Superstructured Porphyrins as Effectors in Dynamic Supramolecular Assemblies: Receptors, Rotaxanes and Catenanes

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The development of porphyrinic systems specifically functionalised to recognise photoactive and electroactive substrates has been a study in the evolution of supramolecular assemblies, from receptors, through pseudorotaxanes to catenanes, to thermodynamically-controlled synthesis, and eventually to solid-appended self-assembling supermolecules. We describe how crown ether-capped porphyrins act as efficient receptors for bipyridinium dications, where the complexes have an in-built addressability through the porphyrin, and are monitored through physical and chemical stimuli. Conceptual extension allows production of porphyrin[2]- and -[3]-catenanes, and a series of these offers opportunities for a structure-activity profile through a variety of dynamic processes, including motional, translational, chemical (acid/base), photochemical and electrochemical methods. Related design concepts extend the study into neutrally-charged diimide-based catenanes. The recognition processes responsible for their synthesis have then been extended into equilibrating conditions, so that the thermodynamically most favourable rotaxanes can be assembled by simple mixing of components. Finally, these concepts have led to the direct real-time study by gel-phase HRMAS methodology of the self-assembly of porphyrin rotaxanes on polymer supports, under equilibrating conditions between solid and solution phases.

Introduction

Supramolecular chemistry has already advanced from more or less simple beginnings of molecular recognition (host-guest systems) to the second generation of systems with inbuilt functionality to address and stimulate the assemblies to perform useful chemistry, and further still to arrays which can emulate meso-scale processes. Molecular machines,[1−5] nanotechnology,[6−8] synthetic enzymes,[9,10] artificial photosynthesis,[11−13] molecular scale electronic devices[14] − wires, switches, diodes, relays, etc. are just some of the applications that have derived from the controlled and rational development of new-age supramolecules.

Many whose interests span a range of fundamental aspects of modern chemistry have been attracted to the concept of molecular receptors incorporating porphyrins as fundamental components, either as a potential reactive site[15] or as part of the structural architecture for assembling the various components of an array.[16] Furthermore, metalloporphyrins have been the molecules of choice for photoactive systems designed with photo-induced electron transfer (PET) or energy transfer (EnT) as fundamental operational principles in materials chemistry.[17,18] This is

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MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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hardly surprising, given the remarkable range of properties that can be accessed by appropriate variation in both the substituents and the metal ion in metalloporphyrins.

Most of the systems built around the PET or EnT concept have relied on the covalent bond for control of the overall design, whether it be for rigidity, flexibility, stereoselectivity, or geometric requirements, and the chemical literature abounds with beautiful molecules that seem only to be limited by the chemists' imaginations. On the other hand, we and many others have been attracted by the potential for noncovalent interactions as a fundamental design motif in assembling supramolecular systems with the desired properties for a variety of potential functions. Several of these ideas are illustrated in this microreview, where we describe some approaches to novel supramolecular systems which utilise porphyrins or their metallo derivatives as both a fundamental structural unit and the origin of the trigger or stimulus to activate the arrays in various ways.

Photoactive Receptors

In the first series, a new family of receptor molecules was developed from two design concepts: (i) bipyridinium dications have been shown to bind noncovalently to certain dibenzo-crown ethers, and (ii) bipyridinium dications are efficient electron acceptors, and indeed can be used in systems which can photochemically generate hydrogen from water under appropriate conditions when a metalloporphyrin is used as electron donor. Thus, the appendage of a specifically designed dibenzo-crown to a metalloporphyrin should result in a molecule in which an electron donor (the metalloporphyrin) and electron acceptor (the bipyridinium dication) can be brought together through noncovalent bonding, thus allowing for efficient PET under suitably chosen conditions.

The design was based upon the principles established some time ago by Stoddart et al, where *ortho*- and *meta*-substituted crown ethers of the appropriate size such as **1** were shown to be excellent receptors for bipyridinium dications such as diquat and paraquat.[19,20] The binding geometry is such that the dibenzo crown enfolds the bipyridinium in an "ear-muff" or "headphone" fashion. The operating complexation forces include π−π interactions between the aromatic rings, as well as C−H−O hydrogen bonding, electrostatic interactions, and CH−π interactions. The binding could be enhanced by strapping the crown ethers at the benzo rings, **2**,[21] resulting in a higher degree of pre-organisation. As far as we were concerned an obvious evolution of such a molecule would be to replace the linking unit with a porphyrin, **3**. The conceptual evolution and design is depicted in Figure 1.

In such a porphyrinic system, after efficient photoinduced electron transfer from the metalloporphyrin to the adjacent bipyridinium receptor, it was envisaged that the supramolecular complex would be destabilised and the photoproducts might escape, thus alleviating an inherent problem in most covalently linked donor-acceptor systems, that of back electron transfer. This is shown schematically in Figure 2. In other words, *charge separation* might be achieved, an essential factor for any effective photoactive system, and indeed the fundamental requirement for any system that would hope to model or mimic the basic functions of photosynthesis.

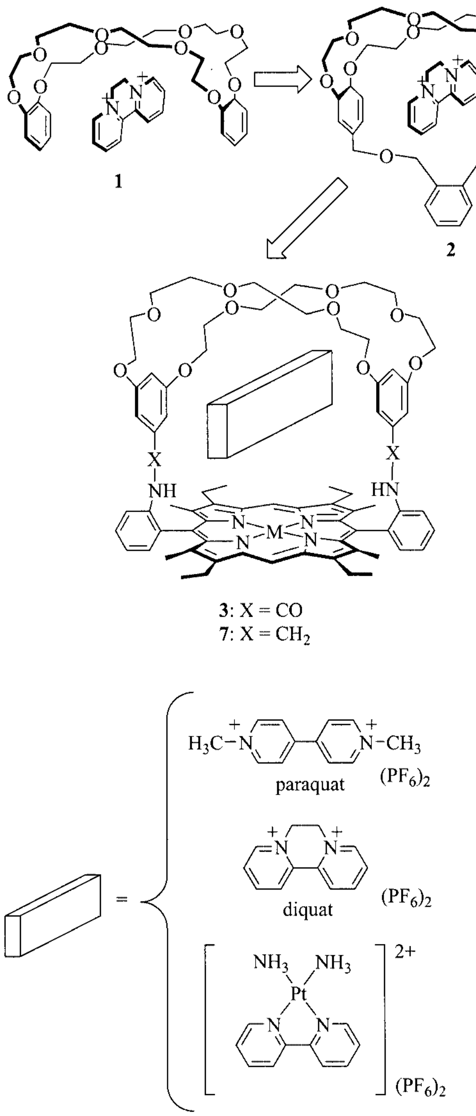


Figure 1. Conceptual evolution of porphyrin-based crown ether co-receptors for bipyridinium guests

In our initial systems a dibenzo-crown ether, containing *meta*-substituted aromatic rings and tetraethylene glycol ether chains, was strapped across a porphyrin to produce a series of macrotricyclic hosts **3** (Figure 1).[22−24] The strapped porphyrin systems were derived from the α,α-atropisomer of the 5,15-bis(*o*-aminophenyl)octaalkylporphyrin **4**[25] by high dilution condensation with the dicarbonyl chloride derivative of the dibenzo crown (Scheme 1).

As a result of the amide bond linkage, the crown ether subunit of **3a** was found to be conformationally solvent dependent. From characteristic ^{1}H NMR shifts, two conformational extremes were identifiable; in acetone the crown

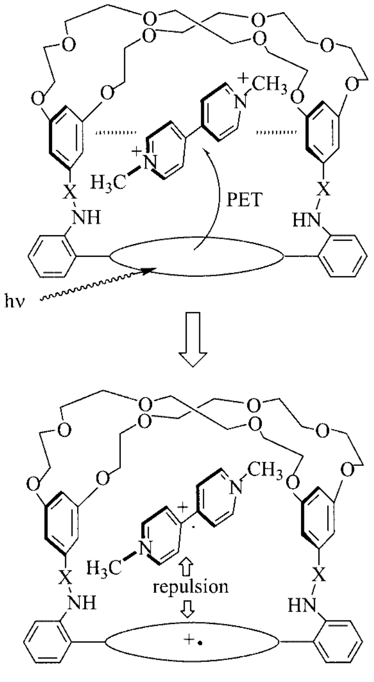


Figure 2. Proposed charge escape mechanism after photoinduced electron transfer (PET) for the porphyrin/bipyridinium complexes

aromatic rings are essentially co-planar with the *meso*-phenyl plane, whereas in chloroform they are nearly orthogonal to it (Figure 3).

Nevertheless, this host could complex methyl viologen (paraquat) (K_a = 50 M^{-1} at 298 K) and

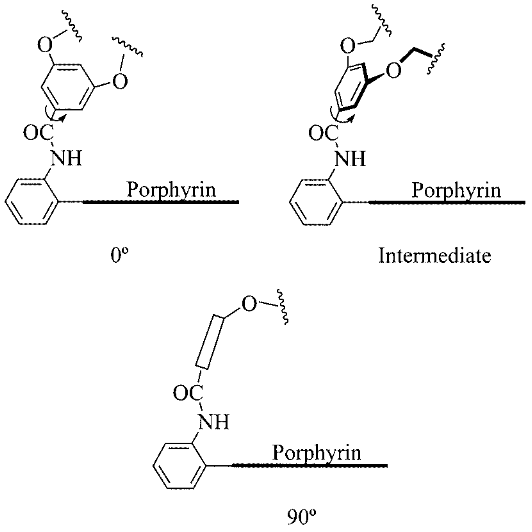
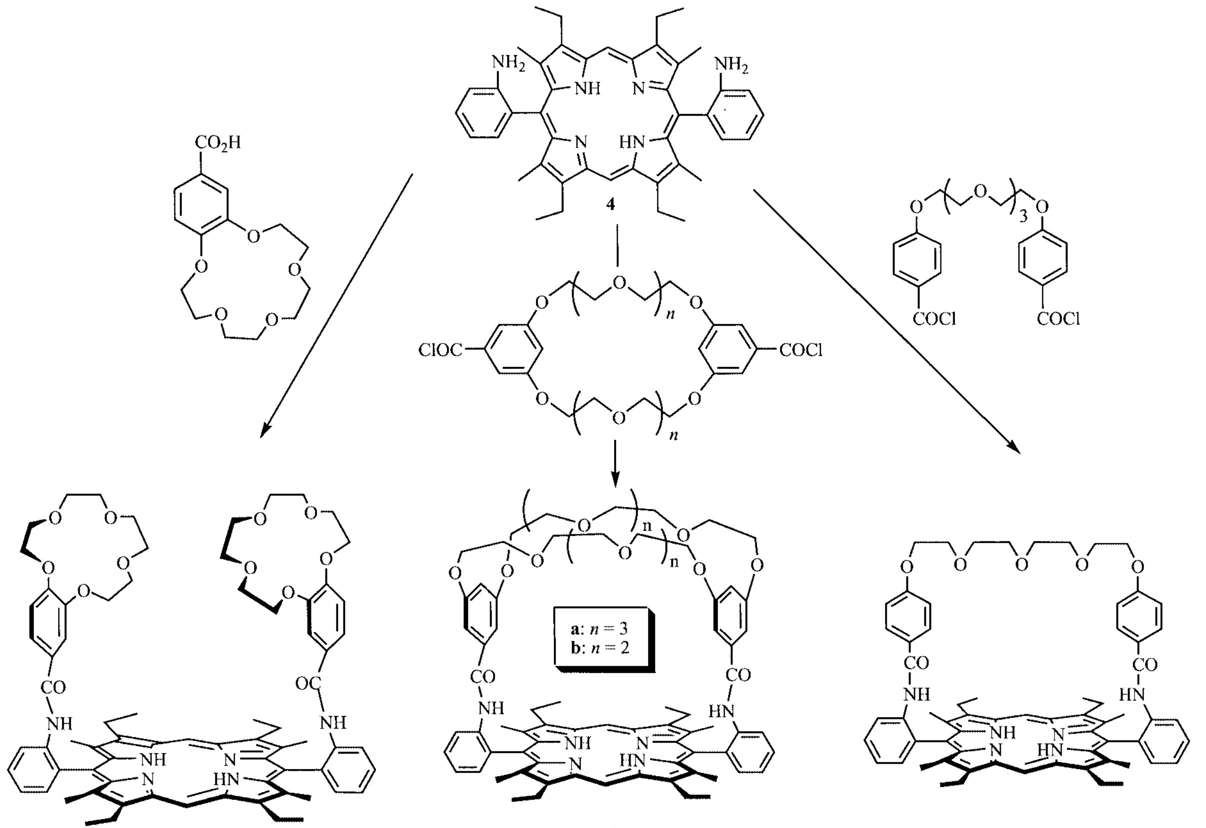


Figure 3. Possible solvent and substrate-dependent conformations of the amide-based receptors



Scheme 1

$[Pt(bpy)(NH_3)_2](PF_6)_2$ (K_a = 1350 M^{-1} at 298 K) by a solvent-dependent *induced fit* mechanism, as a result of rotational barriers associated with the diaryl amide linkage (clearly for effective binding the crown aromatic rings are required to be perpendicular to the *meso*-aryl ring, at a cost of decreased resonance stabilisation which is maximised by a co-planar orientation of both aryl rings and the amide).

Efforts to improve the complexing ability of these types of hosts involved a shortening of the linking ether chains **3b**[23] (for a gain in entropy through a more preorganised structure), and reduction of the amide group linking the crown ether and porphyrin moieties, **7** (which alleviates the problem of the conformationally restrictive amide). Of these two directions the reduced host **7** was most successful, complexing all the bipyridinium dications examined, although ligand exchange reactions complicated the binding of the platinum complex (for paraquat K_a = 480 M^{-1} at 298 K; for diquat K_a = 80 M^{-1} at 298 K). By contrast, the host containing shortened ether chains **3b** was observed to have similar complexing abilities to its predecessor, as a result of comparable solution conformations (for paraquat K_a = 50 M^{-1} at 298 K; for $[Pt(bpy)(NH_3)_2](PF_6)_2$ K_a = 365 M^{-1} at 298 K). However, in this case binding by the platinum complex within the constricted cavity of the host resulted in deformation of the porphyrin and an increased activation barrier to complexation.

To gauge the minimal structural requirements for efficient receptors for bipyridinium groups, we simplified the design, and indeed the syntheses, by making a single polyether strapped derivative **5**,[24] and also by a *bis*-crown appended porphyrin in which the porphyrin is surmounted by two separate benzo-15-crown-5 units **6**, which might bind the guest in the manner of a pair of tweezers.[23,26]

However, the simplified macrobicyclic receptor **5** failed to complex either the paraquat or diquat dications to any significant extent, although it formed an inclusion complex with $[Pt(bpy)(NH_3)_2]^{2+}$ (K_a = 155 M^{-1}) with an orthogonal orientation of the guest relative to the porphyrin plane, as for the macrotricyclic host. The lack of paraquat and diquat complexation may be due to either an incorrect number or geometry of ether oxygen atoms for electrostatic interactions, and/or unfavourable orientations of the crown aromatic rings due to their increased conformational mobility within **5** when compared to the macrotricyclic analogue **3**. This suggests that (i) decreasing the number of ether chains from two to one only partially removes the steric effects from the ether chain on the crown aromatic rings, or (ii) the amide bond is still dominant in influencing the solution conformations of the crown aromatic rings.

On the other hand, the tweezer **6** does bind paraquat, diquat, and $[Pt(bpy)(NH_3)_2]^{2+}$ in acetone solution with association constants of 32, 20, 140 M^{-1}, respectively. The stronger complexation of $[Pt(bpy)(NH_3)_2]^{2+}$ presumably reflects the additional stabilisation of the inclusion complex by hydrogen bonding between the ammine ligands of $[Pt(bpy)(NH_3)_2]^{2+}$ and the oxygen atoms of the crown tweezer. The inclusion geometry of these guests within the pincers of **6** was confirmed by NMR measurements, and was again consistent with the aromatic rings of the guest sandwiched between the aromatic benzo-crown rings as predicted.[23,26]

To simplify the receptor design even further, an analogous minimal tweezer molecule where the crown ether chains were replaced by simple methoxy substituents was easily prepared, but did not bind any of the guests; clearly some oxygen donor atoms in the over-arching moiety are essential to the design.

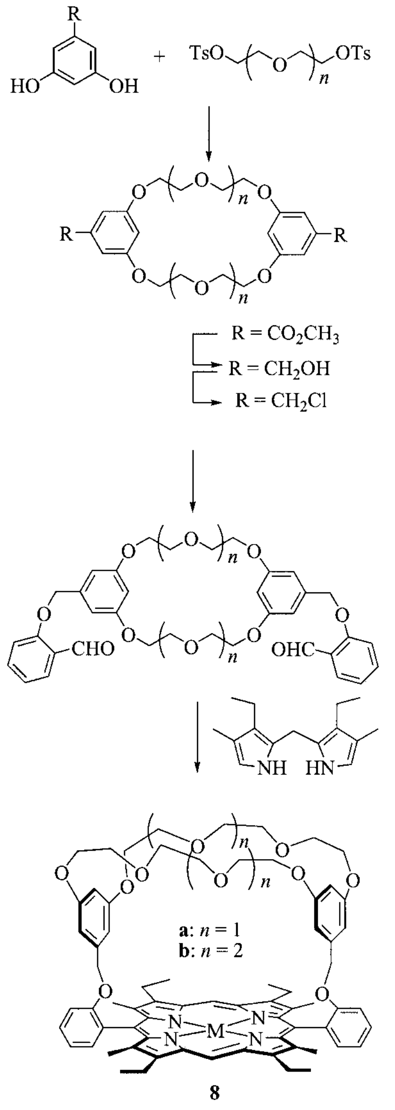
Although **6** was observed to complex all three guests, the smaller association constants and free energies of complexation compared to the nonporphyrinic receptors of the Stoddart type reflects the lesser degree of pre-organisation present in the crown ethers of the complexing subunit of **6**. Thus, although the removal of the bridging ether chains allowed an increase in the conformational mobility of the crown aromatic rings the net result was a decrease in the level of pre-organisation, and a reduction in the receptor binding strength.

To overcome the problems resulting from the conformational preferences and restricted rotation about the amide bond which added extra kinetic and thermodynamic barriers to the binding process, we next produced a new series of porphyrin-base receptors **8** for paraquat and diquat with the same over-arching dibenzo-crown ethers, but in these cases the appended superstructure was connected to the porphyrin through ether linkages from the *o*-positions of the *meso*-aryls of the porphyrins.[27] We found that in these cases that the synthesis was easier if a dialdehyde is incorporated at each end of the strap, and this is then condensed in a "2+2" method with a dipyrromethane (Scheme 2).

We were surprised to find in these complexes, at variance with the amide series, conformations in which the complexed bipyridinium is parallel to the porphyrin sub-unit rather than perpendicular to it, as indicated in Figure 4. Solid state structures of several representative members of this series confirmed the solution NMR evidence for this binding geometry such as shown in Figure 5.[27]

The range of binding constants measured for all of the free-base and zincporphyrin derivatives in this series with both paraquat and diquat in various solvents allowed several important principles to be established: (i) the binding strength decreases with increasing solvent polarity, (ii) there is little difference in the binding strength between the free base and zinc derivatives for a given receptor, (iii) binding is stronger for the more constrained compared to the looser host systems, (iv) in general paraquat binds more strongly than diquat, (v) the single strapped analogues **5** are relatively ineffective as receptors for these bipyridinium guests, (vi) for a given sized dibenzo-crown ether cap or polyether strap, the substitution of ether linkages for the amide linkages in the related family of receptors **3** and **8** results in stronger binding.

Since the rationale of the design of these receptors was based on the binding motif of Stoddart's nonporphyrinic *ortho*- and *meta*-substituted benzo crown ethers such as BMP32C10, and because of the parallel binding geometry



Scheme 2

evident in these host systems, we were encouraged to adjust the design to incorporate the *para*-substituted series **9**, where the bipyridinium guests are threaded through the annulus of the crown as shown in **10**, rather than being enfolded by it in "headphone" fashion.[28−31] For this series of receptor then, we needed a porphyrin strapped by a hydroquinol or naphthoquinol-containing polyethylene glycol strap; conceptually, we were replacing one of the quinol units with an electron-rich porphyrin unit. We expected that similar stabilising forces to those responsible for the simpler crown ether adducts would prevail in our molecules, and that any electron acceptor bipyridinium guest would be threaded underneath the strap and parallel to the porphyrin, in a pseudo-rotaxane binding motif with π-stacking forces maximised, as indicated by **11:PQ^{2+}** in Figure 6.

Thus we synthesised a new series of strapped porphyrins **11** and **12** (Figure 7) where we varied both the length of the strap and the electron-donor quinol unit; diethylene-, triethylene- and tetraethylene-glycol chains on each side of either a hydroquinol or naphthoquinol unit.[32,33] The link to the porphyrin was an ether, deliberately chosen again to proscribe any complications associated with amide conformational restrictions.

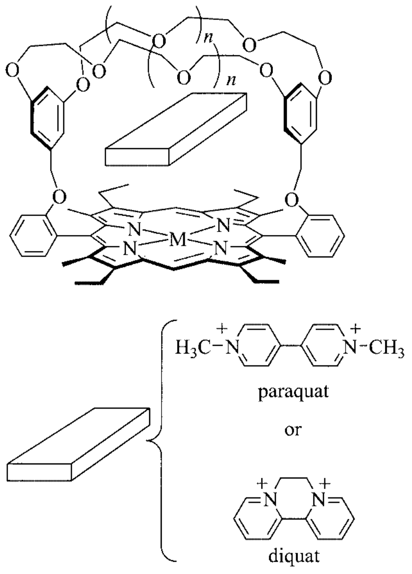


Figure 4. Parallel geometry of bipyridinium guest binding in the ether-linked crowned porphyrins

These adjustments to the design allowed for simpler systems than the crown-appended porphyrins describe above. Here, the porphyrin itself is used as part of the receptor systems; the bipyridinium dication is now stabilised in the complex principally by π−π interactions between the electron-rich porphyrin and the hydroquinol. The result is a family of particularly stable complexes, for which the same principles apply in PET processes as the molecules described above and shown in Figure 2.

We were able to establish that a similar binding geometry to the nonporphryinic analogues is indeed maintained for all of the strapped porphyrins in the series. The solution studies are supported by X-ray crystal structures of representative complexes; an example is shown in Figure 8.[33]

The synthesis of this family of strapped porphyrins followed a similar strategy to that of the ether-linked crowned derivatives; a strap with a dialdehyde functionality at each end was condensed in a "2+2" method with a dipyrromethane (Scheme 3). However, there is a caveat here. If the strap is long, then a mixture of atropisomeric porphyrins is formed, as a result of restricted rotation around the *meso*-carbon to aryl bond in the *ortho*-substituted *meso*-aryl substituent.[34] The result is a mixture of "over-the-top" or α,α-, such as **11c** and **12c** and "twisted" or α,β- isomers **13** and **14**. Nevertheless, although the atropisomers can be separated, they undergo equilibration slowly in solution at room temperature, and more rapidly at higher temperatures. We have identified atropisomers of the tetraethyleneglycol-strapped hydroquinol and naphthoquinol derivatives,[34] and we have also structurally characterised one of the "twisted" isomers in the amide-appended crown series of receptors **15**.[24] On the other hand for the short strap de-

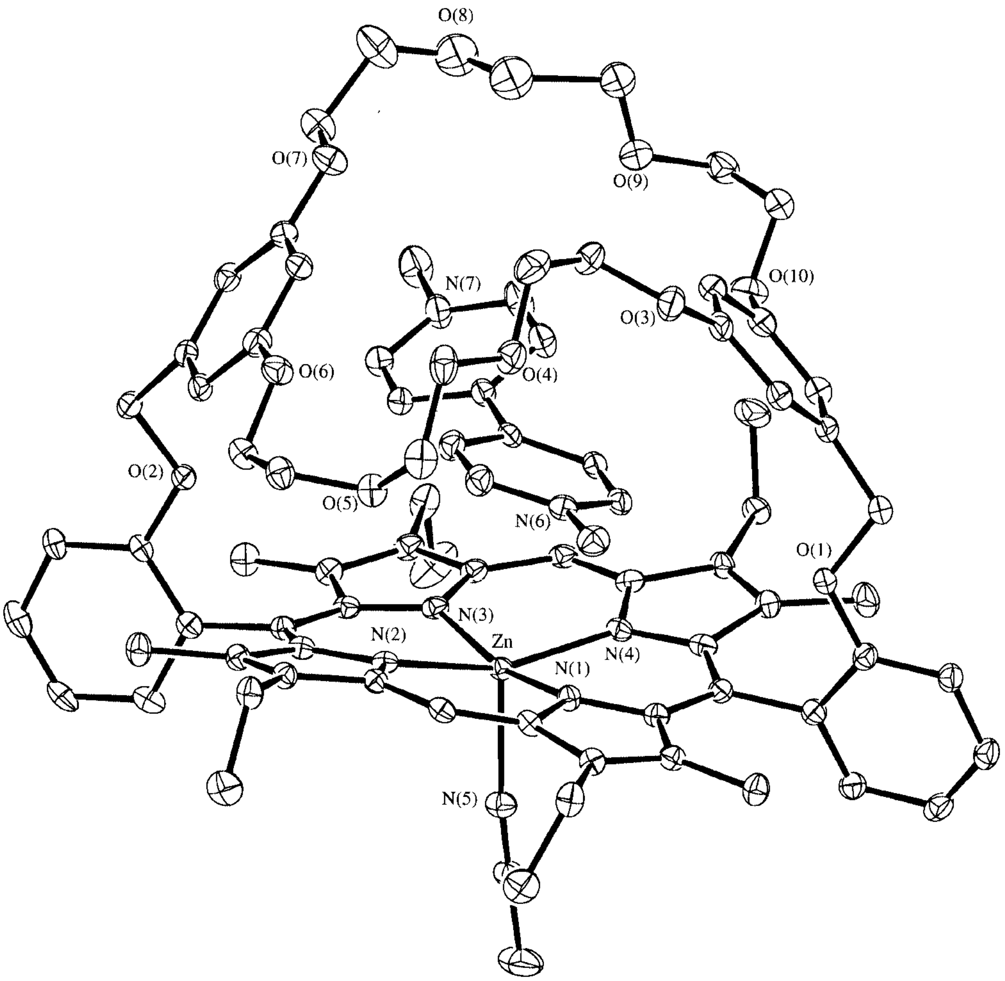


Figure 5. A labelled projection of the complex **8b:PQ^{2+}** from X-ray crystal data; carbon atoms are unnumbered

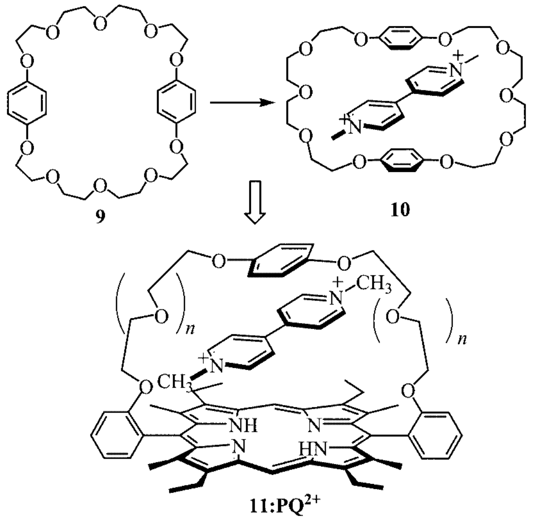
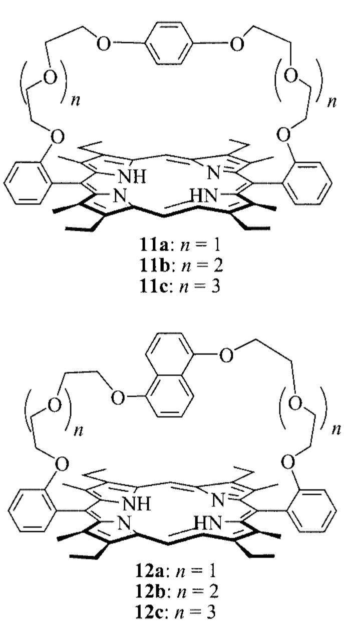


Figure 6. Conceptual evolution of hydroquinol-strapped porphyrin co-receptors for paraquat



11a: $n = 1$
11b: $n = 2$
11c: $n = 3$

12a: $n = 1$
12b: $n = 2$
12c: $n = 3$

Figure 7. The series of hydroquinol- and naphthoquinol-strapped porphyrins described in this study

rivatives, dimers and higher oligomers are formed, and these can also show atropisomerism.[34] Care is thus advised in identifying the correct fraction when synthesising these

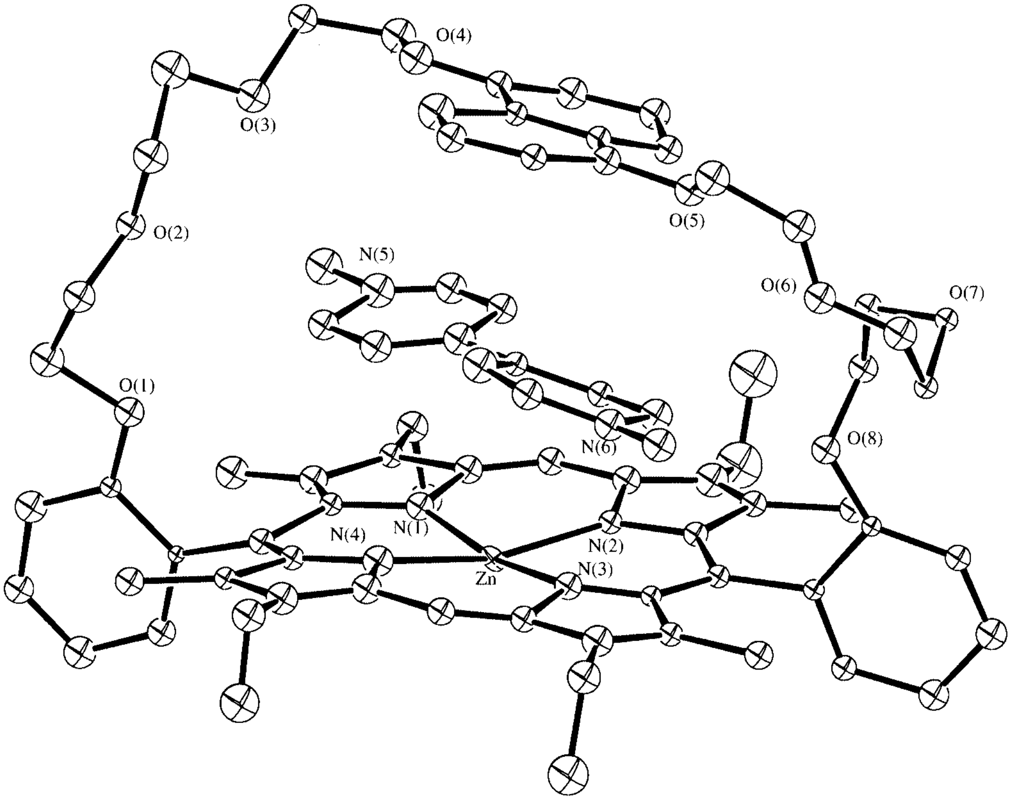
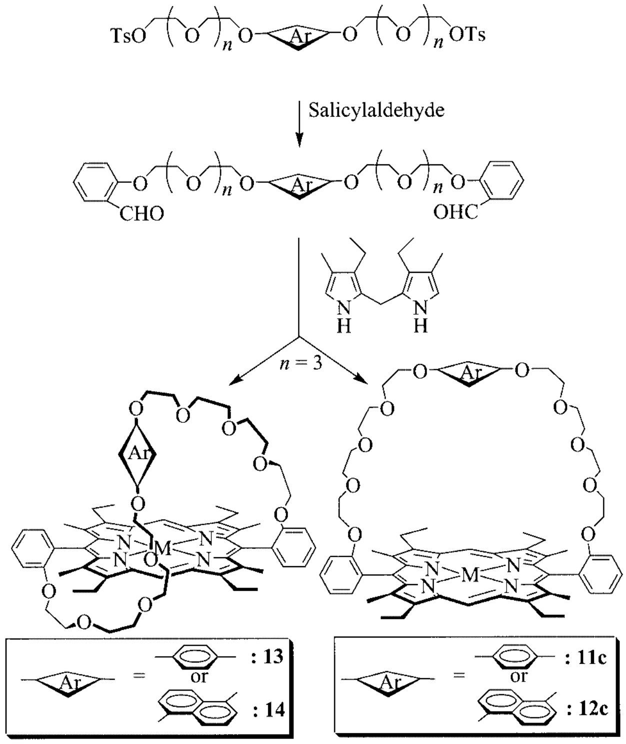


Figure 8. Projection of the complex **12b:PQ^{2+}** from X-ray crystal data; carbon atoms are unnumbered

types of receptors. Although NMR and mass spectrometry can distinguish between isomers and oligomers, it is often not straightforward, and generally requires careful comparison of data for each of the components. Representative members of the series have been structurally characterised by X-ray crystallography.

The complete series of strapped porphyrin receptors has allowed a rational comparison of the structural influences on their binding abilities towards paraquat, as an archetypal example of general bipyridinium dications (Table 1).[33,34] For each of the untwisted singly-strapped porphyrins, there is significant binding of the paraquat within the cavity formed by the strap, and the binding constants range over about two orders of magnitude. These results show that binding of paraquat is strongest in the tight diethylene-strapped naphthoquinol porphyrin. As expected, the strength of binding in the naphthoquinol-strapped porphyrin series is weaker as the length of the strap increases where entropic terms predominate in the overall free energy of complexation. Furthermore, the replacement of a naphthoquinol unit for a hydroquinol in analogous length strapped porphyrins reduces the effectiveness of π−π interactions and this is reflected in a significant decrease in the strength of binding.

Also, this series of complexation studies highlights the solvent effect on binding strength, which generally decreases as the polarity of the solvent increases, as we have



Scheme 3

Table 1. Binding constants (K_a) for several hydroquinol and naphthoquinol containing crown-ether-strapped porphyrin hosts with paraquat at 303 K[a]

Host	K_a (M^{-1})	$\Delta G°$ ($\mathrm{kJ\cdot mol^{-1}}$)[a]
11a	2.0×10^3	-18.9
11b	1.6×10^3	-18.5
11c	1.0×10^3	-17.2
12a	5.6×10^3	-21.5
12b[b]	2.3×10^3	-19.3
12c	3.1×10^2	-14.3
12b[a]	2.1×10^4	-24.7

[a] Measured in [D_7]DMF.[b] Measured in 20% [D_6]acetone/[D_6]DMSO.

also found in the related crowned porphyrins discussed above.

Having established the binding ability of these hosts, we set out to find if these systems function as predicted under photochemical stimulation. Indeed they do, albeit not particularly efficiently in the experiments conducted thus far. Although early experiments did point to relatively efficient charge separation,[35,36] we have since established that interpretation of these results was compromised by the fact that they were conducted under conditions in equilibrating solutions where the complex was overshadowed by significant amounts of free host in solution.

We subsequently repeated and extended the photophysical characterization of the complexes in solutions containing more than 95% of associated porphyrin component.[37] A photoinduced electron transfer from the porphyrin excited state to the paraquat guest, responsible for the porphyrin luminescence quenching, takes place with $\tau << 20$ ps and is followed by a very fast recombination of the resulting charge separated state. In only a few cases could the charge separated state be detected and a lifetime of 20 ps was measured, whereas in most complexes the recombination is faster than this. The slower rates in the charge recombination reaction have been correlated to the dimensions and internal structure of the receptor site. In none of the examined complexes was escape from the geminate recombination of the charge separated state observed; it has now been confirmed that the previously postulated escape of the reduced guest from the complex to freely diffuse in solution with a consequent dramatic increase of the charge separated state lifetime, does not occur in these types of complexes.

Nevertheless, these results have established certain ground rules for a more successful model, and we are now in a position to improve the design in the light of these findings.

Dynamic Catenanes

The second approach to potential photo-responsive supramolecular systems evolved from an obvious extension to those described above. Pioneering work by Stoddart had shown that families of interlocked macrocyclic rings could be synthesised efficiently using the concepts of self-assembly.[38–41] The design motif used similar principles outlined above: hydroquinol-containing crown ethers bind bipyridinium dications within their annulus as in **10**, and conversely bipyridinium-containing macrocycles **17** bind hydroquinol-containing linear polyethers in similar fashion. Alignment of the two concepts led logically to catenanes such as **16** where rings of both crown ethers and bipyridinium groups are interlocked. The pre-complexation and assembly of the component parts result in an assembly in which the interactions live through into the final products, in the form of mutual donor-acceptor or π−π interactions between the electron-rich hydroquinol of the crown and the electron-deficient bipyridinium, amongst other factors.

To replace one of the hydroquinol units in these symmetrical catenane structures with an electron-rich porphyrin was an obvious target; the resultant catenane **18** would thus have in-built addressability through chemistry, photochemistry or electrochemistry. The design concept is cartooned in Figure 9; realisation of the concept was nontrivial initially, but it is now a relatively simple matter to produce porphyrin catenanes to order.

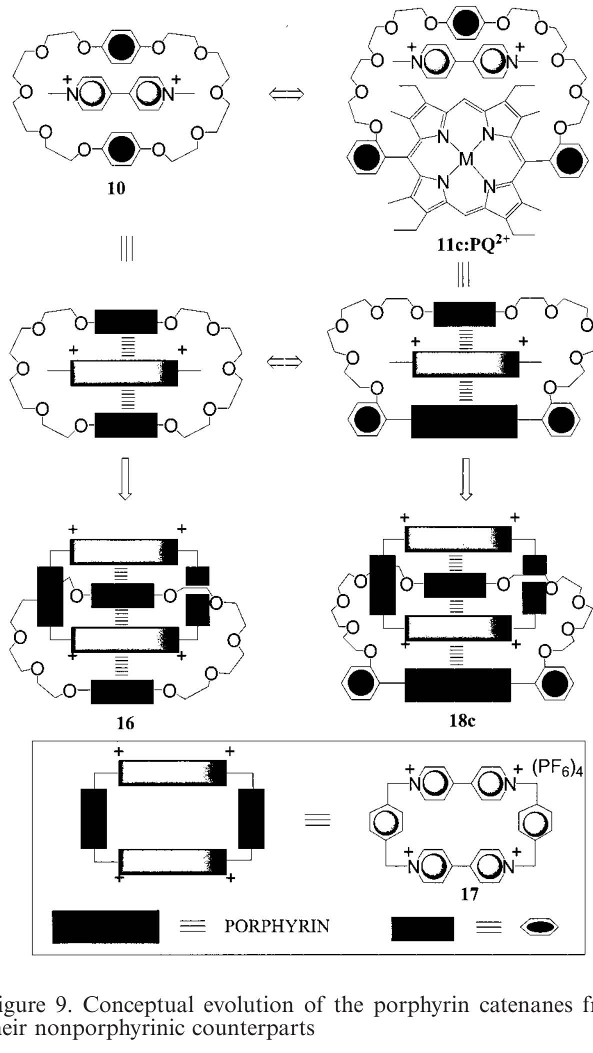
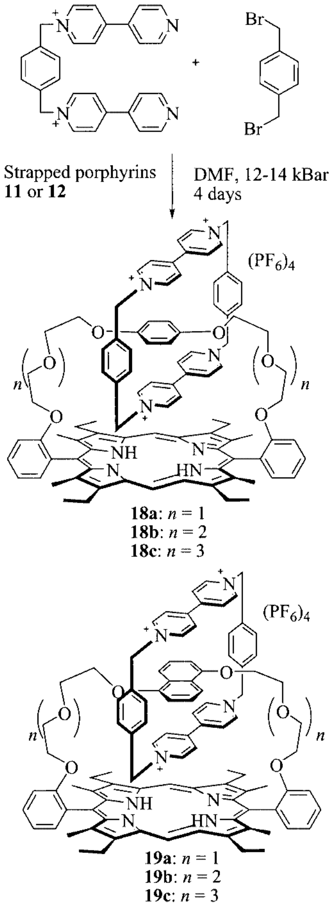


Figure 9. Conceptual evolution of the porphyrin catenanes from their nonporphyrinic counterparts

Naturally, the family of strapped porphyrin bipyridinium receptors described above were produced with the synthesis of the corresponding series of catenanes in mind. By utilising the "clipping" procedure that was successful in the Stoddart catenanes,[38] we were able to produce the complete set of catenanes where the length of the polyethylene glycol strap over the porphyrin is regularly increased from diethylene to triethylene to tetraethylene, and the central electron-donor component is either hydroquinol- or naphthoquinol-based (Scheme 4).[32−34]



Scheme 4

It is interesting to note that a potential complication associated with the longer strapped derivatives, in the production of equilibrating atropisomeric mixtures **11c/13** and **12c/14**, turned out not to be a hindrance to catenane synthesis.[34] Although the atropisomers for both the hydroquinol- and naphthoquinol-strapped porphyrins with tetraethylene glycol-based straps can be separated and catenated individually, they can be equilibrated in solution, and catenation under high pressure conditions of *either* an equilibrated mixture *or* the individual isomers, results in only a single [2]catenane in each case, **18c** and **19c** respectively. Under the high pressure conditions used for the catenation (typically 12−14 kbar for several days, in dimethylformamide solvent), equilibration was rapid enough so that only the catenane from the "untwisted" isomer was formed (indeed perusal of structural models suggest that formation of a catenane from the "twisted" isomer would be sterically unlikely).

For the family of catenanes, NMR studies show that in each case the overall structural motif is the same, with the bipyridinium side of the macrocyclic ring oriented parallel to the porphyrin plane, so that the bipyridinium rings, the quinol, and the porphyrin are stacked in a face-to-face fashion. This is similar to the structures observed for the simple complexes between the corresponding strapped porphyrins and paraquat. An alternative structure where the rectangular bipyridinium macrocycle is rotated through 90 ° is not consistent with the NMR evidence.

Dynamic NMR studies were particularly informative,[33,34] as they allowed for a comparison with the nonporphyrin analogues incorporating BPP34C10 **16** and 1,5-DN38C10, which have been studied in detail by Stoddart. In the simpler systems with hydroquinol electron donor units in the crowns, several types of dynamic processes have been identified, including "rotating" (where the bipyridinium macrocycle passes through the crown), "pirouetting" (the crown passing through the tetracationic macrocycle) and "rocking" of the hydroquinol within the cavity of the tetracation. Clearly in our systems, pirouetting is impossible, as the porphyrin is too large to pass through the tetracation. However, rotating and rocking are expected: rotation where the "outside" bipyridinium unit of the macrocycle exchanges with the "inside" (a process driven by extra stabilisation of the inside unit which has stabilising interactions with both porphyrin and hydroquinol, compared to the outside unit which has only one such interaction − that with the hydroquinol; in effect this exchange is described as a "rotation"). For the naphthoquinol series, and additional process is also evident, described as "out-turn-around-and-in-again" whereby the exchange between two inherently asymmetric orientations of the naphthalene unit over a bipyridinium ring requires that the naphthalene removes itself from the centre of the macrocycle to re-orient itself before re complexing.

The temperature-dependent dynamic properties of the catenanes vary dramatically across the series (Table 2).[34] There is clearly a trend within the rates of rotation of the macrocycle around the central quinol axis, which is critically dependent on the length of the strap on the one hand, and on the nature of the quinol unit on the other. Within the hydroquinol series **18**, the rates of rotation increase from 50 to 25000 to 340000 s^{-1} at room temperature as the length of the strap increases by one ethylene glycol unit on each side. This compares with a rate of about 2000 s^{-1} for the related nonporphyrinic analogue from the simple BPP34-C-10 [2]catenane, and indicates that the relatively large π-surface of the porphyrin provides an effective "brake" on the macrocycle rotation in the tight-strapped derivatives, but has little influence when the strap is loose enough not to impose any steric restriction.

For the similarly sized naphthoquinol derivatives **19**, which have an increased π-surface area, the rotation rates are reduced by many orders of magnitude, ranging from

Table 2. Kinetic parameters from dynamic ^{1}H NMR studies of the porphyrin [2]catenanes for tetracation rotation and reorientation

Catenane	Rotation rates at 25 °C (Hz)	“Out-turnaround-in” rate at 25 °C
16	2000	–
18a	50	–
18b	2500	–
18c	340000	–
1,5-DN38C10.cat	1200	10
19a	0	2
19b	10	400
19c	100	110000

essentially zero to 10 to 100 times per second at 25 °C through the same increase in chain length as for the hydroquinol analogues. This compares to the modest decrease in rate for the simple nonporphyrinic 1,5-DN38-C-10 [2]catenane compared to its phenyl analogue (1500 vs. 2000). It is thus apparent that $\pi-\pi$ interactions between the naphthoquinol and porphyrin are sufficiently strong to cause a significant barrier to rotation. Nevertheless, the second process also needs to be considered in the naphthoquinol cases − that of a barrier imposed by the “out-turn-around-and-in-again” process, as a mechanism by which the naphthoquinol unit can rotate only by slipping out from the enclosing macrocycle first. This ranges from 2 to 400 to 110000 s^{-1} at 25 °C in this porphyrin series, compared to about 10 s^{-1} for the nonpophyrinic analogue. Clearly, this is not a significant barrier to rotation in the porphyrin catenanes, and may arise from the porphyrin catenane being conformationally less flexible than its nonporphyrinic counterpart, and having fewer sites available for [CH···O] hydrogen bonding.

A stronger $\pi-\pi$ interaction as a the major influence in restricting rotation in the naphthoquinol series compared to the hydroquinol series, is indicated by the stronger binding constants of the corresponding strapped porphyrins for the simple guest paraquat. However, it is interesting to note that the electronic spectra of the catenanes themselves do not show any significantly enhanced charge-transfer bands over the hydroquinol counterparts.

Thus armed with a regular series of the catenanes, we could now prime them with chemical and physical stimuli. Quite simply, protonation of the free base derivatives of catenanes such as those shown in Scheme 4 results in an intriguing outcome.[42] The interactions that were responsible for the production of the molecules, and which controlled the motion in these dynamic systems (the tetracationic macrocyclic “wheel” rotating about the hydroquinol “axle” at variable rates depending on the “tightness” of the strap across the porphyrin, amongst other factors) are destroyed on porphyrin protonation. Moreover, electrostatic repulsions between the tetracationic macrocycle and the dipositively charged porphyrin are clearly to be avoided; since the two rings of the catenane are *mechanically* linked, departure of either component part is impossible. The result is a movement to position the like charges as remotely as possible, and the spinning rate is dramatically increased; thus protonation may be likened to removing the “brake” in the form of the porphyrin.

There is yet a further dramatic effect of protonation. That is the effects of catenation and strap length on the protonation constants (pK_a) of the various porphyrin subunits.[43] For the strapped porphyrin precursors, the length of the strap has a small effect on the apparent pK_a values of the porphyrin, although minor effects are seen for the tighter strapped derivatives compared to the looser analogues, which are little different to the related unstrapped porphyrins. The apparent pK_a values for both the strapped porphyrins and their corresponding catenanes are plotted in Figure 10.

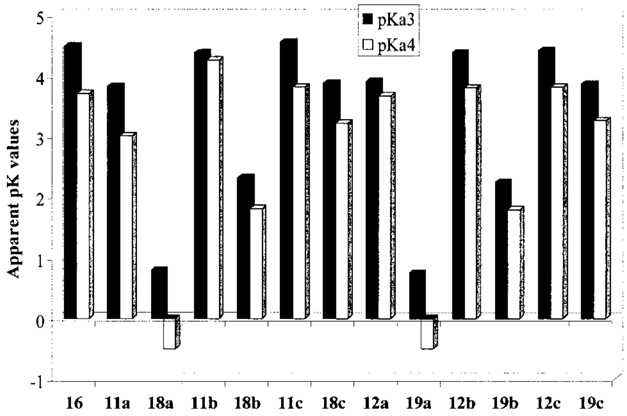


Figure 10. Apparent pK_a values for the charged porphyrin catenanes compared to their strapped porphyrin precursors; pK_{a3} and pK_{a4} refer to the formation of the porphyrin mono- and dications, respectively; values were calculated from pH/UV titrations by addition of aliquots of HCl to solutions of the catenanes in acetone/dimethyl sulfoxide/0.1 M NaCl (5:6:1)

In all cases, it is evident that (i) the catenanes have consistently lower apparent pK_a values than those observed for the strapped porphyrin analogues and (ii) the electronic structures of the porphyrin dications are strongly influenced by the proximity and restrictions of the tetracation. The “tighter” systems with diethylene glycol chains **18a** and **19a** showed a resistance to forming the porphyrin diacid species with apparent pK_{a3} values (0.75 and 0.5, respectively) being significantly lower than those compounds with the more flexible tri- and tetraethylene glycol chains. Indeed the apparent pK_{a4} values for these two compounds could not be experimentally determined, although they were estimated to be about -0.5. Electronic spectral evidence also indicates that at low pH $(0-1)$ the protonated forms of these [2]catenanes are not an equilibrium of the free base and diprotonated species, but are distinctly different and characteristic of the *monoprotonated* acid form, a species that has avoided detection previously except as a transient during diprotonation.

Thus the protonation of the porphyrin subunits in these porphyrin [2]catenanes is effectively controlled by coulombic interactions which are in turn governed by essentially steric effects. These effects are cartooned in Figure 11.[43] For the tighter strapped derivatives **18a** and **19a**, separation of the repulsive charges of the tetracationic macrocycle and the porphyrin cation is restricted; reorientation of the oblong-shaped macrocycle through 90 ° to relieve the coulombic repulsion would induce even further steric interactions. Thus, there is considerable resistance to protonation in these systems, and even greater difficulty in forming the dicationic species. As the size of the central quinol unit of the strap changes from hydroquinol to naphthoquinol, there is only a minor difference in behaviour, as the major controlling factor is the restriction induced by the strap rather than the central electron donor π-system. On the other hand for the looser strapped members of the series **18b** and **c**, and **19b** and **c**, the coulombic repulsions can be relieved by a 90° rotation of the rectangular macrocycle, and there is sufficient flexibility and space for this to occur without major steric difficulties. This is indicated by higher apparent pK_a values, approaching those for unrestricted porphyrins for the longest strapped tetraethylene glycol analogues **18c** and **19c**, and with intermediate values for the triethylene glycol derivatives **18b** and **19b**.

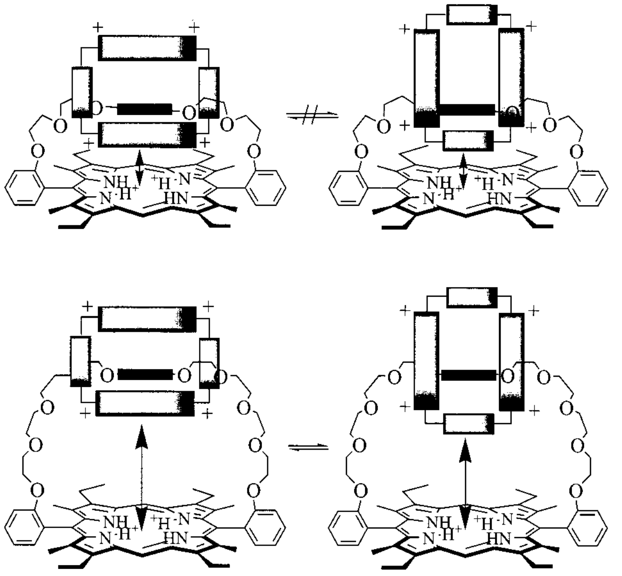


Figure 11. Cartoon indicating the effects of protonation on "tight" and "loose" porphyrin catenanes

These findings point towards the structural, dynamic and spectral differences observed as being mainly sterically based, with π−π electronic perturbations playing only a minor role. The most restricted members of the series provide an ideal opportunity to study the monocationic porphyrin species free from the more usual dications. Furthermore, these results have significant implications for photoinduced electron transfer experiments, where initial photoexcitation of the metalloporophyrin subunit and subsequent electron transfer to the bipyridinium unit of the macrocycle results in similar repulsive situations, in this case between the porphyrin π-radical cation and the tricationic macrocycle radical.

We have also undertaken photophysical and electrochemical studies of representative members of this family of catenanes.[44] The electron transfer rates leading to charge separation and the recombination rate to the ground state have been determined, and these have been compared to the simpler paraquat complexes of the same strapped porphyrins. The rates of electron transfer are faster in the complexes **11:PQ^{2+}** and **12:PQ^{2+}** than in the catenanes **18** and **19**, and this is attributed to a looser structure in the complexes which favors a closer approach of the partners in the charge separation reaction. Accordingly, a slower charge separation reaction is measured in the systems with looser straps and the same occurs for charge recombination in the complexes. Charge recombination in the catenanes occurs with the same rate regardless of the strap length and suggests the involvement of a further, subsequent electron transfer to a more stabilized reduction site of the macrocyclic electron acceptor, identified as the outer paraquat unit of the cyclic electron acceptor macrocycle. These processes and their energy profile are indicated in Figure 12.

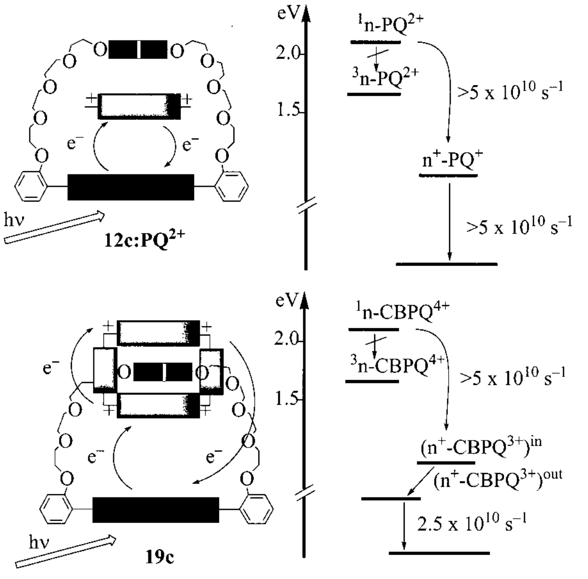


Figure 12. Cartoon and energy level diagram of the PET processes in the porphyrin complex **12c:PQ^{2+}** and its corresponding catenane **19c**

A photoinduced electron transfer from the porphyrin excited state (charge separation CS) occurs with τ = 20 ps in the catenanes with a looser strap and faster than 20 ps in the more constrained catenane with the tighter straps. The resulting charge separated state recombines to the ground state (charge recombination CR) with lifetimes similar in all cases, about 40 ps. Comparison of the electron transfer rates CS and CR in the host−guest complexes **11:PQ^{2+}** and **12:PQ^{2+}** of the same porphyrins with the electron acceptor paraquat, indicate slower reactions in the [2]catenanes. This behavior is explained by the different separation between reacting partners determined by the type of bond (weak interaction or mechanical) and to a two-step consecutive electron transfer to different sites of the macrocyclic electron acceptor in the catenanes which retards charge recombination.

Likewise electrochemical studies[44] reveal a structural dependence on the reduction potentials. Representative members across the series of catenanes all reveal two single-electron reduction processes for reduction of the two possible bipyridinium sites, the "outer" and "inner" (indicating too that rotation of the macrocycle is slower than the timescale of the electrochemistry experiment). However, while the "loose" naphthoquinol **19c** derivative shows two single-electron processes for the third and fourth reductions, the "tighter" analogue **19a** shows a single dielectronic reduction.

This indicates a conformational change where the macrocycle is now oriented "end-on" to the porphyrin, making both bipyridinium sides of the rectangular macrocycle spatially eqivalent, and indistinguishable in the reduction process. Presumably this is a result of release of steric interactions in the two-electron reduced species where any charge transfer interactions have been negated by the reduction. A similar situation is observed for the "loose" hydroquinol derivative **18c**. These effects are illustrated in Figure 13.

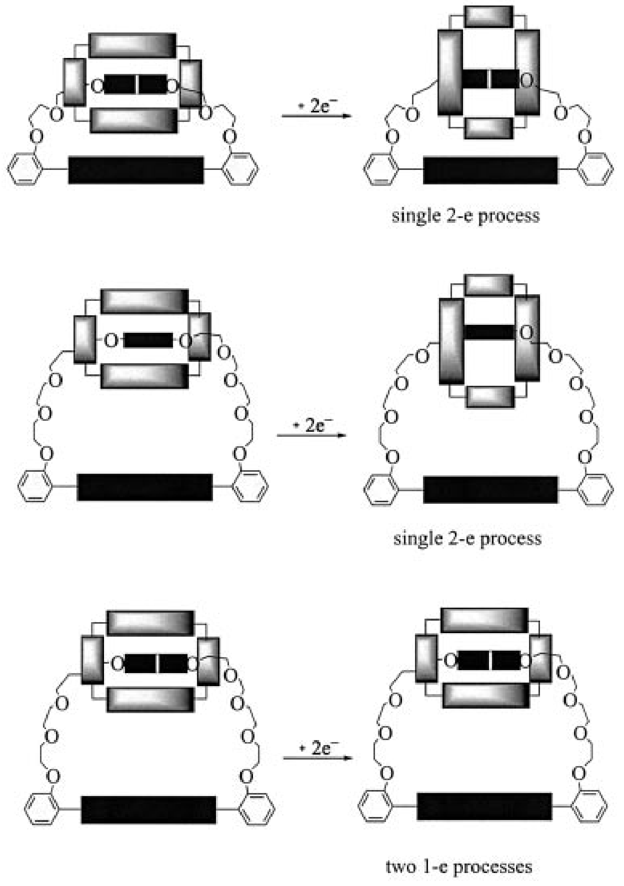
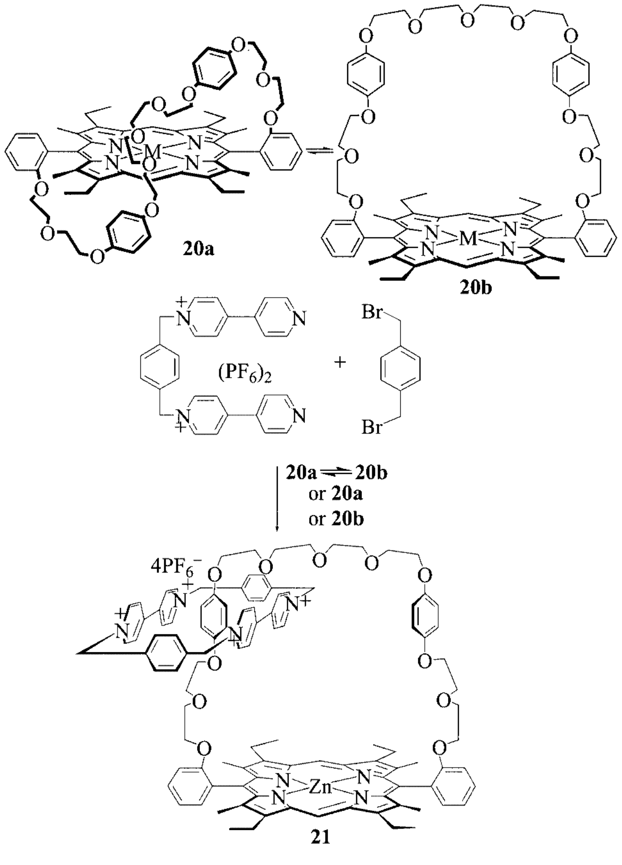


Figure 13. Cartoon of the electrochemical reduction processes for representative porphyrin catenanes

Thus with this set of catenanes, we have been able to delineate their structure-activity profile by studying their behaviour under a range of stimuli. We can now provide a complete catalogue of their fundamental properties, to allow a more systematic and rational structure−activity relationship across the whole series.

Higher Order Catenanes

Although the porphyrin [2]catenanes undergo rotational isomerisation, we sought to extend the dynamic possibilities by higher order catenanes which could undergo translational motion as well.[45] These types of molecules are of particular interest for the production of molecular switches, relays, and other electronic components.



Scheme 5

Thus we designed another series of porphyrins again strapped between *ortho*-positions of 5,15-(*meso*)-diaryl groups, and interlinked with the same bipyridinium macrocycle cyclobis(paraquat-4,4′-biphenylene) **17** as for the [2]catenanes; however, in this case we armed the polyether chains with two or three hydroquinol units with a view to the production of new porphyrin-containing [2] and [3]catenanes with the added possibility of acting as movable shuttles.

As for the longer strapped single quinol porphyrins, these porphyrins were isolated as mixtures of atropisomers, where the linking strap spans across the face of the porphyrin (α,α-isomer) **20b**, or "twisted" around its side (α,β-isomer) **20a**. Their structures were determined by detailed ^1H NMR spectroscopy.[45]

These bis(hydroquinol)-strapped derivatives have also been shown to undergo atropisomerisation on heating, to produce an equilibrium mixture. Catenation under high pressure conditions of the mixture, or of the individual isomers, produced only a single catenane, that of the α,α-isomer **21**. Its dynamics were measured, and rates were determined for (i) translational motion or "shuttling" between hydroquinols; (ii) "rotation" of the macrocycle around the hydroquuinol axis; and (iii) "rocking" of the hydroquinol within the macrocycle.

The atropisomers of the strapped derivatives containing three hydroquinol units were also separated, and subjected to catenation (Scheme 6).[45] Both [2]- and [3]catenanes **23−26** have been isolated, and shown to be stable to further atropisomerisation. Their solution structures were probed in detail by dynamic ^{1}H NMR measurements, although these were complicated. The rates for shuttling and rotation were obtained in certain cases, although the complexity of the spectra of the [3]catenanes precluded a more detailed investigation.

Neutral Porphyrin Catenanes

As an alternative approach to self-assembled catenanes, Sanders and co-workers[46−49] have shown that hydroquinol and naphthoquinol crown ethers such as 1,5-DN38C10 form pseudorotaxanes with substituted naphthodiimides and pyromellitimides, and that it is possible to form *neutral* catenanes using a variety of approaches for assembling diimide-containing macrocycles of various dimensions and constitutions interlinked with the crown ether (Scheme 7). In particular, Cu^I mediated Glaser coupling of propynyl-substituted diimides **28** or **29** in the presence of **27** led to excellent yields of the catenanes **30**.

Thus it was logical for us to extend the concepts of our charged porphyrin-containing catenanes of the Stoddart type to those of the Sanders type. Such neutral catenanes retain the inherent interest and potential of the charged analogues, but now provide an entry into noncharged systems which can be studied in a wider variety of solvents, and which allow variation in photophysical and photochemical studies by virtue of the diimide subunits. The successful synthesis of porphyrin containing [2]catenanes also establishes a methodological basis for the construction of more elaborate porphyrinic molecular assemblies.

Thus, we set out to assemble an analogous series of neutral porphyrin-containing catenanes consisting of the same polyethyleneglycol-strapped zincporphyrins **11** and **12** that were used for the charged porphyrin [2]catenanes, interlinked with a naphthalene diimide or pyromellitimide macrocycle (Scheme 8).[50] For increased solubility, we also synthesised the *n*-hexyl analogues. Although the naphthalene diimide precursor units exhibit only weak binding with the strapped porphyrins (K_a between 8 and 0.02 M^{-1}), good yields of the catenanes were obtained by Glaser coupling of the alkynyl naphthalene diimide precursors in the presence of the strapped porphyrins. However, we soon established that naphthalene units in both the strap and the macrocycle were essential for success, and only **31** and **32** were produced. It appears that the binding between hydroquinol-strapped porphyrins and the pyromellitimide, or between naphthoquinol-strapped porphyrins and naphthalene diimide precursors, is too weak to provide sufficient pre-organisation and self-assembly of the catenanes.[50]

Structures and solution conformations of this new family of catenanes were determined by mass spectral and detailed ^{1}H NMR studies. These catenanes **31** and **32** exhibit similar dynamic processes to their charged bipyridinium cousins **19a** and **19c**; for the longer strapped porphyrins, the diimide macrocycle rotates around the central naphthoquinol unit at about 450 times per second, while rotation is virtually prevented in the tighter strapped derivatives. It is interesting to note by comparison that the analogous charged [2]catenane **19b** gave a tetracationic macrocycle spinning rate of around 400 s^{-1} at 298 K,[33] which demonstrates similarities of size and other criteria that determine the interplanar interactions between the two different electron deficient macrocycles with similar strapped porphyrin compounds.[50]

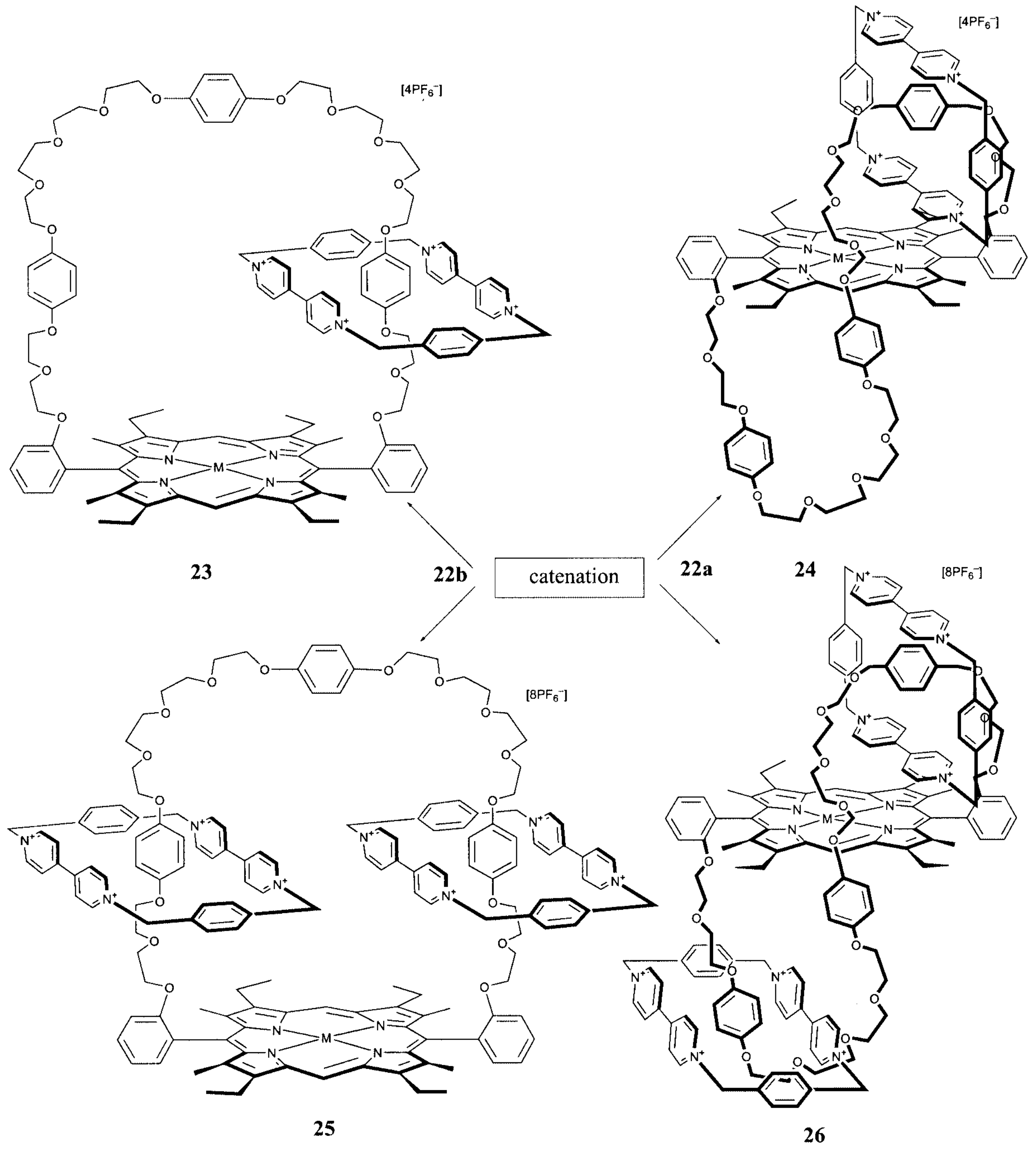
A second dynamic process occurring in these catenanes and described as "yawing" leads to inequivalence in the naphthalene moieties of both the porphyrin and the diimide macrocycle, and we were able to obtain rates for this process as well.

UV/Vis spectra indicate charge transfer interactions and electronic communication between the two components of these catenanes. A feature of the absorptions is the appearance of broad band with a maximum in the region of 670−700 nm with a molar extinction coefficient in the range 10^{2}–10^{3} $\text{dm}^3\cdot\text{m}^{-1}\cdot\text{cm}^{-1}$, which is assigned to CT bands originating from the interaction between the porphyrin component and the diimide units of the macrocycle. Similar CT bands have been observed in spectroscopic studies on the charged porphyrin catenanes **18** and **19**, although the maxima of these bands appeared at longer wavelengths (720−760 nm).

The neutral nature of the interlocked macrocycle in these catenanes, in contrast to the tetracationic charge of the bipyridinium systems discussed above, provided an interesting comparison of the effects of protonation of the porphyrin. In this case, the apparent pK_a's of the porphyrin in **31** and **32** are little affected by catenation, and the rotation rates of the macrocycle show only relatively small differences to the free base or metallated derivatives. In fact there is a slight *slowing* of the rotation rates in these cases, presumably as a result of an electrostatically induced "drag" as the polar groups of the diimide pass by the positively charged porphyrin core.

Rotaxane Assembly Under Thermodynamic Control

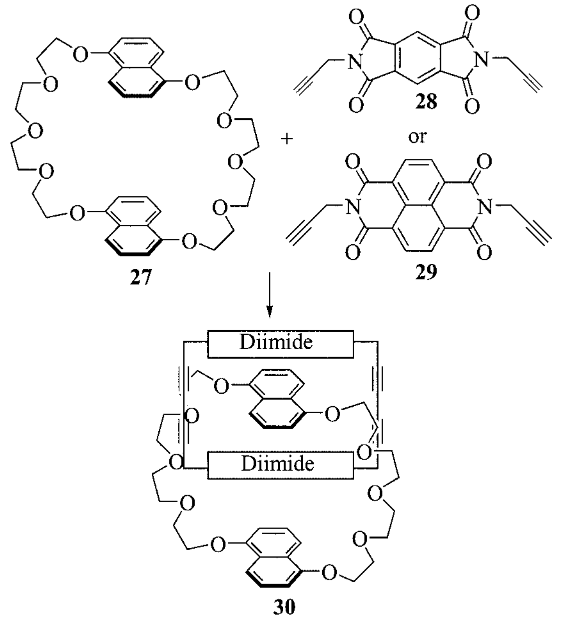
Although in all of the above systems we have been able to produce relatively complex systems after pre-assembly of



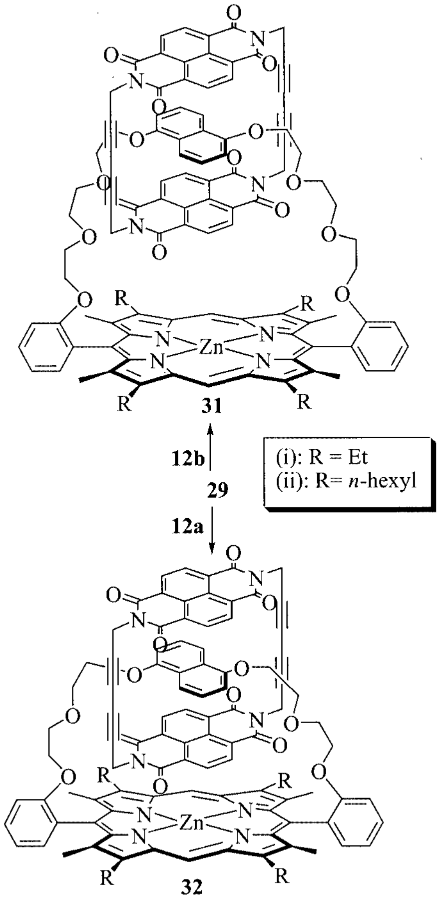
Scheme 6

the component parts, the final reactions to lock in the structures have been kinetically controlled and irreversible. To simplify the synthetic process and to allow the most stable system to self assemble under strict thermodynamic control, we were encouraged to investigate the possibility of utilising the usual recognition processes that are inherent in the self assembly processes of our previous systems (including π−π, C−H−O, and electrostatic), together with coordinate covalent bonding, to allow the most stable system to predominate at the expense of all intermediate possibilities in an equilibrating system.[51]

In these cases, we began with using metalloporphyrins as stopper units in rotaxane structures which contain the same recognition motifs as those of the neutral catenanes of Sanders et al. discussed above. By judicious choice of components and temperatures we produced a variety of porphyrin-stoppered rotaxanes under conditions of thermodynamic reversibility. An admixture of a thread unit comprising of a central naphthodiimide **34** with terminal pyridines, a ring unit dinaphtho-38-crown-10 (see **33**) and either Zn^{II} (**35a**), Ru^{II}(CO) (**35b**) or Rh^{III}I (**35c**) as stoppers was shown to form an equilibrating mixture of pseudorotaxanes and the



Scheme 7



Scheme 8

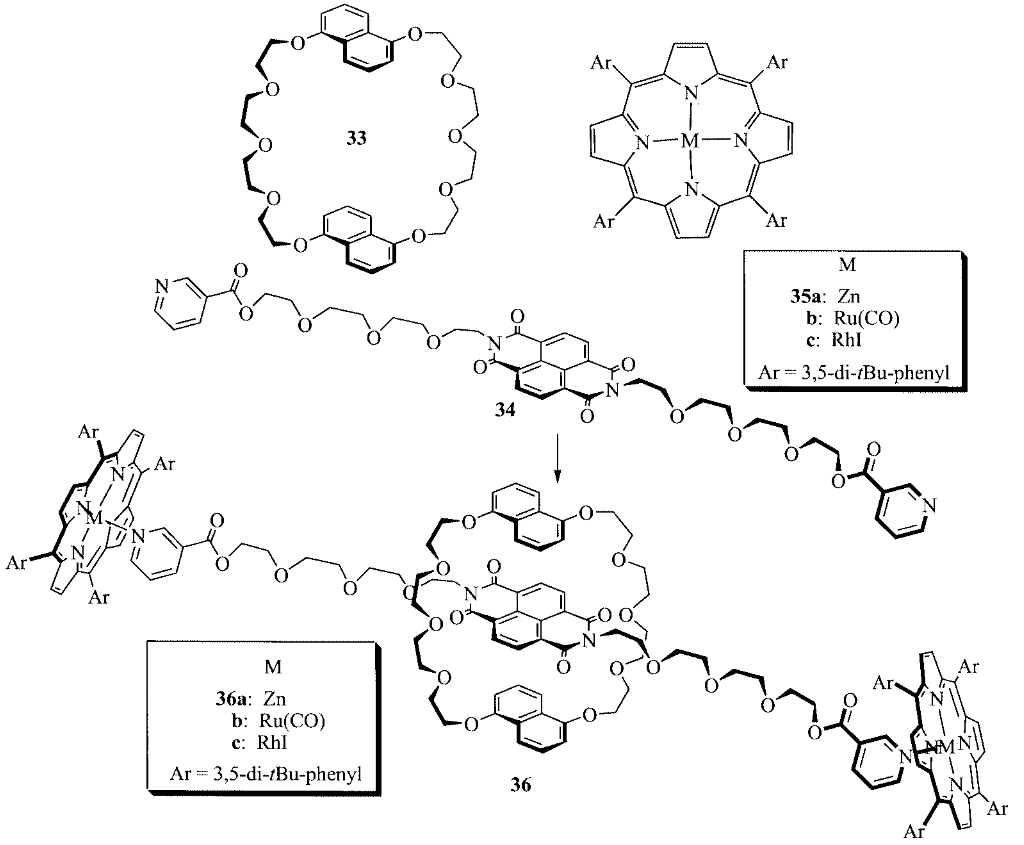
porphyrin-stoppered rotaxanes **36** (Scheme 9). A representative energy profile considering each of the possible reversible interactions is cartooned in Figure 14, and clearly the most stable product is the complete rotaxane.

The choice of metal ion in the porphyrin is crucial for success. For these three metalloporphyrin stoppers **35**, we could show that the equilibrium is still dynamic at room temperature but the rotaxane could be stabilised at low temperatures. Much lower temperatures are required to stabilise the rotaxane **36** when the more labile Zn porphyrin stoppers are used, compared to Ru(CO) or RhI which have significantly higher binding constants for pyridine-based ligands.[51]

When using the Ru(CO) or RhI metalloporphyrin stoppers, from the mixture of components, the intact rotaxane **36b** or **36c** could be crystallised from solution, and could be chromatographed at low temperatures (< 230 K); at higher temperatures only a mixture of the components separated on chromatography. ^{1}H NMR revealed NOE correlations between all three components for the rotaxane, and exchange peaks for related free and complexed species. The temperature and concentration dependence of the equilibria were studied by NMR methods, and van't Hoff plots for the Ru(CO) stoppered system **36b** enabled an estimation of $\Delta H°$ and $\Delta S°$, $-41.4\ \mathrm{kJ{\cdot}mol^{-1}}$, and $-95\ \mathrm{J{\cdot}mol^{-1}\ K^{-1}}$, respectively, and a K_a at 273 K of 790 M^{-1}, rising to $5.39 \times 10^4\ \mathrm{M}^{-1}$ at 223 K. For the unstoppered pseudorotaxane systems **33:34**, the $R\ln K$ vs. $1/T$ plots were not linear, implying a temperature-dependent ΔH and a nonzero ΔC_p, indicative of a folding/unfolding of the extended thread unit on complexation.

Nevertheless, although the thermodynamic stability of the overall rotaxane is expected to be similar to that of the pseudorotaxane, there is clearly an enhanced kinetic barrier for the formation of the metalloporphyrin-stoppered rotaxanes **36b** and **36c**, but not for the more labile Zn analogue **36a**. While mixing of all three components of the rotaxanes **36** at room temperature resulted in rapid rotaxane assembly irrespective of the order of addition (thermodyamic control), it was shown that at low temperatures it was possible to "lock out" or "lock on" the central thread unit under conditions of kinetic control. These concepts were further extended to the assembly of more complex multi-porphyrin arrays such as **37** (Figure 15), where the central ring unit is the same naphtho-crown-strapped zincporphyrin used in the catenanes discussed above. It is therefore possible to use the kinetics of the remote event (metal ligation/coordination) to control the overall kinetics of rotaxane formation.[51]

Thus by appropriate choice of components, we have shown that it is feasible to fine tune the conditions necessary for porphyrin-stoppered rotaxane self-assembly by simple mixing of the constituent parts. It is clear that this choice can be extended to a range of threads, rings and stoppers where the appropriate combinations can be guided by the relative values of the kinetic and stability constants. Furthermore, the principles established in the reversible and thermodynamically controlled assembly of these rotaxanes should facilitate the construction of more complex struc-



Scheme 9

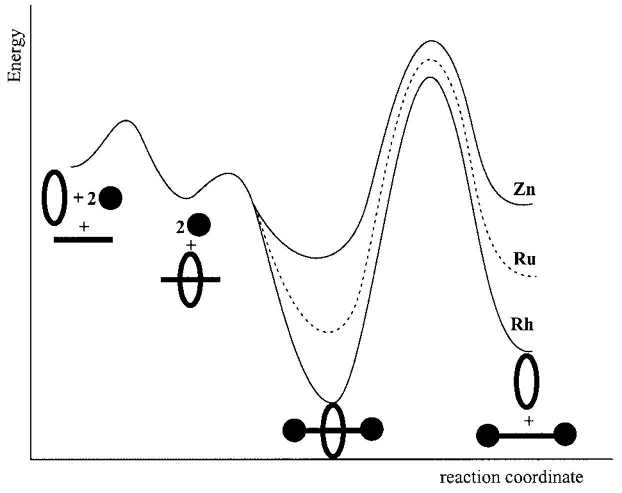


Figure 14. Schematic energy profiles for the assembly of the rotaxanes **36** from their constituent parts

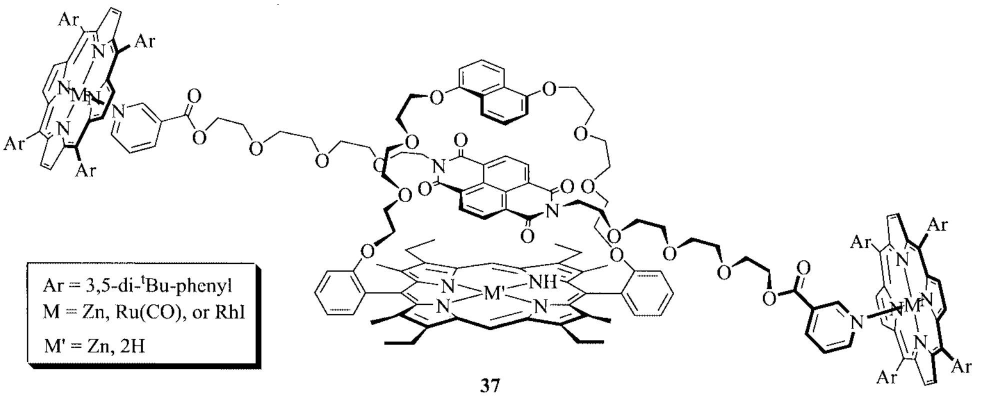
tures, and indeed may form the basis for combinatorial libraries of supramolecular interlocked structures.

Polymer-bound Rotaxanes

Although the use of catenane and rotaxane systems as components of potential molecular electronic devices has been extensively reported and discussed, fabricating them into real nanometre scale devices creates a new dimension to the problem. Many such artificial supramolecular machines have been shown to operate efficiently in solution, but in an incoherent manner. For the next generation of these systems to operate at a macroscopic level, they need to be organised at interfaces, on solid supports, or at surfaces, so that they can operate in unison. There are at least several approaches being adopted in attaching these systems to solid surfaces in order to optimise their ability to work in a practical sense.[52,53] However, it is often difficult to study such systems in their solid form.

We had previously utilised HRMAS NMR techniques to analyse a rotaxane and various other supramolecular systems bound to polystyrene beads.[54,55] Using the above concepts of solution thermodynamically controlled assembly, we have now adapted them to the immobilised phase where the solution-solid phase dynamics are probed using high-resolution magic angle spinning gel-phase (HRMAS) NMR spectroscopy.[56] This technique gives remarkable resolution of the resonances for both the surrounding solution phase and the solid-bound phases, and dynamic equilibria between the phases can be studied in real time.

Using this technique, in parallel with solution measurements, we can now monitor reversible processes that occur between the solution and solid phases as the components of



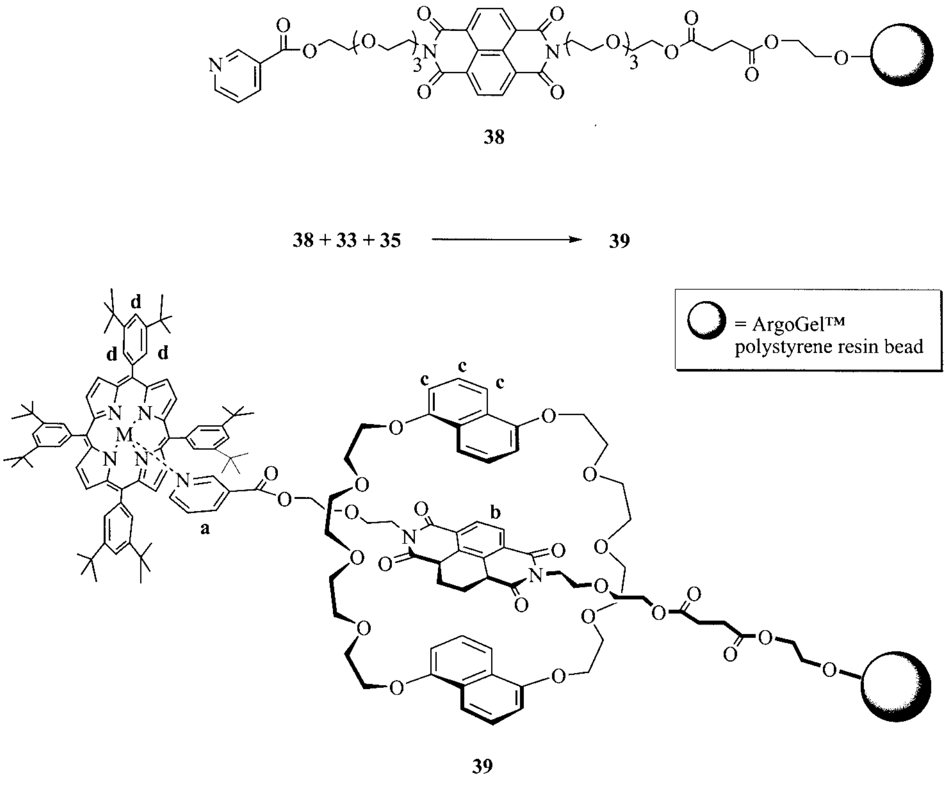
37

Figure 15. Thermodynamically assembled multi-porphyrin rotaxane

porphyrin-based rotaxanes and pseudorotaxanes assemble under thermodynamic control. It was conceptually a relatively straightforward progression to apply similar principles gleaned from solution to gel-phase solid supports.

The synthesis of rotaxane **39** tethered to ArgoGel^{TM}-OH polystyrene resin beads through terminal polyethylene glycol groups was accomplished as shown in Scheme 10.[56] The complete rotaxane has the three basic components of the solution system discussed above, except that in this case the naphthodiimide thread component with terminal pyridine group **38** is tethered at one end to a polystyrene bead. The bead acts as a permanent stopper at one end of the thread, while at the other end the pyridine group coordinates to the ruthenium porphyrin stopper. When the components of the rotaxane (**38** + **33** + **35**) are mixed in a suitable solvent in which the beads swell, both the loop and stopper components freely exchange between the solution phase and the immobilised phase complexed to the thread **38**, resulting in an equilibrium between a number of states, with the complete rotaxane again being the most stable thermodynamically.

HRMAS NMR proved to be an ideal technique for analysing this exchanging rotaxane system as it allows both solution and solid-bound components to be studied concurrently. The HRMAS ^{1}H NMR spectra of **38** showed typical pyridine (**a**) and diimide (**b**) aromatic peaks (Figure 16). Upon addition of a solution of the dinaphtho crown **33** the diimide peak shifts upfield (**b**) due to the shielding effect of



Scheme 10

the crown naphthalene groups (Figure 16, b). The diimide (**b**) and crown (**c**) peaks are an average between the threaded and dethreaded states due to their fast exchange rate on the chemical shift timescale. In this respect, the system is similar to the analogous solution state system. Addition of a solution of the ruthenium porphyrin **35b** results in a large shift upfield of the pyridine protons (**a**) as the pyridine groups coordinate to the ruthenium porphyrin (**d**) (Figure 16, c). Stoppering the system also slows down the threading-dethreading complexation between the crown and diimide thread, resulting in observable bound and unbound crown (**c**, **c′**) and diimide (**b**, **b′**) peaks in an approximate 1:1 ratio. A third set of peaks (**c′′**) which remained after filtering and washing the beads, indicated a third environment in which one or more crowns are threaded on the long terminal polyethylene glycol tethers of the ArgoGel beads, still stoppered by the porphyrin complexation.[56]

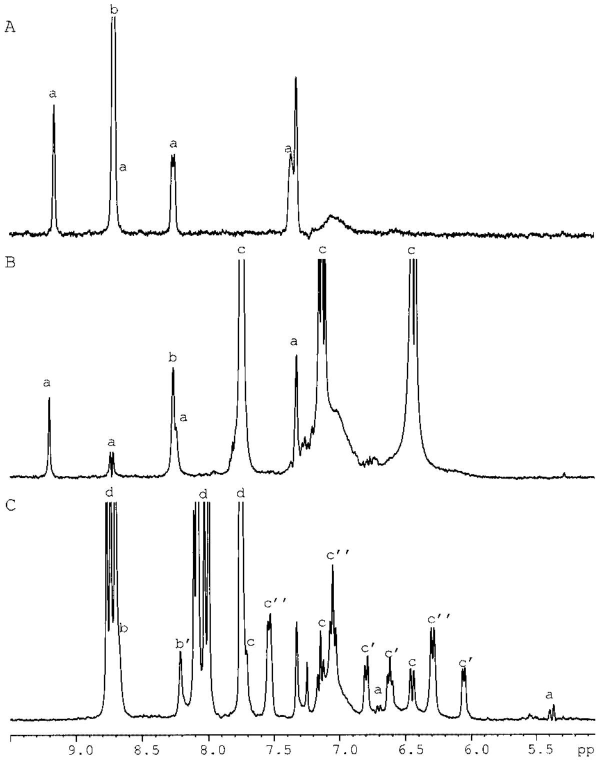


Figure 16. HRMAS ^{1}H NMR data for: (A) **38**, (B) **38** + **33**, (C) **38** + **33** + **35**; the lettering corresponds to the protons indicated in Scheme 10

The excellent resolution and line-shape provided by gel-phase HRMAS NMR has proven to be an invaluable technique for characterising and probing the inter-component interactions of our thermodynamically controlled, self-assembling solid-bound rotaxane. We are continuing to utilise this technique to develop variations on this theme with each component of the exchanging system tethered separately and in combinations on the beads. In this way we are in an excellent position to extend this methodology to study higher-order solid-bound supramolecular systems in the future.

Conclusion

We have demonstrated the viability of the synthesis of porphyrin receptors, catenanes, pseudorotaxanes and rotaxanes in which the porphyrin subunit provides an ideal trigger for control of the dynamics, as it can be addressed by chemical, photochemical, or electrochemical stimuli. In this way, each of the assemblies can be regarded as components of molecular machinery, in which mechanical motion can be controlled in a systematic and predictable manner.

An added advantage of these types of systems is that the changes at the molecular level can easily be detected through macroscopic signalling (such as detectable colour changes and other spectroscopic probes). The induced charge movements within the assemblies have obvious similarities to the operational principles of photodiodes, relays, switches, shift registers and other electronic components. They are indeed molecular scale electronic devices, and useful components for the science of nanotechnology. The way is now clear for the next generation of experiments.

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