Synthesis, Structure and Photophysics of Neutral π-Associated [2]Catenanes

Darren G. Hamilton, John E. Davies, Luca Prodi, and Jeremy K. M. Sanders*

Abstract: The supramolecular utility of a neutral π-stacking system of aromatic donors and acceptors is illustrated with the syntheses of three neutral [2]catenanes. These templated syntheses are based on the oxidative dimerisation of electron-deficient aromatic diimide derivatives, equipped with terminal acetylene functions, in the presence of a preformed crown macrocycle containing complementary electron-rich aromatic diethers. X-ray crystallographic study of one of the catenanes and a precatenane crown/diimide inclusion complex reveals the ordered donor–acceptor stacking responsible for templating the catenane syntheses and subsequently organising the packing of the interlocked molecules in the solid state. NMR investigation of the catenanes reveals a dominant dynamic process at room temperature involving the sweeping of the crown macrocycle around the periphery of the interlocked structures; NOESY exchange spectra reveal a higher-energy process involving the revolution of the crown macrocycle through the centre of the second ring. This combined dynamic picture has been used to support the observed photophysical behaviour. Room-temperature fluorescence of the catenanes is only partially quenched by neighbouring chromophores, implying some mobility in the constituent rings; for one of the catenanes fluorescence quenching data enables an estimate to be made of the ratio of translational isomers present in solution. In contrast, low-temperature (77 K) fluorescence is totally quenched as a consequence of freezing all dynamic movement. Collectively, the results presented in this work lend support to the assertion that the robust, neutral building blocks employed in the catenane syntheses are ideal vehicles for the development of complex [*n*]catenane syntheses.

Keywords: catenanes · donor–acceptor systems · photochemistry · template synthesis

Introduction

The development of several efficient templating mechanisms for the covalent assembly of topologically complex molecules has facilitated the synthesis of numerous catenanes, rotaxanes, and even knots.[1] Isolated yields are often impressively high, this efficiency being the direct consequence of the high level of structural ordering imposed by the specific noncovalent interactions established between the converging molecular precursors. Accordingly, one method for the classification of studies of mechanically interlocked molecules is by the nature of the intermolecular association employed in templating their formation. Contemporary organic synthesis has yielded three distinct approaches to such templating: i) chelation of metal cations, ii) stacking of electron-deficient aromatic dications with electronically complementary aromatic molecules and iii) amide hydrogen-bonding interactions.[2] The application of these disparate approaches has allowed the construction of an array of topologically fascinating molecules and has provided considerable impetus to the development of supramolecular chemistry in the past decade.[3]

Stoddart's development of a methodology for the synthesis of interlocked molecules based on the π-stacking of electron-rich aromatic ethers with electron-poor bipyridinium derivatives remains a landmark in the field.[4] The work we present here represents an attempt to answer two questions raised by the sheer simplicity, efficiency and elegance of Stoddart's syntheses. Firstly, because the molecular recognition process responsible for templating the synthesis of existing π-associated systems arises as a consequence of the first bond-forming reaction, the question is raised whether such in situ programming of components is a prerequisite for efficient molecular interlocking.[5] Secondly, if we can utilise building blocks with preprogrammed recognition characteristics, are there other macrocyclisation reactions of potential utility in the synthesis of complex structures? These two approaches are illustrated for the assembly of a tetracationic catenane using the methodology of Stoddart (Figure 1), and for our proposed

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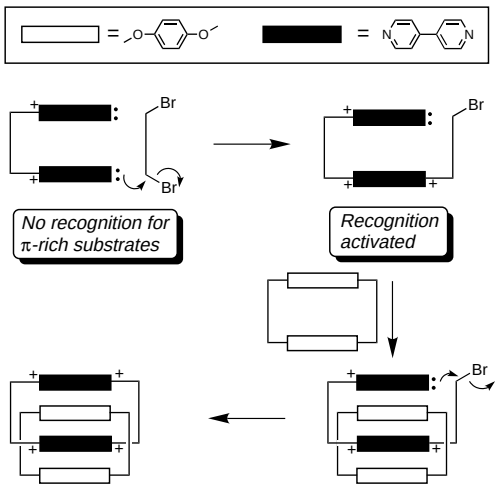


Figure 1. Tetracationic catenane assembly strategy of Stoddart, highlighting the crucial recognition step involving a tricationic intermediate formed on the reaction pathway.

construction of a neutral catenane from precursors with established, complementary recognition characteristics (Figure 2).[6]

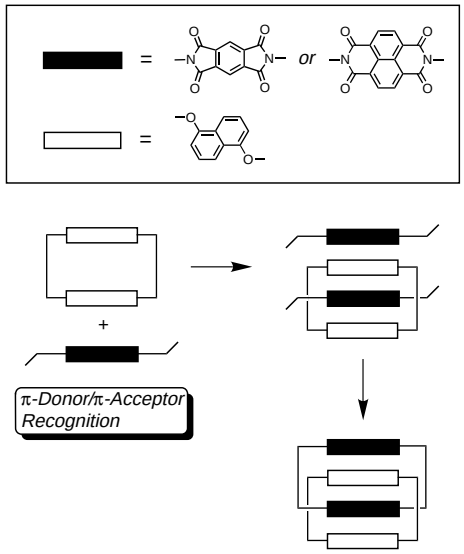


Figure 2. Catenane assembly from neutral building blocks: preexisting recognition characteristics are employed to ensure assembly in a geometry favouring molecular interlocking.

The photophysical[7] and electrochemical[8] properties of pyromellitic and related diimides have led to their incorporation in a variety of supramolecular systems. Some of the earliest examples involved the use of a pyromellitimide derivative to bridge a porphyrin centre in macrocyclic species designed as model photosynthetic systems.[9] A variety of electron donor–acceptor cyclophanes derived from pyromellitic and 1,4,5,8-naphthalenetetracarboxylic diimides have also been reported.[10] The naphthalenediimide is a rather strong electron acceptor and has previously been employed in several supramolecular systems which rely on π-stacking associations: a cryptand that effectively binds nitrobenzene,[11] a molecular host that self-assembles in the presence of dimethoxybenzene[12] and a linear covalently linked alternating donor–acceptor oligomer that spontaneously adopts a pleated conformation in aqueous solution.[13]

We have previously shown that pyromellitic diimide, like 1,4,5,8-naphthalenetetracarboxylic diimide, forms alternating donor–acceptor π-stacks with electron-rich naphthalene diethers.[14] The packing arrangement of donor and acceptor subunits revealed by these solid-state analyses led to the design of a [2]catenane synthesis: pairs of electron-rich naphthalene residues are linked with polyether chains to form the known macrocycle bis(1,5-dinaphtho)-38-crown-10;[15] this preformed ring is then used as the template to direct the coupling and cyclisation of two bis-acetylenic diimide derivatives, one bound inside the crown macrocycle, the other stacked outside (Figure 3). We selected the oxidative coupling of terminal acetylenes as the key ring-closing

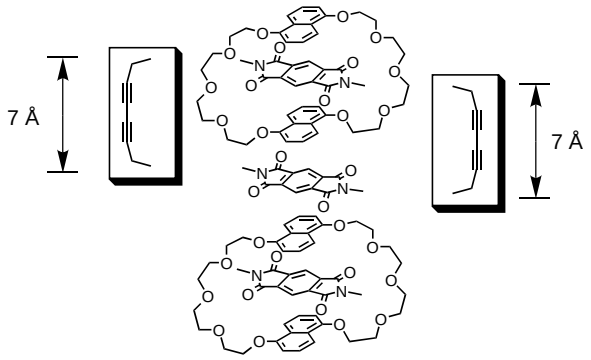


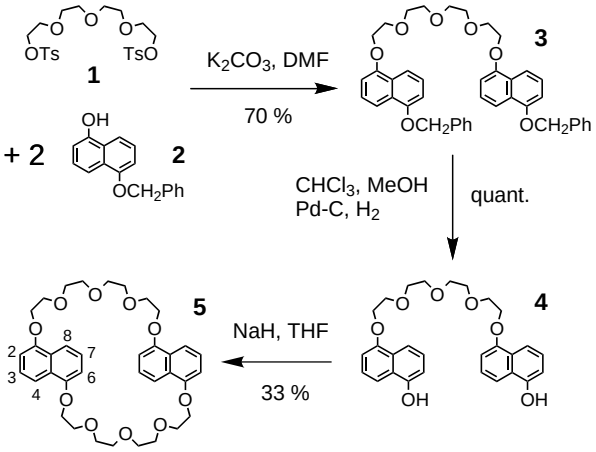
Figure 3. From neutral donor–acceptor π-stacks to neutral interlocked supermolecules.

reaction for several reasons. This process has previously been employed in the synthesis of a variety of macrocyclic host systems,[16] including some phenanthroline-based catenates,[17] and the butadiyne linker generated from the coupling of two terminal acetylenes is ideally suited to bridge the ca. 7 Å span demanded by the target structure. Additionally, the reaction proceeds under the mild conditions conducive to effective supramolecular templating by means of weak noncovalent interactions.

In this paper[18] we do not present the exhaustive analyses of a series of closely related systems that would be required for the detailed examination of subtle structural and dynamic characteristics. Our intention is to demonstrate the applicability and versatility of a neutral system of π-complementary components for the templated formation of interlocked molecules. The solid-state structures of a bis-acetylene building block, a representative preassembled complex and one of the [2]catenanes are used to illustrate this programmed structural approach. NMR experiments are described which reveal the nature of the dynamic solution processes occurring within the [2]catenane structures, and also serve as a model for rationalising the results of photophysical measurements. By way of conclusion, a brief discussion of the applicability of this system to the development of reversible, thermodynamically controlled catenane syntheses is presented.

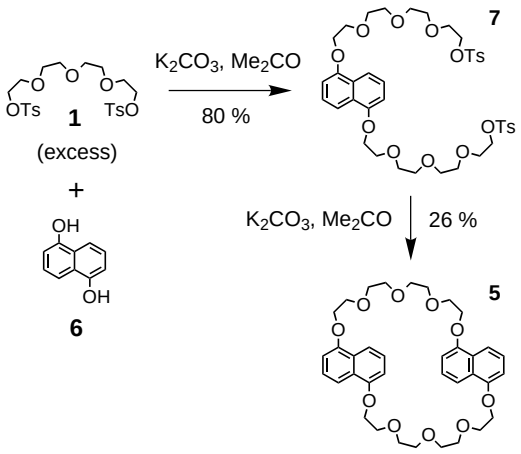
Results and Discussion

Synthesis: Bis-1,5-(dinaphtho)-38-crown-10 **5** is a known compound,[15] and we first prepared this macrocycle utilising the literature synthesis briefly described in 1987 (Scheme 1).[19] Whilst the chemistry involved in this route is



Scheme 1. Literature synthesis of dinaphtho crown **5** from a protected naphthalenediol.

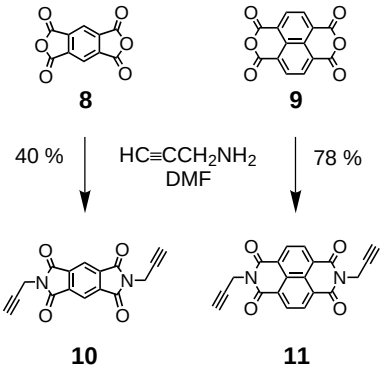
straightforward and provided adequate quantities of the desired crown for our early studies, we found the initial monobenzylation protection step (to yield **2**) rather troublesome. The yield of this aromatic monoether could be raised substantially from that reported in the original synthesis by use of an excess of 1,5-dihydroxynaphthalene in the alkylation step, but the procedure remains difficult to reproduce on a reasonable scale. However, the synthesis of **5** from **2** proceeds satisfactorily, and a typical overall yield for the four-step route detailed in Scheme 1 is around 10%. Recently a two-step route to the well-known hydroquinone analogue of **5** was reported.[20] Adaptation of this chemistry to the synthesis of **5** involved alkylating the starting naphthalenediol **6** with a large excess of glycol ditosylate **1** to afford naphthalene ditosylate **7** (Scheme 2). Macrocyclisation of **7** with a further equivalent of **6** in a refluxing suspension of potassium carbonate in acetone



Scheme 2. Two-step synthesis of crown **5** from 1,5-dihydroxynaphthalene.

afforded the dinaphtho crown ether **5** after chromatographic separation and recrystallisation from methanol. The overall yield for this more reliable, two-step procedure is around 20%.

To equip the electron-accepting diimide components of our system with terminal acetylene functions we condensed each dianhydride with two equivalents of commercially available propargylamine. In each case, treatment of a dimethylformamide (DMF) solution of the appropriate dianhydride, **8** or **9**, with the amine led to precipitation of the ring-opened diacid diamide derivatives. This precipitate could then be collected and heated in acetic anhydride to form the desired diimide products. More conveniently, simple warming of the DMF suspension obtained in the first step also leads to ring closure and dehydration (Scheme 3). The crystalline bis-acetylene derivatives **10** and **11** are obtained in analytically pure form following recrystallisation from aqueous DMF.



Scheme 3. Synthesis of terminal acetylene functionalised aromatic diimides **10** and **11**.

A 2:1 molar ratio of bis-acetylene **10** and crown **5**, when mixed in dry DMF (approx. 15 mM crown concentration), gave a strongly orange-coloured solution indicative of donor–acceptor complex formation. The weak, reversible nature of this interaction is readily demonstrated by warming the mixture to around 80 °C, whereupon the colour virtually disappears; it is gradually restored as the solution cools. To effect the coupling process, large excesses of anhydrous copper(I) chloride and copper(II) chloride were added to the mixture under an atmosphere of dry air (Scheme 4). After stirring for two days, [2]catenane **12** was isolated from the reaction mixture by simple work-up and chromatography as an orange-red solid in 38% yield.[52] Compelling evidence that molecular interlocking had been accomplished was provided by the observation that solutions of the crude reaction products remained deeply orange at elevated temperatures.

It was found that **10** and **5** tended to precipitate from the reaction solvent at ambient temperature, and the initial couplings were performed at 50 °C simply to ensure dissolution of all material. However, couplings at ambient temperature, despite containing suspended material, proceed perfectly well and afford generally higher yields than the coupling experiments at higher temperature. Under identical reaction conditions (50 °C, DMF, 15 mM concentration), a 2:1 mixture of **11** and **5** gave the [2]catenane **13** as a purple solid in 29%

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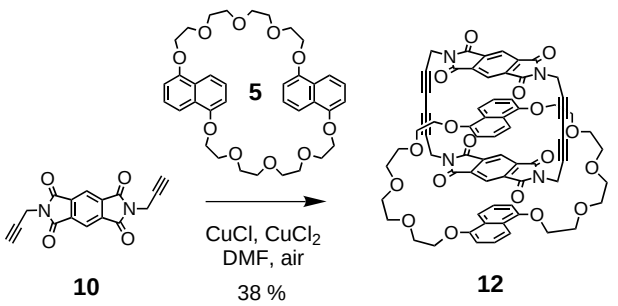
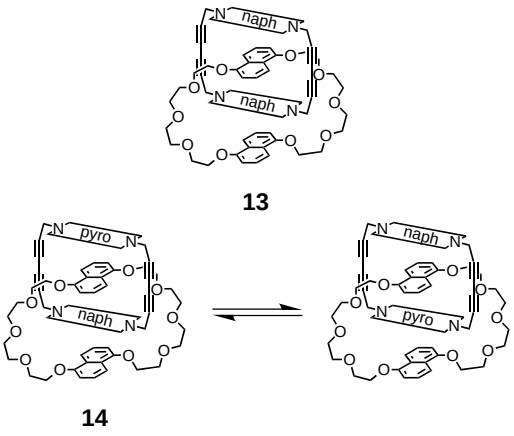


Scheme 4. Synthesis of catenane **12**.

yield. When the reaction was repeated at ambient temperature the isolated yield of **13** rose to 52%,[21] a yield which demonstrates the comparable efficiency of this templating process to previous catenane syntheses. The increase in yield obtained at lower temperatures also highlights the predictably weak nature of the intermolecular association between the molecular components.

Since 1,4,5,8-naphthalenetetracarboxylic diimide derivatives are known to be rather stronger electron acceptors than pyromellitic diimides it is perhaps unsurprising that the isolated yields of [2]catenane are higher with the naphthalene derivative. Support for this hypothesis is provided by exposing a 1:1:1 ratio of diimide **10**, diimide **11** and crown **5** to the standard coupling conditions. After work-up and preparative chromatographic separation the red unsymmetrical catenane **14** (the two translational isomers are shown) was obtained as



the major product (23%), accompanied by smaller amounts of the symmetrical catenanes **12** (5%) and **13** (6%).[22] This product distribution is the inevitable consequence of the majority of the crown binding sites being occupied by naphthalenediimide **11**, so ensuring that the bulk of the catenation process occurs by coupling with the excess of diimide **10** left uncomplexed in solution.

The unequivocal demonstration of molecular interlocking requires the joint application of a number of spectroscopic techniques. However, catenanes have long been regarded as having a unique mass-spectral signature since the first bond-breaking process is highly likely to involve rupture of one of the macrocyclic rings and unthreading of the interlocked molecule. Mass spectra of catenanes display peaks at the molecular weight of the parent catenane and then present no further spectral features until the weight of one or other of the component rings is reached. Liquid secondary ion mass spectral (LSIMS) analyses of catenanes **12**, **13** and **14** all reveal this distinctive behaviour. Mass spectral analysis under electrospray ionisation (ESI) conditions, a more gentle ionisation source, did not induce fragmentation, and each catenane could be detected intact, typically as its sodium ion adduct, $[M+\mathrm{Na}]^+$.

X-ray crystal structures: Contrary to our expectation, cocrystallisation of a 2:1 ratio of bis-acetylene **11** with crown **5** afforded a mixture of high-quality crystals of both the 1:1 **11**·**5** inclusion complex, and of free bis-acetylene **11**. Our intention in selecting this host:guest ratio was to allow the potential formation of an alternating internal–external complex stack and so demonstrate the validity of the structural design outlined in Figure 3; it is surprising that crystal packing forces lead to a structural arrangement that does not display extended donor–acceptor stacks.[23]

A view of the solid-state structure of terminal bis-acetylene **11** is shown in Figure 4. The rather simple structure presents a

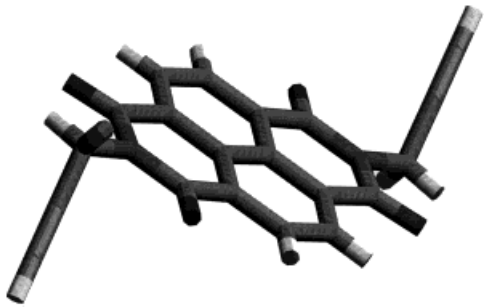


Figure 4. View of the solid-state structure of diimide **11** (displayed with Cerius Molecular Simulations software).

planar tetracyclic framework ideally suited for complexation between complementary aromatic planes.[24] The bond angles for the sp and sp^3 hybridised centres of the *N*-propargyl substituents are 176.2(4)° and 112.9(3)°, respectively. Inclusion complexation of bis-acetylene **11** within the cavity of crown **5** appears to have few structural consequences other than to increase the angle between the diimide framework and the axis of the propargyl substituents from 62° to 89°.[25] The sp and sp^3 bond angles for the propargyl substituents of the included substrate are 179.8(8)° and 110.3(5)°, respectively. The perpendicular arrangement of propargyl substituents neatly highlights the degree of preorganisation of the complex towards an eventual catenation process (Figure 5). In the crystal structure, the included diimide is inserted centrosymmetrically through the centre of the crown with an interplanar spacing between the electron-rich aromatic ethers and electron-deficient diimide units of around 3.5 Å, although the planes of the respective π systems subtend an angle of around 4°. The value of the interplanar spacing is very similar to that observed in a 4,4′-bipyridinium complex of the same crown; unsurprisingly the *all-gauche* conformation of the

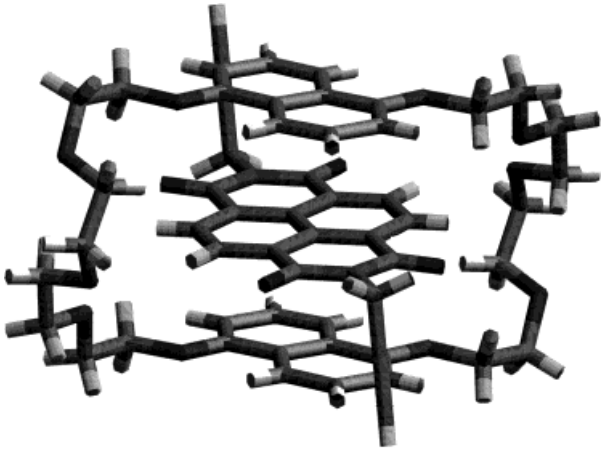


Figure 5. View of the solid-state structure of the **11**·**5** inclusion complex.

crown polyether chains is also noted in both complexes.[15] The overlap orientation of the complementary π systems, with the long axes of the components approximately parallel (Figure 6), is similar to that noted in a related cocrystal,[13] though

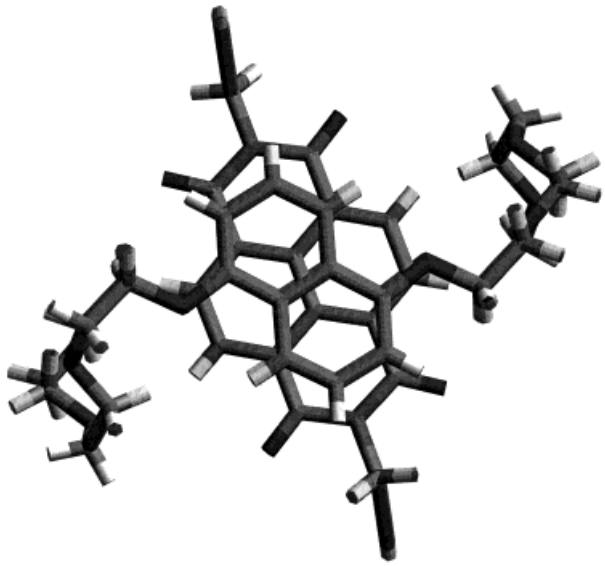


Figure 6. Plan view of the solid-state structure of the **11**·**5** inclusion complex showing the overlap of the aromatic components.

this previously reported system does display alternating donor–acceptor stacks.[26]

The solid-state structure of catenane **12** was obtained from a rather tiny crystal ($0.30 \times 0.12 \times 0.10$ mm) by synchrotron X-ray diffraction, the crystals being too small to allow the structure to be solved using commercial radiation sources.[18] The orders-of-magnitude increase in X-ray intensity provided by the synchrotron allowed the structure to be solved with comparative ease. The solid-state structure of **12** is represented in Figure 7. The mutually interlocked neutral macrocycles that comprise the catenane adopt a relative orientation where the electronically complementary π systems are aligned such that their long axes are nearly perpendicular. Similar overlap orientation has previously been reported for an alternating donor–acceptor stack comprised of the same

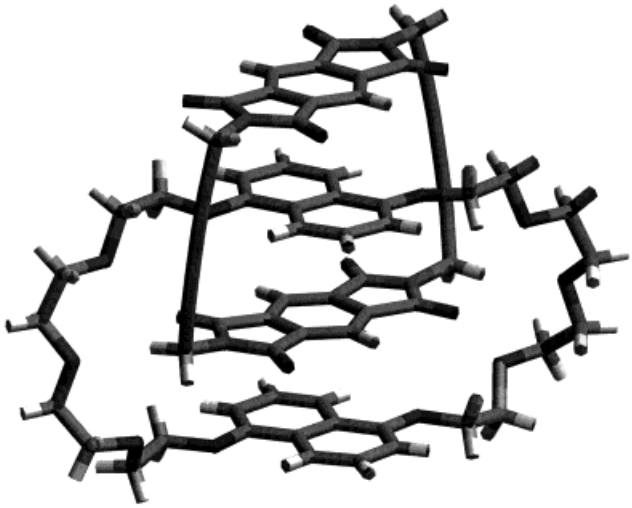


Figure 7. View of the solid-state structure of [2]catenane **12**.

aromatic components, but lacking any macrocyclic architecture.[14] Further vindication of the choice of supramolecular building blocks is provided by the generation of a packing diagram for **12** that reveals stacks of individual catenane molecules parallel to the crystallographic *a* axis, continuing the donor–acceptor stack (Figure 8). The interplanar spac-

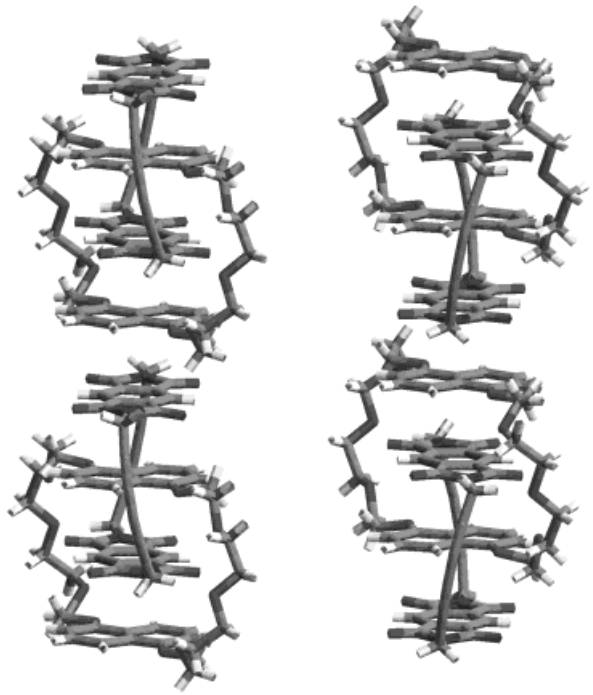


Figure 8. View of the packing of enantiomeric [2]catenanes in the solid-state structure of **12**.

ings of the π-rich and π-poor components, both within individual catenane molecules and between adjacent members of the extended stacks, are around 3.4 Å. The hexadiyne linkers between the pyromellitimide units are substantially bowed, the average sp bond angle being around 171° (< C–C≡C). It is clear that all of the conformational flexibility

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required to form the pyromellitimide macrocyclic component is provided by these nominally linear connections since the sp^3 hybridised centres at the corners of the cyclophane exhibit almost ideal tetrahedral geometry ($\measuredangle N-CH_2-C$ 109.4–110.1°).

The planes of the aromatic components of **12** are essentially parallel (deviation $<1°$), but the two identical aromatic subunits of each neutral ring are twisted relative to each other. For the crown macrocycle the twist angle is only 6°, but for the pyromellitimide ring a twist of 15° is subtended by the long axes of the diimide components. The result of this skewing is to induce a distinct helical turn and thus, in the solid state, to confer chirality on the macrocycle, and therefore also the catenane.[27] Close inspection of the packing (Figure 8) of the individual catenanes reveals that each donor–acceptor column contains a single helical enantiomer. Adjacent columns are comprised of catenanes in which the pyromellitimide macrocycle exhibits the opposite helical twist. The two catenane molecules in the unit cell are enantiomers (space group $P\bar{1}$), related by an inversion centre, and the crystals are therefore racemic. A similar phenomenon has been noted by Breslow in the binding of benzene by a host containing three diyne linkers.[28] The rigidity, in a linear sense, of the diyne link ensures that the only mechanism by which Breslow's receptor can adjust its binding of a guest species is for the top and bottom components of the host to rotate in opposite directions, inducing a helical twist and conferring chirality on the inclusion complex. Crystals of Breslow's complex form in the same space group as **12**, and the unit cell contains one left- and one right-handed helical enantiomer. The helicity of the diimide macrocycle of **12** arises from the need for the aromatic planes to conform with the consistent 3.4 Å interplanar spacing that characterises donor–acceptor arrays. The chirality of this catenane in the solid state may thus be considered a result of freezing conformational mobility during crystallisation.

The solid-state structure of the **11**·**5** inclusion complex does not reveal any significant intramolecular hydrogen bonding interactions of the sort that characterise the structures of donor–acceptor complexes involving bipyridinium units as the electron-deficient components. However, relatively strong intramolecular hydrogen bonds (2.20, 2.24 Å) linking the NCH_2 protons of the included pyromellitimide unit to the central oxygen atoms of the crown polyether chains may be identified in the structure of **12**.[29] Although these interactions may play a role in directing the templated synthesis of **12**, their importance is difficult to quantify. The donor–acceptor overlap orientation revealed in the solid-state structure of the **11**·**5** complex does not permit the formation of similar hydrogen bonds, yet the formation of catenane **13** proceeds efficiently. The success of this catenane synthesis, apparently directed solely by favourable donor–acceptor interactions, leads one to question the importance of the polyether link to the efficiency of assembly of this particular class of interlocked structures. Our recent synthesis of an unusual [2]catenane[30] containing three hexadiyne linkers demonstrates that one of the crown polyether chains in **5** may indeed be replaced without preventing molecular interlocking. However, the flexible polyether chains in crowns such as **5** also allow these macrocycles to breathe and adjust to the inclusion of a guest, and the effects of completely removing this degree of flexibility have not as yet been addressed.

^{1}H NMR spectroscopy: The building blocks employed in our catenane syntheses present rather simple ^{1}H NMR spectral characteristics and allow the changes enforced by the mechanical interlocking of components to be followed with relative ease. The room-temperature ^{1}H NMR spectra of catenanes **12** and **13** present distinctive shifts of the aromatic resonances of both their π-electron-deficient diimide and π-electron-rich aromatic ether constituents (Figure 9). These shifts are the result of the ordered donor–acceptor interactions revealed in the solid-state analysis of **12** being retained in solution. The spectra clearly demonstrate how the symmetry of the preformed crown ether macrocycle is broken by catenation with a second ring, the doublet–triplet–doublet pattern arising from coupling of the aromatic protons of the 1,5-substituted naphthalene systems being doubled in each case. For **12** the aromatic pyromellitimide protons appear as a sharp singlet ($\delta = 6.90$) indicating fast exchange of the two diimide subunits on the chemical shift time scale. *Ortho* coupling of the aromatic protons on the naphthalenediimide macrocycle in **13** results in two doublets ($\delta = 8.07$, 7.86; $^3J = 8$ Hz), but the observation of just one set of doublets again confirms fast exchange of the two constituent diimide subunits. For both **12** and **13** the NCH_2 protons appear as an AB system ($^2J = 17-18$ Hz) between $\delta = 4$ and 5.

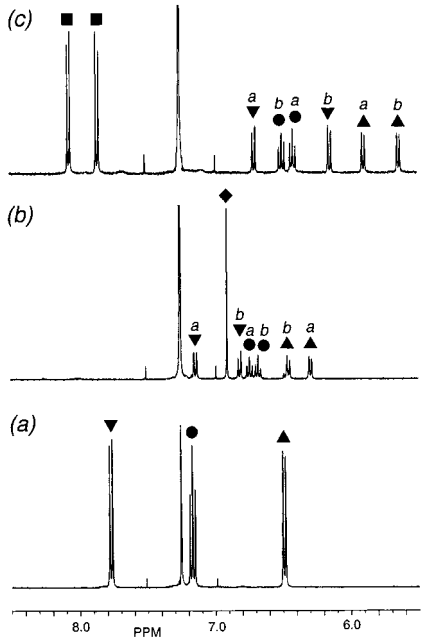

Figure 9. Aromatic region of the 400 MHz ^{1}H NMR spectra ($CDCl_3$) of a) crown **5**, b) [2]catenane **12** and c) [2]catenane **13**. Key: Naphthalene $H_{2,6}$ (▼), naphthalene $H_{3,7}$ (●), naphthalene $H_{4,8}$ (▲), pyromellitimide (◆), naphthalenediimide (■). Coupling patterns (*a, b*) were determined from 500 MHz COSY spectra (these patterns cannot be unambiguously assigned to *inside* and *outside* residues and are therefore simply designated as two distinct sets).

The relative shifts of the aromatic resonances in these structures can to some extent be rationalised by considering

the nature of the overlap of the respective π systems. From our solid-state analyses we know that the preferred overlap orientation of the subunits in **12** places the long axes of the components essentially perpendicular to one another (Figure 10). Such an arrangement situates the pyromellitimide protons directly over the π-rich naphthalene ring system and leads to a significant upfield shift of this resonance (≈ 1.4 ppm).[31] In contrast, the naphthalene protons do not overlap significantly with the pyromellitimide π system and are not appreciably shifted from their positions in the free crown **5**. The reverse situation is observed with [2]catenane **13**, for which the predicted overlap orientation places the crown naphthalene protons directly over the naphthalenediimide π system and induces large upfield shifts of these

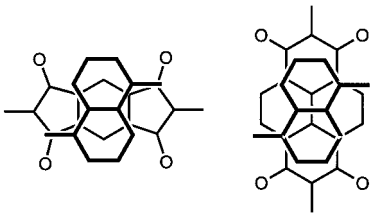

Figure 10. Optimum relative π-system overlaps for catenanes a) **12** and b) **13**.

resonances (Figure 10). The naphthalenediimide protons are situated clear of the adjacent π-rich aromatic system and as a consequence are not shifted appreciably from their positions in typical naphthalenediimide precursors.

The number and appearance of the resonances in the 400 MHz ^{1}H NMR spectrum of unsymmetrical [2]catenane **14** are a predictable composite of those recorded for symmetrical analogues **12** and **13**, but the observed chemical shifts do not represent a linear combination of these spectra. The resonances of the crown naphthalene systems once again appear as two distinct sets, confirming environmental differences for these subunits. Further signals in the aromatic region may be ascribed to the aromatic protons of the pyromellitic and naphthalenediimide units. However, the overlap of the π systems in this unsymmetrical derivative must of necessity reflect a compromise between the situations found for the individual diimides in the symmetrical catenanes; the environmental differences of the naphthalenediimide subunits in [2]catenanes **13** and **14** are confirmed by the chemical shift difference of the ortho protons of this component in each system: for **13**, $\Delta\delta \approx 0.25$ ppm; for **14**, $\Delta\delta \approx 1.00$ ppm. It is, therefore, not possible to use the relative shifts of these signals from their positions in **12** and **13** to gain a measure of the conformational equilibrium of **14** between the two translational isomeric states where each of the electron-deficient diimide units is bound within the cavity of the electron-rich crown.

The observation of a single resonance for the pyromellitimide protons in catenane **12** implies that, at ambient temperature in $CDCl_3$, the two sites of each diimide subunit *and* the two subunits themselves are in rapid exchange on the chemical shift time scale, and are therefore magnetically equivalent. The pyromellitimide singlet does not represent a very informative structural probe since no dynamic process need be invoked to explain the equivalence of the two protons of a single subunit.[32] However, site exchange of the two distinct diimide subunits does demand molecular reorganisation, and two mechanisms are possible. Either the pyromellitimide macrocycle can revolve through the centre of the crown ring or, alternatively, the outer naphthalene diether can sweep around the periphery of the catenane, thus encircling the formerly outer diimide (Processes A and B, Figure 11). Additionally, the latter process requires only one donor–acceptor stacking interaction to be broken during the exchange process. The extensive studies of crown-containing [2]catenanes by the Stoddart group suggest that the latter of these mechanisms is the lower energy dynamic process.[33] This

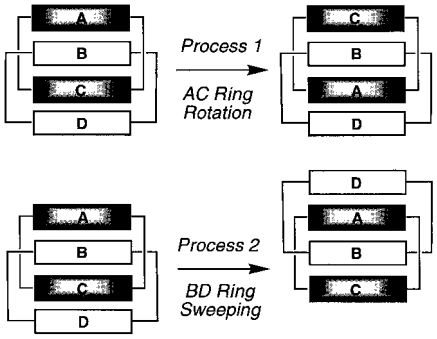

Figure 11. Site-exchange processes in a [2]catenane leading to equivalence of subunits A and C, whilst differentiating B and D. Process 1: exchange of A and C by *rotation* of the AC ring through the BD ring. Process 2: exchange of A and C by *sweeping* of the BD ring around the periphery of the AC ring.

exchange mechanism is also consistent with the presence of the two distinct naphthalene diether components revealed in the ^{1}H NMR spectrum since the outside diether always remains on the outside of the catenane, and the inner remains bound within the diimide macrocycle. However, the 500 MHz NOESY spectrum[34] of **12** does reveal exchange cross-peaks for the interchange of the two naphthalene diether components, implying that whilst this process is slow on the chemical shift time scale it is fast on the NOESY time scale.[35] Additional exchange cross-peaks are revealed between the diastereotopic NCH_2 protons; the similarity of intensity with those for the naphthalene diether components indicates that a single exchange mechanism is responsible for equilibrating both sets of resonances.

As before, two site-exchange mechanisms may be envisaged which lead to magnetic equivalence of the aromatic diether subunits. The crown ring can revolve through the rigid diimide macrocycle, or this more rigid ring can sweep around the outside of the catenane to encircle the outer diether residue. CPK models reveal that this latter process is most unlikely, as the short linkers confer far greater rigidity on this macrocycle than the flexible polyether chains present in the crown component. Therefore, the exchange mechanism must involve the revolution of the crown through the diimide

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macrocycle, a process which inevitably breaks *all* of the donor–acceptor interactions within the catenane. Necessarily, this exchange is energetically expensive, and therefore relatively slow, and is only apparent on the NOE time scale. The observed exchange of the NCH_2 signals is consistent with this process. These protons are distinct by virtue of their different spatial relationship to the adjacent naphthalene diether systems: equivalence can only be achieved by rotating the adjacent π-rich systems about their O–O axes (Figure 12).[36] Reformation of the ordered catenane structure, after the total disruption of the donor–acceptor stack required by exchange of the two aromatic diether units, would not favour the orientation of a particular combination of π-faces, and the environments of the neighbouring NCH_2 protons would become averaged as a result.

The ^{1}H NMR spectrum of [2]catenane **13** reveals just two doublets for the *ortho* protons of the diimide component, confirming the same environmental exchange on the chemical

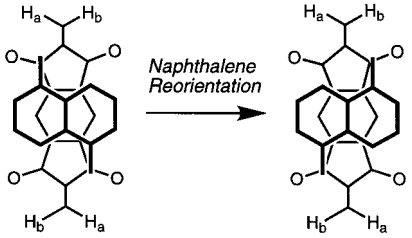

Figure 12. Dynamic process leading to equivalence of H_a and H_b through reorientation of the neighbouring naphthalene diether.

shift time scale of the two diimide subunits of the hexadiyne-linked macrocycle witnessed in **12**. All of the arguments presented for catenane **12** also apply to this system, suggesting that the same dynamic processes are in operation. This is also the situation for the unsymmetrical composite [2]catenane **14** where, despite the inevitable complication of the spectrum arising from the desymmetrising of the diimide-derived ring, the 500 MHz COSY and NOESY spectra support the proposition of identical dynamic phenomena.

Absorption spectra, luminescence spectra and excited-state lifetimes: Photophysical experiments were conducted in CH_2Cl_2 solution at room temperature and in an opaque rigid CH_2Cl_2 matrix for the low temperature (77 K) luminescence measurements. The results are summarised in Table 1.

Table 1. Luminescence properties of the catenanes **12–14** and their parent compounds **5**, **10** and **11**.

	Room temperature			77 K			
	λ_{max} (nm)	τ (ns)	I_{rel} (%)	λ_{max} (nm)	τ (ns)	λ_{max} (nm)	τ (ms)
5	345	7.5	100[a]	345	9.6	488	1200
10	–	–	–	–	–	477	410
11	408	<0.4	100[b]	413	0.5	619	41
12	345	7.5	6[a]	–	–	–	–
13	345	1.7, 7.5	15[a]	–	–	–	–
	411	<0.4	49[b]				
14	345	7.5	51[a]	–	–	–	–
	411	<0.4	15[b]				

The absorption spectra of the catenanes differ from the sum of the absorption spectra of their respective components. Most noticeably, the absorption bands of crown **5**, and of the diimides **10** and **11**, undergo a noticeable decrease in intensity when incorporated into a catenated structure. These decreases are accompanied by small red-shifts of these features, the appearance of a tail in the 340–440 nm region, and, significantly, the presence of a new broad band in the 480–650 nm region (Figure 13). All these observations are consistent with the introduction of a reasonably strong donor–acceptor interaction between the electron-rich naphthalene diethers and the electron-deficient diimide derivatives.[37] The new absorption bands may be assigned to a charge-transfer transition, and it is important to note the following characteristics: i) the absorption maximum depends on the nature of the electron acceptor; the stronger the acceptor, the lower the energy of the transition, and ii) the absorption band of the unsymmetrical [2]catenane **14** appears as approximately half

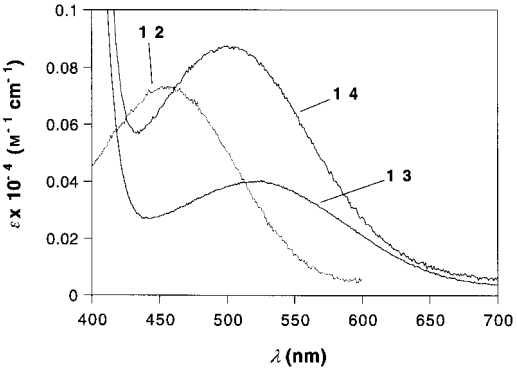

Figure 13. Absorption spectra (CH_2Cl_2) of [2]catenanes **12**, **13** and **14**.

the sum of the bands noted for **12** and **13**. The implication is that in the ground state both the pyromellitimide and naphthalenediimide units of **14** interact with the macrocyclic crown component **5**, and the absorption spectrum represents the sum of the absorptions of the different conformers present in solution. The difficulty involved in extracting quantitative data from these measurements, because of the number of structural factors involved to which the electronic interaction is sensitive, means that it is not possible to measure a ratio of conformers for **14** from absorption measurements.

At room temperature the crown macrocycle **5** presents a structured luminescence band, with maxima at 330 and 345 nm ($\tau = 7.5$ ns), previously ascribed to a $\pi-\pi^*$ transition.[38] A structured, weak fluorescence band is also exhibited by naphthalenediimide **11** (387 and 408 nm; $\tau < 400$ ps), that may also be assigned to a $\pi-\pi^*$ transition. No room-temperature luminescence was observed for pyromellitimide derivative **10**. The naphthalenediimide-containing catenanes **13** and **14** display a similar, but lower-intensity, fluorescence band to that observed for the free diimide **11** (Figure 14), and again the lifetime is shorter than 400 ps. All three catenanes **12–14** exhibit a similar, though once again weakened, fluorescence band to that observed for the parent crown **5** if excitation is performed at wavelengths shorter than 330 nm. The lifetime of this band for catenanes **12** and **14** is equal to

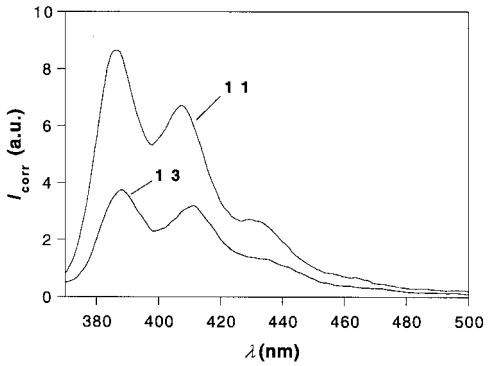

Figure 14. Corrected fluorescence spectra (CH_2Cl_2, $\lambda_{exc} = 345$ nm) of naphthalenediimide **11** and its derivative [2]catenane **13**.

that observed for the fluorescence of **5** (7.5 ns), whilst for catenane **13** the decay profile can be fitted only by employing two exponential terms revealing the presence of a double lifetime ($\tau_1 = 1.3$ ns and $\tau_2 = 7.5$ ns, attributed to diimide **11** and crown **5**, respectively).

Luminescence spectra measured at 77 K reveal that whilst pyromellitimide derivative **10** does not show any fluorescence, both the crown ether **5** ($\lambda_{max} = 345$ nm, $\tau = 9.6$ ns) and the naphthalenediimide **11** ($\lambda_{max} = 413$ nm, $\tau = 0.5$ ns) exhibit intense, structured fluorescence bands. All the parent components (**5**, **10** and **11**) show relatively strong phosphorescence. In stark contrast both to these observations and to the room-temperature measurements, neither fluorescence nor phosphorescence is observed for any of the catenanes at this lower temperature.

The modification of the $\pi-\pi^*$ transition of the parent chromophores when incorporated in catenates **12**, **13** and **14**, and the previously mentioned introduction of new low-energy absorption bands, clearly indicate the presence of an electronic donor–acceptor interaction. The presence of the new charge-transfer excited state in the interlocked molecules results in the partial (room-temperature) and total (77 K) quenching of the luminescence of the parent compounds. The total quenching observed in the low-temperature experiments demonstrates that the intense residual emission observed for the catenanes at room temperature cannot be due to the presence of emitting impurities, since contamination by noncatenated chromophores would also be observed at 77 K. Quenching must therefore be ascribed to a frozen molecular structure where each diimide subunit is locked in close proximity with a naphthalene diether. Incomplete fluorescence quenching at room temperature can be attributed to the dynamic movement of the catenane donor and acceptor subunits. The NMR investigation revealed that for all three catenanes a dominant dynamic process involves the circumrotation of one of the electron-rich naphthalene units of the crown around the periphery of the molecule, weakening its interaction with the electron-deficient diimides and consequently its ability to quench the fluorescence of these units. In the case of [2]catenane **13**, at any given time only one of the naphthalenediimide units will be complexed between the naphthalene diether components. If this complexed form is assumed to lead to efficient quenching then this scenario would explain the 50% residual luminescence intensity of this catenane. Additionally, if we accept that efficient fluorescence quenching can only occur when the naphthalenediimide subunit is bound within the crown, the 15% residual luminescence of this diimide in unsymmetrical [2]catenane **14** could indicate a ratio of solution conformers of 85:15 in favour of that with the naphthalenediimide included within the crown.

The residual fluorescence of the naphthalene diether components of each of the catenanes can also be rationalised in terms of the strength of the interaction between adjacent donor and acceptor units. In the case of pyromellitimide catenane **12** the residual luminescence is rather low (6%), indicating that only a small fraction of the naphthalene diethers find themselves distanced from fluorescence-quenching pyromellitimide units. The considerable residual fluorescence of unsymmetrical catenane **14** (51%) indicates a nonoptimal orientation of donor and acceptor units, supporting the proposition from NMR evidence that the overlap of subunits must necessarily reflect a compromise of the preferred overlap orientations of the different constituent diimides. The preexponential terms for **13** show that about 50% of the naphthalene diether chromophores have a relatively short lifetime, presumably those sandwiched between the two naphthalenediimide components. Once again, the residual fluorescence with the longer lifetime can be ascribed to a peripheral, less strongly interacting diether residue.

The significant room-temperature fluorescence of the naphthalenediimide-containing catenanes **13** and **14** may be contrasted with the complete quenching observed for bipyridinium-derived [2]catenanes containing the same crown.[38] The conclusion is that catenanes **13** and **14** do not have available radiationless decay routes, as a result of unfavourable donor–acceptor overlap or dynamic reorientation of these units.

Conclusion

In this work we have shown how donor–acceptor interactions between neutral aromatic components may be used to assemble superstructures favouring, under macrocyclisation conditions, the formation of [2]catenane supermolecules. The use of a familiar coupling reaction and building blocks with preexisting recognition characteristics serves to demonstrate that the rather special combination of reactivity and self-assembly involved in the synthesis of the Stoddart catenanes does not represent the only viable approach to these systems. We regard our modular approach as essentially complementary to existing methods: some building blocks are common to both approaches, while others present complementary electrochemical and photochemical properties;[39] one approach is *reagent-free* whereas that presented in this paper utilises a traditional *reagent-mediated* coupling procedure. In an emerging area of chemical technology and development, such flexibility and diversity of approach must be regarded as both desirable and important.

In particular, the present systems offer possibilities for post-assembly modification of the catenated structure, in the reduction of the imide or acetylenic groups, that would be expected to modify or eliminate the donor–acceptor proper-

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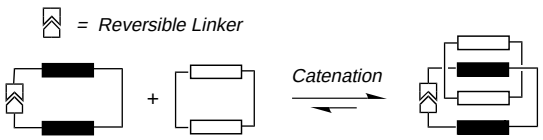
ties of the catenanes. Removal of the templating interaction employed to assemble these structures would represent an irreversible counterpart to Sauvage's use of transition metal ion coordination to assemble [*n*]catenates, from which the templating metals can subsequently be removed. Additionally, the use of rather robust and readily functionalised imide derivatives allows the consideration of different ways in which to close macrocyclic links and achieve catenation. Of particular current interest is the area of coupling or macrocyclisation using reversible, thermodynamically controlled reactions such as transesterification[40] or olefin metathesis;[41] in recent studies using the former of these reactions we have introduced the concept of predisposition as a thermodynamic driving force for the formation of particular macrocyclic architectures.[42] In the present context, the establishment of favourable donor–acceptor interactions between two macrocyclic components would ensure a thermodynamic preference for the interlocked form of two separate, complementary rings (Scheme 5).[43] We envisage that the promise of potentially high macrocyclisation efficiency provided by thermodynamic ring closure, and the robust characteristics of our neutral building blocks, may allow access to thus far inaccessible [*n*]catenanes with fascinating topologies.[44,53]



Scheme 5. Schematic representation of thermodynamic catenation.

Experimental Section

General methods: All chemicals were purchased from Aldrich and were used without further purification. Solvents were dried according to literature procedures:[45] tetrahydrofuran (THF) from Na/benzophenone ketal, acetone from 4 Å molecular sieves, DMF from CaH_2 (under reduced pressure). *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled prior to use. Anhydrous CuCl[46] and $CuCl_2$[47] were prepared according to literature procedures, stored in an efficient desiccator and used within one week of preparation. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on silica gel (Merck 9385, 230–400 mesh). Melting points were determined on a Gallenkamp Electrothermal melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AC-250, AM-400 or DRX-500 MHz spectrophotometers; chemical shifts in $CDCl_3$ are expressed relative to $CHCl_3$ (7.25 ppm); *J* values are given in Hz. The following abbreviations are employed: pyro (pyromellitimide), naph (naphthalenediimide). ^{13}C NMR spectra (100 MHz) were recorded on the AM-400 Bruker machine. Liquid secondary ion mass spectrometry (LSIMS) was performed with a Kratos MS50 double-focussing electric/magnetic sector instrument (NOBA matrix). Electrospray mass spectrometry (ESMS) was performed with a VG BioQ triple quadrupole spectrometer (MeCN solution). Absorption spectra were recorded with a Perkin Elmer Elmer λ16 spectrophotometer. Uncorrected emission spectra, corrected excitation spectra, and phosphorescence lifetimes were obtained with a Perkin Elmer LS50 spectrofluorimeter. The fluorescence lifetimes (uncertainty ±5%) were obtained with an Edinburgh single-photon counting apparatus (D_2-filled flash lamp). Emission spectra in a CH_2Cl_2 rigid matrix at 77 K were recorded in quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects and phototube sensitivity were performed.[48]

1-Benzyloxy-5-hydroxynaphthalene (**2**): Dry, powdered potassium carbonate (1.44 g, 10 mmol) was added in small portions over 3 h to a stirred solution of 1,5-dihydroxynaphthalene (5.00 g, 31 mmol) and benzyl bromide (1.78 g, 1.24 mL, 10 mmol) in dry DMF (120 mL). After stirring further for 16 h the solvents were removed under vacuum, and the residue was extracted with boiling dichloromethane (3 × 75 mL). The organic extracts were washed with water (50 mL), dried ($MgSO_4$) and purified by column chromatography (SiO_2, $CHCl_3$; typically two sequential purifications were required) to afford the product as a pale yellow solid (1.10 g, 44%). M.p. 135–137 °C (ref. [15] 136–138 °C); R_f = 0.40 (SiO_2, MeOH/$CHCl_3$, 0.2:99.8); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.96 (d, 1H, ^3J = 6 Hz), 7.78 (d, 1H, ^3J = 6 Hz), 7.55 (d, 2H), 7.47–7.27 (m, 5H), 6.94 (d, 1H, ^3J = 6 Hz), 6.87 (d, 1H, ^3J = 6 Hz), 5.27 (s, 2H).

1,11-Bis(5′-benzyloxy-1′-naphthoxy)-3,6,9-trioxaundecane (**3**): This material was prepared by a procedure directly analogous to that described for its 1,4-phenyl analogue.[33] Column chromatography (SiO_2; DCM/Et_2O, 98:2) afforded the pure material as an oil that slowly crystallised on standing (71%). M.p. 103–104 °C (ref. [15] 106–108 °C); R_f = 0.30 (SiO_2; DCM/Et_2O, 98:2); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.01–7.86 (m, 4H), 7.53–7.30 (m, 14H), 6.89–6.80 (m, 4H), 5.13 (s, 4H), 4.27 (m, 4H), 3.97 (m, 4H), 3.79 (m, 4H), 3.74 (m, 4H).

1,11-Bis(5′-hydroxy-1′-naphthoxy)-3,6,9-trioxaundecane (**4**): This material was prepared, directly prior to use in macrocyclisation reactions, by the procedure previously reported for its 1,4-phenyl analogue[33] (quantitative yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.82 (d, 2H, ^3J = 8 Hz), 7.71 (d, 2H, ^3J = 8 Hz), 7.32 (t, 2H, ^3J = 8 Hz), 7.22 (t, 2H, ^3J = 8 Hz), 6.78 (t, 4H, ^3J = 8 Hz), 5.49 (s, 2H), 4.23 (t, 4H, ^3J = 5 Hz), 3.95 (t, 4H, ^3J = 5 Hz), 3.78 (m, 4H), 3.73 (m, 4H).

Bis(1,5-naphtho)-38-crown-10 (**5**) **by Method A**: A suspension of sodium hydride (140 mg, 5.7 mmol) in dry THF (100 mL) was treated dropwise under Ar over 2 h with a solution of dinaphthol **4** (910 mg, 1.9 mmol) and ditosylate **1** (960 mg, 1.9 mmol) in dry THF (100 mL). The reaction was stirred under reflux for 5 days and cooled to ambient temperature, and excess hydride was quenched with water, added dropwise. The solvent was removed under reduced pressure, and the residue was partitioned between DCM and water. The organic layer was separated and dried ($MgSO_4$). The pure crown was obtained by column chromatography (SiO_2; $CHCl_3$/Et_2O/MeOH, 30:69:1) and recrystallisation from MeOH as a cream-coloured crystalline solid (363 mg, 30%). M.p. 125–126 °C (ref. [15] 125–127 °C); R_f = 0.30 (SiO_2; $CHCl_3$/Et_2O/MeOH, 30:69:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, 4H, ^3J = 8 Hz), 7.17 (t, 4H, ^3J = 8 Hz), 6.49 (d, 4H, ^3J = 8 Hz), 4.05 (m, 8H), 3.92 (m, 8H), 3.77 (m, 8H), 3.73 (m, 8H).

1,5-Bis[13-(*p*-toluenesulfonyl)-1,4,7,10,13-pentaoxatridecyl]naphthalene (**7**): A solution of 1,5-dihydroxynaphthalene (**6**, 0.46 g, 2.9 mmol) and ditosylate **2** (7.23 g, 14.4 mmol) in dry acetone (75 mL) was added dropwise over 2 h under N_2 to a refluxing suspension of K_2CO_3 in dry acetone (75 mL). The mixture was refluxed for 2 days and subsequently allowed to cool to room temperature, filtered and evaporated to dryness under reduced pressure. The residue was partitioned between DCM and water, and the organic layer was separated and washed with 3N NaOH (100 mL) and water (100 mL). The organic layer was then dried ($MgSO_4$) and evaporated, and the residue was purified by flash column chromatography (SiO_2; EtOAc/60–80 °C petroleum ether, 3:1) to afford the ditosylate as a pale yellow oil (1.48 g, 63%). R_f = 0.53 (SiO_2; EtOAc/60–80 °C petroleum ether, 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.83 (d, ^3J = 8 Hz, 2H), 7.76 (d, ^3J = 8 Hz, 4H), 7.31 (t, ^3J = 8 Hz, 2H), 7.30 (d, ^3J = 8 Hz, 4H), 6.81 (d, ^3J = 8 Hz, 2H), 4.26 (t, ^3J = 5 Hz, 4H), 4.10 (t, ^3J = 5 Hz, 4H), 3.96 (t, ^3J = 5 Hz, 4H), 3.77–3.72 (m, 4H), 3.65–3.52 (m, 16H), 2.38 (s, 6H); HRMS (FAB+): found 821.2893, $C_{40}H_{53}S_2O_4$ $[M+H]^+$ calcd 821.2877.

Bis(1,5-naphtho)-38-crown-10 (**5**) **by Method B**: A solution of ditosylate **7** (1.13 g, 1.4 mmol) and 1,5-dihydroxynaphthalene (**6**, 0.22 g, 1.4 mmol) in dry acetone (50 mL) was added dropwise over 3 h under N_2 to a refluxing suspension of K_2CO_3 in dry acetone (150 mL). The reaction was stirred under reflux for 2 days, cooled, filtered and evaporated to dryness under reduced pressure. The residue was partitioned between DCM and water, and the organic layer was separated, dried ($MgSO_4$) and evaporated. The pure crown was obtained after column chromatography and recrystallisation from methanol (232 mg, 26%); this material had identical spectral characteristics to that obtained by Method A.

Bis-*N,N'*-(prop-2-ynyl)pyromellitic diimide (**10**): Pyromellitic dianhydride (**8**, 1.07 g, 5 mmol) was added to a stirred solution of propargylamine (0.54 g, 10 mmol) in dry DMF (20 mL). Soon after dissolution of the anhydride a thick precipitate started to form. After 2 h the reaction was warmed to 140–150 °C (complete dissolution of precipitate) and stirred further for 2 h. The reaction was cooled to ambient temperature and poured into ice-cold water, and the solid precipitate was collected at the pump. Recrystallisation from DMF/water afforded a cream-coloured crystalline solid (400 mg, 28 %). M.p. >280 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 8.30$ (s, 2H), 4.44 (d, $^4J = 2.5$ Hz, 4H), 3.33 (t, $^4J = 2.5$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 165.20$, 137.02, 118.04, 79.28, 74.42, 27.35; MS (EI): m/z (%) = 292.0 M^+ (100); $C_{16}H_8N_2O_4$ (292.25): calcd C 65.76, H 2.76, N 9.59; found C 65.74, H 2.77, N 9.58.

Bis-*N,N'*-(prop-2-ynyl)-1,4,5,8-naphthalenetetracarboxylic diimide (**11**): Condensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride **9** (1.34 g, 5 mmol) with propargylamine (0.54 g, 10 mmol) in dry DMF (35 mL), by an identical procedure for that described for **10**, gave fine, brown-pink needles (1.14 g, 67 %) after work-up and recrystallisation from DMF/water. M.p. >280 °C; ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 8.73$ (s, 4H), 4.81 (d, $^4J =$ 2.5 Hz, 4H), 3.23 (t, $^4J = 2.5$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 161.94$, 130.82, 126.34, 79.24, 73.55, 29.57; MS (EI): m/z (%): 343.1 $[M+H]^+$ (50), 307.1 (100); $C_{20}H_{10}N_2O_4$ (342.31): calcd C 70.18, H 2.94, N 8.18; found C 70.12, H 2.90, N 8.16.

[2]-{[Cyclobis(pyromellitimide-hexa-2,4-diyne)][bis(1,5-naphtho)-38-crown-10]}-catenane (**12**): Crown **5** (144 mg, 0.23 mmol) and bis-acetylene **10** (132 mg, 0.45 mmol) were added to dry DMF (12 mL) in an atmosphere of dry air. Anhydrous CuCl (2.25 g, 23.0 mmol) and anhydrous $CuCl_2$ (0.61 g, 4.5 mmol) were then added, and the reaction was stirred for two days. The mixture was diluted with dichloromethane (100 mL), extracted with water (2 × 50 mL), dried ($MgSO_4$) and evaporated. Residual DMF was removed under high vacuum, and the residue was purified by column chromatography (SiO_2; MeOH/$CHCl_3$, 1:99 increasing to MeOH/$CHCl_3$, 10:90) to afford the [2]catenane as an orange-red solid (105 mg, 38 %). M.p. >280 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): $\delta = 7.16$ (d, $^3J = 8.7$ Hz, 2H; *a*-H$_{2,6}$), 6.93 (s, 4H; diimide-H), 6.83 (d, $^3J = 8.2$ Hz, 2H; *b*-H$_{2,6}$), 6.75 (t, $^3J = 7.8$ Hz, 2H; *a*-H$_{3,7}$), 6.69 (t, $^3J = 7.8$ Hz, 2H; *b*-H$_{3,7}$), 6.47 (d, $^3J = 7.6$ Hz, 2H; *b*-H$_{4,8}$), 6.28 (d, $^3J = 7.5$ Hz, 2H; *a*-H$_{4,8}$), 4.39 (d, $^2J_{AB} = 17.7$ Hz, 4H; NCH_2), 4.22 (d, $^2J_{AB} = 18.1$ Hz, 4H; NCH_2), 4.11 (m, 4H; OCH_2), 4.01 (m, 8H; OCH_2), 3.93–3.86 (m, 20H; OCH_2); MS (ES$^+$): m/z (%) = 1241.1 $[M+Na]^+$ (100), 1256.6 $[M+K]^+$ (12); MS (LSI): m/z (%) = 1239.2 $[M+Na]^+$ (100), 766.0 (20), 659.1 (30), 636.1 (20); $C_{68}H_{56}N_4O_{18}$ (1217.22): calcd C 67.10, H 4.64, N 4.60; found C 66.92, H 4.74, N 4.43.

[2]-{[Cyclobis(1,4,5,8-naphthalenetetracarboxylic diimide-hexa-2,4-diyne)][bis(1,5-naphtho)-38-crown-10]}-catenane (**13**): A solution of crown **5** (34 mg, 53 μmol) and bis-acetylene **11** (37 mg, 107 μmol) in dry DMF (8 mL) was treated with anhydrous CuCl (0.53 g, 5.3 mmol) and anhydrous $CuCl_2$ (0.14 g, 1.1 mmol), and the mixture was stirred in an atmosphere of dry air for 2 days. It was then poured into water (50 mL) and extracted with $CHCl_3$ (2 × 50 mL). The organic extracts were dried ($MgSO_4$) and evaporated to afford a residue which was purified by column chromatography (SiO_2; MeOH/$CHCl_3$, 0.5:99.5 increasing to MeOH/$CHCl_3$, 2:98) to yield the [2]catenane as a purple solid (36 mg, 52 %). M.p. >280 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): $\delta = 8.14$ (d, $^3J = 7.5$ Hz, 4H; diimide H), 7.92 (d, $^3J = 7.5$ Hz, 4H; diimide H), 6.78 (d, $^3J = 8.2$ Hz, 2H; *a*-H$_{2,6}$), 6.58 (t, $^3J = 7.9$ Hz, 2H; *b*-H$_{3,7}$), 6.48 (t, $^3J = 7.9$ Hz, 2H; *a*-H$_{3,7}$), 6.23 (d, $^3J = 8.3$ Hz, 2H; *b*-H$_{2,6}$), 5.96 (d, $^3J = 7.5$ Hz, 2H; *a*-H$_{4,8}$), 5.71 (d, $^3J = 7.5$ Hz, 2H; *b*-H$_{4,8}$), 4.86 (d, $^2J_{AB} = 17.1$ Hz, 4H; NCH_2), 4.79 (d, $^2J_{AB} =$ 16.9 Hz, 4H; NCH_2), 4.07–3.69 (m, 28H; OCH_2), 3.49 (m, 4H; OCH_2); MS (ES$^+$): m/z (%) = 1341.2 $[M+Na]^+$ (100); MS (LSI): m/z (%) = 1317.5 M^+ (36), 636.3 (100); $C_{76}H_{60}N_4O_{18}$ (1317.34): calcd C 69.29, H 4.59, N 4.25; found C 69.02, H 4.41, N 4.14.

[2]-{[Cyclo(1,4,5,8-naphthalenetetracarboxylic diimide)(pyromellitimide)bis(hexa-2,4-diyne)][bis(1,5-naphtho)-38-crown-10]}-catenane (**14**): A mixture of crown **5** (50 mg, 79 μmol), bis-acetylene **10** (23 mg, 79 μmol) and bis-acetylene **11** (27 mg, 79 μmol) in dry DMF (6 mL) was treated with anhydrous CuCl (780 mg, 7.9 mmol) and $CuCl_2$ (210 mg, 1.6 mmol) and subsequently stirred in an atmosphere of dry air for 2 days. The mixture was poured into water (100 mL) and continuously extracted with $CHCl_3$ for 4 h. The chloroform extracts were evaporated, and the residue was subjected to preliminary chromatography (SiO_2; MeOH/$CHCl_3$, 7:93) to afford a mixture of catenane products. The mixture was successfully separated by preparative thin layer chromatography (SiO_2; MeOH/$CHCl_3$, 7:93) to afford (in order of increasing polarity) symmetrical [2]catenane **13** (5 mg, 5 %), the desired red unsymmetrical [2]catenane **14** (24 mg, 24 %) and symmetrical [2]catenane **12** (6 mg, 6 %). The unsymmetrical catenane had m.p. >280 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.31$ (d, $^3J = 7$ Hz, 2H; naph), 7.83 (d, $^3J = 7$ Hz, 2H; naph), 6.98 (s, 2H; pyro), 6.84 (d, $^3J = 8$ Hz, 2H; *a*-H$_{2,6}$), 6.62 (t, $^3J = 8$ Hz, 2H; *b*-H$_{3,7}$), 6.52 (overlapping d and t, 4H; *b*-H$_{2,6}$ and *a*-H$_{3,7}$), 6.01 (d, $^3J =$ 8 Hz, 2H; *a*-H$_{4,8}$), 5.98 (d, $^3J = 8$ Hz, 2H; *b*-H$_{4,8}$), 4.94 (d, $^2J_{AB} = 17$ Hz, 2H; naph–CH_2), 4.75 (d, $^2J_{AB} = 17$ Hz, 2H; naph–CH_2), 4.35 (d, $^2J_{AB} = 18$ Hz, 2H; pyro–CH_2), 4.22 (d, $^2J_{AB} = 18$ Hz, 2H; pyro–CH_2, and 2H; overlapping OCH_2 resonance), 4.10–3.75 (m, OCH_2; 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 164.25$, 163.98, 161.66, 161.50, 153.07, 152.83, 134.64, 134.37, 130.86, 130.00, 125.34, 124.96, 124.83, 124.03, 123.68, 115.72, 113.71, 112.77, 104.91, 103.89, 78.06, 74.52, 71.00, 70.86, 69.74, 69.27, 68.00, 67.38, 67.18, 29.97, 28.02; MS (ES$^+$): m/z (%) = 1290.5 $[M+Na]^+$ (100); MS (LSI): m/z (%) = 1290.5 $[M+Na]^+$ (20), 1267.5 M^+ (50), 636.5 (20); $C_{72}H_{58}N_4O_{18}$ (1267.28): calcd C 68.24, H 4.61, N 4.42; found C 68.10, H 4.50, N 4.37.

X-ray structure determinations: Single crystals of both bis-acetylene **11** and the **11**·**5** inclusion complex were obtained from a slowly cooled DMF/water mixture of **11** and **5** (2:1 molar ratio). Data reduction was performed within the TEXSAN program.[49] The structures were solved by direct methods with SIR 92[50] and refined by full-matrix least-squares on F^2 with SHELXL 93.[51] Hydrogen atoms were fixed geometrically, riding on the relevant heavy atom and refined with isotropic temperature factors. Crystal data and collection parameters for the structures are given in Table 2. Details of the data collection and structural solution of **12** have been reported elsewhere.[18]

Table 2. Crystal data and data collection parameters for **11** and **11**·**5**.

	Bis-acetylene **11**	Complex **11**·**5**
formula	$C_{20}H_{10}N_2O_4$	$C_{56}H_{54}N_2O_{14}$
formula weight	342.3	979.0
colour	colourless	red
T, K	150	150
λ(Mo$_{K\alpha}$), Å	0.71069	0.71069
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
cell dimensions		
a, Å	9.746(5)	11.704(4)
b, Å	6.310(6)	11.628(5)
c, Å	12.867(5)	17.963(7)
α, °	90	90
β, °	111.78(3)	97.91(4)
γ, °	90	90
V, Å^3	734.8(8)	2421(2)
Z	2	2
ρ_{calcd}, g cm^{-3}	1.547	1.343
μ, mm^{-1}	0.110	0.097
$2\theta_{max}$, °	22.49	22.50
crystal size, mm	0.30 × 0.12 × 0.10	0.25 × 0.22 × 0.20
θ range, °	3.32–22.49	2.63–22.50
reflns collected	1761	3349
independent reflns	964	3164
absorption correction	none	none
data/restraints/parameters	962/0/119	3159/0/325
goodness-of-fit on F^2	1.042	1.016
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0402$, $wR_2 = 0.0906$	$R_1 = 0.0586$, $wR_2 = 0.1240$
R indices (all data)	$R_1 = 0.1111$, $wR_2 = 0.1141$	$R_1 = 0.1899$, $wR_2 = 0.1793$
largest diff. peak and hole, e Å^{-3}	0.211 and −0.257	0.274 and −0.228

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Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-100717 (**11** · **5**) and CCDC-100718 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ (UK) (Fax: (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[22] At a **12**:**13**:**14** ratio of around 1:1:5 these yields represent a significant deviation from the statistical ratio of 1:1:2 expected if precursor **10** did not bind preferentially to crown **11**. However, the greater solubility of **14** may prove an exaggerating factor, enhancing its isolation during work-up; **14** is the only catenane in this series which proved sufficiently soluble in common organic solvents to allow a ^{13}C NMR spectrum to be recorded.

[23] An alternating internal–external stack of the intended type is formed between a 4,4′-bipyridinium derivative and the enlarged crown bis(1,5-dinaphtho)-44-crown-12: J.-Y. Ortholand, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1989**, *101*, 1402; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1394–1396. It is intriguing that although the solid-state structure of this complex provided at least part of the inspiration for the first π-associated catenane syntheses, all of these derivative syntheses were based around smaller crown components like **5**.

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