Photo- and Redox-active [2]Rotaxanes and [2]Catenanes

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1 General Introduction

[2]Rotaxanes and [2]catenanes represent a fascinating class of compounds in which two components are inseparable not because they are tethered covalently, but as a result of their molecular topology[1] (Figure 1). The chemistry of these molecules is now well established and forms a major part of supramolecular science. Recent synthetic improvements[2a,b] have not only led to enhanced yields of rotaxanes/catenanes, but also an ability to build-in further functionality at any stage of the synthesis. As a consequence, there are now numerous examples of such systems which have been termed photoactive or redoxactive since residing within the architecture is a subunit which can be photochemically and/or electrochemically activated. Nevertheless, the question arises should, for example, a rotaxane be defined as redoxactive even when the redox centre incorporated in the superstructure appears to serve no purpose? Such a point is clearly open to debate, but for this review an assembly is deemed photoactive or redoxactive if the active subunit(s) and molecular architecture are mutually important to the operation of the system.
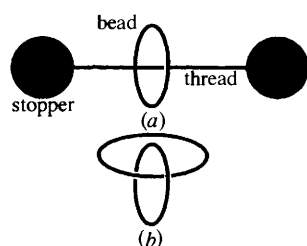

Figure 1 Simple cartoons representing (a) a [2]rotaxane (nomenclature commonly used when referring to [2]rotaxanes is also shown), and (b) a [2]catenane

Andrew C. Benniston was born in Walsall (West Midlands) in 1966. After obtaining his BSc in 1987 from the University of Warwick, he undertook a PhD under the supervision of Professor Peter Moore. After a one year Royal Society Fellowship in 1991 at the Université Louis Pasteur de Strasbourg with Dr Jean-Pierre Sauvage, he moved to Austin, Texas, to work at the Center for Fast Kinetics Research with Dr Anthony Harriman. After two and a half years he moved back to Britain in November, 1994 to take up his current lecturing position in the Inorganic Department at the University of Glasgow. His major research interests concern donor–acceptor complexes and their photophysical properties and ways in which to incorporate them into multi-dimensional structures using cation chelation.
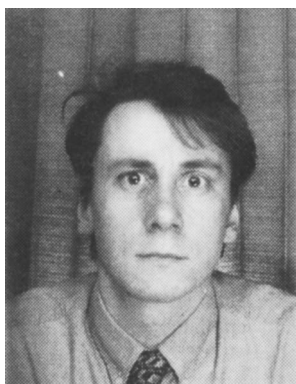
1.2 Relevance–Supramolecular Devices

To undergo and complete a desired task any machine requires not only an external trigger, but also each independent component performing in the correct sequence a specific function. Usually, machines are regarded as large items with many moving parts, however more recently the same notions have been applied to chemical systems, whereby individual subunits are made to perform unique operations but now at the molecular level (supramolecular devices).[3] Examples of such devices are molecular switches in which the relative positioning of molecular subunits is altered by an external agent such as light or through redox changes.[4] Because of the unique structural features of catenanes and rotaxanes research into these molecules as switches is growing, especially rotaxanes where control of bead positioning on a thread forms the basis of a simple molecular abacus.

1.2.1 Photosynthetic Models

Light-harvesting by plants is possibly the single most important natural process occurring on the Earth, and since solving of the X-ray structure of the photosynthetic reaction centre (RC) for the bacterium Rhodopseudomonas viridis a great deal of research has resulted in an attempt to understand and mimic this natural process. At a simplified level, within the RC photonic excitation of a donor molecule (D) causes an electron to migrate along a series of electron acceptors (A), leading ultimately to generation of a pair of redox ions.[5] In the natural system unique donor–acceptor separation and orientation play a major role in controlling individual electron transfer steps, and as a consequence chemists have turned to rotaxanes and catenanes in an attempt to create suitable synthetic prototypes. The two strategies depicted in Figure 2 attempt to illustrate how using the structural traits of [2]rotaxanes, spatial separation of charge is possible through either initial photonic excitation of: (a) a stopper entity, or (b) bead portion, coupled with concomitant electron transfer to an acceptor-based stopper.

Molecular devices and synthetic models for photosynthetic RCs are merely two potential areas of research pertaining to photoactive and redoxactive [2]rotaxanes/[2]catenanes and many more applications are being explored. However, it is fair to say that research is still at a very early stage and there is a long way to go before working molecular devices are commonplace. Thus, it is the inten-
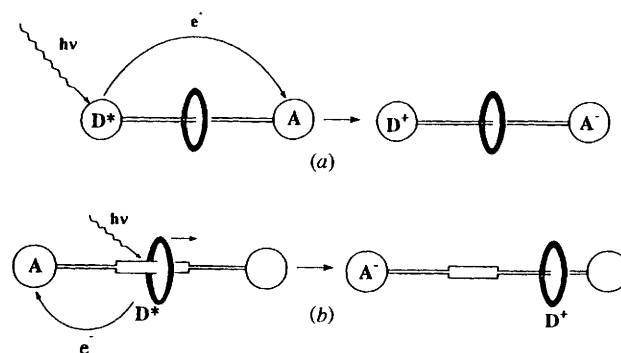

Figure 2 Two modes of charge-separation in a [2]rotaxane through an initial photonic excitation of either: (a) a stopper, or (b) bead. Note: in (a) the bead does not participate in the forward electron transfer process, but may play a role in the restoration of the ground-state by return electron transfer.
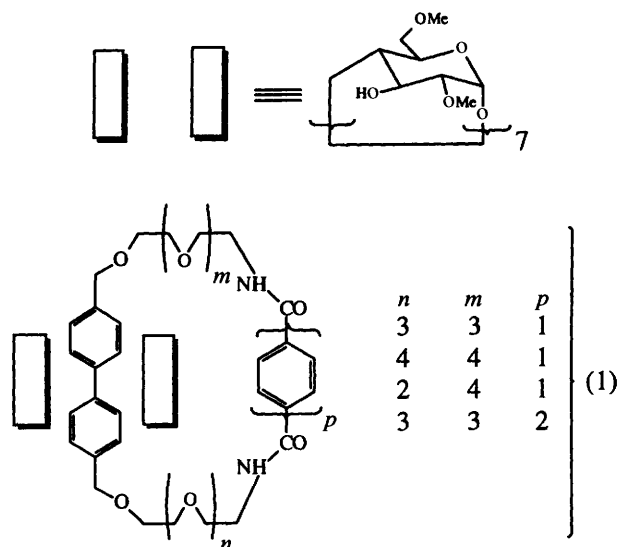
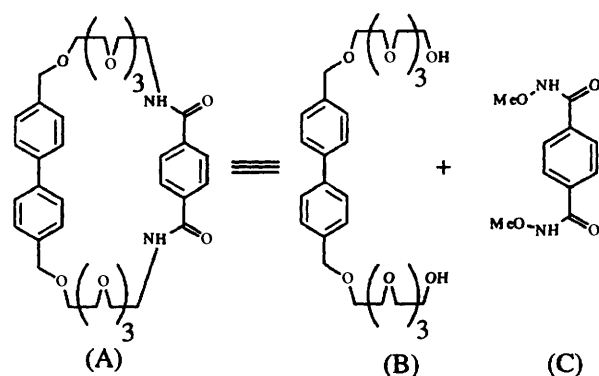**Figure 3** Examples of [2]catenanes incorporating a β-cyclodextrin as one of the interlocked rings

tion of this review to cover some of these recent developments, and in particular give illustrations of real chemical systems supporting photoactive and/or redoxactive groups. Where possible the relationship between structural features and physicochemical properties will be highlighted, especially where an understanding of both helps explain observed findings.

2 Cyclodextrin-based Superstructures

Cyclodextrins (CD) are well known 'bucket-shaped' cyclic sugar compounds ideally suited for inclusion of organic-based guests into their hydrophobic cavity. As a result early research, particularly into redoxactive [2]rotaxanes, utilised the inclusion properties of CDs. A review of this early research can be found in ref. 2(b) and therefore these systems will not be discussed.

Up until very recently, examples of analogous [2]catenanes incorporating CDs have been noticeably lacking. Recently however, Stoddart and coworkers[6] have been successful in producing workable quantities of cyclodextrin-derived interlocked rings. Consequently, examples of catenanes comprising of luminescent bitolyl groups linked via polyethoxy chains to bislactam subunits are shown in Figure 3. As pictorially depicted in Figure 3, the X-ray structure of [2]catenane 1 ($n = 3, m = 3, p = 1$) fully confirms the bitolyl unit exclusively occupying the cyclodextrin and the bislactam residue lying on the outer casing. In contrast, in the solution phase (C_6D_6) detailed nuclear Overhauser enhancement experiments confirm both the bitolyl and terephthaloyl units residing within the CD cavity. In an apparent contradiction 2D rotating Overhauser enhancement spectroscopy (ROESY) data obtained in the same solvent supports the existence of a single translational isomer in which the bitolyl is encapsulated within the CD. This apparent discrepancy however is explained by the less sensitive nature of ROESY experiments. Detailed photophysical data on (1) ($n = 3, m = 3, p = 1$) in MeCN are also entirely consistent with the interlocked nature of the two molecular components. For simplicity, 1 can be viewed as three simple components (A–C) plus the cyclodextrin.

Unlike the absorption spectrum of (A), which is simply a superimposition of the spectra of (B) and (C), the fluorescence spectrum is somewhat different to those of the individual units and contains two weak bands centred around 320 nm ($\tau < 0.5$ ns) and 420 ns ($\tau = 2.5$ ns). The emission at 420 nm is accredited to formation of an excited state complex (exciplex), resulting from initial photonic excitation of the bitolyl unit. However, in the resulting [2]catenane no exciplex emission is observed, and only luminescence at 320 nm from the bitolyl group is detected. Such photophysical data would be expected if both bitolyl and terephthaloyl units are well separ-

ated and accordingly is entirely in keeping with the interlocked nature of the [2]catenane and structural data.

3 π–π Stacked Assemblies

Simple mixing in an appropriate polar solvent of the electron-accepting N,N'-dimethyl-4,4'-bipyridinium dication and electron-rich 1,4-dimethoxybenzene results in creation of an electron donor–acceptor (EDA) complex, and formation of a charge-transfer (CT) absorption band. This CT absorption band of the EDA complex arises from an electronic transition within molecular orbitals formed by direct overlap of appropriate HOMO–LUMO π-orbitals of the two interacting aromatics.[7] Although highly coloured, the resultant solution phase EDA complex is loosely held ($K < 1$ dm^3 mol^{-1}) and consequently of little practical use in the construction of larger molecular assemblies such as rotaxanes and catenanes. Added extra complex stability is however readily obtained through cyclisation of either components into their corresponding macrocyclic counterparts. Using such an idea Stoddart and coworkers[8] have been particularly successful, especially regarding the bipyridinium-based cyclophane 2 (Figure 4) whose internal cavity dimension of ca. 6.8×10.3 Å is optimal for encapsulation of varying electron-rich aromatics and formation of EDA complexes.[9]
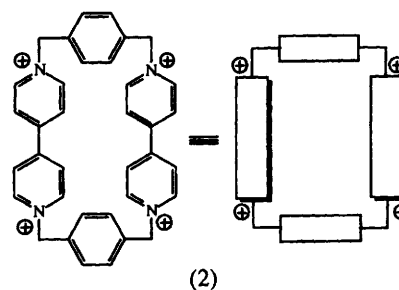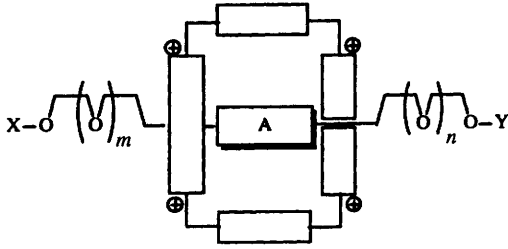

(2)

**Figure 4** An illustration of the bipyridinium-based cyclophane synthesised by Stoddart et al.
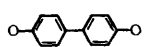
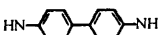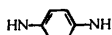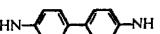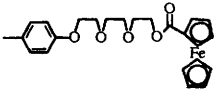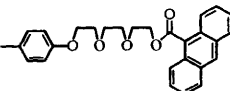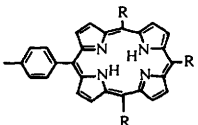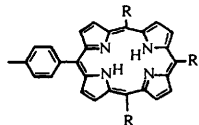Indeed, cyclophane 2 is now commonly used as the bead in a multitude of [2]rotaxane examples, or alternatively the ring in analogous [2]catenanes. The ability to address such systems photochemically,[10,11] and electrochemically[12,13] has resulted in intense research into such molecular assemblies.

3.1 [2]Rotaxanes

Relevant examples of [2]rotaxane assemblies in which the cyclophane 2 forms an integral part of the overall structure are listed in Table 1.

The [2]rotaxanes 3–5 represent recently developed systems by Kaifer and coworkers,[12b,c] synthesised specifically for influencing properties of the systems through electrochemical means. A closer examination of the electrochemistry of 4–5 is particularly noteworthy as subtle differences in electrochemical attributes of the benzidine- and p-phenylenediamine-station rotaxanes are observed.

Table 1 Examples of [2]rotaxanes

X	Y	A	$CT\lambda_{max}/nm^a$	Ref.
		o—⬡—⬡—o (3) ($m = n = 2$)	685	11b
		HN—⬡—⬡—NH (4) ($m = n = 2$)	480	11b
		HN—⬡—NH (5) ($m = n = 2$)	745	11c
		HN—⬡—⬡—NH (6) ($m = n = 2$)	690 480	11a
		o—⬡—o (7) ($m = n = 2$)	478	10c
		o—⬡—o (8) ($m = n = 2$)	480	10a
		o—⬡—o (9) ($m = 3, n = 2$)	475	10a
		o—⬡—o (10) ($m = n = 2$)	486	10b
		o—⬡—o (11) ($m = 3, n = 2$)	485	10a
		o—⬡—o (12) ($m = 3, n = 3$)[b]		11d

^{a} in CH_3CN. ^{b} Charge-transfer band obscured by porphyrin Soret bands

Primarily, the anodic electrochemistry of the two [2]rotaxanes can be summarised as follows:

$$S - e \rightleftharpoons S^+$$

$$S^+ - e \rightleftharpoons S^{2+}$$
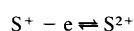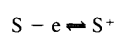
where S represents the bound station. In both cases, because of proximity to the tetracationic bead oxidation of the bound stations is significantly more difficult than in simple uncomplexed threads. This effect, however, is far more pronounced in **5** compared to **4** and is attributed to the larger size of the benzidine moiety as compared to the corresponding p-phenylenediamine which permits extended positive charge delocalisation over the extended π-orbital.

Electrostatic repulsion between bead and oxidised station is especially important when considering two-station [2]rotaxanes, as the possibility of 'driving' a bead from alternate stations constitutes an electroactive molecular switch. Accordingly, the [2]rotaxane **6** has been developed containing both a benzidine and biphenol station, which under normal conditions (room temperature, CD_3CN) displays bead shuttling. At reduced temperatures shuttling rate is significantly reduced and from 2D NMR experiments confirms the bead predominantly residing on the benzidine (86%) rather than the biphenol (14%) subunit. More significantly, electrochemical one-electron oxidation of the benzidine station is able, due to generation of enough electrostatic repulsion, to 'switch' the bead exclusively over to the biphenol site. It should be noted that similar switching is also possible by protonation of the benzidine basic nitrogens.
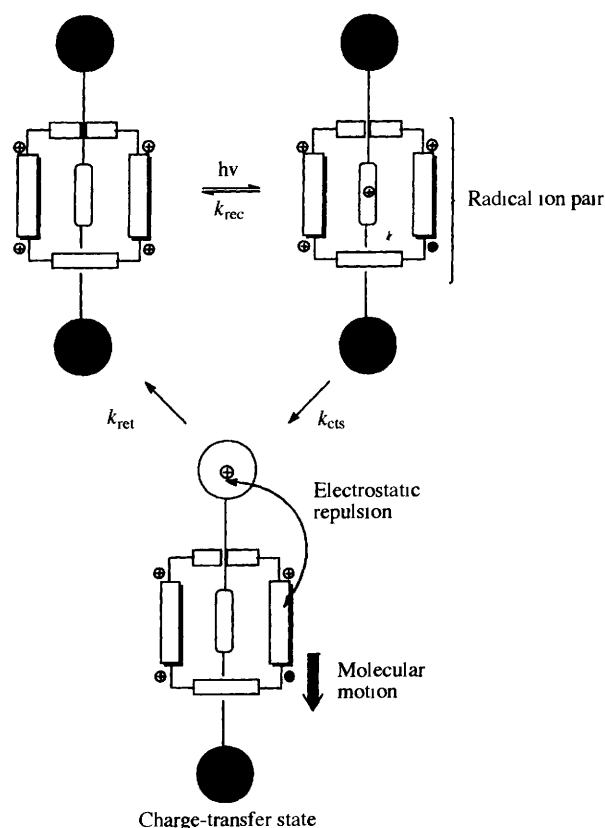
Figure 5 Photoprocesses occurring in the ferrocene containing [2]rotaxanes illustrated in Table 1

Conformational control of rotaxanes, but this time using light-induction instead of electrochemical means, is again the goal behind the research carried out by Harriman and co-workers,[9,10] on a series of one- and two-station [2]rotaxanes 7–11 (Table 1) As CT absorption bands of these EDA complexes occur in the visible region selective excitation of these rotaxanes is possible, resulting in a destabilisation of the charge-transfer interaction For simplicity, the cartoon (Figure 5) is intended to explain the general photoprocesses occurring in [2]rotaxanes 7–11

In general, excitation of the rotaxanes 7–11 using an ultra-short laser pulse generates a radical ion pair (RIP) through electron transfer from the bound hydroquinol unit to the proximal 4,4'-bipyridinium dication acceptor of the bead The lifetimes of the RIPs in rotaxanes 7–11 are ultrashort ranging from 14 to 30 ps, as a result of rapid charge recombination from back electron transfer (k_{rec}) In rotaxanes 10–11 these short lifetimes exclude the possibility of molecular bead motion, and all initial photonic energy is converted to heat in the surrounding solvent However, in 7–9 an additional secondary electron transfer process occurs in which the ferrocene stopper is oxidised (with a rate constant k_{cts}) by the photo-generated dialkoxybenzene π-radical cation, leading ultimately to formation of a spatially remote charge-transfer state (CTS) The CTS quantum yields range from 8% for 9 to a modest 25% for 7, and represent direct competition between the two rate constants k_{rec} and k_{cts} To fully explain this successful competition, proximity of the ferrocene to the charge-transfer reaction centre has to be invoked Indeed, a solid-state X-ray crystallographic structure of 7 reveals the ferrocene stoppers π-stacking to the cyclophane bipyridinium units and forming a more compact closed conformer in which the competitive electron-transfer processes occur (Figure 6)

Interestingly, lifetimes of generated CTSs are relatively long (0 5–1 µs), indicative of an increase in separation between the ferricinium and reduced bipyridinium-based cyclophane groups This increased component separation is accredited to strong intramolecular electrostatic repulsion inducing bead motion away from the ferricinium unit and towards the opposing stopper (Figure 2b) It is also interesting to note that whilst the lowest CTS quantum
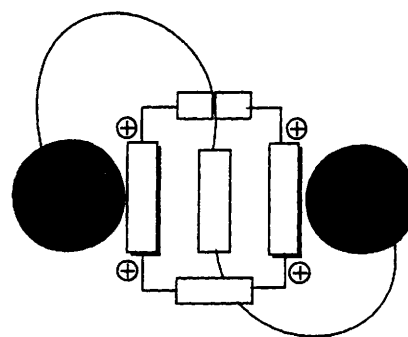

Figure 6 A cartoon representing π stacking of the ferrocene stoppers to the cyclophane bipyridinium groups

yield is observed for two-station rotaxane (9) the lifetime is the greatest (1 µs), and at a first glance could be attributed to the bead shuttling to the opposing station However, this is not the case as ^{1}H NMR studies indicate that bead interchange between the two stations occurs on a much longer timescale than is required for return electron transfer between the ferricinium and reduced cyclophane

Finally, 12 represents another example of a recently reported assembly in which the stopper is itself photoactive [12d] Although no detailed photophysical measurements on such an assembly have been reported it is interesting to note that ^{1}H NMR experiments are consistent with the bead residing proximal to the photoactive porphyrin stopper as well as at the expected hydroquinol station of the thread

3.2 [2]Catenanes

Relevant examples of [2]catenane systems recently developed by the group of Stoddart[13] incorporating both photoactive and electroactive subunits, are listed in Figure 7 Within such assemblies, control of translational isomerism is expected by trans–cis switching of the bis(pyridinium)ethylenes, or preferential electrochemical bipyridinium reduction

Rather disappointingly, photoexcitation of catenanes 13–18 via the bis(pyridinium)ethylene subunits results in no changes attributable to molecular component switching Even using external sensitizers no photoreactions occur and the catenanes remain unperturbed The lack of reactivity, however, is explained by fast photoexcited state deactivation, caused by strong electronic coupling to a low-lying charge-transfer state More encouragingly, switching is observed through electrochemical reduction of bipyridinium units in 13–15, and relying on the preferred translational isomer being that with the bis(pyridinium)ethylene unbound For instance, variable-temperature ^{1}H NMR experiments on 13 in $(CD_3)_2CO$ confirms the catenane predominantly existing as the translational isomer in which the bipyridinium unit is sandwiched 'inside' the two hydroquinol groups of the polyether crown (as shown) Complete switching of this translational isomer is performed through removal of the charge-transfer 'braking' action by means of preferential reduction of the inside bipyridinium unit Upon reduction of the bipyridinium unit, diminished aromatic binding allows circumrotation of the cationic cyclophane and a subsequent encapsulation of the bis(pyridinium)ethylene unit Re-oxidation of the reduced bipyridinium cation generates the non-preferred isomer, which by ring rotation reforms the starting translational isomer A simple cartoon representing this process is depicted in Figure 8, starting from the preferred translational isomer in the top left-hand corner

Returning to photoactive assemblies, three examples of azobenzene-based catenanes recently reported by Vogtle and coworkers [14a,b] are illustrated in Figure 9 Catenanes 19–21 differ from those described previously by virtue of the fact that the photoisomerizable (E)-azobenzene is not in direct contact with the charge-transfer centre Photoisomerization of (E)-azobenzene subunits in catenanes 19–21 leads to generation of a photostationary state in which a mixture of the Z/E isomers exists Thermal repopulation of

13 R= R'—⟨ ⟩—

14 R=⟨naphthyl⟩ R'=—⟨ ⟩—

15 R= R'⟨naphthyl⟩

16 R= R'—⟨ ⟩—

17 R=⟨naphthyl⟩ R'=—⟨ ⟩—

18 R= R'⟨naphthyl⟩
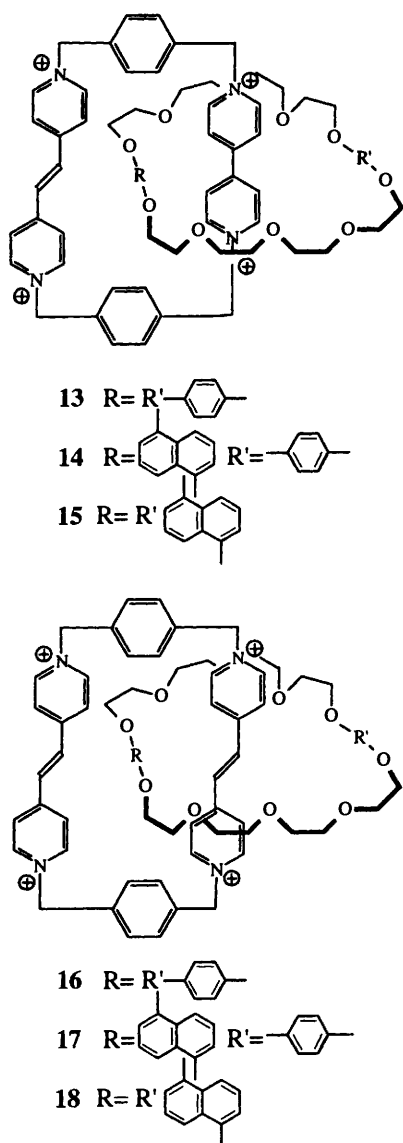
Figure 7 Illustrations of photo and redox active [2]catenanes containing bis(pyridinium)ethylene units

19

20

21
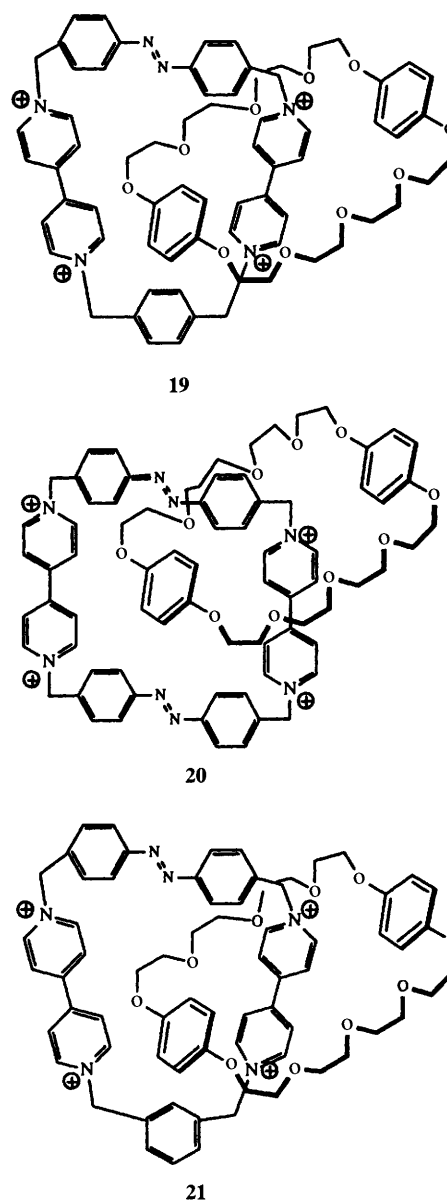
Figure 9 Examples of photoswitchable [2]catenanes synthesised by the group of Vogtle
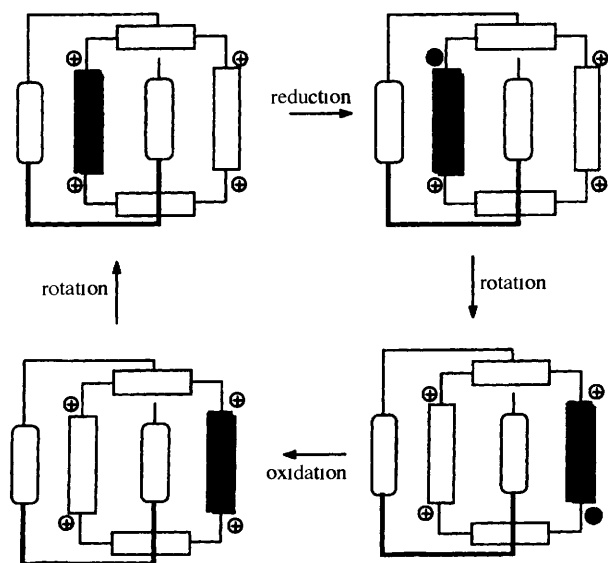
Figure 8 A simple cartoon representing electrochemical and physical pro cesses occurring in [2]catenane **13**

ground state conformation is somewhat dependent on the size of the catenanes, with half-lives of 20 5 h and 12 days reported for **19** and **20**, respectively More importantly, in both cases internal space reduction by generation of the (Z)-azobenzene moiety is manifested in an increased 'friction' between the bipyridinium and hydroquinol subunits, in a simple sense photoisomerization acts a kind of molecular brake to the circumrotation process Interestingly, unlike **19–20** no (E–Z)-photoisomerization is observed within **21**, which is not surprising considering the highly compressed nature of the cate nane In contrast, it is worth noting that isomerization in the simple cyclophane ($i\,e$ without the interlocked crown ether) is possible, hence reiterating the significant influence interlocking two rings in catenanes imposes

Finally, to conclude this section on catenanes examples of por phyrin-based assemblies developed by the group of Gunter[15a,b] are illustrated in Figure 10

As depicted, control of catenane conformation is exerted by way of close porphyrin proximity to the cyclophane **2** Specifically, within catenanes **22–23** a face-to-face arrangement of the cyclo phane bipyridinium units and porphyrin rings is maintained Strong evidence for such a phenomenon is a shift in the porphyrin Soret band, ca 20 nm **22**, which is most likely due to electronic perturbations from secondary π–π interactions However, protonation of the
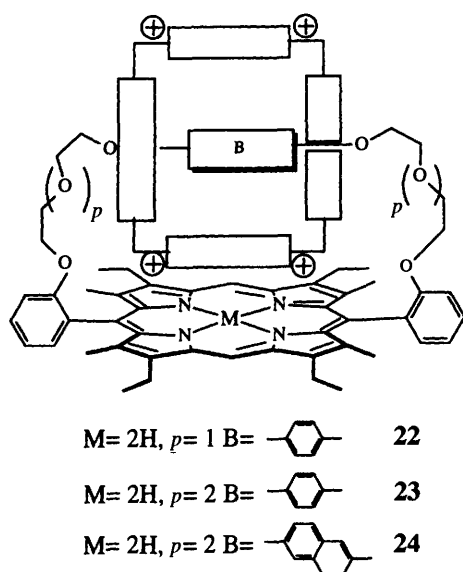
Figure 10 Porphyrin-based [2]catenanes containing cyclophane 2 prepared by Gunter *et al.*

basic porphyrin nitrogens leads to heightened electrostatic repulsion between the components and an increase in their separation. It is interesting to note that whilst increased molecular separation in catenanes 23–24 allows circumrotation of the cyclophane 2, no such rotation in the more restricted catenane 22 is observed. As this example of dynamic control is brought about by protonation, the system is consequently *ionactive*, but it is worthy of a mention as clearly there is scope for even more interesting work using the photoactive properties of the porphyrin groups.

### 3.3 Miscellaneous Examples

Although 25 (Figure 11) cannot be labelled a true [2]rotaxane, and is best described as a pseudorotaxane, the work reported by Balzani *et al.*[12] exemplifies a potential alternative method for photochemically addressing [2]rotaxanes. Balzani's approach again relies on destabilisation of the CT interaction but this time by use of 9-anthracenecarboxylic acid as an external photochemical reducing reagent.

Without the influence of stoppers, 25 is in dynamic equilibrium with its individual components, namely the tetracationic cyclophane 2 and naphthalene-based thread. Owing to a favourable thermodynamic driving force, electron transfer from photoexcited 9-anthracenecarboxylic acid results in rapid reduction of a single bipyridinium unit in 25. Under normal conditions restoration of the ground state by back electron transfer is too fast to permit dethreading, and as a result is of little practical use. However, through the use of a sacrificial reductant (triethanolamine) photooxidised 9-anthracenecarboxylic acid is immediately removed and recycled. With removal of the fast destructive return electron transfer pathway dethreading readily takes place. Indeed, under employed conditions after some 25 min of irradiation up to 35% of the pseudorotaxane becomes dethreaded.
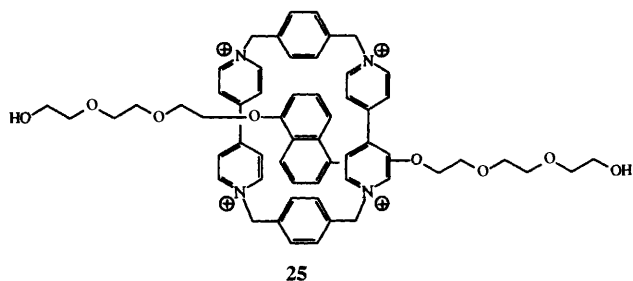

25

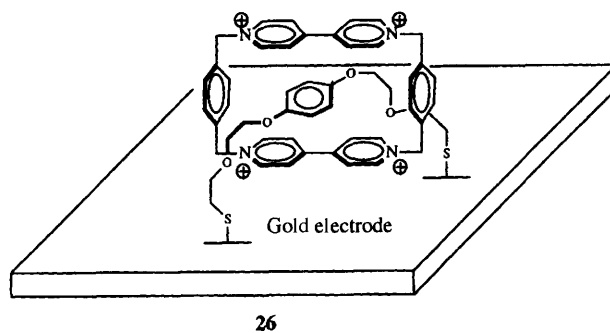Figure 11 An illustration of the pseudorotaxane studied by Balzani and coworkers

26

Figure 12 The surface-modified [2]catenane incorporating cyclophane 2 prepared by Kaifer and coworkers

The necessity to think of modes in which to externally manipulate well-organised [2]rotaxane and [2]catenane superstructures is gaining in momentum. To this extent, the use of an electrode as not only a [2]catenane component but also the electroactive support, has recently been explored by Kaifer and coworkers.[16] In this instance, [2]catenane 26 (Figure 12) is formed by sulfur surface attachment of a thiol functionalised thread and cyclophane 2, by simply leaving a clean gold electrode exposed to a solution of the individual ingredients. Cyclic voltammetry of the modified electrode displays typical reversible bipyridinium reduction centred at *ca.* −0.46 V (*vs.* saturated calomel electrode, SCE). Even though the extent of surface bound catenane is small (*ca.* 8%) such an example is encouraging for future development of macroscopic devices based on surface-modified electrodes.

4 Cation Chelating Supramolecular Systems

It is well established that preorganisation of molecular components on metal ions prior to final cyclisation, leads to significant enhancement in yields of macrocyclic ligands. The first successful synthetic application of such an approach to the field of rotaxane and catenane chemistry came through the work of Sauvage and Dietrich–Buchecker.[2a] Through fashioning of two bidentate 2,9-diphenyl-1,10-phenanthroline ligands around Cu[I] they were able to prepare a tetrahedral complex ideal for cyclisation to the [2]catenane assembly 31 (Table 3). Leading on from this work Sauvage and coworkers have now prepared corresponding rotaxane assemblies, again using the preferential tetrahedral coordinating properties of Cu[I]. In particular, [2]rotaxane systems developed by Sauvage and studied by Harriman[17a,b] using fast kinetic techniques have shown to be prime models for the light-harvesting photosynthetic reaction centre [Figure 2(a)].

4.1 [2]Rotaxane Assemblies

Examples of rotaxanes based upon entwined 2,9-phenyl-1,10-phenanthroline moieties and in which the large bulky stoppers inhibit dethreading are illustrated in Table 2.

The rotaxanes 27–29 incorporating gold(III) and zinc(II) porphyrins were primarily developed as models for determining spacer effects on electron transfer between two well-separated porphyrin subunits. Specifically, previous work on analogous non-rotaxane systems supported the view that photoinduced electron transfer proceeded *via* a superexchange mechanism employing the HOMO/LUMO orbitals of the phenanthroline-based spacer moiety.[18a-d] Modulation in energy of these spacer-based orbitals through cation changes in 27–29 was expected to determine the effectiveness of the superexchange mechanism at promoting photoinduced electron transfer.[19]

In general, selective excitation of 27–29 by way of the zinc porphyrins causes rapid singlet excited-state electron transfer to the adjacent gold porphyrin, and generation of a charge-separated state (CST) [eqn. (1)].
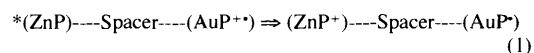
$$*(ZnP)\text{----}Spacer\text{----}(AuP^{+\bullet}) \Rightarrow (ZnP^{+})\text{----}Spacer\text{----}(AuP^{\bullet})$$
$$(1)$$

Table 2 Examples of [2]rotaxanes incorporating phenanthroline metal chelators

	R	R	M		Ref
			Cu⁺	27 (n = 1)	19
			no metal	28 (n = 1)	19
			Zn²⁺	29 (n = 1)	19
			Cu⁺	30 (n = 0)	20

In rotaxanes **28–29** the rates of formation (ca 3×10^{10} s⁻¹) and decay (ca 2×10^9 s⁻¹) of the CTSs are somewhat slower than those measured for **27** (ca 5×10^{11} s⁻¹ and ca 5×10^{10} s⁻¹, respectively) clearly demonstrating the influence on electron transfer the copper(i) ion imposes Alternatively, excitation of **27–29** via the gold(iii) porphyrin subunits results in generation of the gold(iii) porphyrin triplet state, which again rapidly decays to form the CTS [eqn (2)]

$$(ZnP) \quad Spacer \quad (AuP^+)^* \Rightarrow (ZnP^{+\bullet}) \quad Spacer \quad (AuP^\bullet)$$
(2)
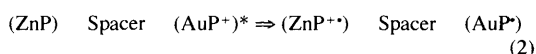
As before, influence of the copper(i) results in significant lifetime differences in the gold(iii) porphyrin triplet states, ranging from ca 60 ps for **28–29** to 17 ps for **27** As surmised, observed differences in electron transfer properties of the individual rotaxanes are to a first approximation explained using a through bond superexchange mechanism More specifically, rate constants (k) for the aforementioned electron transfer processes are governed weakly by the following expression $k \, \alpha \, (1/\delta E_{AB})^2$, where δE_{AB} represents the energy gap between the spacer LUMO or HOMO and the donating or accepting orbitals of the appropriate porphyrin subunits Generally, for rotaxane **27** δE_{AB} has the minimum value and accordingly corresponds to the highest electron transfer rate constant

Moving away from porphryin rotaxanes the teaming up of Sauvage and Diederich[20] has recently resulted in the preparation of the novel fullerene stoppered rotaxane **30** Electrochemical results indicate a significant anodic shift in the redox potential for the Cuⁱ/Cuⁱⁱ couple attributable to destabilisation of the higher copper oxidation state by the strong electron withdrawing power of the fullerenes Proximity effects of the fullerene stoppers also account for complete quenching of the ³MLCT luminescence of the Cuⁱ complex

4.2 [2]Catenane Assemblies

Illustrations of Cuⁱ based [2]catenanes (catenates) in which the linker between individual phenanthroline ligands either maintain

structural integrity, or are themselves photo/redox active groups are listed in Table 3

Influence of interlocking two coordinating subunits is particularly noticeable in the electrochemistry of catenates **31–32**, especially the kinetic stability of formal low oxidation state species[21a] Comparison of redox potentials for Cuⁱⁱ/Cuⁱ and Cuⁱ/Cu⁰ in similar non catenated phenanthroline based copper(i) complexes to **31–32** reveals only minor differences in recorded values However, for catenanes **31–32** an additional highly reversible redox couple exists

Table 3 Illustrations of copper I [2]catenanes

R	R	Ref
		31 21
		32 21
		33 24
		34 25

at ca −1 9 V (vs SCE) assigned to the reduction process Cu⁰/Cu ¹ Complete electrochemical and chemical reversibility of this redox couple is attributed to the catenanes exhibiting an enhanced kinetic inertness towards decomplexation, as a consequence of the entwined nature of the ligands This kinetic inertness also accounts for the 'free' catenane ligands (catenands) being very effective in production of other stable low oxidation state metal species (e g Ni⁺,Zn⁺),²¹ᵇ ᶜ which are otherwise inaccessible in other 'simple' phenanthroline-based metal complexes

In solution (CH₂Cl₂) at room temp , relatively long-lived excited state luminescence (τ ca 190–280 ns) at λ_max ca 720 nm is observed for catenanes 31–32, consequently making them ideal photosensitizers It should be noted however that these emission lifetimes are not particularly unusual, as other Cuᴵ complexes incorporating 2,9-aryl substituted phenanthroline ligands exhibit similar photophysical properties ²² Luminescence is also observed in other metal complexes of the catenand corresponding to 31, with emission maxima being able to be tuned from 730 nm (Cu⁺) to 400 nm (Li⁺) ²³

As a continuation, recently the assembly 33²⁴ has been synthesised containing the electron-donating tetrathiafulvalene unit It is hoped that photoactive properties of the Cuᴵ site, coupled with its strong excited state reducing properties, can be harnessed to eventually produce a catenane capable of yielding charge-separation comparable to the counterpart [2]rotaxanes Along the same line, insertion of two photoactive porphyrinic moieties in [2]catenane 34²⁵ is expected to allow study of through-space electron transfer

To conclude, an example of a novel [2]catenane²⁶ in which molecular switching is induced through changes in oxidation state of the central copper ion is shown in Figure 13 Again, because copper(ı) prefers a tetrahedral arrangement, 35 exists exclusively with the two phenanthroline ligands of the catenane coordinated to the metal Upon electrochemical oxidation however the five coordinate geometry requirement of copper(ıı) results in a 'swinging round' of one ring, and attachment of the tridendate terpyridine ligand Reduction of the system back to copper(ı) consequently returns the assembly back to the starting geometry
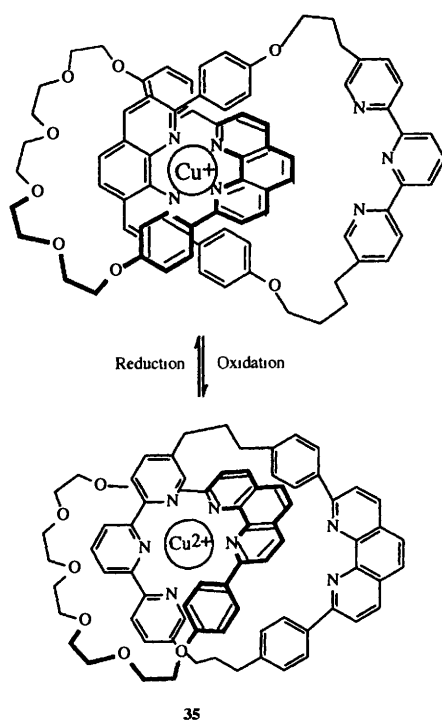

Reduction ‖ Oxidation

35

Figure 13 Conformation changes induced by oxidation/reduction of a copper containing [2]catenane

5 Concluding Remarks

Clearly at the present, studies into utilising the unique structural features and physiochemical properties of rotaxanes and catenanes are still in the early development stage Currently, we are still limited to mainly probing the properties of aforementioned molecular systems in the solution phase, and have only just commenced on the long road of rotaxane/catenane surface attachment for 'outside world' manipulation On top of this, the most conducive method for external stimulation is still debatable, but clearly issues such as selectivity, speed of switching, compound degradation, overall control, etc will certainly play a major role in the final choice

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