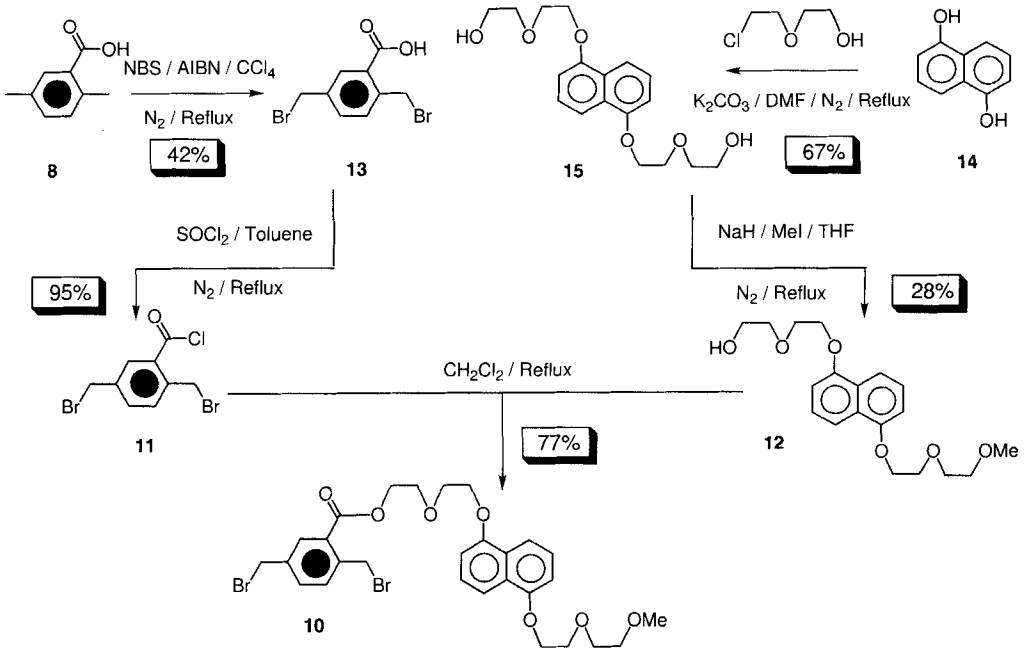
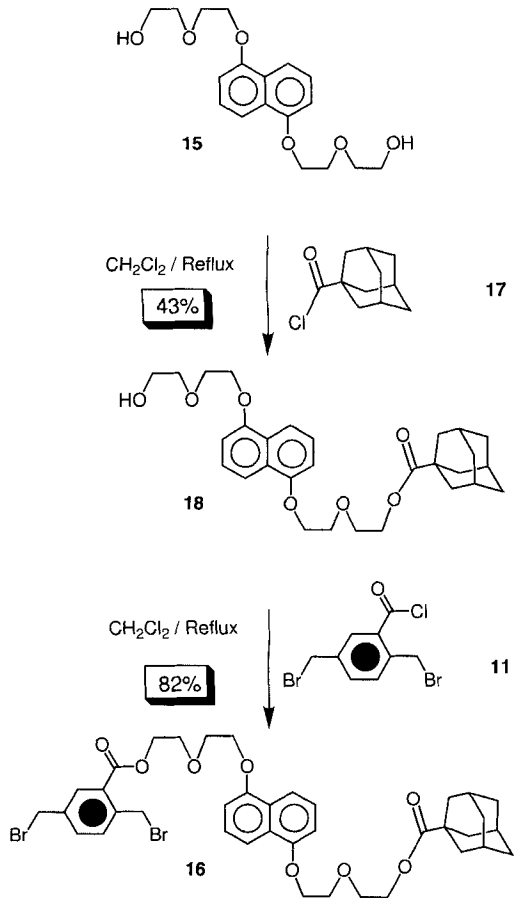
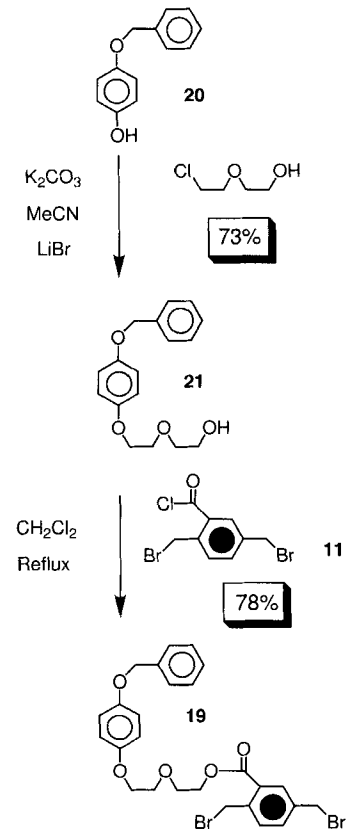


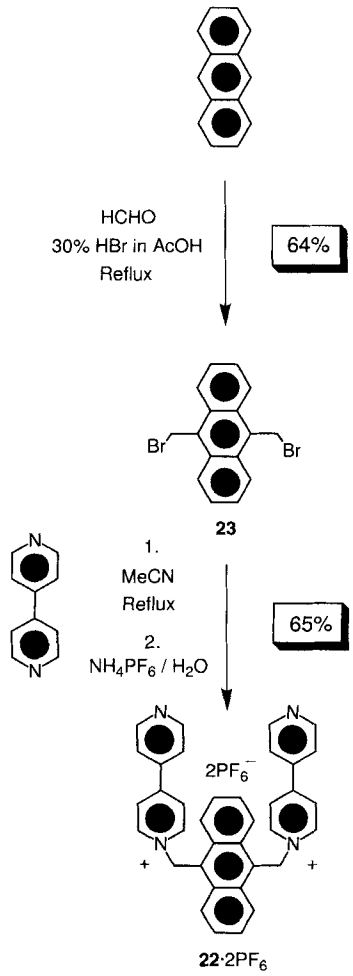
Scheme 3. The synthesis of the dibromide **10**, a precursor of the self-complexing macrocycle **29**·4PF$_6$.



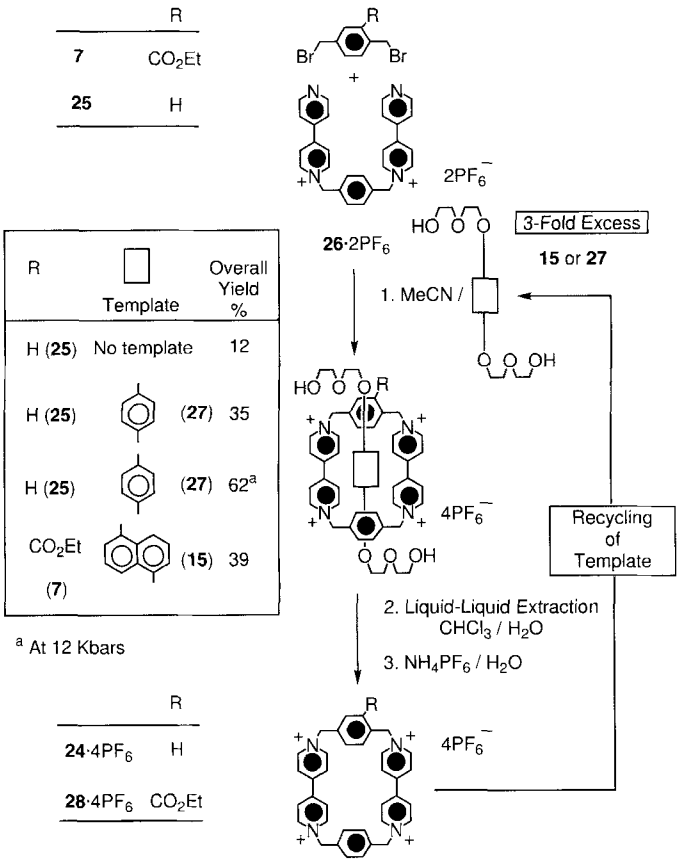
Scheme 4. The synthesis of the dibromide **16**, a precursor of the self-complexing macrocycle **30**·4PF$_6$.



Scheme 5. The synthesis of dibromide **19**, a precursor of the self-complexing macrocycle **31**·4PF$_6$.



Scheme 6. The synthesis of the dicationic salt **22**·2PF$_6$, a precursor of the self-complexing macrocycle **32**·4PF$_6$.



Scheme 7. The self-assembly of tetracationic cyclophanes **24**·4PF$_6$ and **28**·4PF$_6$, assisted by noncovalent templates **15** and **27**.

permitting *p*-xylenedibromide (**25**), the bis(pyridylpyridinium) salt **26**·2PF$_6$, and 3.0 molar equivalents of the template 1,4-bis(2-(2-(2-hydroxy)ethoxy)ethoxy)benzene[12c] (**27**) to react in MeCN. This template-directed synthesis, which follows the general methodology described in Scheme 1 b, is even more efficient (62%) when it is carried out in an ultra-high-pressure reaction vessel at 12 kbar.[12e] The self-assembly of the functionalized tetracationic cyclophane **28**·4PF$_6$ was achieved in a 39% yield by treating the modified dibromide **7** with the dicationic salt **26**·2PF$_6$ in the presence of the template, 1,5-bis(2-(2-(2-hydroxy)ethoxy)ethoxy)naphthalene **15**.

All attempted purifications of the dibromides **10**, **16**, and **19** by silica gel column chromatography were unsuccessful, so the crude dibromides were used without further purification. Nonetheless, the reactions to give the tetracationic cyclophanes yielded the respective self-assembled products **29**·4PF$_6$–**32**·4PF$_6$ (Scheme 8), which could be isolated by silica gel column chromatography. This fact illustrates the error-checking nature of the self-assembly process, in which molecular recognition selects the appropriate molecular components and dispenses with those which are not recognized by the noncovalent bonding interactions that control the self-assembly process. The self-assembly of the self-complexed compound **29**·4PF$_6$ proceeded (Scheme 8) in a yield of 24% when 1.0 molar equivalents of **10** and **26**·2PF$_6$ were stirred together in DMF for 10 days at room temperature. The self-assembly of the adamantoyl derivative **30**·4PF$_6$, from 1.0 molar equivalent of dibromide **16** and **26**·2PF$_6$ under the same conditions, was achieved in a 13% yield. The lower yield in this latter reaction might be explained as a result of the steric hindrance produced by the larger adamantoyl substituent. The self-assembly of the intramolecularly complexed macrocycle **31**·4PF$_6$ took place in a modest 7% yield when 1.0 molar equivalent of the dibromide **19** and **26**·2PF$_6$ were stirred together in DMF at room temperature for 10 days. The low yield obtained from this reaction could be a consequence of i) the reduction of the template effect caused by the less π-electron-rich moiety during the macrocyclization and ii) the lack of hydrogen-bonding interactions between the polyether oxygen atoms and the acidic α-bipyridinium protons as a result of the replacement of one terminal polyether chain by a benzyl group. The anthracene-containing analogue **32**·4PF$_6$ was formed in a yield of 30% when 1.0 molar equivalent of the dibromide **10** and **22**·2PF$_6$ were subjected to an ultra-high-pressure reaction for three days. These yields are particularly good when one considers that the yield of **24**·4PF$_6$ obtained from a threefold excess of the naphthalene template **15** is only 13% based on **15**. Additionally, the yield of **24**·4PF$_6$ when ultra-high pressure is employed to promote the reaction is only 15% based on the template **15**. Therefore, by covalently attaching the noncovalent naphthalene template to one of the components of the cyclophane, we witness a doubling of the yield to 24%.[40]

Possible structures for the new tetracationic cyclophanes: The characterization of **29**·4PF$_6$–**32**·4PF$_6$ poses some interesting questions. The very reasonable yields of products associated with the reactions described in Scheme 8 indicate that the formation of these compounds involves the π-electron-donating appendage templating the formation of the tetracationic cyclophane to which it is covalently linked. As a consequence, if there is an equilibrium between the π-electron-rich naphthalene unit residing inside the associated cavity and the π-electron-rich ring remaining uncomplexed outside the cavity, then the equilibrium should lie predominately on the side of the naphthalene residue being "self-complexed" (Scheme 9). However, if there is an equilibrium, as depicted in Scheme 9 between self-complexed and uncomplexed species, then the question arises: does the π-electron-rich residue template the formation of the tetracationic cyclophane by an intermolecular route as well as by the intramolecular one? If this intermolecular route operates, then: is the system able to self-replicate? Additionally: are dimers, trimers, tetramers, etc., and indeed cyclic counterparts, possible? These *n*-mers would lead to a novel class of polymeric materials, analogous to a macroscopic daisy chain.

In order to find answers to the structural questions, X-ray crystallographic analysis was employed to study the solid-state structure of **31**·4PF$_6$, mass spectrometry was used to investigate gas-phase structures of **29**·4PF$_6$–**32**·4PF$_6$, and ^{1}H NMR and UV/Vis spectroscopy and, wherever possible, electrochemistry were employed to study the solution-state structures.

X-ray crystallography: The X-ray crystal structure analysis of **31**·4PF$_6$ (Figure 3) reveals that it has a disordered arrangement. The compound crystallizes in a space group requiring there to be a C_2 axis of symmetry passing through the centers of the two bonds linking the two pyridinium rings of the bipyridinium

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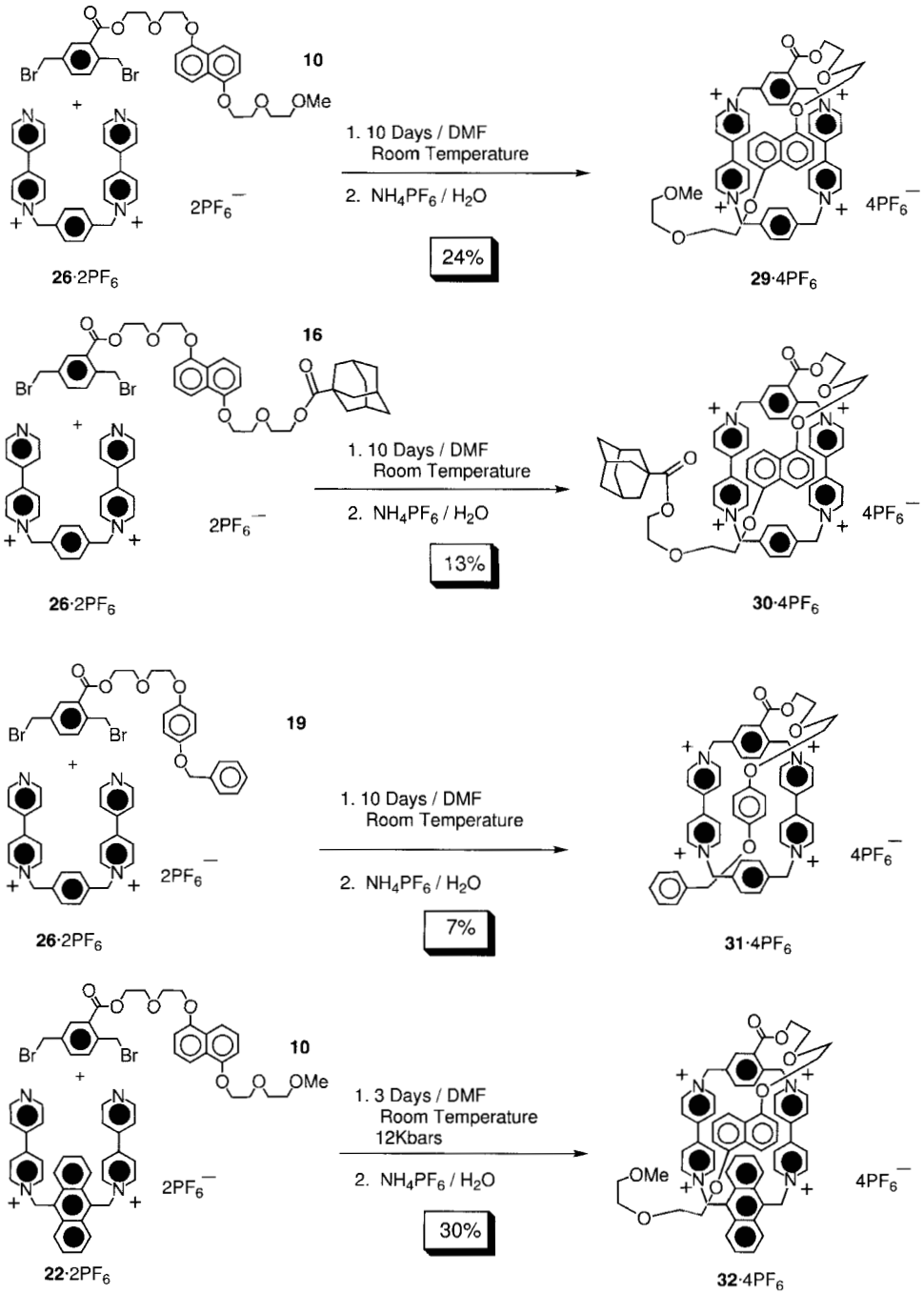


Scheme 8. The self-assembly of the self-complexing macrocycles **29**·4PF$_6$, **30**·4PF$_6$, **31**·4PF$_6$ and **32**·4PF$_6$.

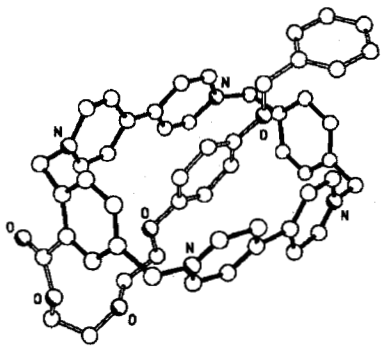
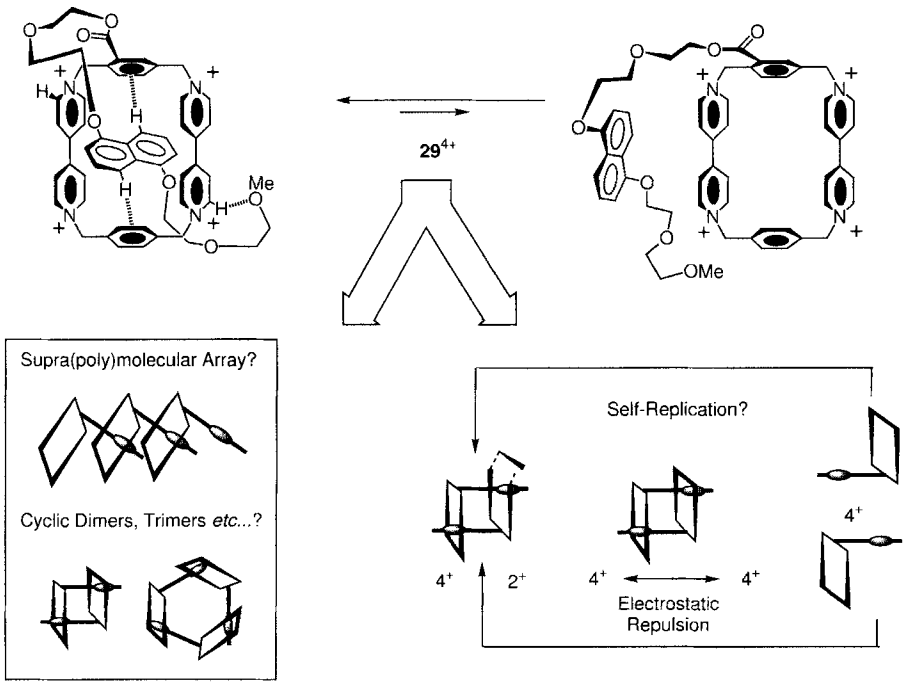


Fig. 3. A ball-and-stick representation of the X-ray crystal structure of self-complexing macrocycle **31**·4PF$_6$.

units. The self-threading nature of the structure could quite clearly be identified and a meaningful geometry for the disordered component (i.e., the chain that originates from one of the *para*-xylyl rings of the tetracationic cyclophane and is terminated by a benzyl group) could be defined. Although the bond lengths and bond angles within this fragment were both optimized and constrained, they were permitted to move relative to the crystallographic C_2 axis. The π-electron-rich hydroquinone ring portion of the thread component is positioned almost centrally within the tetracationic cyclophane component sandwiched[41] between the π-electron-deficient bipyridinium rings. In addition to these π–π stabilizing interactions, there are [C–H···π] T-type edge-to-face interactions between hy-



Scheme 9. A representation of the equilibrium between the self-complexed conformation and the uncomplexed conformation of the macrocycle **29**·4PF$_6$. The uncomplexed conformation can give rise to cyclic or linear polymeric arrays and even a self-replicating system.

droquinone ring hydrogen atoms and the *para*-xylyl residues.[23f] This substituted tetracationic cyclophane exhibits twisting and bowing distortions that are very similar to those observed for the parent cyclophane. Two aspects of the geometry of the thread component that merit mention are the coplanar relationship between the ester and its associated *para*-xylyl residue,[42] and the apparent edge-to-face arrangement between the terminal benzyl group and the other *para*-xylyl residue. In this latter case, although the ring centroid/ring centroid separation is 4.8 Å, the degree of overlap is not conducive to a significant stabilizing T-type interaction. Inspection of the packing of the molecules reveals no significant intermolecular $\pi-\pi$, [C–H$\cdots\pi$], or [C–H$\cdots$O] stabilizing interactions.

Mass spectrometry: The mass spectrometric analysis of **29**·4PF$_6$ by Liquid Secondary Ion Mass Spectrometry (LSIMS) revealed major ions corresponding to the successive loss of three PF_6^- counterions from the parent molecule (Figure 4). Additionally, a small amount of a dimeric species of **29**·4PF$_6$ was observed: again, the major peaks correspond to the loss of PF_6^- counterions from the parent molecule. There could be at least two reasons for observation of the dimeric species: i) there is real dimer formation as depicted in Scheme 9 in the gas-phase conditions of the mass spectrometer, or ii) the dimer is only an artifact of the LSIMS technique, and what is really being observed is a dimeric cluster of **29**·4PF$_6$. Previously, we have observed[43] dimeric forms of catenated molecules when these supramolecular systems have been characterized by electrospray mass spectrometry. The basis for the dimerization may be the electrostatic interactions involving the PF_6^- counterions and the tetracationic **29**·4PF$_6$.

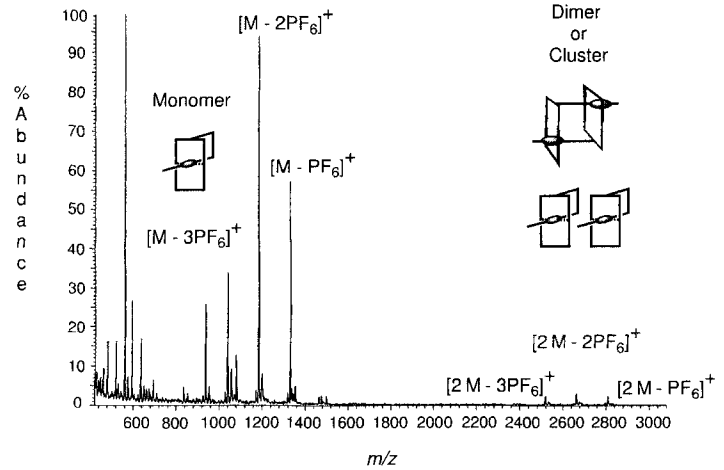


Fig. 4. Mass spectrum of the self-complexing macrocycle **29**·4PF$_6$.

^{1}H NMR spectroscopy: The one-dimensional ^{1}H NMR spectrum of **29**·4PF$_6$, not surprisingly, reveals a complex set of resonances. However, this spectrum can be interpreted broadly on the basis of relative integrations and the expected chemical shifts for resonances associated with the α- and β-bipyridinium, the phenylene, the CH_2N^+, and the CH_2O protons. A closer examination of the spectrum (see the COSY spectrum shown in Figure 5) reveals three other interesting features, namely: i) There are no "uncomplexed" naphthalene proton reso-

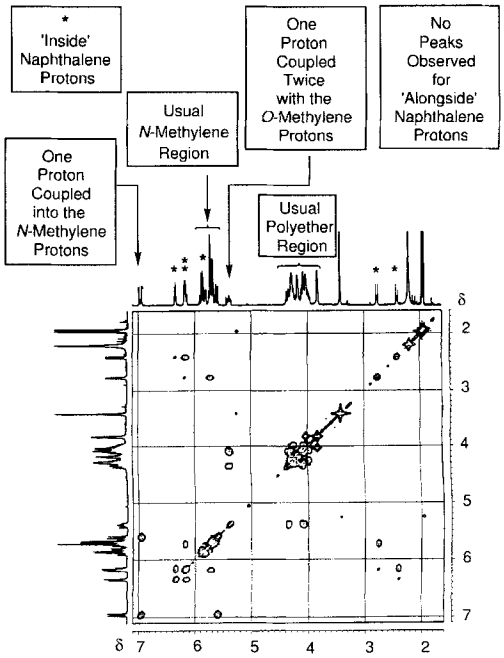


Fig. 5. Partial ^{1}H NMR 2D COSY spectrum recorded in CD_3CN of the self-complexing macrocycle **29**·4PF$_6$.

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nances, as indicated by the lack of the doublet–triplet–doublet splitting pattern of a 1,5-disubstituted naphthalene residue in the range $\delta = 6.8–7.9$. However, there are two doublets (Figure 5) centered on $\delta = 2.43$ ($J = 8$ Hz) and $\delta = 2.80$ ($J = 8$ Hz). These resonances are diagnostic of the 4,8-naphthalene protons on a 1,5-disubstituted naphthalene residue pointing into the π-faces of the *p*-xylyl units of the tetracationic cyclophane when the naphthalene residue is included within the cavity of the cyclophane.[44] ii) There is a multiplet centered on $\delta = 5.39$, which also integrates for one proton (Figure 5). iii) There is a doublet centered on $\delta = 6.97$ ($J = 13$ Hz), which integrates for one proton (Figure 5).

The origin of the resonances centered on $\delta = 5.39$ and 6.97 was not immediately obvious. A COSY spectrum was recorded in order to determine to which other protons the protons giving rise to these resonances were coupled. Figure 5, which illustrates this COSY spectrum in the region $\delta = 2–7$, reveals that the doublet resonance at $\delta = 6.97$ is coupled with the *N*-methylene protons, while the multiplet resonance at $\delta = 5.39$ is coupled twice with *O*-methylene protons in the polyether region. Moreover, these two resonances are shifted approximately 1.5 ppm downfield with respect to the usual chemical shifts of *N*-methylene and *O*-methylene protons. An examination of a CPK space-filling molecular model of this molecule and the X-ray crystal structure in its self-complexed state (Figure 6) reveals that two protons—one from the *N*-methylene closest to the ester function, one from the *O*-methylene group attached to the ester function on the polyether thread—are perfectly positioned to lie inside the deshielding environment of the anisotropic carbonyl group of the ester function. The positioning of these two protons in this particularly deshielded environment causes them to resonate at much lower frequencies than would normally be expected. The proposed structure in Figure 6 for an intramolecularly "complexed" species requires that the two *N*-methylene protons, H_a and H_b, are diastereotopically related, and thus they should resonate as an AX system. Such an AX system is indeed observed. The *O*-methylene protons, H_x and H_y, are also diastereotopically related, and as a result, H_x is geminally coupled to H_y and vicinally coupled to the pair of adjacent polyether (diastereotopically related) protons, giving rise to the multiplet associated with H_x centered on $\delta = 5.39$. The structure for **29**$^{4+}$ represented in Figure 6 is also supported by four other sets of ^{1}H NMR spectroscopic data. i) The COSY spectrum in the region $\delta = 7.0–9.5$ (Figure 7) shows that there are eight couplings

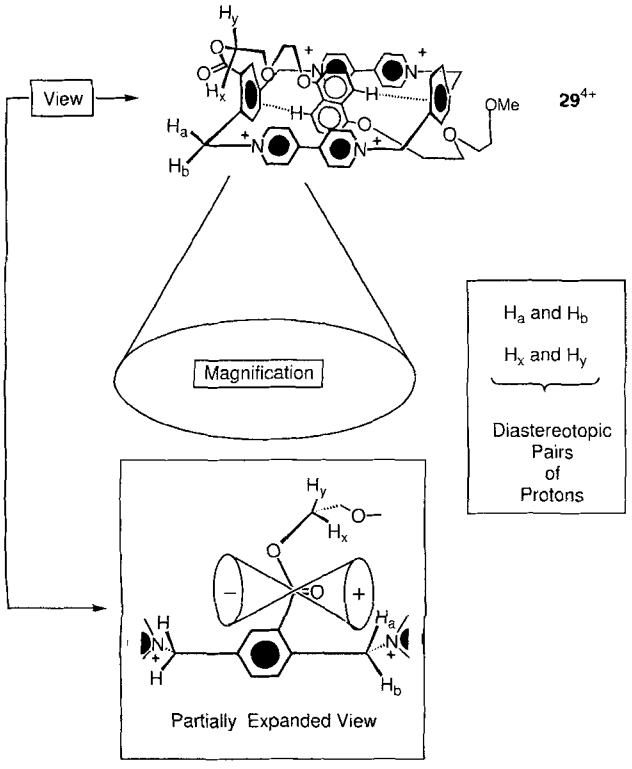

Fig. 6. A three-dimensional representation of the self-complexing conformation of **29**·4PF$_6$. The expanded view of the selected area reveals that the *N*-methylene protons and a proton belonging to γ-CH_2O in the polyether chain are located within the deshielding environment of the anisotropic carbonyl group.

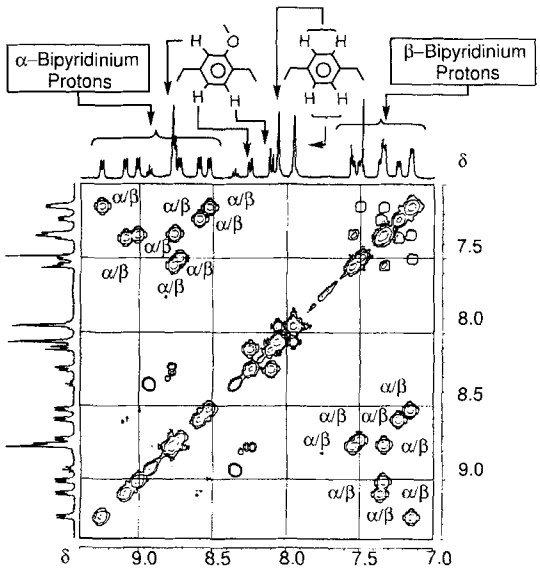

Fig. 7. Partial ^{1}H NMR 2D COSY spectrum recorded in CD_3CN of the self-complexed macrocycle **29**·4PF$_6$ showing the correlation between the signals for the α- and the β-bipyridinium protons.

between the eight vicinally related α- and β-bipyridinium protons. Thus, all eight α- and all eight β-bipyridinium protons in the tetracationic cyclophane are anisochronous. This observation means that, at least on the ^{1}H NMR timescale (400 MHz, 298 K), the decomplexation of the naphthalene residue followed by rotation of the substituted *p*-xylyl unit and then recomplexation of the naphthalene residue from the opposite face of the tetracationic cyclophane, and/or the rotation of the bipyridinium units of the tetracationic component of the self-complexing macrocycle, are slow processes. ii) A ^{1}H NMR spectroscopic study (400 MHz) on the model ethyl ester derivative **28**·4PF$_6$ (Figure 8) shows that, even upon cooling the NMR sample down to 213 K in CD_3COCD_3, rotation about the substituted *p*-xylyl unit and/or rotation of the bipyridinium units occur rapidly on the ^{1}H NMR timescale. These fast rotations are evidenced by the appearance of only four α- and four β-bipyridinium proton doublet resonances at all temperatures. This means that **28**·4PF$_6$ must have an averaged plane of symmetry passing through the four nitrogen atoms: it follows that, in the solution state, this molecule must belong to the C_s point group

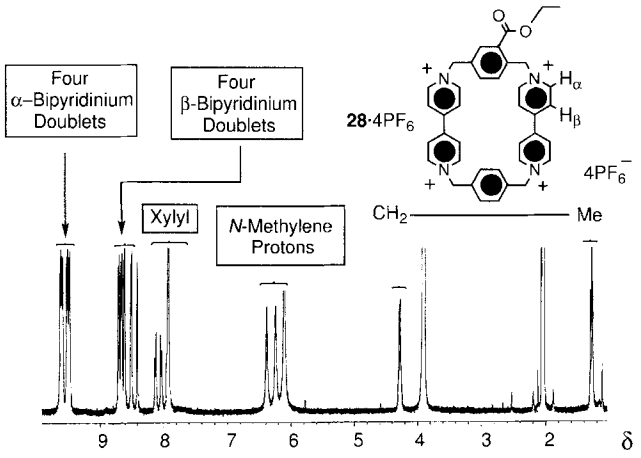

Fig. 8. Partial ^{1}H NMR spectrum recorded in CD_3CN of the modified tetracationic cyclophane **28**·4PF_6.

on the average. iii) Also, the ^{1}H NMR spectrum (400 MHz) of **31**·4PF_6 in CD_3COCD_3 at room temperature reveals four resonanaces for the α- and four resonances for the β-bipyridinium protons, indicating that, at this temperature, rotation around the modified *p*-xylyl spacer and/or rotation of the bipyridinium units occur rapidly on the ^{1}H NMR timescale. However, on cooling the NMR sample to 200 K, we observe the appearance of eight resonances for both the α- and β-bipyridinium protons, clearly indicating that the rotation of the *p*-xylyl group and/or the rotation of the bipyridinium are slow on the ^{1}H NMR timescale at this temperature (Figure 9). iv) The COSY spectrum for the model adamantoyl-substituted compound **30**·4PF_6 is completely consistent with the data obtained for **29**·4PF_6: although there are no "uncomplexed" resonances for the naphthalene protons, there are two doublets centered on $\delta = 2.75$ ($J = 8$ Hz) and $\delta = 3.01$ ($J = 8$ Hz); there is also a multiplet centered on $\delta = 5.45$ assignable to an *O*-methylene proton coupled twice with other *O*-methylene protons in the polyether region; and there is a doublet centered on $\delta = 7.23$ ($J = 13$ Hz) assignable to an *N*-methylene proton coupled geminally with its vicinal *N*-methylene proton. Since these resonances can be explained in the same way as for the compound **29**·4PF_6, the existence of both **29**·4PF_6 and **30**·4PF_6 as intramolecularly complexed structures is indicated.

In summary, these four sets of data support the structure proposed in Figure 6 for the tetracationic cyclophane derivative $\mathbf{29}^{4+}$, in which the naphthalene residue is "complexed" completely inside the cavity of the covalently linked cyclophane, resulting in its conformation becoming rigid. Rotation of the substituted *p*-xylyl is not observed at room temperature, at least on the ^{1}H NMR timescale. The molecular structure of $\mathbf{29}^{4+}$ depicted in Figure 6 possesses no reflection symmetry elements and is, therefore, chiral. The chirality is associated with a plane of chirality.[45] Scheme 10 shows the two possible enantiomers of $\mathbf{29}^{4+}$ in equilibrium with the time-averaged intermediate C_s point group conformation. It must be concluded that, at least on the ^{1}H NMR timescale, the molecule $\mathbf{29}^{4+}$ resides for most, if not all, of its time in one of its two self-complexing enantiomeric forms, and that the rotation of the bipyridinium units is slow or does not occur at all. This conclusion contrasts with the situation for the ethyl ester $\mathbf{28}^{4+}$, which has a time-averaged structure on the ^{1}H NMR timescale corresponding to the point group C_s, even in CD_3CN solution at 213 K. On the other hand, the self-complexing macrocycle $\mathbf{31}^{4+}$ exhibits temperature-dependent behavior: at room temperature, it is equivalent to the model ethyl ester derivative $\mathbf{28}^{4+}$, which lacks a plane of chirality. However, at 200 K, as a result of the slow rotation of the substituted *p*-xylyl spacer and/or the slow rotation of the bipyridinium units, it displays a plane of chirality, as does the self-complexing macrocycle $\mathbf{29}^{4+}$. Thus, although at room temperature there are only four α-bipyridinium proton resonances observed, on cooling to 200 K, eight α-bipyridinium resonances are observed.

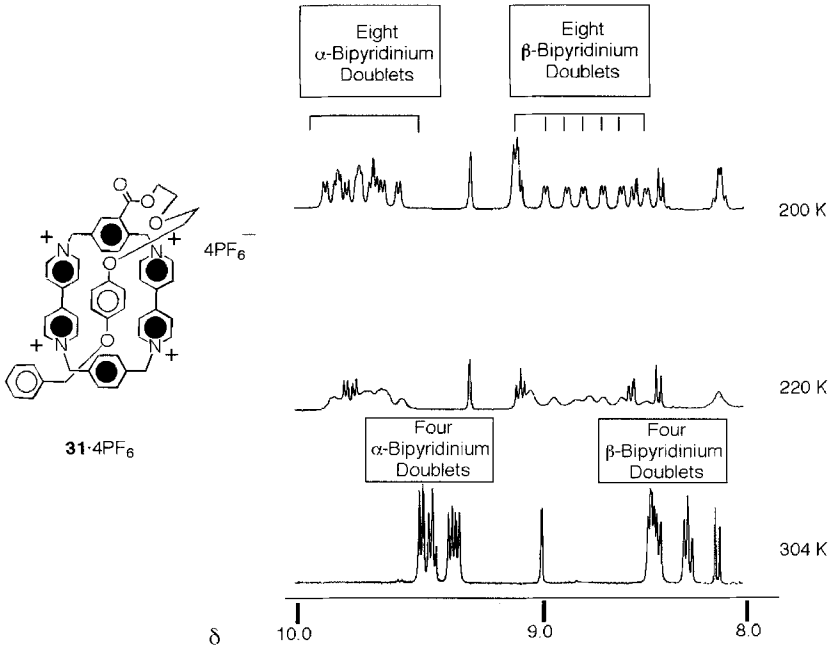

Fig. 9. Partial ^{1}H NMR spectrum recorded in CD_3COCD_3 at different temperatures of the self-complexing macrocycle **31**·4PF_6.

Absorption and luminescence spectra: The tetracationic cyclophane $\mathbf{24}^{4+}$ has a very strong absorption band in the UV region (MeCN solution: $\lambda_{max} = 260$ nm, $\varepsilon_{max} = 40000\,M^{-1}cm^{-1}$).[12e] The absorption spectrum of $\mathbf{28}^{4+}$ (Figure 10) shows the same absorption band observed for $\mathbf{24}^{4+}$, but with a slightly smaller molar absorption coefficient ($\varepsilon_{max} = 33000\,M^{-1}cm^{-1}$). Neither compound is luminescent. The molecular thread **15** exhibits a structured absorption band in the near UV region ($\lambda_{max} = 295$ nm; $\varepsilon_{max} = 8500\,M^{-1}cm^{-1}$, Figure 10) and a strong and structured fluorescence band ($\lambda_{max} = 345$ nm, $\tau = 7.5$ ns, $\Phi = 0.35$)[26] typical of naphthalene derivatives (Figure 10, inset).[46] The absorption spectra of $\mathbf{29}^{4+}$ and $\mathbf{30}^{4+}$ are very similar, but different from the sum of the spectra of their chromophoric model compounds $\mathbf{28}^{4+}$ and **15** (Figure 10). The most important fea-

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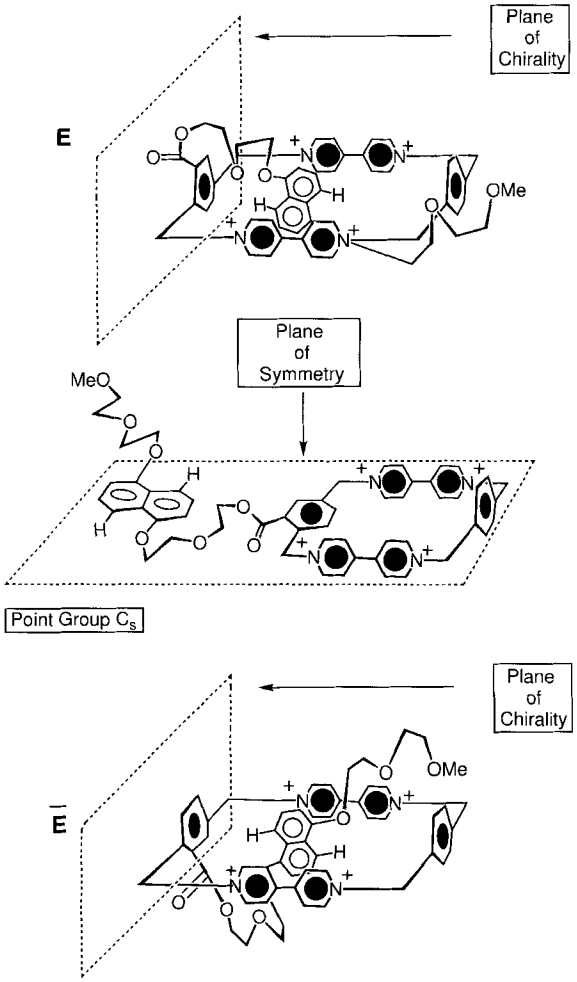


Scheme 10. A representation of the two possible enantiomeric forms for a self-complexing macrocycle **29**·PF_6 and of the unthreaded intermediate possessing a plane of symmetry.

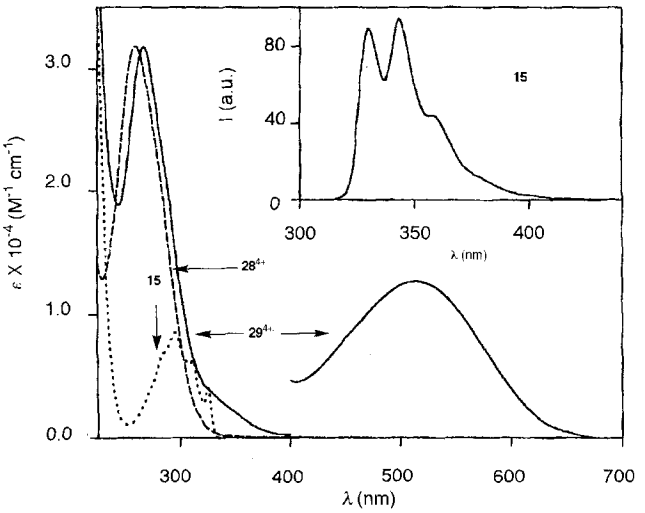


Fig. 10. Absorption spectrum of 29^{4+} (unbroken line) and of its 28^{4+} and **15** components. The fluorescence of **15** (λ_{exc} = 295 nm) is shown in the inset.

ture (as previously observed for related catenanes, rotaxanes, and pseudorotaxanes)[12e, 26, 29] is the presence of a new band in the visible region (λ_{max} = 515 nm, ε = 650 $M^{-1}cm^{-1}$ for 29^{4+}), resulting from a charge-transfer (CT) interaction between the π-electron-rich 1,5-dioxynaphthalene moiety and the π-electron deficient 4,4′-bipyridinium units.

The CT absorption of 32^{4+} in the visible region (Figure 11) is much more intense than that of 29^{4+} and 30^{4+}. Besides a maximum at 445 nm (ε_{max} = 1900 $M^{-1}cm^{-1}$), it shows a shoulder at

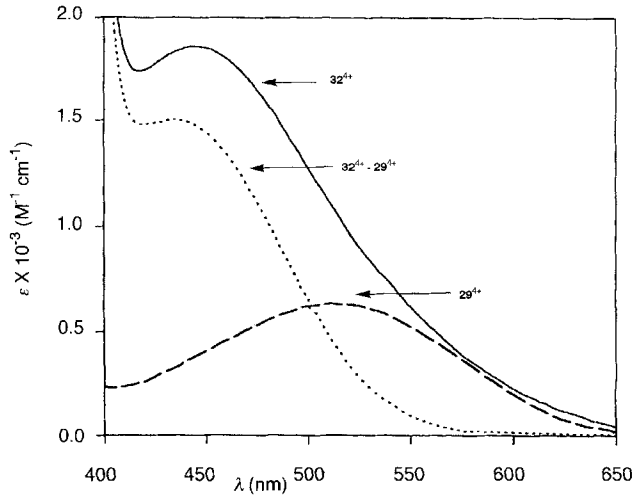


Fig. 11. Absorption spectrum of 32^{4+} (full line) and 29^{4+} (dashed line) in the visible region. The dotted line shows the difference between the two spectra.

about 530 nm. This pattern suggests the presence of two overlapping bands. Subtraction of the CT band of 29^{4+} from that of 32^{4+} in the 400–700 nm region yields a broad band with λ_{max} = 435 nm, ε = 1500 $M^{-1}cm^{-1}$ (Figure 11). This analysis indicates that in 32^{4+}, besides the CT interaction between the 1,5-dioxynaphthalene moiety and the bipyridinium unit, there is another type of CT interaction involving the anthracene moiety. A study of the absorption spectrum of the parent cyclophane of 32^{4+} would have elucidated this point. Unfortunately, it was not possible to prepare this particular compound.

The strong fluorescence of the 1,5-dioxynaphthalene moiety of **15** (Figure 10, inset) is completely quenched in 29^{4+}, 30^{4+}, and 32^{4+}. Furthermore, no fluorescence from the anthracene chromophoric group is present in 32^{4+}. The lack of fluorescence in 29^{4+}, 30^{4+}, and 32^{4+} is attributed to the presence of the low-lying charge-transfer excited states, which offer fast radiationless decay routes to the 1,5-dioxynaphthalene moiety and (in the case of 32^{4+}) anthracene-type luminescent levels.

We recall that the charge-transfer band of 29^{4+} shows practically the same shape, λ_{max}, and ε_{max} as that of 30^{4+}. This observation clearly indicates that 29^{4+} is 100% complexed, as is 30^{4+}. In order to discover whether 29^{4+} is *intramolecularly* or *intermolecularly* complexed, we measured the changes in absorbance in the maximum of the CT band for 29^{4+} on changing concentration and temperature. In the concentration range from 1.0×10^{-5} to 1.1×10^{-3} M, the absorbance of acetonitrile solutions of 29^{4+} increased linearly with increasing concentration (Figure 12), which means that the molar absorption coefficient is constant. For a 5.0×10^{-4} M acetonitrile solution, in going from 10 to 60 °C, the small decrease (≈7%) observed in the absorbance of the maximum of the CT band is comparable to that exhibited by 30^{4+} (≈5%), which is locked in an in-

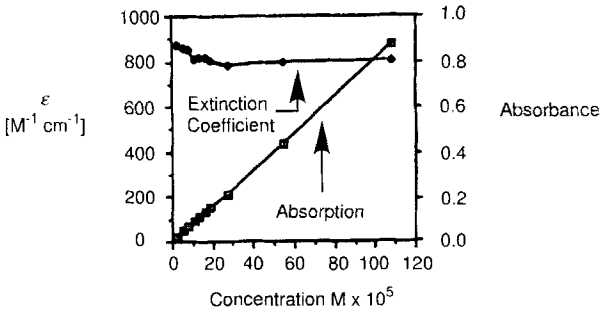


Fig. 12. Absorbance and molar absorption coefficient of **29**·4PF_6 at 520 nm as a function of concentration.

tramolecularly self-complexed conformation. These results confirm that $\mathbf{29}^{4+}$, at least in solution, exists totally as a self-complexed species.

Mechanical molecular and supramolecular machines: The self-complexation of $\mathbf{29}^{4+}$ and the self-assembling process between the cyclophane $\mathbf{24}^{4+}$ and the thread **15** to give the pseudorotaxane $[\mathbf{24}\cdot\mathbf{15}]^{4+}$ (Scheme 11) are a result of donor–acceptor interactions between the π-electron-rich 1,5-dioxynaphthalene moiety of **15** and the π-electron-deficient bipyridinium units of the cyclophane $\mathbf{24}^{4+}$, as well as of the hydrogen-bonding interactions between the polyether oxygen atoms of the naphthalene derivative and the acidic bipyridinium protons of the cyclophane. Upon reduction of the tetracationic cyclophane, the strength of these interactions is expected to decrease,[12e] thereby allowing the naphthalene derivative to dethread from the cavity of the cyclophane. We have devised photochemical and electrochemical methods to control the dethreading processes in these systems. For reasons that will become apparent, dethreading of the pseudorotaxane $[\mathbf{24}\cdot\mathbf{15}]^{4+}$ was performed by photoexcitation and followed by absorption and luminescence spectroscopy, whereas dethreading of the self-complexed system $\mathbf{29}^{4+}$ was observed when the reduction of the tetracationic cyclophane was carried out by electrochemical techniques.

Photochemically driven machines: When the thread **15** is added to an aqueous solution of the cyclophane **24**·4Cl, it threads spontaneously through the center of the tetracationic cyclophane to produce the 1:1 complex or pseudorotaxane $[\mathbf{24}\cdot\mathbf{15}]^{4+}$ (Scheme 11). The occurrence of the threading process is shown by absorption and emission spectra and by NMR spectroscopy. In a 6.0×10^{-5} M aqueous solution of **15** and $\mathbf{24}^{4+}$ (as its tetrachloride salt), a charge-transfer band in the visible region (λ_{max} = 520 nm, ε_{max} ca. 700 $M^{-1}cm^{-1}$), very similar to that of $\mathbf{29}^{4+}$, is formed and the intensity of the fluorescence of **15** (λ_{max} = 345 nm) is quenched (Figure 13, curve a). Since the

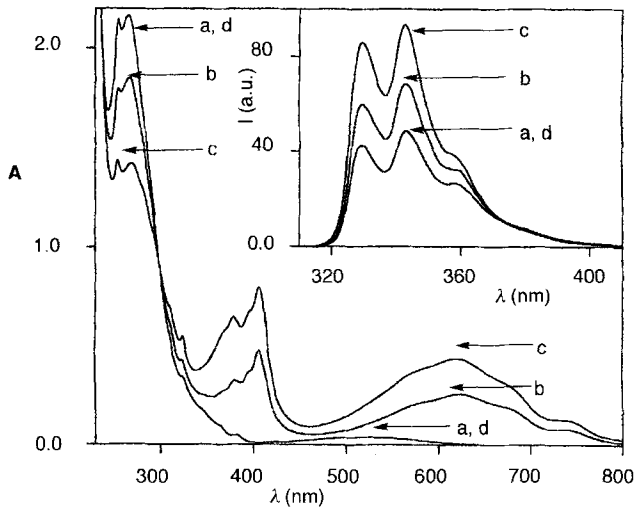
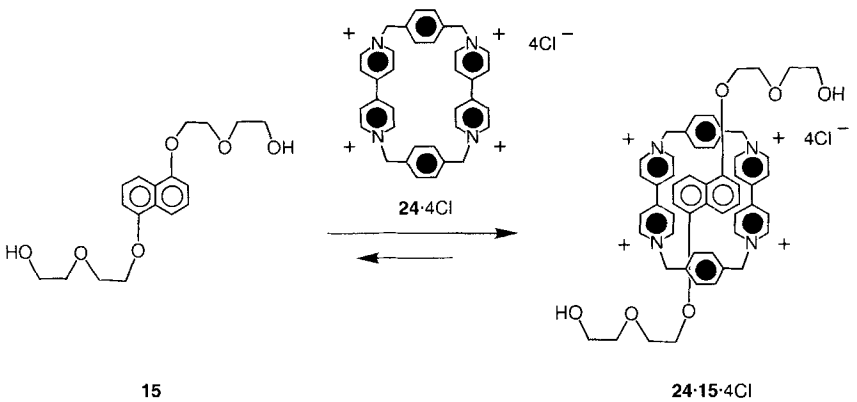


Fig. 13. Absorption and (inset) fluorescence spectra of: a) a 6.0×10^{-5} M solution of **15** and $\mathbf{24}^{4+}$ in water (80% of the species are present as the pseudorotaxane $\mathbf{24}\cdot\mathbf{15}^{4+}$); b) and c) the same solution, irradiated for 4 and 15 min, respectively, in the presence of 5.0×10^{-6} M 9-anthracenecarboxylic acid and 0.01 M triethanolamine; d) solution c after oxidation with O_2. The fluorescence spectra were obtained with λ_{exc} = 295 nm.

excited-state lifetime of **15** is very short (7.5 ns) and the concentration of $\mathbf{24}^{4+}$ is very low, fluorescence quenching can only occur when the two species are associated.[47, 48] ^{1}H NMR spectroscopy (300 MHz) of **15** and $\mathbf{24}^{4+}$ in D_2O (0.013 M each) at room temperature showed significant chemical shift changes for the aromatic protons of **15**. The largest change observed in the ^{1}H NMR spectrum was the one for the H-4/8 protons ($\Delta\delta$ = −4.52 ppm) of the naphthalene ring. This large $\Delta\delta$ value, together with the existence of a strong charge-transfer interaction between the two components, is compelling evidence for the formation of a complex $[\mathbf{24}\cdot\mathbf{15}]^{4+}$ with an aqueous solution-state superstructure best described as pseudorotaxane-like.[49]

The threading process takes place in a variety of solvents,[14b, 25] reaching an equilibrium more or less displaced toward the formation of the pseudorotaxane $[\mathbf{24}\cdot\mathbf{15}]^{4+}$. In water, starting with a 6.0×10^{-5} M solution of **15** and $\mathbf{24}^{4+}$, 80% of the species formed at room temperature is the pseudorotaxane, as measured by the static quenching of the intensity of the luminescence band of **15**. In principle, the interaction between the thread and the cyclophane can be destabilized by reduction of the cyclophane and/or oxidation of the thread. Excitation of the pseudorotaxane in its charge-transfer band formally moves an electron from the 1,5-dioxynaphthalene moiety of the thread to a



Scheme 11. Self-assembly of cyclophane **24**·4Cl and thread **15** to give the pseudorotaxane **24**·**15**·4Cl in aqueous solution.

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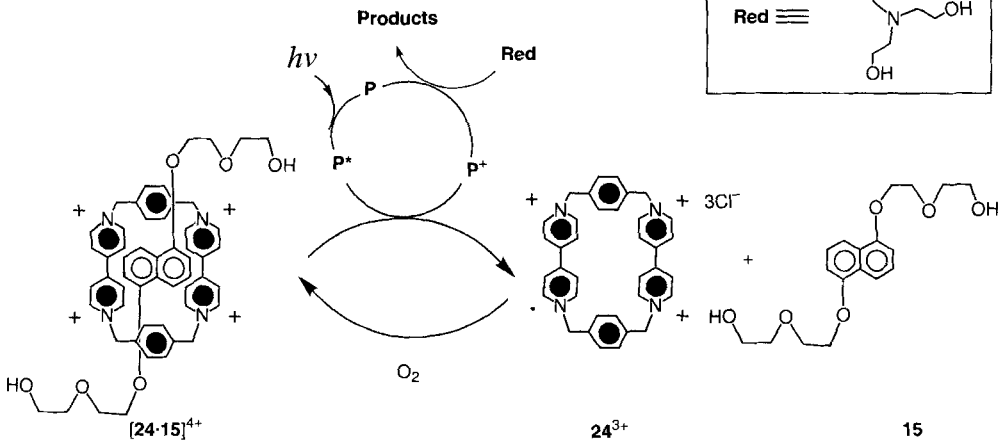
bipyridinium moiety of the cyclophane. Therefore, one can expect that in the CT excited state the strength of the interaction will be strongly reduced, with displacement of the equilibrium toward dethreading. However, the CT excited state undergoes a fast (picosecond timescale)[27] back electron transfer reaction, whereas the dethreading process is very slow, because it involves complex nuclear motions. Therefore, direct light excitation in the CT band does not cause any dethreading. In order to achieve a light-induced dethreading, we have resorted to a photosensitization technique schematically illustrated in Scheme 12.



Scheme 12. Schematic representation of the photosensitized dethreading process.

It is well known that intermolecular redox reactions can be driven by light by means of suitable photosensitizers (hereafter denoted by **P**).[50, 51] For example, the lowest excited state of 9-anthracenecarboxylic acid (hereafter abbreviated as **P***, where the asterisk indicates excitation) is a long-lived (250 μs) and powerful reductant ($E_{red}(P^+/P^*) = -0.88$ V vs. SCE).[52] Therefore, we irradiated a deoxygenated aqueous solution containing 9-anthracenecarboxylic acid (5.0×10^{-6} M) and $[24\cdot15]^{4+}$ (4.8×10^{-5} M) with 365 nm light to cause the reduction of the electron-acceptor component of the pseudorotaxane ($E_{red} = -0.35$ V for the "alongside" bipyridinium unit of an analogous [2]catenane)[29b] [Eqs. (1) and (2)]. After photoreduc-

$$P + h\nu \longrightarrow P^* \quad \text{[Light excitation]} \quad (1)$$

$$P^* + [24\cdot15]^{4+} \longrightarrow P^+ + [24\cdot15]^{3+} \quad \text{[Photoreduction]} \quad (2)$$

tion, one might expect the dethreading process to occur. It should be recalled, however, that the departure of the thread from the ring is slow. Therefore, once again, it cannot compete with the relatively fast back electron transfer[52] [Eq. (3)] from

$$P^+ + [24\cdot15]^{3+} \longrightarrow P + [24\cdot15]^{4+} \quad \text{[Back electron transfer]} \quad (3)$$

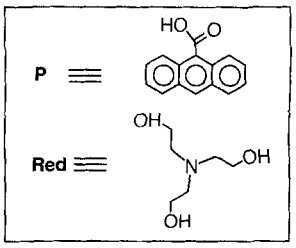
the reduced $[24\cdot15]^{3+}$ to the oxidized P^+ species. However, when a sufficiently large amount of a sacrificial reductant (**Red**, e.g., 0.01 M triethanolamine) is present in the solution, the oxidized P^+ species produced by the excited-state electron transfer reaction can be rapidly scavenged [Eq. (4)]. As a consequence,

$$P^+ + \text{Red} \longrightarrow P + \text{Products} \quad \text{[Scavenging reaction]} \quad (4)$$

the back electron-transfer reaction [Eq. (3)] is prevented and the pseudorotaxane remains reduced, as indicated by the appearance (Figure 13) of the characteristic absorption bands of reduced bipyridinium units.[53] Under such conditions, the interaction between the thread and the ring is *permanently* weakened, and the dethreading process can take place [Eq. (5)]. Proof of

$$[24\cdot15]^{3+} \longrightarrow 24^{3+} + 15 \quad \text{[Dethreading]} \quad (5)$$

the occurrence of the dethreading process is the increase in the fluorescence of the 1,5-dioxynaphthalene moiety, which can only take place from "free" **15** (Figure 13, inset). It should be pointed out that the fluorescent excited state **15*** can be quenched by the reduced form 24^{3+} of the cyclophane by energy transfer (since 24^{3+} possesses low-energy excited states) and electron transfer (since 24^{3+} is a strong reductant and **15*** is an oxidant). Quenching, however, implies either close association between the two species or many random encounters of the excited **15*** (during its short lifetime, 7.5 ns) with 24^{3+}. The recovery of the fluorescence therefore indicates that 24^{3+} and **15** are not only dethreaded, but also far from each other, as expected for two noninteracting, dilute solutes. As will become apparent later, for the covalently linked system 29^{3+} the impossibility of separating the 1,5-dioxynaphthalene moiety from the reduced bipyridinium moiety prevents the recovery of fluorescence even if the reductive dethreading takes place.



Under the experimental conditions used for the photosensitization experiments on $[24\cdot15]^{4+}$ (deaerated aqueous solution; 3 mL reaction cell; excitation with 365 nm light; incident light intensity 2×10^{-6} N hν min^{-1}, 13% of which was absorbed by the photosensitizer), 35% of the pseudorotaxane species was dethreaded after 25 minutes of irradiation (Figure 13). Similar results have been obtained on changing experimental conditions (pH and type of sacrificial reductant, e.g., disodium EDTA). The dethreading reaction was also performed with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) as a photosensitizer, but with a lower efficiency, because of its shorter excited-state lifetime and a less efficient cage escape.[50–52] After dethreading has occurred, if oxygen is allowed to enter the solution the reduced cyclophane is promptly back-oxidized [Eq. (6)] and **15** threads through it again [Eq. (7)] as shown by the decrease in the intensity of

$$24^{3+} \xrightarrow{\text{Oxygen}} 24^{4+} \quad \text{[Oxidation]} \quad (6)$$

$$15 + 24^{4+} \longrightarrow [24\cdot15]^{4+} \quad \text{[Rethreading]} \quad (7)$$

the fluorescence band and the recovery of the initial absorption spectrum (Figure 13). We recall that the covalently linked system 29^{4+} is a self-complexed species where low-energy CT levels

prevent the fluorescence of the 1,5-dioxynaphthalene moiety. On the basis of the results obtained with the pseudorotaxane $[\mathbf{24}\cdot\mathbf{15}]^{4+}$, experiments were performed to examine the possibility of prompting a photochemical dethreading of $\mathbf{29}^{4+}$. A degassed aqueous solution containing 6.0×10^{-5} M $\mathbf{29}^{4+}$, 5.0×10^{-6} M 9-anthracenecarboxylic acid as a photosensitizer, and 10^{-2} M disodium EDTA as sacrificial reductant[54] was irradiated with 365 nm light. After 15 min, changes in the absorption spectrum of the solution comparable to those observed for $[\mathbf{24}\cdot\mathbf{15}]^{4+}$ were obtained, showing that, following light excitation of the photosensitizer [Eq. (1)] and scavenging of $\mathbf{P}^+$ by the sacrificial reductant [Eq. (4)], 45% of the (total) bipyridinium units have been reduced (threaded and unthreaded $\mathbf{29}^{3+}$ are hereafter indicated as $\mathbf{29}^{3+}$ (Np in) and $\mathbf{29}^{3+}$ (Np out), respectively) [Eq. (8)].

$$\mathbf{P}^* + \mathbf{29}^{4+}\text{ (Np in)} \longrightarrow \mathbf{P}^+ + \mathbf{29}^{3+}\text{ (Np in)} \quad \text{[Photoreduction]} \quad (8)$$

Dethreading of $\mathbf{29}^{3+}$ (Np in) is therefore expected to occur [Eq. (9)]. However, unlike what happens on dethreading of

$$\mathbf{29}^{3+}\text{ (Np in)} \longrightarrow \mathbf{29}^{3+}\text{ (Np out)} \quad \text{[Dethreading]} \quad (9)$$

$[\mathbf{24}\cdot\mathbf{15}]^{4+}$, no recovery of the 1,5-dioxynaphthalene moiety fluorescence was observed upon the photochemical reduction of $\mathbf{29}^{4+}$. This nonrecovery, however, is not evidence against the photoinduced dethreading process. It should be considered, in fact, that contrary to what happens for the two components of $[\mathbf{24}\cdot\mathbf{15}]^{3+}$, which, after dethreading, are free to diffuse away in the solution, the short and flexible polyether tether keeps the naphthalene moiety close to the reduced $\mathbf{29}^{3+}$ cyclophane and allows the occurrence of many encounters between them within the excited state lifetime of the 1,5-dioxynaphthalene moiety. In such encounters, the fluorescence of the excited state of the naphthalene moiety [Eq. (11)] can be quenched by the reduced cyclophane by energy transfer [Eq. (12)] and/or oxidative electron transfer [Eq. (13)], with the consequent quenching of the naphthalene-type fluorescence.

$$\mathbf{29}^{3+}\text{ (Np out)} + h\nu \longrightarrow \mathbf{29}^{3+}\text{ (Np* out)} \quad \text{[Light excitation]} \quad (10)$$

$$\mathbf{29}^{3+}\text{ (Np* out)} \rightleftarrows \mathbf{29}^{3+}\text{ (Np out)} + h\nu' \quad \text{[Fluorescence]} \quad (11)$$

$$\mathbf{29}^{3+}\text{ (Np* out)} \longrightarrow \mathbf{29}^{*3+}\text{ (Np out)} \quad \text{[Energy transfer]} \quad (12)$$

$$\mathbf{29}^{3+}\text{ (Np* out)} \longrightarrow \mathbf{29}^{2+}\text{ (Np}^+\text{ out)} \quad \text{[Electron transfer]} \quad (13)$$

After irradiation, introduction of oxygen in the solution causes the disappearance of the absorption bands of reduced bipyridinium [Eq. (14)] and gives back the CT absorption band of $\mathbf{29}^{4+}$ [Eq. (15)], indicating that the reduction of a bipyridinium unit of $\mathbf{29}^{4+}$ is reversible.

$$\mathbf{29}^{3+}\text{ (Np out)} \xrightarrow{\text{Oxygen}} \mathbf{29}^{4+}\text{ (Np out)} \quad \text{[Oxidation]} \quad (14)$$

$$\mathbf{29}^{4+}\text{ (Np out)} \longrightarrow \mathbf{29}^{4+}\text{ (Np in)} \quad \text{[Rethreading]} \quad (15)$$

In the case of $\mathbf{32}^{4+}$, a photosensitizer (anthracene) is present in the cyclophane structure. In principle, excitation of the anthracene moiety of $\mathbf{32}^{4+}$ with 365 nm light could be followed by electron transfer to the bipyridinium unit; a reducing scavenger could then react with the oxidized anthracene unit, thereby preventing the back electron transfer and allowing the unthreading process. We found, however, that irradiation of a degassed aqueous solution containing 6.0×10^{-5} M $\mathbf{32}^{4+}$ and 0.01 M EDTA does not produce any variation in its absorption spectrum. This result means that the bimolecular electron transfer process from the scavenger to the oxidized photosensitizer cannot compete with the very fast intramolecular back electron transfer from the reduced bipyridinium unit to the oxidized anthracene.

Electrochemically driven machines: An alternative approach to the reduction of the tetracationic cyclophane (in order to weaken the interaction between the two components of pseudorotaxanes and achieve dethreading) is to use electrochemical techniques. Here, we describe detailed electrochemical experiments performed on the $\mathbf{29}^{4+}$ system in acetonitrile solution at room temperature. The electrochemical behavior of $\mathbf{28}^{4+}$, $\mathbf{29}^{4+}$, and the previously investigated [2]catenane $\mathbf{33}^{4+}$ is compared in Figure 14.[55]

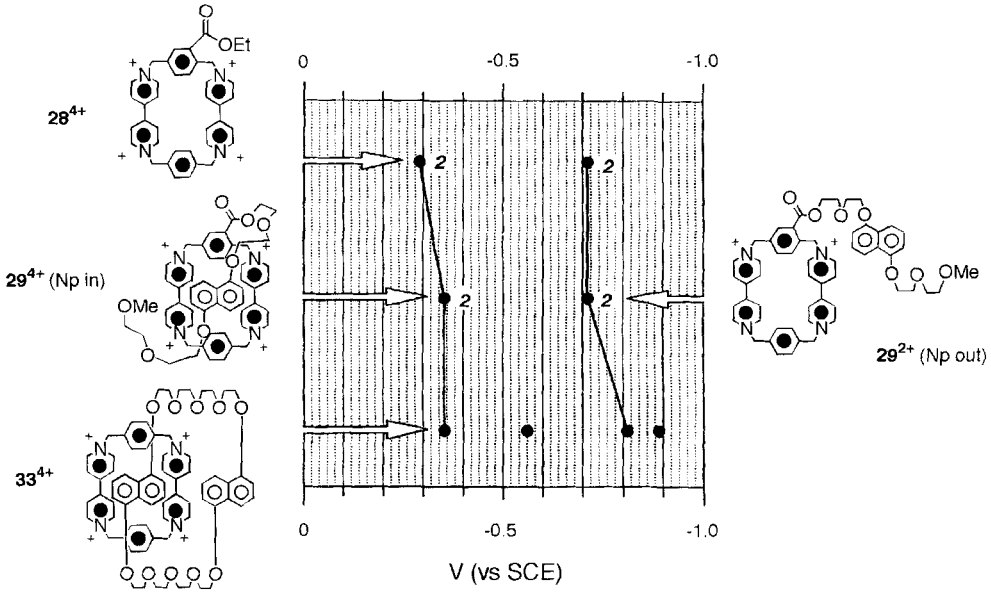


Fig. 14. Comparison of the reduction potentials of $\mathbf{28}^{4+}$, $\mathbf{29}^{4+}$, and $\mathbf{33}^{4+}$.

The behavior of $\mathbf{28}^{4+}$ is practically the same as that shown[11,2e] by $\mathbf{24}^{4+}$: a reversible two-electron reduction process with $E_{1/2} = -0.29$ V is followed by a second reversible two-electron reduction process with $E_{1/2} = -0.71$ V. The first two-electron reduction process corresponds to the one-electron reduction, at the same potential, of the two equivalent and noninteracting bipyridinium units. As shown in Figure 14, the first reversible two-electron reduction process of $\mathbf{29}^{4+}$ takes place at -0.35 V, that is, at more negative potential compared with $\mathbf{28}^{4+}$. This situation is accounted for by the donor–accep-

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tor interaction of the cyclophane with the electron donor 1,5-dioxynaphthalene moiety and confirms the self-threaded structure of 29^{4+}. It should be noted that the two 4,4′-bipyridinium units remain equivalent in 29^{4+} because the 1,5-dioxynaphthalene moiety is positioned symmetrically between them. In [2]catenane 33^{4+}, the two 4,4′-bipyridinium units are not equivalent because only one experiences interaction with two naphthalene units. Therefore, in 33^{4+}, the first reductions of the two bipyridinium units occur at different potentials:[29b] the first one-electron wave (−0.35 V) corresponds to the reduction of the "alongside" unit, and the second one-electron wave (−0.56 V) to the reduction of the "inside" unit. The donor–acceptor interaction experienced by the alongside bipyridinium unit of 33^{4+} is expected to be practically the same as that of the bipyridinium units of 29^{4+}. This expectation is fully confirmed by the fact that the first two-electron reduction of 29^{4+} and the first one-electron reduction of 33^{4+} occur at the same potential (Figure 14).

The results which shed most light on the behavior of 29^{4+} are those concerning the second reduction of the bipyridinium units. In this regard, it should be noted that i) 28^{4+} again shows a two-electron wave (−0.71 V), ii) [2]catenane 33^{4+} shows two one-electron waves (−0.81 and −0.89 V), both at more negative potentials than 28^{4+} because of some residual donor–acceptor interaction, whereas iii) 29^{4+} shows a two-electron wave exactly at the same potential as that of 28^{4+}. These results indicate that for 29^{4+}, at the time of the second reduction, the two bipyridinium units are no longer engaged in any donor–acceptor interaction. As a consequence, we can draw the conclusion that the first reduction [Eq. (16)] of the two bipyridinium units of 29^{4+} to 29^{2+} causes dethreading [Eq. (17), Figure 15].

$$29^{4+}\ (\text{Np in}) + 2e^- \longrightarrow 29^{2+}\ (\text{Np in}) \qquad \text{[Reduction]} \quad (16)$$

$$29^{2+}\ (\text{Np in}) \longrightarrow 29^{2+}\ (\text{Np out}) \qquad \text{[Dethreading]} \quad (17)$$

In agreement with the photochemical results, spectroelectrochemical experiments (macroreduction of 29^{4+} at −0.40 V, monitored by absorption and fluorescence measurements) showed the appearance of the characteristic absorption spectrum of monoreduced bipyridinium units,[53] but no fluorescence from the naphthalene unit. This finding further confirms that in the case of this system, for the reasons discussed above, fluorescence measurements are not sufficient to prove the occurrence of dethreading. The proof that dethreading takes place is given by the fact that the potential value of the second reduction process of 29^{4+} is coincident with that of 28^{4+} (Figure 14).

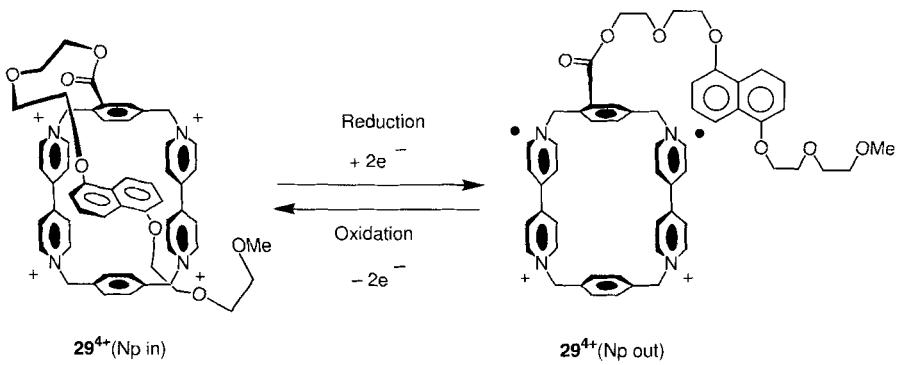

Fig. 15. Electrochemically driven dethreading–rethreading of 29^{4+}.

Electrochemical or chemical oxidation, for example by allowing oxygen to enter the reduced solutions [Eq. (18)], causes rethreading [Eq. (19)], as shown by the disappearance of the absorption band of the reduced bipyridinium units and the reappearance of the CT band.

$$29^{2+}\ (\text{Np out}) \xrightarrow{\text{Oxygen}} 29^{4+}\ (\text{Np out}) \qquad \text{[Oxidation]} \quad (18)$$

$$29^{4+}\ (\text{Np out}) \longrightarrow 29^{4+}\ (\text{Np in}) \qquad \text{[Rethreading]} \quad (19)$$

Conclusion

This research has shown how it is possible to design and construct molecular assemblies and supramolecular arrays with nanometre-scale switching properties by the use of the noncovalent bonding interactions that regulate the self-assembly of π-electron-rich and π-electron-deficient components. For example, we have shown how, by attaching a π-electron-rich aromatic ring to one of the precursors of the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), it is feasible to synthesize molecular assemblies featuring a self-complexing aspect where the tether component acts as a template in the formation of the macrocyclic compound. These self-complexing compounds are not only interesting on account of their rare structures, but also because one of them exhibits electrochemically driven switching properties. In addition, we have described a supramolecular system in which the dethreading of the linear π-electron-donating component from the cavity of the π-electron-deficient tetracationic cyclophane is photochemically driven. Thus, we have constructed molecular and supramolecular systems driven by photons and electrons. This achievement constitutes a step toward storing, processing, and transmitting information at the molecular and supramolecular levels[7]—an activity which is still very much in its infancy.

Experimental Section

Materials and methods: Solvents were purified and dried by literature methods. Reagents were employed as purchased from Aldrich. Thin-layer chromatography (TLC) was carried out with aluminum sheets, precoated with silica gel 60 F (Merck 5554) or aluminum oxide 60 F neutral (Merck 5550). The plates were inspected by UV light prior to development with iodine vapor or by treatment with ceric ammonium molybdate reagent and subsequent heating. Preparative TLC (PTLC) was carried out with TLC plates precoated with silica gel 60 F_{254} (Merck 5717) of layer thickness 2 mm. Column chromatography was performed with silica gel 60 (Merck 7734, 0.063–0.200 mm) or aluminum oxide 90 (neutral, act. II-III, Merck 1097, 0.063–0.200 mm). Melting points were determined on an Electrothermal 9200 apparatus and are uncorrected. Elemental analyses were performed by both the University of Sheffield and the University of Birmingham Microanalytical Laboratories. Mass spectra were recorded on a Kratos Profile spectrometer (EIMS and CIMS) or on a VG ZabSpec instrument equipped with a cesium ion gun (LSIMS). ^{1}H NMR spectra were recorded on a Bruker AC 300 (300 MHz spectra) or a Bruker AMX 400 (400 MHz spectra). ^{13}C NMR spectra were recorded on a Bruker AC 300 (75.5 MHz) by means of the JMOD pulse sequence. All chemical shifts are quoted on the δ scale with TMS or the solvent as an internal standard. Coupling

constants are expressed in Hz. X-ray crystallography was carried out as described in the appropriate compound characterization section. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-43. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

Ethyl 2,5-dimethylbenzoate (9) [38]: 2,5-Dimethylbenzoic acid **8** (3.5 g, 2.3 mmol) and H_2SO_4 (5 mL) in EtOH (50 mL) were heated under reflux overnight. The solution was cooled and solvent removed in vacuo. The residue was dissolved in CH_2Cl_2 (50 mL) and washed with saturated aqueous Na_2CO_3 (2 × 100 mL) and H_2O (2 × 100 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated in vacuo to afford a clear colorless oil (4.2 g, 100%), corresponding to compound **9**. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.73 (d, ^4J = 1 Hz, 1H; Ar–H-6), 7.21 (dd, $^{3,4}J$ = 8 Hz, 1 Hz, 1H; Ar–H-4), 7.12 (d, ^3J = 8 Hz, 1H; Ar–H-3), 4.37 (q, ^3J = 7 Hz, 2H; CH_2CH_3), 2.56 (s, 3H; Ar–CH_3), 2.35 (s, 3H; Ar–CH_3), 1.39 (t, ^3J = 7 Hz, 3H; CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.9, 136.8, 135.2, 132.5, 131.5, 130.9, 129.8, 60.6, 21.2, 20.8, 14.4; MS (70 eV, EI): m/z (%) = 178 (50) [M^+].

Ethyl 2,5-bis(bromomethyl)benzoate (7) [38]: *N*-Bromosuccinimide (4.4 g, 24.7 mmol) and a catalytic amount of AIBN were added to a solution of ethyl 2,5-dimethylbenzoate **9** (2 g, 11.23 mmol) in CCl_4 (50 mL). The suspension was refluxed under nitrogen for 4 h, after which time succinimide was observed floating on the surface of the CCl_4 when the solution was cooled down to room temperature. The succinimide was filtered off under gravity and the filtrate was concentrated. The resulting brown oil was dissolved in CH_2Cl_2 (25 mL), to which hexane (150 mL) was added. The solution was allowed to stand in the refrigerator for 2 h, whereupon a white solid precipitated out. The solid was filtered off under gravity and dried in vacuo; this afforded compound **7** (1.4 g, 40%) in the form of a white powder. M.p. 87 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.98 (d, ^4J = 1 Hz, 1H; Ar–H-6), 7.54 (dd, $^{3,4}J$ = 8, 1 Hz, 1H; Ar–H-4), 7.95 (d, ^3J = 8 Hz, 1H; Ar–H-3), 4.96 (s, 2H; Ar–CH_2Br), 4.49 (s, 2H; Ar–CH_2Br), 4.42 (q, ^3J = 7 Hz, 2H; CH_2CH_3), 1.46 (t, ^3J = 7 Hz, 3H; CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.0, 139.2, 138.3, 132.8, 132.2, 131.7, 130.0, 61.5, 31.8, 30.8, 14.2; MS (70 eV, EI): m/z (%) = 336 (5) [M^+].

2,5-Bis(bromomethyl)benzoic acid (13) [38]: *N*-Bromosuccinimide (26.08 g, 146 mmol) and a catalytic amount of AIBN were added to a solution of 2,5-dimethylbenzoic acid **8** (10 g, 67 mmol) in CCl_4 (200 mL). The suspension was refluxed under nitrogen for 4 h, after which time succinimide was observed floating on the surface of the CCl_4 when the solution was cooled down to room temperature. The succinimide was filtered off under gravity and the filtrate was concentrated. The resulting brown oil was dissolved in CH_2Cl_2 (50 mL) to which hexane (150 mL) was added. The solution was then allowed to stand in the refrigerator for 2 h, whereupon a white solid precipitated out. The solid was filtered off under gravity and dried in vacuo, affording compound **13** (8.4 g, 42%) in the form of a white powder: m.p. 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.11 (d, ^4J = 1 Hz, 1H; Ar–H-6), 7.69 (dd, $^{3,4}J$ = 8, 1 Hz, 1H; Ar–H-4), 7.60 (d, ^3J = 8 Hz, 1H; Ar–H-3), 5.11 (s, 2H; Ar–CH_2Br), 4.73 (s, 2H; Ar–CH_2Br); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 167.6, 140.2, 134.2, 133.5, 132.9, 131.7, 130.1, 33.1, 31.9; MS (70 eV, EI): m/z (%) = 307 (26) [M – H]$^+$.

2,5-Bis(bromomethyl)benzoyl chloride (11) [38]: To a solution of **13** (0.88 g, 2.7 mmol) in dry toluene (50 mL) was added $SOCl_2$ (0.67 g, 5.7 mmol) and one drop of DMF. The solution was heated under reflux for 2 h before being cooled to room temperature. The solution was added to dry PhMe (500 mL), and the solvent was removed in vacuo, affording an oil (0.93 g, 95%). The resulting oil was used as the acid chloride **11** in subsequent reactions without any further purification.

1-[2-(2-Hydroxyethoxy)ethoxy]-5-[2-(2-methoxyethoxy)ethoxy]naphthalene (12): A solution of the diol **15** [12g] (5 g, 14.9 mmol) in THF (30 mL) was added dropwise to a suspension of NaH (60% dispersion in mineral oil) (0.30 g, 7.44 mmol) in dry THF (50 mL) under nitrogen. The solution was stirred for 30 min at room temperature and then for an additional 30 min under reflux. A solution of MeI (1.04 g, 7.44 mmol) in THF (20 mL) was added dropwise over 15 min. The solution was heated under reflux for a further 12 h, then cooled, and MeOH (5 mL) was added. The solvents were removed in vacuo, and the oily residue was taken up in CH_2Cl_2 (50 mL) and washed with saturated aqueous Na_2CO_3 (2 × 50 mL) and H_2O (2 × 50 mL). The organic layer was dried over $MgSO_4$ and filtered under gravity, and the CH_2Cl_2 was removed in vacuo. The resulting oil was subjected to silica gel column chromatography, eluting with Et_2O/$CHCl_3$/MeOH (73:25:2). The fractions containing the product were combined and the solvents were removed in vacuo, affording compound **12** (1.80 g, 28%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.87 (d, ^3J = 8 Hz, 1H; naphthalene *H*-4), 7.85, (d, ^3J = 8 Hz, 1H; naphthalene *H*-8), 7.36 (t, ^3J = 8 Hz, 1H; naphthalene *H*-3), 7.35 (t, ^3J = 8 Hz, 1H; naphthalene *H*-7), 6.84 (d, ^3J = 8 Hz, two coincident doublets, 2H; naphthalene *H*-2,6), 4.33–4.28 (m, 4H; OCH_2), 4.02–3.97 (m, 4H; OCH_2), 3.82–3.72 (m, 6H; OCH_2), 3.62–3.58 (m, 2H; OCH_2), 3.39 (s, 3H; OCH_3), 2.02 (brs, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.4, 154.3, 126.9, 126.8, 125.2, 125.0, 114.8, 114.5, 105.8, 105.8, 72.7, 72.0, 70.9, 69.9, 69.8, 68.0, 61.8, 59.1; MS (70 eV, EI): m/z (%) = 350 (40) [M^+]; $C_{19}H_{26}O_6$: calcd C 65.13, H 7.48; found C 64.91, H 7.45.

(1-[2-(2-Oxyethoxy)ethoxy]-5-[2-(2-methoxy-ethoxy)ethoxy]naphthalene)-2,5-bis(bromomethyl)benzoate (10): A solution of the alcohol **12** (0.94 g, 2.7 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise during 30 min to a solution of **11** (0.93 g, 2.7 mmol) in dry CH_2Cl_2 (50 mL) under N_2. The solution was stirred at room temperature under N_2 for 4 h before being heated under reflux gently overnight. The cooled solution was washed with H_2O (2 × 30 mL) and the organic layer was dried over $MgSO_4$. The $MgSO_4$ was filtered off under gravity and the filtrate was concentrated in vacuo. TLC analysis with hexane/EtOAc (4:1) as the eluent revealed one major component. However, silica gel column chromatography, employing hexane/EtOAc (4:1) as the eluant, failed to separate out the minor fraction observed by TLC. Therefore, the crude mixture (1.3 g, 3.8 mmol) was used without further purification.

1-[2-(2-Hydroxyethoxy)ethoxy]-5-[2-(2-(1-adamantanecarbonyl)ethoxy)-ethoxy] naphthalene (18): 1-Adamantanecarbonyl chloride **17** (2.36 g, 1.19 mmol) was added to a solution of the diol **15** (2 g, 5.95 mmol) in 33% volume C_5H_5N/$CHCl_3$ (30 mL) and the mixture was stirred for 12 h at 25 °C, followed by a further period of stirring for 2 h at 60 °C. The solvent was removed in vacuo leaving a residue, which was dissolved in CH_2Cl_2 (100 mL) and washed with 2 M HCl (50 mL) and distilled H_2O (2 × 100 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed in vacuo. The resultant oil was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH 98:2), giving a yellow oil, which, after being washed with hexane (50 mL), yielded the adamantoyl ester **18** (1.08 g, 36%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.87 (d, ^3J = 8 Hz, 1H; naphthalene *H*-4), 7.84 (d, ^3J = 8 Hz, 1H; naphthalene *H*-8), 7.35 (t, ^3J = 8 Hz, 1H; naphthalene *H*-3), 7.34 (t, ^3J = 8 Hz, 1H; naphthalene *H*-7), 6.84 (d, two coincident doublets, ^3J = 8 Hz, 2H; naphthalene *H*-2,6), 4.31–4.20 (m, 6H; OCH_2), 3.99–3.91 (m, 4H; OCH_2); 3.80–3.72 (m, 2H; OCH_2), 3.75–3.62 (m, 4H; OCH_2), 1.96 (brs, 3H; adamantoyl CH), 1.88 (brs, 6H; adamantoyl CH_2), 1.66 (brs, 6H; adamantoyl CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 27.9, 36.5, 38.7, 40.7, 61.9, 63.3, 68.0, 69.6, 69.8, 69.8, 72.6, 105.7, 114.5, 114.8, 125.1, 125.2, 126.8, 154.3, 154.4; MS (LSIMS): m/z = 498 [M^+]; $C_{29}H_{38}O_7$: calcd C 69.86, H 7.68; found C 69.72, H 7.61.

(1-[2-(2-Oxyethoxy)ethoxy]-5-[2-(2-(1-adamantanecarbonyl)ethoxy)ethoxy]-naphthalene)-2,5-bis(bromomethyl)benzoate (16): A solution of alcohol **18** (1.08 g, 2.16 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise over 30 min to a solution of **11** (0.7 g, 2.16 mmol) in dry CH_2Cl_2 (15 mL). The solution was stirred at room temperature under nitrogen for 4 h and then heated gently under reflux overnight. The cooled solution was washed with water (2 × 30 mL) and the organic layer was dried over $MgSO_4$. The $MgSO_4$ was filtered off and the filtrate was concentrated in vacuo. The crude mixture (1.31 g, 1.60 mmol) was used without further purification.

(1-[2-(2-Oxyethoxy)ethoxy]-4-benzyloxybenzene)-2,5-bis(bromomethyl) benzoate (19): The alcohol **21** (0.66 g, 2.29 mmol) [12g] in dry CH_2Cl_2 (10 mL) was added dropwise over 30 min to a solution of **11** (0.75 g, 2.3 mmol) in dry CH_2Cl_2 (15 mL). The solution was stirred at room temperature under nitrogen for 4 h and then it was heated gently under reflux overnight. The cooled

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solution was washed with H_2O (2 × 30 mL) and the organic layer dried over $MgSO_4$. The $MgSO_4$ was filtered off and the solvent removed in vacuo. The crude mixture (0.98 g, 1.7 mmol) was used without further modification.

9,10-Bis(bromomethyl)anthracene (23) [39]: Anthracene (8 g, 4.4 mmol) was added to a solution of $(CH_2O)_n$ (8 g, 0.26 mol) in 30% HBr/AcOH (100 mL). The solution was heated to 50 °C while being stirred for 30 min, at which point stirring was abandoned on account of the formation of a thick yellow precipitate. Heating was continued for a further 1.5 h. The reaction mixture was cooled overnight. The yellow precipitate was filtered off under reduced pressure and washed well with AcOH, H_2O, aqueous Na_2CO_3 (10%) solution, H_2O, and Et_2O. The yellow solid was dried in vacuo and recrystallized from toluene, affording a fine yellow powder **23** (9.5 g, 64%): m.p. 170 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.41–8.36 (m, 4H; anthracene *H*-1,4,6,9), 7.71–7.66 (m, 4H; anthracene *H*-2,3,5,7), 5.53 (s, 4H; Ar–CH_2Br); MS (NH_3, CI): *m/z* (%) = 364 (2) [M^+], 283 (35) [M – Br]$^+$, 205 (100) [M – 2Br]$^+$.

1,1′-[9,10-Anthracene(methylene)]bis-4,4′-pyridylpyridinium bis(hexafluorophosphate) (22·2PF$_6$): 9,10-Bis(bromomethyl)anthracene **23** (5 g, 13.4 mmol) was added to a solution of 4,4′-bipyridine (20 g, 134 mmol) in refluxing MeCN (100 mL) over a period of 5 days under nitrogen. The solution was heated under reflux for one more day and then cooled. In order to induce full precipitation of the salt that had formed during the course of the reaction, Et_2O was added (100 mL). The precipitate was filtered off and washed with Et_2O and $CHCl_3$ to remove any soluble impurities. The resulting white solid was subjected to silica gel column chromatography with MeOH/NH_4Cl (2M)/$MeNO_2$ (7:2:1) eluent. The fractions containing the product were combined and concentrated. H_2O (50 mL) was added to dissolve the chloride salts, followed by the addition of an aqueous NH_4PF_6 solution to precipitate the product as its bis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure, washed well with H_2O, and dried in vacuo, yielding compound **22**·2PF$_6$ (7.0 g, 65%) as a white solid: m.p. 250 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.83 (d, $^3J_{AB}$ = 6 Hz, 4H; bipyridinium α-CH), 8.72 (d, $^3J_{AB}$ = 6 Hz, 4H; bipyridinium β-CH), 8.43–8.37 (m, 4H; anthracene *H*-1,4,6,9), 8.26 (d, $^3J_{AB}$ = 6 Hz, 4H; bipyridinium α-CH), 7.82–7.75 (m, 4H; anthracene *H*-2,3,7,8), 7.76 (d, $^3J_{AB}$ = 6 Hz, 4H; bipyridinium β-CH), 6.89 (s, 4H; Ar–CH_2); ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ = 155.8, 152.2, 145.5, 141.2, 132.8, 129.7, 127.3, 126.4, 125.3, 122.8, 57.4; MS (LSIMS): *m/z* (%) = 661 (100) [M – PF$_6$]$^+$; $C_{36}H_{28}N_4P_2F_{12}$: calcd C 53.61, H 3.5, N 6.95; found C 53.71, H 3.36, N 6.76.

Cyclo[ethyl 2,5-(paraquat-*p*-phenyleneparaquat)benzoate] tetrakis(hexafluorophosphate) (28·4PF$_6$) [38]: A solution of **7** (0.14 g, 0.43 mmol), the bipyridinium salt **26**·2PF$_6$ (0.25 g, 0.36 mmol) and the template **15** were stirred in DMF (5 mL) for 5 days at room temperature and ambient pressure. In order to ensure full precipitation of the salt, Et_2O (50 mL) was added. The precipitate was filtered off under reduced pressure and subjected to a liquid–liquid extraction in order to partition the salts and the template **15** between H_2O and $CHCl_3$. The aqueous layer was concentrated and the salts were precipitated with aqueous NH_4PF_6 solution. The precipitate was filtered off and subjected to silica gel chromatography with MeOH/NH_4Cl (2M)/$MeNO_2$ (7:2:1) eluent. The fractions containing the product were combined and concentrated. H_2O (50 mL) was added to dissolve the chloride salts, followed by the addition of aqueous NH_4PF_6 solution to precipitate the product as its tetrakis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure, washed well with H_2O, and dried in vacuo at 40 °C, yielding **28**·4PF$_6$ (0.16 g, 39%) as a white solid: m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 8.93–8.85 (m, 8H; bipyridinium α-CH), 8.21–8.16 (d, ^4J = 1 Hz, 1H; Ar–H-6), 8.19 (m, 6H; bipyridinium β-CH), 8.12 (d, $^3J_{AB}$ = 6 Hz, 2H; bipyridinium β-CH), 7.67 (dd, $^{3,4}J$ = 8 Hz, 1 Hz, 1H; Ar–H-4), 7.57 (d, ^3J = 8 Hz, 1H; Ar–H-3), 7.53 (s, 4H; xylyl *H*), 6.15 (s, 2H; NCH_2), 5.83 (s, 2H; NCH_2), 5.75 (s, 4H; NCH_2), 4.42 (q, ^3J = 7 Hz, 2H; CH_2CH_3), 1.43 (t, ^3J = 7 Hz, 3H; CH_2CH_3); ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ = 166.8, 150.8, 150.5, 146.8, 146.2, 146.0, 137.2, 136.9, 136.7, 134.6, 133.3, 131.6, 131.3, 131.1, 128.3, 128.3, 128.2, 127.7, 65.6, 65.5, 65.0, 63.3, 62.5, 14.2; MS (LSIMS): *m/z* = 1027 [M – PF$_6$]$^+$, 882 [M – 2PF$_6$]$^+$, 737 [M – 3PF$_6$]$^+$; $C_{39}H_{36}F_{24}N_4O_2P_4$: calcd C 39.95, H 3.09, N 4.78; found C 40.24, H 3.08, N 5.05.

Cyclo[1-[2-(2-oxyethoxy)ethoxy]-5-[2-(2-methoxyethoxy)ethoxy)naphthalene 2,5-(paraquat-*p*-phenyleneparaquat)benzoate] tetrakis(hexafluorophosphate) (29·4PF$_6$): A solution of the dibromide **10** (0.14 g, 0.22 mmol) and the bipyridinium salt **26**·2PF$_6$ (0.13 g, 0.19 mmol) was stirred in DMF (5 mL) for 5 days at room temperature and ambient pressure. In order to ensure full precipitation of the purple salt, Et_2O (50 mL) was added to the reaction mixture. The precipitate was filtered off under reduced pressure and subjected to silica gel chromatography with MeOH/NH_4Cl (2M)/$MeNO_2$ (7:2:1) as eluent. The fractions containing the product were combined and concentrated. H_2O (50 mL) was added to dissolve the chloride salts, followed by the addition of an aqueous NH_4PF_6 solution to precipitate the product as its tetrakis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure, washed well with H_2O, and dried in vacuo at 40 °C, yielding **29**·4PF$_6$ (0.065 g, 24%) as a purple solid: m.p. > 270 °C; ^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ = 9.27 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-CH), 9.11 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-CH), 9.03 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-CH), 8.81–8.72 (m, 4H; 3 × bipyridinium α-CH and Ar–H-6), 8.61 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-CH), 8.53 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-CH), 8.26 (dd, $^{3,4}J$ = 7 Hz, 1 Hz, 1H; Ar–H-3), 8.12 (d, ^3J = 7 Hz, 1H; Ar–H-4), 8.07 (s, 2H; xylyl H), 7.97 (s, 2H; xylyl H), 7.57–7.49 (m, 3H; bipyridinium β-CH), 7.39–7.31 (m, 2H; bipyridinium β-CH), 7.26 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium β-CH), 7.19–7.11 (m, 2H; bipyridinium β-CH), 6.97 (d, ^3J = 13 Hz, 1H; NCH_2), 6.36 (d, ^3J = 7 Hz, 1H; naphthalene), 6.22–6.13 (m, 2H; naphthalene), 5.90–5.81 (m, 3H; 2 × NCH_2 and naphthalene), 5.75–5.68 (m, 4H; NCH_2), 5.66 (d, ^3J = 12 Hz, 1H; NCH_2), 5.44–5.34 (m, 1H; OCH_2), 4.40–4.21 (m, 6H; OCH_2), 4.20–4.10 (m, 3H; OCH_2), 4.09–3.97 (m, 2H; OCH_2), 3.86–3.78 (m, 4H; OCH_2), 3.42 (s, 3H; OCH_3), 2.88 (d, ^3J = 8 Hz, 1H; naphthalene), 2.42 (d, ^3J = 8 Hz, 1H; naphthalene); MS (LSIMS): *m/z* = 1333 [M – PF$_6$]$^+$, 1187 [M – 2PF$_6$]$^+$, 1043 [M – 3PF$_6$]$^+$; $C_{56}H_{56}F_{24}N_4O_7P_4$: calcd C 45.54, H 3.82, N 3.82; found C 45.26, H 3.72, N 3.69.

Cyclo[1-[2-(2-oxyethoxy)ethoxy]-5-[2-(2-(1-adamantanecarbonyl)ethoxy)ethoxy]naphthalene 2,5-(paraquat-*p*-phenyleneparaquat)benzoate] tetrakis(hexafluorophosphate) (30·4PF$_6$): A solution of the dibromide **16** (1.35 g, 1.71 mmol) and the bipyridinium salt **26**·2PF$_6$ (1.04 g, 1.48 mmol) in DMF (10 mL) was stirred for 7 days at room temperature and pressure. In order to ensure full precipitation of the purple salt, Et_2O (50 mL) was added to the reaction mixture. The precipitate was filtered off under reduced pressure and subjected to column chromatography (SiO_2, MeOH/NH_4Cl (2M)/$MeNO_2$ 4:1:4). The fractions containing the product were combined and concentrated. H_2O (50 mL) was added to dissolve the chloride salts, followed by the addition of an aqueous NH_4PF_6 solution to precipitate the product as its tetrakis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure, washed well with H_2O, and dried in vacuo, yielding **30**·4PF$_6$ (0.3 g, 13%) as a purple solid. M.p. > 270 °C (decomp.); ^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C): δ = 9.55 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-H), 9.48–9.31 (m, 3H; bipyridinium α-H), 9.25 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-H), 9.21 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-H), 9.16 (d, ^3J = 1 Hz, 1H; Ar–H-6), 9.15 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-H), 9.06 (d, $^3J_{AB}$ = 6 Hz, 1H; bipyridinium α-H), 8.59 (dd, ^3J = 1, 7 Hz, 1H; Ar–H-4), 8.45 (d, ^3J = 7 Hz, 1H; Ar–H-3), 8.38 (brs, 2H; xylyl *H*), 8.28 (brs, 2H; xylyl H), 8.24–8.18 (m, 2H; bipyridinium β-H), 7.97–7.92 (m, 2H; bipyridinium β-H), 7.67–7.64 (m, 2H; bipyridinium β-H), 7.50–7.48 (m, 2H; bipyridinium β-H), 7.26 (d, ^3J = 13 Hz, 1H; NCH_2), 6.50 (d, ^3J = 7 Hz, 1H; naphthalene), 6.42–6.40 (m, 2H; naphthalene), 6.25–6.12 (m, 4H; 3 × NCH_2 and naphthalene), 6.09–6.06 (m, 3H; NCH_2), 6.05 (d, ^3J = 13 Hz, 1H; NCH_2), 5.38 (m, 1H; OCH_2), 4.62–4.47 (m, 5H; OCH_2), 4.42–4.33 (m, 6H; OCH_2), 4.18–4.08 (m, 6H; OCH_2), 3.04 (d, ^3J = 8 Hz, 1H; naphthalene), 2.76 (d, ^3J = 8 Hz, 1H; naphthalene), 1.84 (brs, 3H; adamantoyl CH), 1.71 (brs, 6H; adamantoyl CH_2), 1.67 (brs, 6H; adamantoyl CH_2); MS (LSIMS): *m/z* = 1647 [M – Na]$^+$, 1479 [M – PF$_6$]$^+$, 1334 [M – 2PF$_6$]$^+$, 1189 [M – 3PF$_6$]$^+$; HRMS (LSIMS): $C_{66}H_{68}N_4O_8F_{18}P_3$: [$M$ – PF$_6$]$^+$, calcd 1479.3962, found 1479.3915.

Cyclo[1-[2-(2-oxyethoxy)ethoxy]-4-benzyloxybenzene-2,5-(paraquat-*p*-phenyleneparaquat)benzoate] tetrakis(hexafluorophosphate) (31·4PF$_6$): A solution of the dibromide **19** (1.15 g, 2.06 mmol) and the bipyridinium salt **26**·2PF$_6$ (1.21 g, 1.72 mmol) was stirred in DMF (10 mL) for 10 days at room temperature and ambient pressure. In order to ensure full precipitation of the red salt, Et_2O (50 mL) was added to the reaction mixture. The red precipitate was filtered off under reduced pressure and subjected to silica gel column chromatography with MeOH/NH_4Cl (2M)/$MeNO_2$ (7:2:1) as eluent. The fractions containing the product were combined together and solvent was

removed in vacuo. H_2O (50 mL) was added to dissolve the chloride salt, followed by the addition of a saturated aqueous solution of NH_4PF_6 to precipitate the product as its tetrakis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure and washed well with H_2O and then dried in vacuo. Crystallization by vapor diffusion of iPr_2O into an MeCN solution of the salt afforded **31**·4PF_6 (0.16 g, 7%) as a red crystalline solid: ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C, TMS): δ = 9.44–9.34 (m, 4H; bipyridinium α-CH), 9.29–9.22 (m, 4H; bipyridinium α-CH), 8.87 (d, ^4J = 8 Hz, 1H; Ar–H-6), 8.41–8.34 (m, 6H; bipyridinium β-CH), 8.26–8.21 (m, 3H; 2× bipyridinium β-CH and Ar-H-4), 8.11 (d, ^3J = 7 Hz, 1H; Ar–H-3), 7.78–7.7 (m, 4H; xylyl H), 7.66–7.61 (m, 2H; OCH_2Ar–H), 7.59–7.56 (m, 2H; OCH_2Ar–H), 7.48–7.40 (m, 1H; OCH_2Ar–H), 6.54 (s, 2H; NCH_2), 6.16 (s, 2H; NCH_2), 6.02 (s, 2H; NCH_2), 5.99 (s, 2H; NCH_2), 4.78–4.74 (m, 2H; OCH_2), 4.67 (s, 2H; OCH_2Ar), 4.31–4.25 (m, 2H; OCH_2), 4.12–4.06 (m, 2H; OCH_2), 3.96–3.93 (m, 2H; OCH_2), 3.81–3.72 (m, 4H; hydroquinone); MS (LSIMS): m/z = 1437 $[M+Na]^+$, 1269 $[M-PF_6]^+$, 1124 $[M-2PF_6]^+$, 979 $[M-3PF_6]^+$; HRMS (LSIMS): $C_{54}H_{50}N_4O_5F_{18}P_3$: $[M-PF_6]^+$ calcd 1269.2670, found 1269.2706. Crystal data for **31**·4PF_6: single crystals suitable for X-ray crystallography were obtained by vapor diffusion of iPr_2O into an MeCN solution of **31**·4PF_6. $C_{54}H_{50}N_4O_5F_{24}P_4 \cdot 2Me_2CO \cdot MeCN$, M = 1572.1, monoclinic, a = 11.446(3), b = 22.292(3), c = 14.450(2) Å, β = 109.84(1)°, V = 3468(1) Å^3, space group C_2, Z = 2 (the molecule has crystallographic C_2 symmetry), ρ_c = 1.505 g cm^{-3}, μ ($Cu_{K\alpha}$) = 20.8 cm^{-1}, $F(000)$ = 1608. Data for a crystal of dimensions 0.35 × 0.21 × 0.02 mm^3 were measured at −70 °C on a Siemens P4/RA diffractometer ($2\theta \leq 124°$) with $Cu_{K\alpha}$ radiation (graphite monochromator) and ω-scans. Of the 2821 independent reflections measured, 1823 had $|F_0| > 4\sigma(|F_0|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods, and only the major occupancy portions of the disordered PF_6^- anions were refined anisotropically. The structural disorder about the C_2 axis and the relative lack of observed data precluded anisotropic refinement of any of the remaining parts of the structure. Although the cyclophane component of the structure is ordered about the C_2 axis, the self-threading component is not and even those parts that could adopt a C_2 symmetric arrangement do not do so. The central hydroquinone ring is displaced sideways with respect to the crystallographic C_2 axis. The geometry of the whole of the polyether chain, the hydroquinone ring and the terminal benzyl group were optimized and restrained to an idealized geometry. Hydrogen atoms were placed in calculated positions and assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. The refinement was by full-matrix least-squares based on F^2 to give R_1 = 0.126, wR_2 = 0.3442 for the observed data and 366 parameters. The maximum and minimum residual electronic densities in the final ΔF map were 0.71 and −0.45 e Å^{-3}. Computations were carried out on a 486 PC with the SHELXTL-PC version 5 program system [56].

Cyclo[1-[2-(2-oxyethoxy)ethoxy]-5-[2-(2-methoxyethoxy)ethoxy]naphthalene-2,5-(paraquat-9,10-anthraceneparaquat)benzoate] tetrakis(hexafluorophosphate) (32·4PF$_6$): A solution of the dibromide **10** (0.14 g, 0.22 mmol) and the anthracene-containing bipyridinium salt **22**·2PF_6 (0.15 g, 0.186 mmol) in DMF (5 mL) was subjected to 12 kbar pressure for 3 days at room temperature. In order to ensure full precipitation of the red salt, Et_2O (50 mL) was added to the reaction mixture. The precipitate was filtered off under reduced pressure and subjected to silica gel chromatography with MeOH/NH_4Cl (2M)/$MeNO_2$ (7:2:1) as eluent. The fractions containing the product were combined and concentrated. H_2O (50 mL) was added to dissolve the chloride salts, followed by the addition of an aqueous NH_4PF_6 solution to precipitate the product as its tetrakis(hexafluorophosphate) salt. The precipitate was collected under reduced pressure, washed well with H_2O, and dried in vacuo at 40 °C, yielding a red solid **32**·4PF_6 (0.087 g, 30%): m.p. > 270 °C; MS (LSIMS): m/z = 1576 $[M^+]$, 1432 $[M-PF_6]^+$, 1286 $[M-2PF_6]^+$, 1141 $[M-3PF_6]^+$; $C_{60}H_{60}F_{24}N_4O_7P_4$: calcd C 48.96, H 3.94, N 3.73; found C 48.74; H 3.83, N 3.55. The room-temperature ^{1}H NMR spectrum (300 MHz) in CD_3CN solution indicates that there is a slow exchange process occurring between complexed and uncomplexed species. Thus, the spectra cannot be interpreted without an extensive variable-temperature ^{1}H NMR spectroscopic investigation. This study was not carried out in view of the fact that photochemical switching was not observed for the simpler compound **32**·4Cl.

Absorption spectra, luminescence, photochemical and electrochemical experiments: Absorption and emission spectra were recorded with a Perkin–Elmer λ6 spectrophotometer and a Perkin–Elmer LS-50 spectrofluorimeter, respectively. Fluorescence lifetimes were measured with Edinburgh 199 single-photon counting equipment. Photochemical experiments were carried out in argon-purged water solutions, by means of a Hanau Q400 medium-pressure mercury lamp. The 365 nm wavelength was isolated by means of an interference filter. The incident light intensity on the 3 mL reaction cell was 2×10^{-6} N hν min^{-1}. Electrochemical measurements (cyclic voltammetry, CV, and differential pulse voltammetry, DPV) were carried out in argon-purged acetonitrile solutions with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer. A glassy carbon electrode (0.08 cm^2, Amel) was used as the working electrode. The counter electrode was a Pt wire and the reference electrode was an SCE (saturated calomel electrode) separated with a fine glass frit. The concentration of the examined compounds was 5.0×10^{-4} M; 0.05 M tetraethylammonium tetrafluoroborate ($TEABF_4$) was added as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates of 20, 50, 200, 500, and 1000 mV s^{-1}; DPV experiments were performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. For the observed processes, the same $E_{1/2}$ values were obtained from the DPV peaks and from an average of the cathodic and anodic CV peaks. Both CV and DPV techniques have been used to measure the number of the exchanged electrons in each redox process. The criteria for reversibility were i) a separation of 60 mV between cathodic and anodic peaks, ii) a ratio of the intensities of the cathodic and anodic currents close to unity, iii) and constancy of the peak potential on changing sweep rate. The experimental error on the half-wave potential values was estimated to be ±10 mV. Spectroelectrochemical experiments were perfomed on argon-purged acetonitrile solutions of 1.0×10^{-4} M of the examined compound and 0.01 M of $TEABF_4$ contained in a spectrofluorimetric cell (optical path 1 cm), with a Pt grid as working electrode, a Pt wire separated with a fine glass frit as a counter-electrode, and an Amel Ag/AgCl reference electrode. Absorption spectra of the reduced species were recorded with a Kontron Uvikon 860 spectrophotometer, and emission spectra were recorded with a Perkin–Elmer LS 5 spectrofluorimeter with appropriate corrections for inner filter effects.

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