Synthesis of macrocycles and an unusually asymmetric [2]catenane *via* templated acetylenic couplings

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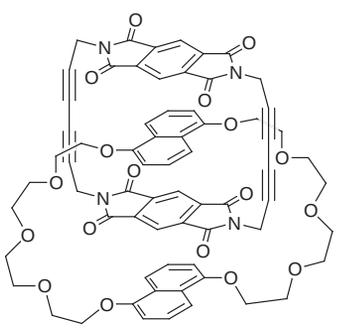
An unusually asymmetric [2]catenane has been prepared by interlocking a hybrid crown macrocycle (containing one polyether and one butadiyne linker) with a diimide-derived macrocycle itself constructed with a pair of rigid butadiyne links. This system of complementary building blocks and connectors has proved a versatile vehicle for demonstration of a number of templating effects. Synthesis of the hybrid crown monomer by intramolecular cyclisation is promoted by the presence of a benzene diimide, acting as a positive template, but a sufficiently different effect is exerted by a naphthalene diimide derivative that intermolecular dimerisation becomes significant. Templating the hybrid crown synthesis with an 'active' benzene diimide, itself bearing acetylene functions, allows the first tandem synthesis of a catenane comprising two different rings: the diimide first acts as a template for the formation of the hybrid crown, which itself in turn acts as a template for cyclodimerisation of the acetylenic diimide. Remarkably, the yield of catenane is essentially independent of the initial cyclisation state of the crown component. No significant production of covalently linked donor–acceptor species is observed from these reactions, supporting the presence of an intermediate complex pre-organised to catenane formation. In contrast, oxidative coupling of an alkyl solubilised diimide gave no interlocked products and yielded only small amounts of cyclic poly-imide macrocyles.

Introduction

The identification of a variety of efficient templating mechanisms for the controlled positioning of molecular components has allowed the development of several high-yielding syntheses of catenanes.[1] One early approach to [2]catenane synthesis employs the tetrahedral coordination of two 9,10-phenanthroline ligands around a copper(I) ion to establish a complex favouring [2]catenane formation.[2,3] Donor–acceptor interactions between complementary π-rich and π-deficient aromatic substrates have been employed to assemble a wide variety of [*n*]catenanes using 'structure directed' syntheses where the molecular recognition properties of the building blocks are activated by the self-assembly process.[4,5] To be more precise these products, and the intermediate complexes on the reaction pathway, certainly exhibit (through strong solid and solution state colours) the presence of donor–acceptor interactions, but the question of whether these interactions are the driving force for, or simply the result of, complexation, is not clear. [2]Catenanes have also been identified as major, and unexpected, products from the attempted syntheses of amide-linked macrocycles *via* a mechanism in which amide hydrogen bonding interactions direct the threading of a second ring through the cavities of initially formed macrocycles.[6–8] More recently, we have shown that complexes of aromatic diethers with aromatic diimides may be used to prepare neutral π-associated [2]catenanes (*e.g.* **1**).[9,10] We describe here some additions to the structural and conceptual frameworks of this latter approach.

In terms of the complexity of accessible interlocked systems the cation chelation approach has proved by far the most flexible, allowing access to a variety of [*n*]catenanes, doubly interlocked catenanes[11,12] and even knots.[13–16] The donor–acceptor approach has provided an enormous number of [*n*]catenanes but the more exotic of these depend on the synthesis of large ring macrocycles prior to molecular interlocking.[17,18] The amide hydrogen bonding templating mechanism is fascinating in that



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the 'first-formed' macrocycle directs threading of a copy of itself through its central cavity. However, almost by definition, this approach affords only [2]catenanes and provides no obvious route to more complex systems.

Tolerance of structural variation in the catenane components would allow the design of assemblies incorporating an interchangeable and varied set of linkers and interacting components. However, the efficiency of self-assembly of bipyridinium derived catenanes decreases markedly if the linker in the pre-formed macrocyclic component is altered from a tetraethylene-pentaoxy chain,[19] and also if the central heteroatom is replaced by furan oxygen[20] or pyridine nitrogen.[21] Such observations indicate a significant templating role for the tetraethylene glycol linker employed in the original syntheses; numerous hydrogen bonding interactions help to organise the solid state structure of these catenanes and the establishment of these interactions during the assembly process contributes to the observed templating. Since hydrogen bonding interactions do not appear to be dominant structural features of our donor–acceptor systems[10] we sought to examine their importance to the assembly process by replacing one of the crown polyether

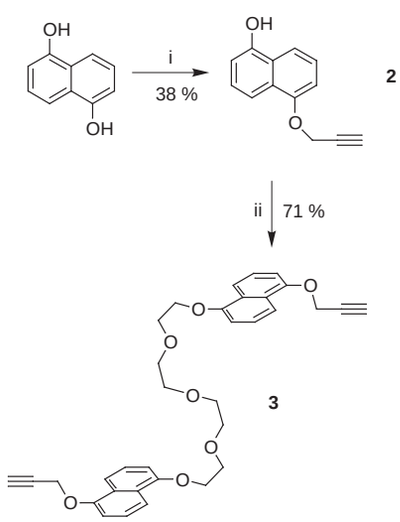
chains with a spacer of comparable length. An obvious choice was the butadiyne linker which is both geometrically and chemically compatible with catenane assembly.[22]

In this paper we discuss the tolerance of the components of our original [2]catenane **1** towards such structural alteration. We first report the design and synthesis of a hybrid macrocycle containing both polyether and butadiyne linkers and discuss the contrasting distribution of macrocyclic products obtained when this macrocyclisation is conducted in the presence of two different template molecules. We then show how the product hybrid macrocycle can act as a template for assembly of an unusually asymmetric [2]catenane containing three butadiyne linkers. Remarkably, we also show that the synthesis of this catenane may be achieved from wholly acyclic precursors in a tandem ring closure reaction, the first double ring closure synthesis of a [2]catenane comprised of two *different* rings.[22] The solid-state structure of this unusual molecule, obtained by X-ray synchrotron diffraction, is also presented.

Results and discussion

Templated macrocycle syntheses

The synthetic approach to a desymmetrised electron-rich macrocycle involved initial monoalkylation of 1,5-dihydroxynaphthalene with propargyl bromide prop-2-ynyl bromide, affording naphthol **2** in a yield of around 38%. Two equivalents of this naphthol were subsequently linked by further alkylation with tetraethylene glycol ditosylate to yield the acyclic bisacetylene derivative **3** in 71% yield based on **2** (Scheme 1). At



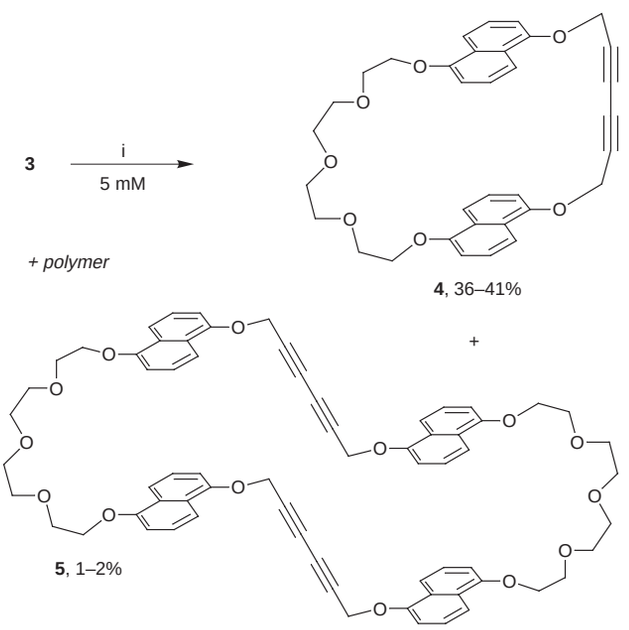
Scheme 1 *Reagents and conditions*: i, K_2CO_3, DMF; ii, $TsO(CH_2CH_2O)_4Ts$, K_2CO_3, acetone.

5 mM concentration in CH_2Cl_2 this precursor could be cyclised, by coupling of the terminal acetylene functions, to hybrid macrocycle **4** in 36–41% yield by treatment with anhydrous CuCl. A small amount (1–2%) of the dimeric product **5** could also be isolated (Scheme 2), the remainder of the product mixture is comprised of uncharacterised higher oligomers. At 5 mM the cyclisation mixture is delicately balanced between *intramolecular* cyclisation to form **4** (Process **B**, Fig. 1), and *intermolecular* couplings leading to higher oligomers (Process **A** followed by either Process **D** to give polymer, or Process **G** to afford cyclic dimer **5**). It seemed likely that this fine balance could be influenced by the intervention of a template molecule and we therefore sought to reverse the roles of donor and acceptor from our previous catenane syntheses and employ electron-deficient diimide derived templates to direct the cyclisation process. Highly organic-soluble di-*n*-hexyl templates

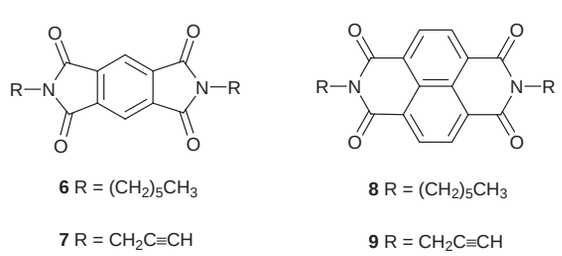
Table 1 Summary of yield ranges for macrocyclisation of acyclic bisacetylene **3**

	Yield[a] (%)			
Reaction	Monomer **4**	Dimer **5**	Trimer	Polymer[b]
Untemplated	36–41	1–2	—[c]	*ca.* 60
Template **6**	68–74	3–4	—[c]	*ca.* 25
Template **8**	52–56	13–17	3–4	*ca.* 27

[a] Yield range from a minimum of three cyclisation reactions. [b] Defined as all uncharacterised higher oligomers. [c] Not observed.



Scheme 2 *Reagents and conditions*: i, CuCl, TMEDA, CH_2Cl_2, air.



6 and **8** were readily prepared from the condensation of the appropriate tetracarboxylic dianhydride with *n*-hexylamine in hot DMF (see Experimental section).

When the oxidative coupling of Scheme 2 was conducted in the presence of a five-fold excess of the *N*-hexyl pyromellitimide derivative **6**, the isolated yield of macrocycle **4** rose to 68–74%; a slightly increased amount of dimeric material was also noted (3–4%). The increases in the isolated yields of both macrocycles are at the expense of the uncharacterised higher oligomers. Repetition of the macrocyclisation reaction in the presence of five equivalents of the *N*-hexyl naphthalene diimide template **8** led to isolated yields of the monomeric **4** and dimeric **5** macrocycles of 52–56 and 13–17% respectively; a small amount of cyclic trimer (3–4%) was also formed. The yield ranges for the various cyclisations are summarised in Table 1.

The approximately two-fold increase in the isolated yield of **4** when the macrocyclisation reaction is templated with **6** suggest that a positive templating effect[23,24] is operating, attributable to a binding event that brings the reactive acetylenic functions of acyclic precursor **3** into close proximity and facilitates macrocyclisation (Process **C**). Additionally, in order to favour

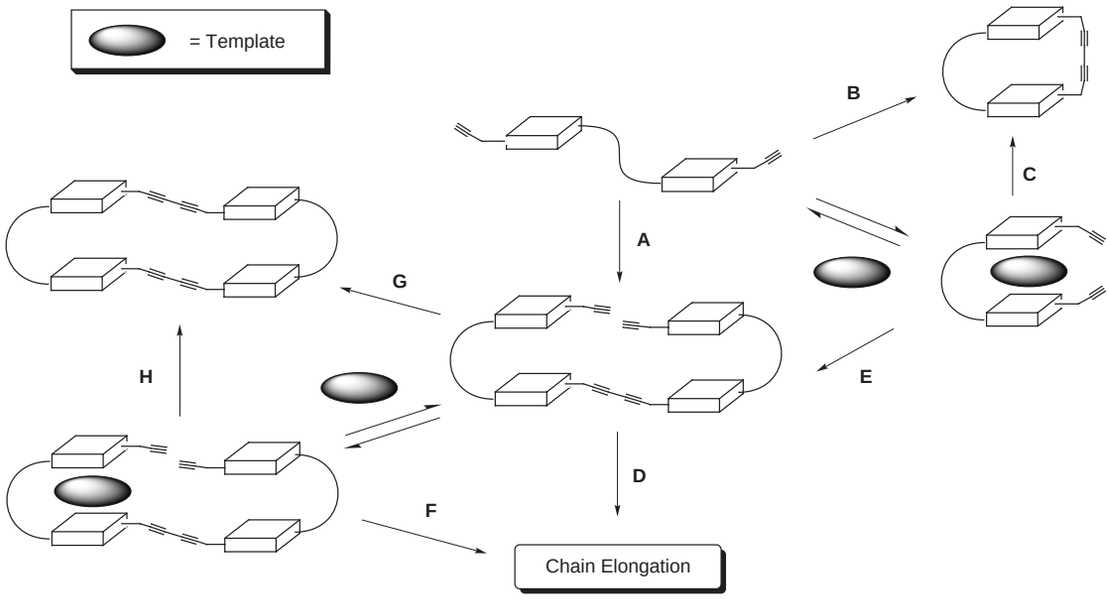


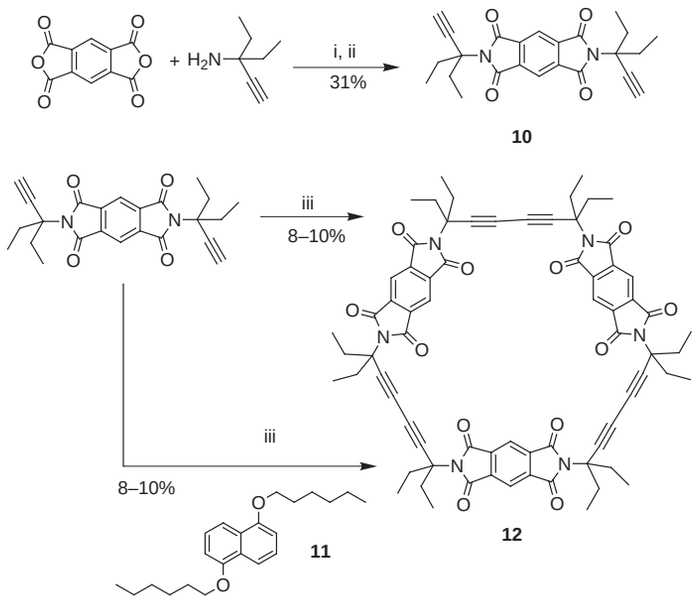
Fig. 1 Proposed binding processes and complexes responsible for the templating effects in the macrocyclisation of bis-acetylene **3**.

intramolecular cyclisation the overlap orientation of the naphthalene diether π-donor and diimide π-acceptor units must be such that reaction can readily occur between the terminal acetylene functions and it is clear this situation is satisfied in the case of the pyromellitimide template. The untemplated reaction (Process **B**) affords around 40% of monomeric macrocycle **4** and 60% polymer, while the ratio is shifted to 70 : 30 in the presence of excess template **6**. These results therefore reveal a 3.5-fold macroscopic increase in the rate of cyclisation of **3** to **4** in the presence of template **6**, derived using the simple arithmetical approach described previously (see ref. 24, Table 2). The approximate binding constant of around 80 M^{-1} measured for the 1 : 1 **3.6** complex[22] allows one to calculate that in the presence of a five-fold excess of **6** around 65% of **3** would find itself bound to the template. The contribution to the 70% yield of **4** from the 35% of *unbound* material (Process **B**) is *ca.* 14% (0.40 × 0.35 = 14%) so the cyclisation of *bound* **3** (Process **C**) must be highly efficient.

The situation becomes both more intriguing, and more complex, when the macrocyclisation is conducted in the presence of naphthalene diimide derivative **8**. Cyclisation reactions conducted in the presence of this template took noticeably longer to reach completion than untemplated reactions, or those involving pyromellitimide template **6**. This qualitative observation suggests that in the **3.8** complex the reactive acetylenic functions are held in such a fashion that they cannot readily react in a fast intramolecular fashion. Secondly, when compared with the action of pyromellitimide template **6**, naphthalene diimide template **8** is seen to enhance the yield of dimeric macrocycle **5** at the expense of monomeric macrocycle **4**. The ratio of monomeric **4** to dimeric **5** generated in the presence of template **6** is around 20 : 1 whereas in the presence of **8** the cyclisation yields a product ratio of approximately 4 : 1. These yields support the view that intramolecular cyclisation within the **3.8** complex is inhibited to such an extent that intermolecular reaction more effectively competes (Process **E**). There now exists the possibility that the locking of **3** into a U-shaped geometry that cannot readily undergo intramolecular reaction might preorganise the reactive functions towards cyclo-dimerisation and favour production of dimeric macrocycle **5** (Process **H**) over further intermolecular reaction (Process **F**). However, the current yield data do not allow us to determine whether the cyclo-dimerisation process is favoured solely as a consequence of disfavouring monomer cyclisation, or whether template **8** has such a subsequent positive role to play in dimer formation.†

The successful template mediated syntheses of macrocycles **4** and **5** encouraged us to re-examine the preparation of the diimide macrocyclic component of **1**: this box-like molecule should have interesting host properties. Early attempts to promote cyclodimerisation of acetylenic diimide **7** in the absence of a crown or other template had been unsuccessful and we suspected that the extremely poor solubility characteristics of this material were responsible. We therefore prepared a more soluble bis-acetylene diimide **10** (Scheme 3) and a complementary hexyl naphthalene diether template **11** (see Experimental section). Addition of anhydrous CuCl to a 5 mM solution of **10** in CH_2Cl_2 resulted in rapid production of a number of oligomeric products, but preparative chromatographic separation of these gave only one characterisable fraction which mass spectrometry revealed as principally cyclic trimer **12** (contaminated with around 15% of cyclic tetramer). Repetition of the cyclisation reaction in the presence of five equivalents of template **11** gave an unchanged yield of the same trimeric product, containing an identical proportion of tetramer, and a similarly complex mixture of higher oligomers, *i.e.* the template does not have any detectable influence on the product distribution and no cyclic dimer is formed. We have no firm explanation for this result, but it seems likely that the intermediate acyclic dimer formed from coupling of two molecules of **10** is insufficiently flexible to form a well defined π-associated complex with template **11** and so promote dimer formation. In the absence of a favourable templating interaction some preorganisation of **10** might favour trimer formation, though clearly the bulk of **10** becomes incorporated in uncharacterised higher oligomers. A successful template for cyclodimerisation of acetylenic diimides **7** and **9** will perhaps need to be macrocyclic in nature since, to date, we have only been able to prepare the diimide macrocycles as integral components of [2]catenanes: diimide **10** failed to yield any interlocked products when coupled in the presence of a crown

† The reasons underlying the slowing of the coupling rate in these reactions remain unclear, though a similar phenomenon has been noted in attempts to prepare several cyclic porphyrin oligomers *via* acetylenic couplings.[25] It is conceivable that for these systems strong binding to a complementary template might 'lock' the acyclic precursor into a conformation which cannot cyclise *via* intramolecualar coupling. Such ultimate slowing of the coupling rate leads, at least at low concentration, only to the recovery of starting material.



Scheme 3 *Reagents and conditions*: i, THF, room temp.; ii, Ac_2O, 130 °C; iii, CuCl, TMEDA, CH_2Cl_2, air.

macrocycle, further illustrating its unfavourable interaction geometry. Equipping the crown component of a catenane with a cleavable link would allow subsequent release of the topologically bound diimide macrocycle; and this tactic has been successfully employed by Stoddart and co-workers to obtain an otherwise elusive bipyridinium cyclophane.[26]

Sequential and tandem catenane synthesis

Mechanical interlocking of hybrid macrocycle **4** was achieved by exposing the cyclophane to two equivalents of bis-acetylene **7** under the coupling conditions developed for the synthesis of **1** (Scheme 4).[10] The unsymmetrical [2]catenane **13** can be isolated from this reaction in a rather low, but reproducible, yield of 13–16%. For the first time with a reaction of this type we also noted the production of a small amount of a [3]catenane, the product of intermolecular rather than intramolecular ring closure of the pre-catenane intermediate (Fig. 2). This observation, and the rather low yield of the desired [2]catenane, lead to the not unexpected conclusion that **4** presents a rather constrained central binding cavity. The inevitable result is that interlocking of this macrocycle is less efficient than with the symmetrical crown ether employed in the preparation of **1**.

The room temperature ^{1}H NMR spectrum of [2]catenane **13** in $CDCl_3$ is extremely complex, reflecting the lack at ambient temperature of site-exchange processes involving rotation of the constituent rings. The appearance of the system could only be simplified by recording the spectrum in deuterated tetrachloroethane ($C_2D_2Cl_4$) at 120 °C. Resonances attributable to the six distinct proton environments of the naphthalene residues and for the single pyromellitimide proton were identified in the aromatic region, a situation consistent with fast inside–outside exchange of pairs of aromatic sub-units on the chemical shift time scale. The FAB mass spectrum of **13** is consistent with an interlocked structure displaying the characteristic fragmentation pattern for compounds of this type.

In the light of our observation that the efficiency of macrocyclisation of **3** is significantly enhanced by the presence of template **6**, it was irresistible to determine whether bis-acetylene diimide **7** might also act as a template for this cyclisation. The presence of identical reactive functions in both **3** and **7** dictates that material will be consumed in an unprofitable fashion through any direct coupling of **3** to **7**; reactions of this kind will lead to *covalently* connected donor–acceptor conjugates rather than *mechanically* linked ring systems. However, when exposed

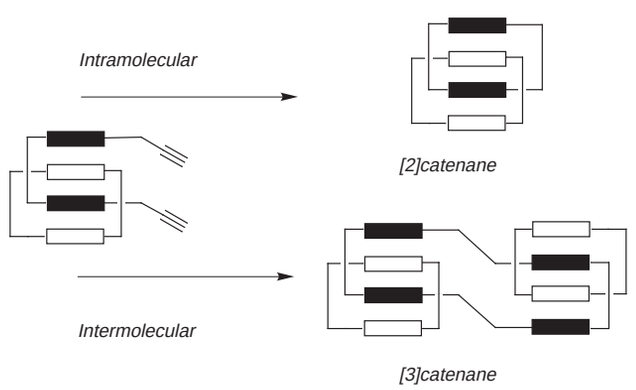
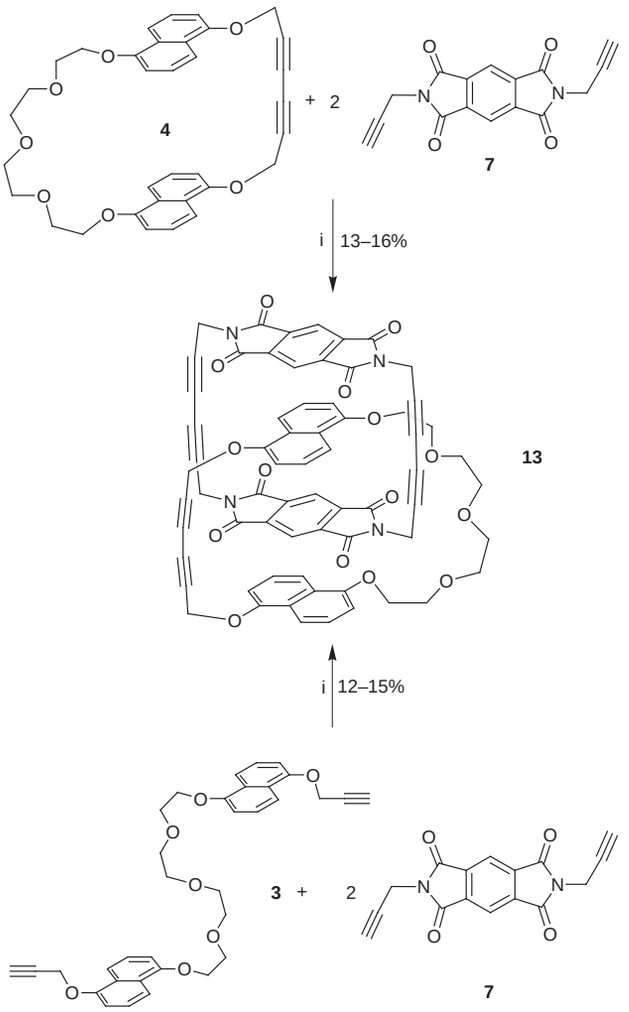


Fig. 2 Intra- and inter-molecular coupling pathways of a proposed pre-catenane intermediate, leading to [2]- and [3]-catenanes, respectively.

to the standard coupling conditions (CuCl–$CuCl_2$–DMF; 5 mM crown concentration), a 1:2 molar ratio of **3** and **7** affords isolated yields of [2]catenane **13** in the range 12–15% (Scheme 4). This tandem ring closure process is clearly of comparable efficiency to the sequential route where one of the two rings of the product catenane is preformed. An interpretation of this result is that the *initial* role of bis-acetylene **7** is, as anticipated, to template formation of macrocycle **4** *via* a complex whose geometry prevents intermolecular coupling. This *in situ* formed macrocycle could subsequently act as a template for the cyclodimerisation of bis-acetylene **7** leading to the catenane product.

Support for this picture of the assembly process is provided by association constant (CH_2Cl_2) estimates for the binding of template **6** by acyclic and cyclic naphthalene diether derivatives **3** and **4**. These order of magnitude estimates of binding strength were made from fluorescence quenching measurements (see Experimental section). For the interaction of template **6** with a *single* 1,5-naphthalene diether such measurements yield an upper limit for the association constant (K_a) of around 20 M^{-1}. This value increases to 80 M^{-1} for the complex of *acyclic* bis-naphthalene diether **3** with **6**, and to around 400 M^{-1} for the association of the corresponding *macrocycle* **4** with **6**. If the bulk of acyclic **3** were converted to macrocycle **4** by the templating action of **6**, then we would expect the yield of [2]catenane **13** to be similar to that obtained from the sequential reaction; the starting materials for the tandem reaction are converted *in situ* to those employed in the sequential assembly route. Further-



Scheme 4 *Reagents and conditions*: i, CuCl, $CuCl_2$, DMF, air.

more, we would also expect to observe a substantial amount of free macrocycle **4** in the tandem reaction since we know catenation of *pre-formed* **4** to be rather inefficient. Significantly, **4** is the major product isolated from the tandem ring closure reactions. Finally, the one-pot process also generates a small amount of [3]catenane, paralleling the situation found with the sequential reaction.

Attempted catenane formation with macrocycle **4** and naphthalene diimide **9** was reproducibly unsuccessful. We have already seen that a diimide of this type may act as a negative template for cyclisation of **3** and is, perhaps, unlikely to be effectively bound by the product macrocycle **4**. Since acetylenic pyromellitimide **7** can act as a positive template for macrocyclisation of bisacetylene **3**, mimicking its unfunctionalised analogue **6**, we might have expected some hint of production of interlocked systems based around dimeric macrocycle **5** from this reaction. No products of this kind were observed.

Solid-state structure

Single crystals of **13** proved as difficult to obtain as those of the previously reported [2]catenane **1**. After numerous attempts it was found that very small single crystals could be obtained by slow cooling of solutions of the catenane in DMSO–water mixtures. Though perfect and single, these crystals measured only a few tens of microns along an edge and proved too small for structural determination using a typical laboratory X-ray source. However, as was the case with **1**,[9] an excellent quality crystal structure was determined using a high intensity synchrotron radiation source. The data refined to a final *R* value of 5.6%.

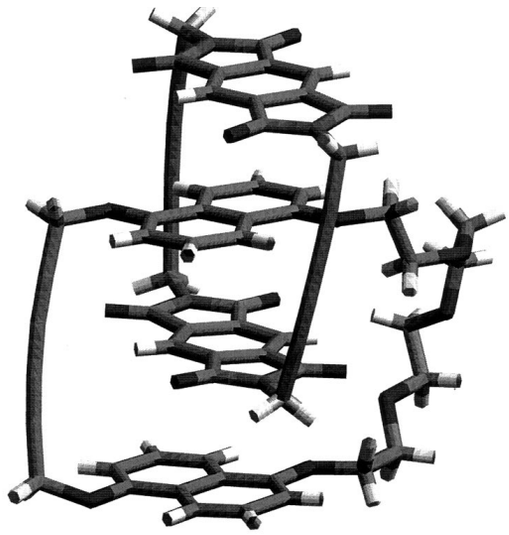


Fig. 3 Solid-state structure of **13** (displayed using Cerius Molecular Simulations software) demonstrating the orthogonal arrangement of naphthalene residues.

The most striking feature of the solid-state structure of **13** (Fig. 3) is the unusual disposition of the two naphthalene units comprising the recognition elements of the electron-rich hybrid macrocycle. This asymmetric arrangement of naphthalene residues, with the long axes defining an angle of around 100°, is to the best of our knowledge a unique structural feature: all previous reported structures of crowns, complexes and catenanes incorporating dinaphtho-crown macrocycles display a parallel arrangement of aromatic residues.[1]

In an earlier paper we discussed the solid-state structure of **1**; the butadiyne links of the diimide macrocycle are twisted by around 15° relative to one another, allowing establishment of the optimum 3.4 Å separation of complementary components.[10,27] A reduced twist angle of around 7° is observed for this same macrocycle when incorporated in [2]catenane **13**. Continuing this argument, a parallel arrangement of naphthalene residues in **4**, the crown component of **13**, would lead to an interplanar spacing of greater than optimum for establishing ideal donor–acceptor interactions. In such an arrangement the butadiyne linker would be forced perpendicular to the planes of the naphthalene diethers and the macrocycle would have no room to adjust to binding of a substrate. The observed orthogonal arrangement of naphthalene diethers can 'breathe' to optimise binding interactions by tilting the butadiyne link between these two units (Fig. 4).

A related observation for the diether component of the catenane involves the torsion angles between the naphthalene units and the first O–C bonds. Three of these bonds are close to being co-planar (≤ 2.5° torsion angle) with the aromatic diether, but the fourth, on the acetylenic side of the macrocycle, defines an angle with this plane of around 19°. This deviation must be an additional result of the adjustment of **4** to optimum accommodation of an acceptor substrate. The four stacked aromatic residues of **13** are coplanar to within 4°, though this value is significantly greater than that for **1** (<1°) perhaps reflecting the reduced level of geometrical flexibility in the present system. The bond angles at the four corners of the macrocycle are all within 0.5° of the ideal tetrahedral angle. Macrocyclic strain is principally accommodated in the sp carbons of the acetylenic linkers (average C–C≡C angle of 172.9°) and to a lesser extent by the bending of the N–C bonds out of the plane of the diimide framework (2–6°).

Extended alternating stacks of donor and acceptor sub-units characterise the solid-state packing of **1** and related co-crystals.[10,27] These are, however, conspicuous by their absence

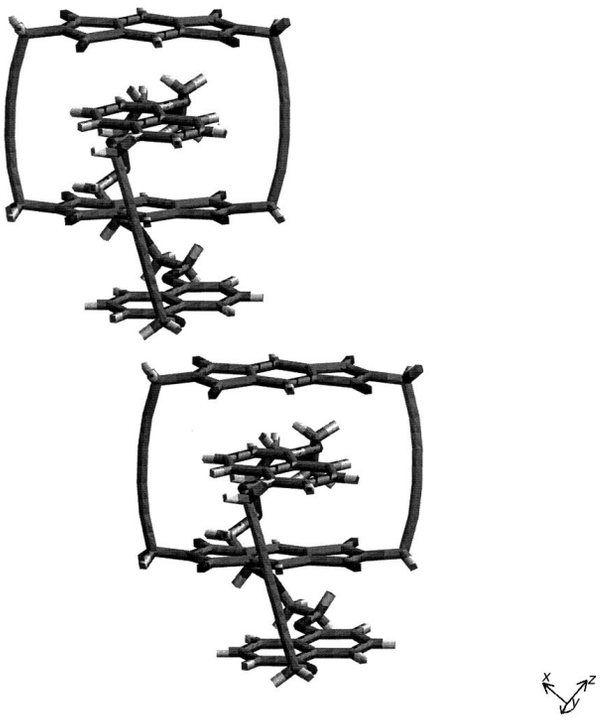


Fig. 4 Packing of individual [2]catenanes in the solid-state structure of **13**, revealing the offset packing and the tilted butadiyne link between naphthalene diether residues.

from the solid-state structure of **13**. Instead, individual catenanes form slipped stacks and the relative orientation of the donor and acceptor units of adjacent molecules is such that no additional stabilisation is achieved (Fig. 4). This unusual packing mode has previously been noted in the solid-state structure of a bipyridinium-derived catenane which, perhaps significantly, also contains one unusually strained macrocycle.[28] It may be the case that the non-optimal overlap of the constituent donor and acceptor units of these systems enforced by the rather constrained nature of the component macrocycles alters the electronic properties of the catenanes. By this mechanism, and contrary to the situation observed for more flexible interlocked systems, the additional stabilisation afforded by the establishment of extended donor–acceptor stacks might be outweighed by competing factors during the crystallisation process. The unit cell of **13** contains four molecules as a result of 'freezing-in' chirality during the crystallisation process. The pyromellitimide-derived macrocycle is chiral by virtue of its left or right handed helical sense.[29] The fact that the hybrid macrocyclic component **4** is non-superimposable on its mirror image leads to the prediction that four distinct catenane molecules should be observed. In the unit cell an inversion centre relates one pair of molecules to another (space group $P2_1/c$) and crystals of **13** are therefore racemic.

Conclusions

With the synthesis of the catenane described in this paper we have demonstrated that our original catenane design can tolerate modification of the crown macrocyclic component, an important step in establishing a set of compatible, interchangeable linkers suitable for inclusion in the design of more complex catenane syntheses. The demonstration of diverse templating effects in the syntheses of monomeric and dimeric hybrid macrocycles increases the repertoire of cyclisation processes that may be influenced by the rational deployment of diimide-derived templates. The extension of these observations to the first tandem assembly of a [2]catenane provides the ultimate demonstration of co-operative templating within this system, though elements of the nature of the driving force for these templated syntheses remain unclear. Building reversibility into this interlocking process, thus allowing the proof-reading of incorrect bond formation, would be likely to increase the admittedly low yield of interlocked product. Efforts to develop our first thermodynamically-controlled catenane syntheses are continuing.[30,31]

Experimental

General methods

All chemicals were purchased from the Aldrich Chemical Company and were used without further purification. Solvents were dried according to literature procedures: Anhydrous CuCl[32] and $CuCl_2$[33] were prepared according to literature procedures and used within one week of preparation. Yield ranges for cyclisation reactions represent the results of at least three individual runs. 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. NMR Spectra were recorded on Bruker AC-250, AM-400 or DRX-500 MHz spectrophotometers, chemical shifts in $CDCl_3$ are expressed relative to $CHCl_3$ (^{1}H, 7.25; ^{13}C, 77.2 ppm), J values are given in Hz. Electrospray mass spectrometry (ESI-MS) was performed using a VG BioQ triple quadrupole spectrometer (MeCN solution). LC-MS Analyses were recorded on a Micromass Platform LC quadrupole mass analyser fed at 20 μL min^{-1} by a Hewlett Packard 1050 HPLC (3 cm Supelcosil ABZ+PLUS column; 10 mM NH_4OAc in H_2O containing 0.1% HCO_2H, then 95:5 MeCN–H_2O containing 0.05% HCO_2H).

5-Propargyloxy-1-hydroxynaphthalene 2

1,5-Dihydroxynaphthalene (5.00 g, 31 mmol) was added to a suspension of K_2CO_3 (4.31 g, 31 mmol) in dry acetone (100 mL) under an argon atmosphere. After stirring for 10 min propargyl bromide (3.72 g, 31 mmol; 3.5 mL of an 80% solution in PhMe) was added and the mixture subsequently brought to reflux for 16 h. After allowing the reaction to cool the solvent was removed under vacuum and the residue extracted with boiling CH_2Cl_2 (3 × 100 mL). The combined extracts were boiled over charcoal, filtered and evaporated to yield a residue which was purified by column chromatography (SiO_2; $CHCl_3$) to afford the desired naphthol as a pale yellow solid (2.35 g, 38%): mp 139–140 °C; R_f = 0.30 (SiO_2; $CHCl_3$); δ_H(250 MHz, $CDCl_3$) 7.86 (d, ^3J 8, 1 H), 7.79 (d, ^3J 8, 1 H), 7.40 (t, ^3J 8, 1 H), 7.30 (t, ^3J 8, 1 H), 6.98 (d, ^3J 8, 1 H), 6.85 (d, ^3J 8, 1 H), 5.17 (br s, 1 H), 4.88 (d, ^4J 2, 2 H), 2.54 (t, ^4J 2, 1 H); δ_C(100 MHz, $CDCl_3$) 153.30, 151.16, 125.39, 124.98, 114.82, 114.71, 109.52, 106.20, 78.58, 75.60, 56.19; ESI-MS (positive ion) m/z 198.0 ([M]$^+$, 100%), 159.0 (40), 154.0 (80); High resolution LSI-MS: Found 197.062, $C_{13}H_9O_2$ ([M − H]$^+$) requires 197.060.

1,11-Bis(5′-propargyloxy-1′-naphthyloxy)-3,6,9-trioxaundecane 3

Naphthol **2** (272 mg, 1.4 mmol) and tetraethylene glycol di(toluene-*p*-sulfonate) (345 mg, 0.7 mmol) were added to a suspension of K_2CO_3 in dry acetone (35 mL). The mixture was stirred at reflux under nitrogen for 2 days, filtered and evaporated. The residue was partitioned between $CHCl_3$ (50 mL) and water (50 mL) and the organic layer separated, dried ($MgSO_4$) and evaporated. Column chromatography (SiO_2; $CHCl_3$–Et_2O–MeOH, 30.5:69:0.5) gave the pure product as a white solid (540 mg, 71%): mp 118–121 °C; R_f = 0.27 (SiO_2; CH_2Cl_2–Et_2O, 98:2); δ_H(250 MHz, $CDCl_3$) 7.90 (d, ^3J 8, 2 H), 7.83 (d, ^3J 8, 2 H), 7.34 (t, ^3J 8, 4 H), 6.93 (d, ^3J 8, 2 H), 6.81 (d, ^3J 8, 2 H), 4.86 (d, ^4J 2, 4 H), 4.25 (t, ^3J 7, 4 H), 3.96 (t, ^3J 7, 4 H),

3.80–3.68 (m, 8 H), 2.53 (t, ^4J 2, 2 H); δ_C(63 MHz, $CDCl_3$) 154.35, 153.12, 126.83, 126.73, 125.35, 124.78, 115.42, 114.44, 106.28, 105.77, 78.65, 75.48, 71.00, 70.79, 69.79, 67.93, 56.18; ESI-MS (positive ion) *m/z* 554.2 ($[M]^+$, 100%); High resolution FAB-MS: Found 554.235, $C_{34}H_{35}O_7$ ($[M + H]^+$) requires 554.230.

Example macrocyclisation of bis-acetylene 3

A solution of acyclic bis-acetylene **3** (260 mg, 0.47 mmol) in dry CH_2Cl_2 (94 mL; 5 mM) containing dry TMEDA (2.18 g, 2.8 mL, 18.8 mmol) was treated with anhydrous CuCl (0.94 g, 9.4 mmol) and stirred for 15 min in an atmosphere of dry air. The mixture was then diluted with 2 M HCl (50 mL), transferred to a separating funnel and washed with 2 M HCl (2 × 50 mL) and water (50 mL). The organic layer was then separated, dried ($MgSO_4$) and evaporated to yield a residue which was purified by column chromatography (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1) to afford hybrid crown **4** (93 mg, 36%): mp 175–177 °C; $R_f = 0.51$ (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1); δ_H(250 MHz, $CDCl_3$) 7.86 (d, ^3J 8, 1 H), 7.73 (d, ^3J 8, 1 H), 7.30 (t, ^3J 8, 1 H), 7.25 (t, ^3J 8, 1 H), 6.86 (d, ^3J 8, 1 H), 6.78 (d, ^3J 8, 1 H), 4.93 (s, 4 H), 4.27 (m, 4 H), 3.95 (m, 4 H), 3.79–3.67 (m, 8 H); δ_C(100 MHz, $CDCl_3$) 154.30, 152.11, 127.04, 125.27, 125.00, 115.76, 114.43, 107.72, 105.80, 74.73, 71.37, 71.21, 70.92, 69.82, 68.62, 56.25, 53.47, 50.95; ESI-MS (positive-ion) *m/z* 575.3 ($[M + Na]^+$, 100%); High resolution FAB-MS: Found 553.220, $C_{34}H_{33}O_7$ ($[M + H]^+$) requires 553.223. Further elution of the column afforded a trace of the dimeric analogue **5** (1–2%): $R_f = 0.33$ (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1); ESI-MS (positive-ion) *m/z* 1126.4 ($[M + Na]^+$, 2%), 591.3 ($[M + 2K]^{2+}$, 100), 575.3 ($[M + 2Na]^{2+}$, 60).

N,*N*′-Di-*n*-hexylpyromellitic diimide 6

A mixture of pyromellitic dianhydride (2.00 g, 9.2 mmol), *n*-hexylamine (1.85 g, 2.4 mL, 18.3 mmol) and dry DMF (40 mL) was stirred and heated at 140 °C for 6 h. The reaction mixture was subsequently cooled in a refrigerator for 2 h and filtered to afford the dihexyl derivative as white plates (2.29 g, 65%): mp 198–200 °C; δ_H(250 MHz, $CDCl_3$) 8.25 (s, 2 H), 3.72 (t, ^3J 7, 4 H), 1.65 (quintet, ^3J 7, 4 H), 1.30 (br s, 12 H), 0.87 (t, ^3J 7, 6 H); LSI-MS (positive ion) *m/z* 385.2 ($[M + H]^+$, 100%); High resolution LSI-MS: Found 385.214, $C_{22}H_{29}N_2O_4$ ($[M + H]^+$) requires 385.213.

N,*N*′-Di-*n*-hexylnaphthalene-1,4,5,8-tetracarboxylic diimide 8

A mixture of naphthalene-1,4,5,8-tetracarboxylic dianhydride (2.00 g, 7.5 mmol), *n*-hexylamine (1.51 g, 2.0 mL, 14.9 mmol) and dry DMF (50 mL) was stirred and heated at 140 °C for 6 h. After cooling the mixture was filtered to afford fine pink needles (2.29 g, 65%): mp 200–202 °C; δ_H(250 MHz, $CDCl_3$) 8.75 (s, 4 H), 4.18 (t, ^3J 7, 4 H), 1.73 (quintet, ^3J 7, 4 H), 1.50–1.30 (br m, 12 H), 0.88 (t, ^3J 7, 6 H); LSI-MS (positive ion) *m/z* 435.4 ($[M + H]^+$, 100%); High resolution LSI-MS: Found 435.226, $C_{26}H_{31}N_2O_4$ ($[M + H]^+$) requires 435.228.

Example templated cyclisation of 3 in the presence of 6

A solution of acyclic bis-acetylene **3** (113 mg, 0.20 mmol) in dry CH_2Cl_2 (41 mL; 5 mM) containing dry TMEDA (0.95 g, 1.22 mL, 8.2 mmol) and dihexyl template **6** (0.39 g, 1.00 mmol) was treated with anhydrous CuCl (0.41 g, 4.1 mmol) and stirred for 15 min in an atmosphere of dry air. The mixture was worked up as detailed above and the residue purified by column chromatography (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1) to afford the hexyl template ($R_f = 0.9$–1.0, >95% recovery), the hybrid crown **4** (78 mg, 70%; $R_f = 0.56$) and a small amount (2–3 mg, 2–3%; $R_f = 0.31$) of the dimeric analogue **5**, ESI-MS (positive-ion) *m/z* 1104.4 ($[M + NH_4]^+$, 100%).

Example templated cyclisation of 3 in the presence of 8

A solution of acyclic bis-acetylene **3** (239 mg, 0.43 mmol) in dry CH_2Cl_2 (86 mL; 5 mM) containing dry TMEDA (2.00 g, 2.60 mL, 17.3 mmol) and naphthalene diimide template **8** (0.94 g, 2.16 mmol) was treated with anhydrous CuCl (0.86 mg, 8.63 mmol) and stirred for 30 min in an atmosphere of dry air. The mixture was worked up as detailed above and the residue purified by preliminary column chromatography (SiO_2; CH_2Cl_2–Et_2O, 98 : 2) to recover the bulk of the template (0.9 g, 95%); further elution of the column with a more polar solvent system (CH_2Cl_2–MeOH, 4 : 1) afforded a mixture of cyclic monomer **4**, cyclic dimer **5** and cyclic trimer. These oligomers were separated by further column chromatography (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1) to afford the hybrid crown **4** (123 mg, 52%) and a mixture of the dimeric analogue **5** with a small amount of the corresponding cyclic trimer. This latter fraction could only be separated by repeated preparative TLC (SiO_2; $CHCl_3$–MeOH, 97 : 3) to ultimately yield cyclic dimer **5** (36 mg, 15%) and cyclic trimer (7 mg, 3%): ESI-MS (positive-ion) *m/z* 846.6 ($[M + (NH_4)_2]^{2+}$, 100%).

N,*N*′-Bis(diethylprop-2-ynyl)pyromellitic diimide 10

To a solution of pyromellitic dianhydride (4.33 g, 39 mmol) in dry THF (40 mL) was added a solution of 1,1-diethylpropargylamine (4.25 g, 19.5 mmol) in dry THF (20 mL). The reaction mixture was stirred overnight and evaporated to afford a white foam. Acetic anhydride (60 mL) was then added and the mixture brought to 130 °C for 2 h. The cooled mixture was poured into vigorously stirred ice-cold water and the solid precipitate collected at the pump. Recrystallisation from DMF–water afforded a pale yellow crystalline solid (2.45 g, 31%): mp 158–159 °C; δ_H(250 MHz, $CDCl_3$) 8.20 (s, 2 H), 2.62 (s, 2 H), 2.61–2.51 (dq, ^2J 15, ^3J 7, 4 H), 2.06–1.92 (dq, ^2J 15, ^3J 7, 4 H), 1.02 (t, 12 H, ^3J 7); δ_C(100 MHz, DMSO-d_6) 165.20, 137.02, 118.04, 79.28, 74.42, 27.35; LSI-MS (positive ion) *m/z* 405.3 ($[M + H]^+$, 100%); High resolution LSI-MS: Found 405.179, $C_{24}H_{25}N_2O_4$ ($[M + H]^+$) requires 405.181.

1,5-Bis(*n*-hexyloxy)naphthalene 11

To a suspension of K_2CO_3 (21.56 g, 156 mmol) in dry acetone (150 mL) were added 1,5-dihydroxynaphthalene (5.00 g, 31 mmol) and *n*-hexyl bromide (11.34 g, 9.60 mL, 69 mmol). The mixture was refluxed in an argon atmosphere for 2 days, filtered and evaporated. The residue was partitioned between CH_2Cl_2 and water and the organic extracts separated and dried ($MgSO_4$). The solid material so obtained was recrystallised several times from EtOAc to afford the product as long straw yellow needles (6.66 g, 65%): mp 95–97 °C; δ_H(250 MHz, $CDCl_3$) 7.84 (d, ^3J 8, 2 H), 7.34 (t, ^3J 8, 2 H), 6.82 (d, ^3J 8, 2 H), 4.11 (t, ^3J 6, 4 H), 1.91 (quintet, ^3J 6, 4 H), 1.56 (m, 4 H), 1.38 (m, 8 H), 0.92 (t, ^3J 6, 6 H); LSI-MS (positive ion) *m/z* 328.3 (M^+, 100%); High resolution LSI-MS: Found 328.240, $C_{22}H_{29}N_2O_4$ (M^+) requires 328.240.

Example macrocyclisation of bis-acetylene 10

To a solution of bis-acetylene **10** (100 mg, 0.25 mmol) in dry CH_2Cl_2 (50 mL; *ca.* 5 mM) were added TMEDA (1.15 g, 1.50 mL, 9.90 mmol) and anhydrous CuCl (500 mg, 4.95 mmol). The mixture was stirred in an atmosphere of dry air until complete (20 min) as revealed by the absence of starting material (TLC; SiO_2, $CHCl_3$). The mixture was then diluted with 2 M HCl (50 mL), transferred to a separating funnel and washed with 2 M HCl (2 × 50 mL) and water (50 mL). The organic layer was then separated, dried ($MgSO_4$) and evaporated to yield a residue which was purified by preparative TLC (SiO_2; $CHCl_3$) to afford cyclic trimer **12** ($R_f = 0.3$) as the sole isolable product (9 mg, 9%): mp (decomp.) >220 °C; δ_H($CDCl_3$, 250 MHz) 8.24 (s, 6 H), 2.65–2.51 (d of q, ^2J 15, ^3J 7, 12 H), 2.09–1.92 (d of q, ^2J 15,

^3J 7, 12 H), 1.05 (t, ^3J 7, 36 H); ESI-MS (positive ion) *m/z* 1224.54 ([M + NH_4]$^+$, 100%); High resolution LSI-MS: Found 1207.487, $C_{72}H_{67}N_6O_{12}$ ([M + H]$^+$) requires 1207.482.

Repetition of the above reaction in the presence of five equivalents of template **11**, employing an identical work-up procedure, afforded a seemingly unchanged distribution of products and 8–10% isolated yields of cyclic trimer **12**. In both the untemplated and templated reactions around 15% of cyclic tetramer could also be detected in the trimer fraction, revealed by an additional ^{1}H NMR singlet at 8.19 ppm and a peak at *m/z* 1609.3 [M + H]$^+$ in the FAB mass spectrum. This oligomer co-ran with the cyclic trimer under all tested chromatographic conditions.

Example synthesis of [2]catenane 13; sequential method

A solution of hybrid crown **4** (41 mg, 74 μmol) and bis-acetylene **7** (43 mg, 149 μmol) in dry DMF (6 mL) was treated with anhydrous CuCl (0.74 g, 5.3 mmol) and anhydrous $CuCl_2$ (0.2 g, 1.1 mmol) and the mixture stirred in an atmosphere of dry air for 2 days. The mixture 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 initially purified by column chromatography (SiO_2; $CHCl_3$–MeOH, 99 : 1 increasing to $CHCl_3$–MeOH, 98 : 2). The orange fraction so obtained was further purified by preparative thin layer chromatography (SiO_2; $CHCl_3$–MeOH, 99 : 1) to afford the [2]catenane product as an orange–yellow solid (12 mg, 14%): mp (decomp.) >250 °C; δ_H(500 MHz, $C_2D_2Cl_4$, 120 °C) 7.31 (br d, 4 H), 7.18 (s, 4 H), 6.89 (d, ^3J 8, 4 H), 6.85 (t, ^3J 8, 4 H), 6.69 (t, ^3J 8, 4 H), 6.63 (d, ^3J 8, 4 H), 6.44 (d, ^3J 8, 4 H), 4.96 (s, 4 H), 4.36 (s, 8 H), 4.08 (br s, 4 H), 3.96 (m, 4 H), 3.91 (m, 8 H); LSI-MS (positive ion) *m/z* 1155.3 ([**13**+Na]$^+$, 100%), 1133.3 ([**13**+H]$^+$, 22), 575.2 ([**4**+Na]$^+$, 35); High resolution LSI-MS: Found 1133.2868, $C_{66}H_{45}N_4O_{15}$ ([M + H]$^+$) requires 1133.2881.

Example synthesis of [2]catenane 13; tandem method

To a solution of acyclic bis-acetylene **3** (53 mg, 96 μmol) and bis-acetylene **7** (56 mg, 191 μmol) in dry DMF (5 mL) were added anhydrous CuCl (0.96 g, 9.5 mmol) and anhydrous $CuCl_2$ (0.26 g, 1.9 mmol). The mixture was stirred in an atmosphere of dry air for 2 days prior to work-up and chromatographic purification according to the above described sequential procedure. The [2]catenane **13** was obtained as an orange–yellow solid (14.8 mg, 14%) and was spectroscopically indistinguishable from the material obtained in the above procedure.

X-Ray structural determination

Single crystals of the catenane were obtained by initial vapour diffusion of water into a solution of **13** in DMSO-d_6 and subsequent recrystallisation by warming and then slow cooling of the DMSO–water mixture. Details of the structure solution and refinement have been reported elsewhere.[22]

Binding constant determinations

UV absorption and emission spectra were recorded using a 3 μL aliquot of a 1×10^{-4} M $CHCl_2$ solution of **3** or **4**. Aliquots (10 μL) of a 5×10^{-3} M solution of **6** were then added *via* micro syringe and the spectra recorded. Residual fluorescence intensity from the naphthalene diether derivatives ($\lambda_{exc} = 295$ nm, $\lambda_{em} = 345$ nm) and from the diimide template **6** ($\lambda_{exc} = 320$ nm, $\lambda_{em} = 425$ nm) was corrected by inner filter effects. Since a dynamic quenching was also observed from lifetime measurements ($k_q = 4 \times 10^{10}$ M^{-1} s^{-1}) this contribution was also taken into account when evaluating the final corrected intensities. The corrected intensities were finally fitted to $I_{corr} = \varphi_c C_c + \varphi_u C_u$, where C_c and C_u are the concentrations of uncomplexed and complexed species, respectively, and φ_c and φ_u are the proportionality constants between the corrected emission intensity (in arbitrary units) and the concentration of the uncomplexed and complexed species, respectively. C_c satisfies the usual binding expression[34] in eqn. (1) where $[\mathbf{6}]_{tot}$ is the total concentration of added **6**. Values of the association constant, K_a, were then obtained by simulation of the data with both K and φ_c as adjustable parameters.

$$C_c^2 - \{(C_c + C_u) + [\mathbf{6}]_{tot} + 1/K\} + [\mathbf{6}]_{tot}(C_c + C_u) = 0 \quad (1)$$

There are inevitable, and rather large, errors associated with these determinations: for the **3.6** complex, $K_a = 80 \pm 50$ M^{-1}; for the **4.6** complex, $K_a = 400 \pm 500$ M^{-1}. These errors are the unavoidable consequence of measuring a weak binding process in the presence of complex quenching phenomena. In particular, internal fluorescence quenching processes in macrocycle **4** hamper accurate determination of the latter value.

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