Synthesis and post-assembly modification of some functionalised, neutral π-associated [2]catenanes

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Two diaryl crown ethers bearing methyl ester functionality on one of the aromatic components of the macrocycle have been used as templates for the cyclodimerisation of acetylenic aromatic diimides, thereby achieving assembly of several functionalised neutral π-associated [2]catenanes. Post-assembly synthetic modification of some of these interlocked structures, and of some previously reported [2]catenanes, by hydrogenation of the butadiyne linkers in the diimide macrocycle has also been achieved. In contrast to their parent systems, these modified catenanes give room temperature ^{1}H NMR spectra which are poorly resolved; at elevated temperatures the constituent rings of the catenanes are in fast exchange on the chemical shift timescale leading to simplification of the spectra. The crystal structure of one of the ester-derivatised [2]catenanes is also presented. The ester functionality present in these interlocked systems provides options for potential chemical modification *via* surface attachment or metal-ion complexation.

A central motivation for our development and introduction of a supramolecular synthetic approach to neutral π-associated interlocked molecules[1] was to provide a general route to chemically robust, functionalised, yet readily modified structures with complex topologies.[2] The approach has proved general for two structurally distinct electron deficient components **2** and **3** (Fig. 1),[2] tolerant of modification in the linkers used to connect the components of individual macrocycles,[3] amenable to macrocyclisation using either kinetically controlled coupling of terminal acetylenes or thermodynamically controlled olefin metathesis,[4] and controllable *via* a form of temporary supramolecular protection of a binding cavity.[5] We now present the assembly of related [2]catenanes bearing functionality suitable for solid-state immobilisation of the interlocked molecules or their precursors. We also describe the synthetic and structural post-assembly modification of these and earlier systems by hydrogenation of the acetylenic links present in one of the constituent macrocycles. The photophysical and electrochemical characterisation of these new interlocked systems, as well as of several earlier catenanes in this series, will be described elsewhere.[6]

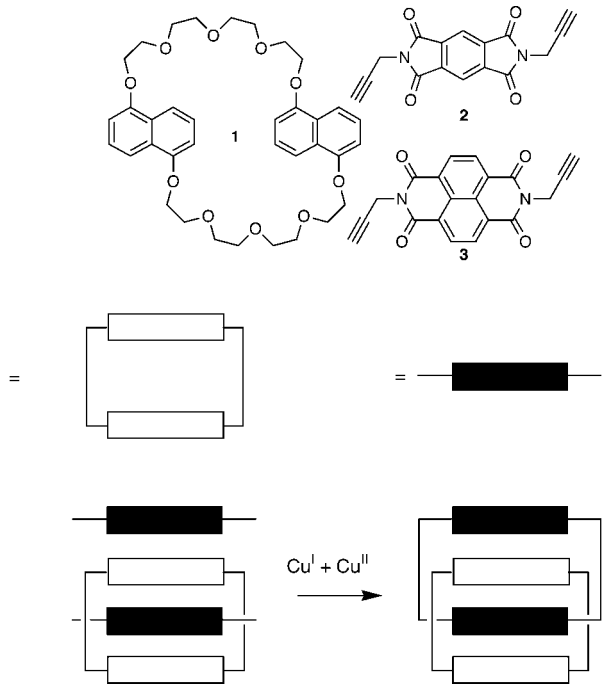


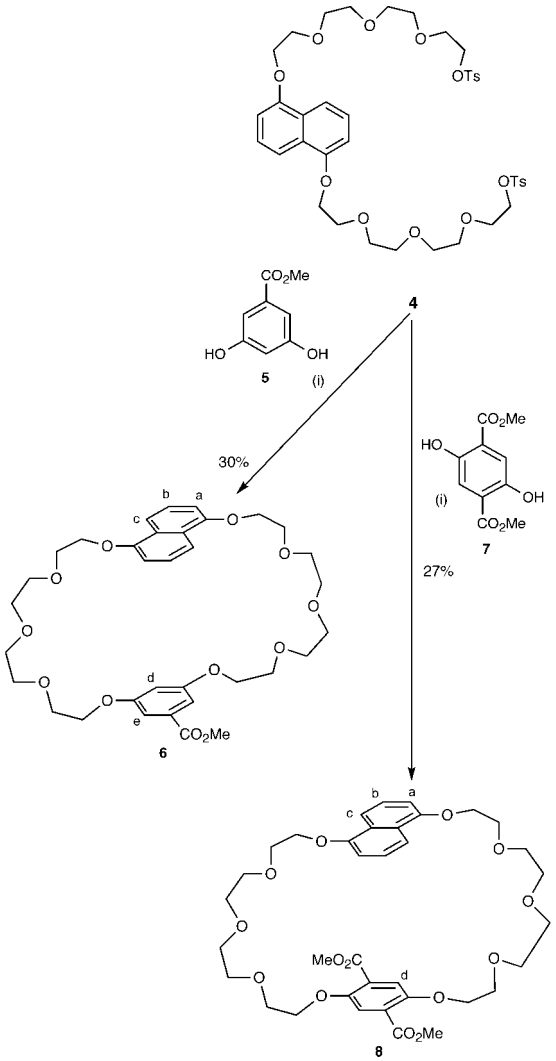
Fig. 1 Chemical and cartoon representations of a system of complementary aromatic donors (empty boxes) and diimides (filled boxes) used in catenane assembly.

Results and discussion

Synthesis

1,5-Bis(dinaphtho)-38-crown-10 **1**, the polyether macrocyclic component of previously reported [2]catenanes **9** and **11**, may be prepared in two steps from commercially available materials *via* ditosylate **4**.[2] We wished to extend this simple synthetic approach beyond the formation of symmetrical diaryl crown ethers by introducing a different aromatic diol in the macrocyclisation step. Accordingly, the diaryl crown polyethers **6** and **8** were synthesised, using ditosylate **4** as the common precursor, from methyl 3,5-dihydroxybenzoate **5** or dimethyl 2,5-dihydroxyterephthalate **7** (Scheme 1). Yields of around 30% were obtained for the macrocyclisation step, values typical for reactions of this type. A full synthetic procedure has previously been reported for macrocycle **6**, though the current procedure affords a similar yield and avoids the use of expensive caesium salts in the macrocyclisation step.[7] An alternative preparation of the diethyl ester analogue of **8** has also recently been reported in abbreviated form.[8]

Molecular interlocking of the new crowns was achieved using the general procedure developed for the synthesis of **9** and related systems,[2] and is based on that reported by Sauvage and co-workers for their preparation of acetylenic transition-metal catenates.[9] Mixing 2 : 1 ratios of acetylenic diimides **2** or **3** with mono-ester crown macrocycle **6** in dry DMF (approx. 5 mM crown concentration) afforded strongly



Scheme 1 (i) K_2CO_3, Me_2CO.

orange or purple coloured solutions respectively, indicative of charge transfer complex formation. To effect coupling of the diimides, large excesses of anhydrous copper(I) and copper(II) chloride were then added to these solution complexes. The reactions were allowed to stir at room temperature for two days prior to aqueous work-up and isolation of the interlocked products by column chromatography on silica, and occasional further purification by preparative silica gel TLC; the new catenanes **13** and **15** were obtained in yields of 30 and 20% respectively.

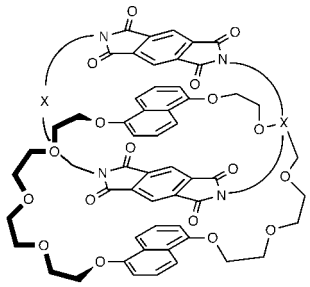
Under identical reaction conditions, a 2 : 1 molar ratio of benzene diimide **2** and diester crown macrocycle **8** gave a 29% yield of [2]catenane **17**, after chromatographic separation and purification. Whilst the parallel reaction involving naphthalene diimide **3** yielded solution complexes indicative of charge transfer complex formation, no interlocked product could be isolated from the coupling reaction. This situation parallels that found for an earlier system, a hybrid crown macrocycle whose rather constrained binding cavity could only be interlocked by coupling in the presence of benzene diimide **2**.[3] It is clear that neither of these macrocycles is capable of forming a suitable intertwined precursor that would lead to [2]catenane formation, perhaps because of their inability to adopt a favourable binding overlap of electron-rich and electron-deficient systems, or to establish stabilising C–H···O hydrogen bonds with the included diimide.

A consideration of the yields of the previously reported [2]catenanes **9** (38%) and **11** (52%) alongside those of the current systems allows related observations to be made concerning the binding abilities of the three macrocyclic polyethers **1**, **6** and **8**. The increased yield of [2]catenane **11**, compared with **9**, has been attributed to the rather stronger electron accepting ability of the naphthalene diimide units present in the latter derivative. This property is certainly supported by electrochemical investigations,[10,11] and by photophysical studies of a [2]catenane comprising a macrocycle made of one benzene and one naphthalene diimide where it is estimated that incorporation of the naphthalene diimide within the crown cavity is favoured in a ratio of 85 : 15 in solution.[2] Clearly the 10% drop in isolated catenane yield when ester functionalised crown **6** is interlocked with naphthalene diimide **3** rather than with benzene analogue **2** contradicts this purely electronic argument. We have previously noted that the optimum overlap geometries in donor–acceptor complexes are sensitive to both the nature of the diimide, and the substitution pattern of the electron-rich component, but are also likely to be influenced by the presence of C–H···O hydrogen bonds.[12] The reduction in catenane yield with the ester functionalised crowns must derive from these factors; in the extreme case of diester crown macrocycle **8** no interlocking with naphthalene diimide **3** is possible. Intriguingly, only a trace amount of a [2]catenane could be obtained from reactions involving the carboxylic acid derivative of **6**, for reasons that are unclear. Our solution to this problem will be reported elsewhere.[13]

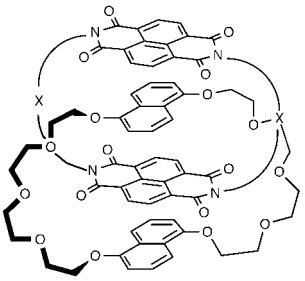
Dinaphtho-crown **1** presents two electron-rich sub-units suitable for the inclusion complexation of an electron deficient guest through formation of a donor–acceptor complex. Although crowns **6** and **8** contain two diaryl ether units, electron withdrawing carbonyl functions are also present in one of the aromatic systems, reducing the electron density associated with this π-system and consequently weakening the overall donor–acceptor interaction between the crown host and an included diimide catenane precursor. The yields of [2]catenanes obtained from benzene diimide **2** with the three crowns **1** (38%), **6** (30%) and **8** (29%) indicate, assuming all other structural factors within this series to be equal, that the binding ability of the diaryl crowns is **1** > **6** ⩾ **8**. Despite the fact that this is the order predicted on the basis of their general electron donating properties the overall drop in catenation efficiency is small and these results demonstrate that the crown component can be elaborated substantially and yet remain capable of effective molecular interlocking. Additionally, these results highlight the recently raised question of how important are donor–acceptor interactions in the syntheses of these structures.[14]

Most routes to topologically complex molecules provide little, and frequently no, opportunity for post-assembly synthetic modification.[1] An understandably much studied property of interlocked molecules is the dynamic behaviour of their constituent rings and, therefore, a way of altering gross molecular structure (and as a consequence the molecular dynamics of the system) would be an attractive feature to build into a synthetic approach. Our route to the assembly of neutral [2]catenanes provides two options for such post-assembly synthetic modification, reduction of the imide carbonyl groups and hydrogenation of the butadiyne linkers. The latter option has been examined in this work.

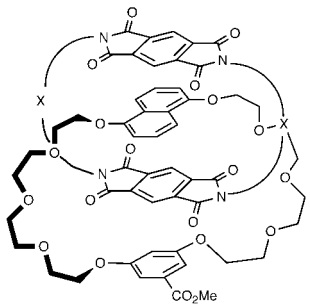
Previously reported [2]catenanes **9** and **11**, and the new ester-equipped [2]catenanes **13**, **15** and **17** were hydrogenated over Pd–C catalyst (5 mol%) at room temperature. In all cases periodic LC-MS analysis of the reaction mixtures indicated clean conversion of the butadiyne linkers to their fully saturated analogues within a period of sixteen hours; peaks were observed at sixteen mass units higher than the parent compounds and no partially hydrogenated products were observed after the first few hours of reaction. All the new hydrogenated catenanes **10**, **12**, **14**, **16** and **18** have been characterised by high resolution mass spectrometry.



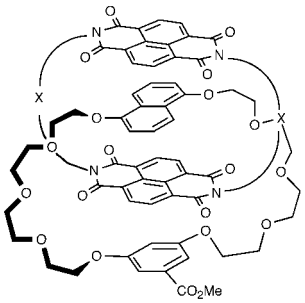
9 X = $-CH_2-C\equiv C-C\equiv C-CH_2-$
10 X = $-(CH_2)_6-$



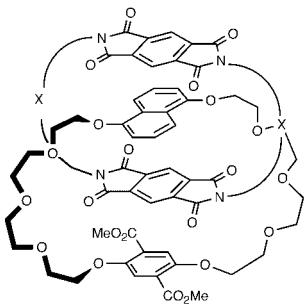
11 X = $-CH_2-C\equiv C-C\equiv C-CH_2-$
12 X = $-(CH_2)_6-$



13 X = $-CH_2-C\equiv C-C\equiv C-CH_2-$
14 X = $-(CH_2)_6-$



15 X = $-CH_2-C\equiv C-C\equiv C-CH_2-$
16 X = $-(CH_2)_6-$



17 X = $-CH_2-C\equiv C-C\equiv C-CH_2-$
18 X = $-(CH_2)_6-$

^{1}H NMR Spectroscopy and molecular modelling

The new crowns **6** and **8** do not possess the two-fold symmetry of **1** and this is reflected in both the dispersion and complication of the signals arising from the methylene groups of their polyether chains; those attached to the ester functionalised phenyl ring of **6** appear somewhat downfield shifted (δ 4.22) compared to the others (δ 3.95–3.58). In the aromatic region, in addition to the familiar three resonance pattern arising from the naphthalene system, two singlets are observed at δ 7.10 and 6.43. Diester crown **8** presents a similar ^{1}H NMR spectrum to **6**, further simplified in that only one aromatic resonance is observed for the ester bearing aromatic ring.

As observed previously in the ^{1}H NMR spectra of catenanes **9** and **11**,[2] the aromatic resonances of **13** and **15** are shielded relative to their positions in the catenane precursors. These shifts are the product of the continued influence of the donor–acceptor interactions initially used to template the synthesis of the catenanes. In pyromellitimide derived catenane **13** the five aromatic resonances of the crown component shift upfield by as much as 1.0 ppm; the diimide singlet appears at δ 7.10, upfield shifted by around 1.2 ppm from its position in free diimide **2**. The larger π-surface of the naphthalene diimide unit results in generally larger upfield shifts of adjacent resonances, the aromatic resonances of crown **6** shift by a maximum value of 1.5 ppm when this macrocycle is incorporated in [2]catenane **15**; this maximum shift corresponds to 4.9 ppm for an aromatic proton and must indicate an overlap geometry in [2]catenane **15** which places this proton in very close proximity to a naphthalene diether π-system. An additional effect of the increased size of the naphthalene diimide unit is to distance its peripheral protons from the shielding effects of the adjacent aromatic diethers. Accordingly, these signals are shifted by only around 0.3 ppm from their initial position in diimide **3**. In both **13** and **15** the NCH_2 protons appear as an AB system (J = 17–18 Hz) between δ 4 and 5.

Only one diimide environment is revealed in the spectra of both **13** and **15**, indicating that the two diimide sub-units of each of these catenanes are in fast exchange on the chemical shift timescale. This situation once again parallels that found for our original catenane systems **9** and **11** and strongly suggests that a similar dynamic behaviour is operating within the new systems. The lowest energy dynamic process that can explain the observed spectra is the sweeping of the whole of the crown macrocycle around the periphery of the catenane, thus exchanging the inner and outer diimide units and averaging their respective chemical shifts; in consequence, the outer aromatic diether always remains on the outside of the catenane whilst the inner remains bound within the diimide macrocycle. This process has frequently been found to operate within interlocked structures involving rather flexible polyether macrocycles.[15]

The 500 MHz COSY spectra of **13** and **15** proved most important in determining the proton connectivities around the aromatic components of the macrocycles. In the case of [2]catenane **15** the COSY spectrum was necessary to unambiguously locate the resonance (at δ 4.9) of H_d by virtue of the presence of a cross-peak to H_e. The most interesting features of the 500 MHz NOESY spectra of these catenanes are numerous through-space connections between protons on different macrocycles; these are connections between non-covalently (*i.e.* mechanically) linked ring systems. Interestingly, and against expectation, such cross peaks are not observed in the NOESY spectra of our original [2]catenane systems **9** and **11**. For both **13** and **15** additional cross-peaks are observed within the crown macrocycle between aromatic protons and the first methylene groups of the polyether chains linking the two aromatic components. It seems likely that through the use of these resonances it would be possible to assign most of these polyether methylene signals to individual resonances. More elegantly, the observation of NOEs between rings demonstrates the intimate, interlocked nature of the catenane structures which place non-covalently linked groups in close proximity to one another. Some of the observed NOEs for [2]catenane **15** are shown in schematic form in Fig. 2.

The one-dimensional and two-dimensional ^{1}H NMR spectra of diester [2]catenane **17** support the proposition of the same dynamic behaviour, operating within a system displaying similar resonances and splittings as described for closely related system **13**.

In spite of repeated preparative TLC purification, it proved impossible to obtain well resolved ^{1}H NMR spectra of the hydrogenated [2]catenanes **10**, **12**, **14**, **16** and **18** at ambient temperature. The exception was diester [2]catenane **18** which presented a reasonably well resolved room temperature spectrum in $C_2D_2Cl_4$. The spectra of pyromellitimide derived [2]catenanes **10** and **14** were both markedly improved by recording their spectra at high temperature (120 °C) in $C_2D_2Cl_4$, revealing shifts consistent with fast exchange of the diimide sub-units on the chemical shift timescale. Perhaps because of the additional structural demands of the larger naphthalene diimide unit present in **12** and **16** little improvement in their spectra was obtained at elevated temperature.

There must exist a lower limit for the length of a saturated carbon chain that can bridge the two aromatic diimide sub-units and maintain the roughly 7 Å separation needed for

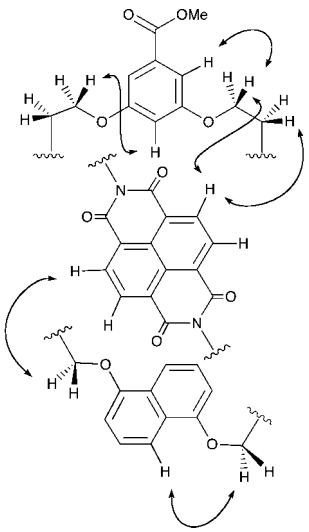


Fig. 2 Proton connectivities revealed in the 500 MHz NOESY spectrum of catenane **15**.

molecular inclusion: we anticipated that we may approach this limit in the conversion of butadiyne-bridged [2]catenane **9** to its saturated analogue **10**. In order to assess the ability of these macrocycles to maintain a rigid receptor-like structure within an interlocked system, we have performed modelling studies using MacroModel (MM2 force-field).[16] We chose as a starting point [2]catenane **9**, the known crystal structure of which could be used to provide starting co-ordinates. Energy minimisation of this structure did not lead to significant changes; the mean interplanar separation of the diimide sub-units was 6.79 Å and the average spacing between the donor–acceptor pairings was 3.36 Å. [2]Catenane **9** was subsequently "converted" to [2]catenane **10** by altering the four sp carbons of each butadiyne link to saturated sp^3 centres. Minimisation did not lead to significant change in the relationship of the two rings, revealing that **10** could readily adopt a familiar stacked conformation of electron-rich and electron-deficient sub-units. Perhaps unsurprisingly, saturation of the butadiyne linked macrocyclic component of the [2]catenane does pull the diimide components together. The minimisation suggests that their interplanar separation is reduced to 6.53 Å and accordingly the average donor–acceptor spacing in [2]catenane **10** is reduced to 3.28 Å. The conformational freedom of **10** was investigated by performing a molecular dynamics simulation (300 K, 1 ns, stochastic dynamics). No gross structural changes were observed, the stacked conformation being retained throughout. Simulations in which the two rings were forced away from this conformation always returned to lower energy conformations with a stacked structure. Energy minimisation of the separate macrocyclic components of both **9** and **10** reveals that both catenanes are 160–170 kJ mol^{-1} lower in energy than the sum of their non-interlocked components. This stabilisation was slightly reduced for **10**, implying that there is a small energetic penalty associated with incorporating the diimide macrocycle in its saturated form.

Of course dynamics simulations on a nanosecond timescale can shed no light on the millisecond timescale gyrations relevant to the NMR chemical shift timescale. Given the many conformational opportunities available to the saturated side chain, and the probable conformational restriction of the transition state relevant to chemical exchange, it is not surprising these processes are slower.

Crystal structure of [2]Catenane 17

In common with all of our previous [2]catenanes, it did not prove possible to grow single crystals of the current systems of a suitable size for structure determination on typical laboratory diffractometers. However, as with three earlier [2]catenanes in this series,[2–4] a very tiny crystal of diester [2]catenane **17** did prove amenable to structural analysis using the very much greater power of an X-ray synchrotron source (Fig. 3). Despite some disorder in one of the polyether chains, and two distinct locations for one of the ester methyl groups, the data refined to a final *R* value of 7.5%.

The most immediately striking feature of the structure is that the diester equipped aromatic residue is rather skewed and offset relative to the remaining three sub-units (Fig. 4), these latter forming a familiar acceptor–donor–acceptor stack of predictable 3.4 Å spacing. Whilst it was expected that the π-rich naphthalene diether residue would be found sand-

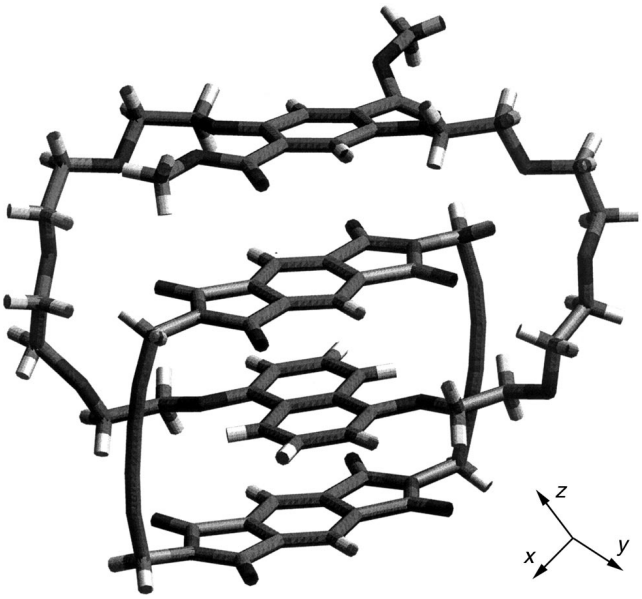


Fig. 3 A view of the structure of [2]catenane **17** in the crystal (displayed using Cerius²).[23]

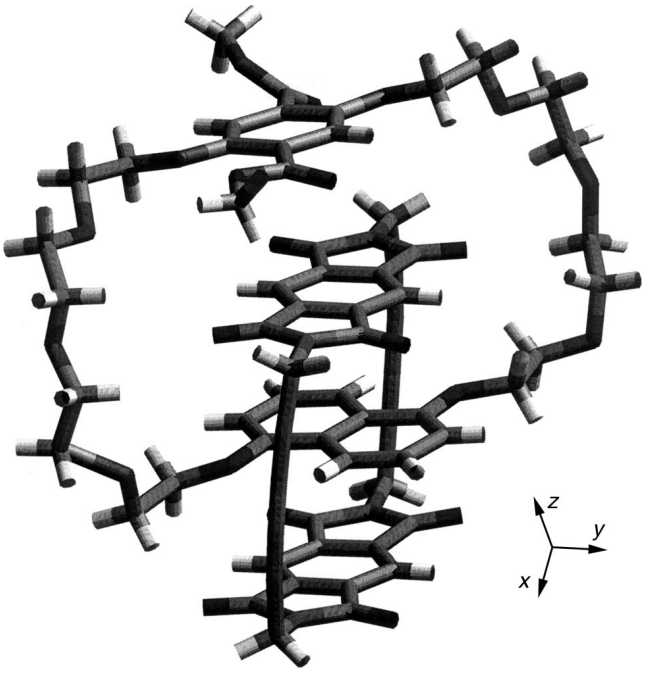


Fig. 4 Alternative view of the solid-state structure of **17** revealing the offset of the ester substituted aromatic ring from the ordered stack of donor and acceptor units.

wiched between the two π-accepting pyromellitimide units, the fact that the diester unit of the crown macrocycle seemingly does not establish donor–acceptor interactions indicates that it should, at best, be regarded as being a π-neutral spectator. In a packing diagram, this reluctant component of the catenane is revealed to be only around 3.5 Å distant from a pyromellitimide unit of an adjacent catenane in a linear stack. However, the overlap of these two residues is not one which would be expected to offer an additional stabilisation in the form of donor–acceptor complex formation; more likely this arrangement is a simple product of close packing effects.

The polyether chains of the crown component exhibit the *gauche* conformations frequently encountered in these macrocycles; the ester carbonyl groups of the benzene residue are twisted out of the plane of the aromatic system by 13 and 47°. The naphthalene diether residue is inserted centrosymmetrically through the cavity of the diimide macrocycle and the planes of the respective π-rich and π-poor components define substantial angles of 4–5°, a far greater deviation from co-planarity than that observed in the solid-state structure of the closely related [2]catenane **9**.[2] The angles at the four sp^3 corners of the diimide macrocycle are close to the ideal tetrahedral angle (average N–CH_2–C 109.3°). As with earlier catenanes of this type, the strain in this macrocycle is accommodated in the acetylenic links (average C–C≡C 173.2°) and by bowing of the N–CH_2 bonds out of the plane of the diimide components (4.8–9.5°). These structural features are in accord with those made for the same diimide macrocyclic component when incorporated within two previously determined catenane structures.[2,3] However, each of these previous structures also revealed this component macrocycle to possess a distinct helical twist; the N–N vectors within each diimide sub-unit defined angles as great as 15°. The axes of the diimides in [2]catenane **17** are only 1.8° from parallel; the substantial twist angle of 15° observed in the solid-state structure of [2]catenane **9** was presumed to be the result of reducing and optimising interplanar spacings between complementary aromatic components. Accordingly, the far smaller twist angle in **17** increases the distance between the diimide sub-units and perhaps in turn necessitates the observed deviation from co-planarity of the included naphthalene diether.

Conclusions

We have demonstrated that our catenane assembly method can tolerate the introduction of additional functionality in the crown macrocycle. Such synthetic elaboration has previously been achieved for other families of catenanes, principally with a view to providing an anchor for polymerisation.[7,17] The provision of a potential attachment point also opens possibilities for surface immobilisation or metal co-ordination. The former of these possibilities provides a means by which to attach a "primer" macrocycle to a solid resin support, a potentially important step in the development of a recursive method to install successive rings in a linear [*n*]catenane.

The conversion of the acetylenic links in these [2]catenanes to saturated methylene chains represents a rare example of *substantial* structural modification of a macrocycle within a pre-assembled interlocked structure. Though there exist examples of [2]catenanes where the component macrocycles have been modified by connection in a polymer chain,[17] or by hydrogenation of an olefin within a macrocyclic constituent,[18] the conversion of two four-carbon linear links to fully saturated chains, within a formerly rigid macrocycle, alters the relationship between the catenane rings in a manner that is made readily apparent by ^{1}H NMR. It seems improbable that the resulting hexyl-linked saturated catenanes could be prepared from any precursor other than the parent catenanes. For example, the minimum number of carbons needed for macrocyclic closure by olefin metathesis is nine.[4] Of course, once mechanically interlocked, the constituent components of any topologically complex molecule can be modified with impunity, as long as no bonds are broken within the macrocyclic loops, since no regard need be given to maintaining the presence of the non-covalent interactions employed in assembling the system.[19] Clearly this is the converse of the situation faced when assembling an interlocked molecule since all contemporary approaches, including that described here, are predicated on establishing and maintaining ordered non-covalent interactions.

Experimental

General methods and materials

All chemicals were purchased from the Aldrich Chemical Company and were used without further purification. Solvents were dried according to literature procedures: acetone from 4 Å molecular sieves, DMF from CaH_2 (under reduced pressure). TMEDA was distilled prior to use. Anhydrous CuCl[20] and $CuCl_2$[21] were prepared according to literature procedures, stored in an efficient dessicator and used within one week of preparation. Ditosylate **4** and [2]catenanes **9** and **11** were prepared as reported.[2] 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, residual solvent peaks were used as a reference, *J* values are given in Hz; the following abbreviations are employed: pyro (pyromellitimide), naph (naphthalene diimide), benz (benzene). Liquid secondary ion mass spectrometry (LSIMS) was performed using a Kratos MS50 double focusing electric/magnetic sector instrument (3-nitrobenzyl alcohol matrix). Electrospray mass spectrometry (ESMS) 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 (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).

Syntheses

Methyl (1,5-naphtho)-35-crown-10-(1,3-dioxybenzene-5-carboxylate) 6.[7] A solution of ditosylate **4** (2.33 g, 2.8 mmol) and methyl 3,5-dihydroxybenzoate **5** (0.53 g, 2.8 mmol) in dry acetone (100 mL) was added dropwise over 3 h under Ar to a refluxing suspension of K_2CO_3 (1.93 g, 14.0 mmol) in dry acetone (200 mL). The reaction was stirred at reflux for three days, cooled, filtered and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water and the organic layer separated, dried ($MgSO_4$) and evaporated. The pure crown was obtained by column chromatography (SiO_2; $CHCl_3$–Et_2O–MeOH, 30 : 69 : 1 v : v) to afford the crown (R_f = 0.25) as a yellow oil that slowly solidified on standing (543 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8 Hz, 2 H; H_c), 7.29 (t, J = 8 Hz, 2 H; H_b), 7.10 (d, J = 2 Hz, 2 H; H_e), 6.75 (d, J = 8 Hz, 2 H; H_a), 6.43 (t, J = 2 Hz, 1 H; H_d), 4.22 (m, 4 H; OCH_2), 3.95 (t, 4 H; OCH_2), 3.86 (overlapping m, 4 H; OCH_2 and s, 3 H, OCH_3), 3.78 (m, 4 H; OCH_2), 3.70–3.58 (m, 16 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.82, 154.34, 131.72, 127.96, 125.10, 114.63, 108.04, 106.38, 105.79, 76.77, 71.06, 70.92, 70.85, 69.83, 69.75, 68.15, 67.69, 52.17.

Dimethyl 2,5-dihydroxyterephthalate 7. Concentrated H_2SO_4 (10 drops) was added to a warm suspension of 2,5-dihydroxyterephthalic acid (1.94 g, 9.8 mmol) in MeOH (40 mL). The mixture was refluxed overnight after which the suspension was cooled and filtered to afford the dimethyl ester as a fluorescent yellow powder (1.72 g, 78%). mp 176–177 °C (lit.[22] 177–179 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ 10.05 (s, 2 H, OH), 7.46 (s, 2 H, CH), 3.96 (s, 6 H, Me). ^{13}C NMR (90 MHz, $CDCl_3$): δ 169.44, 152.90, 118.32, 117.75, 52.71.

Dimethyl-(1,5-naphtho)-36-crown-10-(1,4-dioxybenzene-2,5-dicarboxylate) 8. A solution of ditosylate **4** (0.88 g, 1.1 mmol) and dimethyl 2,5-dihydroxyterephthalate **7** (0.24 g, 1.1 mmol) in dry acetone (75 mL) was added dropwise over 3 h under Ar to a refluxing suspension of K_2CO_3 (0.76 g, 5.5 mmol) in dry acetone (150 mL). The reaction was stirred at reflux for four days, cooled, filtered and evaporated to dryness under reduced pressure. The residue was partitioned between CH_2Cl_2 and water and the organic layer separated, dried ($MgSO_4$) and evaporated. The pure product was obtained by column chromatography (SiO_2; $CHCl_3$–MeOH, 93 : 7 v : v) to afford the crown as a slowly crystallising colourless oil (205 mg, 27%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8 Hz, 2 H; H_c), 7.21 (t, J = 8 Hz, 2 H and s, 2 H; H_b and H_d), 6.68 (d, J = 8 Hz, 2 H; H_a), 4.19 (t, 4 H; OCH_2), 3.97 (t, 4 H; OCH_2), 3.81–3.65 (overlapping m, 24 H, OCH_2 and s, 6 H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.60, 154.24, 151.86, 126.67, 124.97, 117.42, 114.54, 112.62, 105.68, 77.51, 77.00, 76.49, 70.84, 69.88, 69.72, 69.54, 68.02, 52.11. ESI-MS (positive-ion) m/z (%): 720.2 $[M + NH_4]^+$ (77), 671.1 $[M - OMe]^+$ (100): HR-LSIMS: $C_{36}H_{46}O_{14}Na$ requires 725.279, found 725.722. Found C 61.31, H 6.55; $C_{36}H_{46}O_{14}$ requires C 61.53, H 6.60%.

[2]-{[Cyclobis(pyromellitimidehexa-2,4-diyne)]-[methyl(1,5-naphtho)-35-crown-10-(1,3-dioxybenzene-5-carboxylate)]}-catenane 13. To dry DMF (20 mL) were added crown **6** (217 mg, 0.34 mmol) and bis(acetylene) **2** (196 mg, 0.68 mmol) in an atmosphere of dry air. To the stirred mixture was added anhydrous CuCl (1.70 g, 17.0 mmol) and anhydrous $CuCl_2$ (450 mg, 3.4 mmol) and the reaction was stirred for two days. The mixture was then diluted with dichloromethane (50 mL), extracted with water (3 × 50 mL), dried ($MgSO_4$) and evaporated. Residual DMF was removed under high vacuum and the residue purified by column chromatography (SiO_2; MeOH–$CHCl_3$, 1 : 10 v : v) followed by preparative TLC (SiO_2; MeOH–$CHCl_3$, 1 : 10) to afford the [2]catenane as a deep red solid (124 mg, 30%); mp > 200 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (s, 4 H; H_{pyro}), 6.91 (d, J = 8 Hz, 2 H; H_c), 6.73 (t, J = 8 Hz, 2 H; H_b), 6.66 (d, J = 7.6 Hz, 2 H; H_a), 6.52 (s, 2 H; H_e), 6.11 (s, 1 H; H_d), 4.46 (AB d, 4 H, J = 18 Hz; NCH_2), 4.31 (AB d, 4 H, J = 18 Hz; NCH_2), 4.18 (m, 4 H; OCH_2), 4.00 (m, 4 H; OCH_2), 3.90 (m, 4 H; OCH_2), 3.86 (m, 4 H; OCH_2), 3.75 (m, 16 H; OCH_2), 3.67 (s, 3 H; OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.94, 164.17, 159.22, 154.48, 134.89, 131.44, 125.88, 124.65, 116.21, 112.73, 106.75, 106.54, 105.81, 75.75, 70.96, 70.52, 69.60, 69.32, 69.13, 68.64, 67.56, 52.11, 27.99. ESI-MS (positive-ion) m/z (%): 1248.9 $[M + Na]^+$ (100), 1265.1 $[M + K]^+$ (20), 1242.1 $[M + NH_4]^+$ (100). HR-LSIMS: $C_{66}H_{56}N_4O_{20}Na$ requires 1247.338, found 1247.334.

[2]-{[Cyclobis(1,4,5,8-naphthalenetetracarboxylic-diimidehexa-2,4-diyne)][methyl(1,5-naphtho)-35-crown-10-(1,3-dioxybenzene-5-carboxylate)]}catenane 15. A solution of crown **6** (100 mg, 0.16 mmol) and bis(acetylene) **3** (91 mg, 0.31 mmol) in dry DMF (8 mL) was treated with anhydrous CuCl (0.96 g, 9.6 mmol) and anhydrous $CuCl_2$ (0.22 g, 1.6 mmol) and the mixture stirred in an atmosphere of dry air for two days. The reaction mixture was then poured into water (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The organic extracts were then dried ($MgSO_4$) and evaporated under high vacuum to afford a residue which was purified by column chromatography (SiO_2; MeOH–$CHCl_3$, 1 : 10 v : v) followed by preparative TLC (SiO_2; MeOH–$CHCl_3$, 1 : 10 v : v) to afford the [2]catenane as a purple solid (42 mg, 20%). mp > 200 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8 Hz, 4 H; H_{naph}), 8.10 (d, J = 8 Hz, 4 H; H_{naph}), 6.65 (d, J = 8 Hz, 2 H; H_b), 6.55 (s, 2 H; H_e), 6.32 (d, J = 8 Hz, 2 H; H_c), 5.83 (d, J = 8 Hz, 2 H; H_a), 4.86 (s, 1 H; H_d), 4.80 (AB d, 4 H, J = 18 Hz; NCH_2), 4.73 (AB d, 4 H, J = 18 Hz; NCH_2), 3.97 (s, 3 H; OCH_3), 3.94, 3.86, 3.79, 3.70, 3.49, 3.30 (6 × m, 32 H, OCH_2). ESI-MS (positive-ion) m/z (%): 1342.1 $[M + NH_4]^+$ (100). HR-LSIMS: $C_{74}H_{60}N_4O_{20}Na$ requires 1347.369, found 1347.371.

[2]-{[Cyclobis(pyromellitimidehexa-2,4-diyne)]-[dimethyl-(1,5-naphtho)-36-crown-10-(1,4-dioxybenzene-2,5-dicarboxylate)]}catenane 17. A solution of crown **8** (177 mg, 0.25 mmol) and bis(acetylene) **2** (140 mg, 0.48 mmol) in dry DMF (6 mL) was treated with anhydrous CuCl (0.97 g, 9.7 mmol) and anhydrous $CuCl_2$ (0.23 g, 1.7 mmol) and the mixture stirred in an atmosphere of dry air for two days. The reaction mixture was then poured into water (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The organic extracts were then dried ($MgSO_4$) and evaporated under high vacuum to afford a residue which was purified by column chromatography (SiO_2; MeOH–$CHCl_3$, 1 : 10 v : v) followed by preparative TLC (SiO_2; MeOH–$CHCl_3$, 2 : 10 v : v) to afford the [2]catenane as an orange solid (97 mg, 29%). mp > 200 °C (decomp.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 4 H; H_{pyro}), 6.91 (d, J = 8 Hz, 2 H), 6.81 (s, 1 H), 6.76 (t, J = 8 Hz, 2 H), 6.59 (d, 2 H), 4.40 (AB d, 4 H, J = 17 Hz; NCH_2), 4.32 (AB d, 4 H, J = 17 Hz; NCH_2), 4.19 (m, 4 H; OCH_2), 4.03 (m, 4 H; OCH_2), 3.93 (m, 4 H; OCH_2), 3.85 (m, 4 H; OCH_2), 33.77 (m, 16 H; OCH_2), 3.66 (s, 6 H; OCH_3). ESI-MS (positive-ion) m/z (%): 1300.0 $[M + NH_4]^+$ (100). HR-LSIMS: $C_{68}H_{58}N_4O_{22}$ requires 1282.354, found 1282.350.

General procedure for catenane hydrogenation

To a solution of the catenane (typically 20 mg) in MeOH (10 mL) and $CHCl_3$ (10 mL) was added palladium on carbon catalyst (5 mg). The mixture was degassed and saturated with hydrogen (3 cycles) and then stirred under the hydrogen atmosphere. Reaction progress was monitored by LC-MS and after 16 h the chromatographic analysis revealed the presence of a single component corresponding to the appropriate fully saturated catenane derivative. The catalyst was subsequently removed by filtration through a 2 cm bed of Celite and the filtrate evaporated under reduced pressure. The pure hydrogenated catenane products were further purified by, occasionally repeated, preparative TLC (SiO_2; MeOH–$CHCl_3$, 1 : 10 v : v). ^{1}H NMR spectra for naphthalene diimide derived [2]catenanes **12** and **16** were extremely broad even at elevated temperature and no assignments were possible.

[2]Catenane 10. Hydrogenation of [2]catenane **9** (21 mg, 0.02 mmol) gave [2]catenane **10** as a yellow-orange solid (17 mg, 81%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 120 °C): δ 6.91–6.89 (m, 4 H), 6.86–6.83 (m, 4 H), 6.81–6.67 (m, 4 H), 6.57–6.53 (m, 4 H), 4.20 (t, J = 8 Hz, 8 H; OCH_2), 4.05–4.01 (m, 8 H; OCH_2), 3.94 (s, 16 H; OCH_2), 3.58–3.56 (m, 8 H; NCH_2), 1.81 (br s, 8 H; NCH_2CH_2), 1.58 (br s, 8 H; $NCH_2CH_2CH_2$). ESI-MS (positive-ion) m/z (%): 1256.8 $[M + Na]^+$ (100), 1234.8 $[M + H]^+$ (20). HR-LSIMS: $C_{68}H_{72}N_4O_{18}Na$ requires 1255.474, found 1255.474.

Table 1 Crystal data and data collection parameters for **17**

Formula	$C_{68}H_{58}N_4O_{22}$
M	1283.18
T/K	150(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	15.742(2)
b/Å	17.522(2)
c/Å	21.814(3)
V/Å^3	6015.9(13)
Z	4
μ/mm^{-1}	0.107
Reflections collected	35854
Independent reflections	13503
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0751$, $wR_2 = 0.1946$
R indices (all data)	$R_1 = 0.1261$, $wR_2 = 0.2145$

[2] Catenane 12. Hydrogenation of [2]catenane **11** (15 mg, 0.01 mmol) gave [2]catenane **12** as a purple solid (14 mg, 90%). LSIMS (positive-ion) m/z (%): 1332.2 M^+ (15%). HR-LSIMS: $C_{76}H_{76}N_4O_{18}Na$ requires 1356.445, found 1356.441.

[2] Catenane 14. Hydrogenation of [2]catenane **13** (30 mg, 0.02 mmol) gave **14** as a yellow solid (26 mg, 85%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 120 °C): δ 7.18 (s, 4 H), 7.10 (s, 1 H), 6.89–6.87 (m, 2 H), 6.83–6.81 (m, 2 H), 6.80–6.71 (m, 4 H), 4.32 (t, $J = 8$ Hz, 4 H; OCH_2), 4.31–4.10 (m, 4 H; OCH_2), 3.97–3.95 (m, 4 H; OCH_2), 3.88 (s, 3 H; OCH_3), 3.87–3.85 (m, 4 H, OCH_2), 3.82–3.77 (m, 12 H; OCH_2), 3.71 (m, 4 H; OCH_2), 3.64–3.62 (m, 8 H; NCH_2), 1.83 (br s, 8 H; NCH_2CH_2), 1.59–1.57 (m, 8 H; $NCH_2CH_2CH_2$). ESI-MS (positive-ion) m/z (%): 1265.0 $[M + Na]^+$ (100). HR-LSIMS: $C_{66}H_{72}N_4O_{20}Na$ requires 1263.464, found 1263.467.

[2]Catenane 16. Hydrogenation of [2]catenane **15** (30 mg, 0.02 mmol) gave [2]catenane **16** as a purple solid (19 mg, 60%). ESI-MS (positive-ion) m/z (%): 1347.4 $[M + Na]^+$ (60). HR-LSIMS: $C_{74}H_{76}N_4O_{20}Na$ requires 1363.495, found 1363.497.

[2]Catenane 18. Hydrogenation of [2]catenane **17** (14 mg, 0.01 mmol) gave [2]catenane **18** as a yellow solid (11 mg, 77%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 120 °C): δ 7.02 (s, 4 H; H_{pyro}), 6.84 (s, 2 H; H_{benz}), 6.80 (d, $J = 8$ Hz, 2 H), 6.73 (t, $J = 8$ Hz, 2 H), 6.63 (d, $J = 8$ Hz, 2 H), 4.33 (t, $J = 8$ Hz, 4 H; OCH_2), 4.10 (t, $J = 8$ Hz, 4 H; OCH_2), 3.95–3.79 (m, 24 H; OCH_2), 3.74 (s, 6 H; OCH_3), 3.63–3.61 (m, 8 H; NCH_2), 1.86 (br s, 8 H; NCH_2CH_2), 1.64 (br s, 8 H; $NCH_2CH_2CH_2$). ESI-MS (positive-ion m/z (%): 1316.9 $[M + Na]^+$ (100%): HR-LSIMS: $C_{68}H_{74}N_4O_{22}Na$ requires 1321.469, found 1321.468.

Crystal data collection and refinement

Small single crystals of [2]catenane **17** were grown by slow cooling of a d_6-DMSO–H_2O solution. Data were collected on a Bruker SMART CCD diffractometer at the single-crystal diffraction station 9.8 at the Daresbury Laboratory Synchrotron Radiation Source (UK), crystal and data collection parameters are listed in Table 1: corrections were applied for incident beam decay, the structure was solved by direct methods and refined by full-matrix least-squares analysis on F^2. The polyether chains of the crown exhibited a certain amount of disorder, though it was possible to model a portion of one of the ether chains with two distinct conformations. A site occupancy ratio of 60/40 for the two chains gave satisfactory thermal parameters for the atoms concerned. One of the methyl ester groups also appeared to be disordered and was modelled over two sites, this time with a site occupancy ratio of 50/50.

CCDC reference number 440/133. See http://www.rsc.org/suppdata/nj/1999/897/ for crystallographic files in cif. format.

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References

1 D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
2 D. G. Hamilton, J. E. Davies, L. Prodi and J. K. M. Sanders, *Chem. Eur. J.*, 1998, **4**, 608.
3 D. G. Hamilton, L. Prodi, N. Feeder and J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1057.
4 D. G. Hamilton, N. Feeder, S. J. Teat and J. K. M. Sanders, *New J. Chem.*, 1998, **22**, 1019.
5 D. G. Hamilton and J. K. M. Sanders, *Chem. Commun*, 1998, 1749.
6 D. G. Hamilton, M. Montalti, L. Prodi, M. Fontani, P. Zanello and J. K. M. Sanders, submitted for publication.
7 S. Menzer, A. J. P. White, D. J. Williams, M. Belohradsky, C. Hamers, F. M. Raymo, A. N. Shipway and J. F. Stoddart, *Macromolecules*, 1998, **31**, 295.
8 R. Wolf, M. Asakawa, P. R. Ashton, M. Gomez-Lopez, C. Hamers, S. Menzer, I. W. Parsons, N. Spencer, J. F. Stoddart, M. S. Tolley and D. J. Williams, *Angew. Chem., Int. Ed.*, 1998, **37**, 975.
9 C. O. Dietrich-Buchecker, A. Khemiss and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1986, 1376.
10 A. Viehbeck, M. J. Goldberg and C. A. Kovac, *J. Electrochem. Soc.*, 1990, **137**, 1460.
11 G. Heywang, L. Born, H. G. Fitzky, T. Hassel, J. Hocker, H. K. Muller, B. Pittel and S. Roth, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 483.
12 D. G. Hamilton, D. E. Lynch, K. A. Byriel and C. H. L. Kennard, *Aust. J. Chem.*, 1997, **50**, 439.
13 Y. Tong, D. G. Hamilton, J.-C. Meillon and J. K. M. Sanders, submitted for publication.
14 K. N. Houk, S. Menzer, S. P. Newton, F. M. Raymo, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 1479.
15 P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193.
16 F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, M. Lipton, C. Caufield, G. Chang, T. Hendrickson and W. C. Still, *J. Comput. Chem.*, 1990, **11**, 440.
17 J. L. Weidmann, J. M. Kern, J.-P. Sauvage, Y. Geerts, D. Muscat and L. Mullen, *Chem. Commun.*, 1996, 1243.
18 B. Mohr, M. Weck, J.-P. Sauvage and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1308.
19 T. J. Kidd, D. A. Leigh and A. J. Wilson, *J. Am. Chem. Soc.*, 1999, **121**, 1599.
20 R. N. Keller and H. D. Wycoff, *Inorg. Synth.*, 1946, **II**, 1.
21 A. R. Pray, *Inorg. Synth.*, 1957, **V**, 153.
22 M. F. Ansell and G. C. Culling, *J. Chem. Soc.*, 1961, 2914.
23 Cerius^2 (version 3), BLOSYM/Molecular Simulations, San Diego, 1997.

Paper 9/04174E