Reversible five-component assembly of a [2]catenane from a chiral metallomacrocycle and a dinaphtho-crown ether

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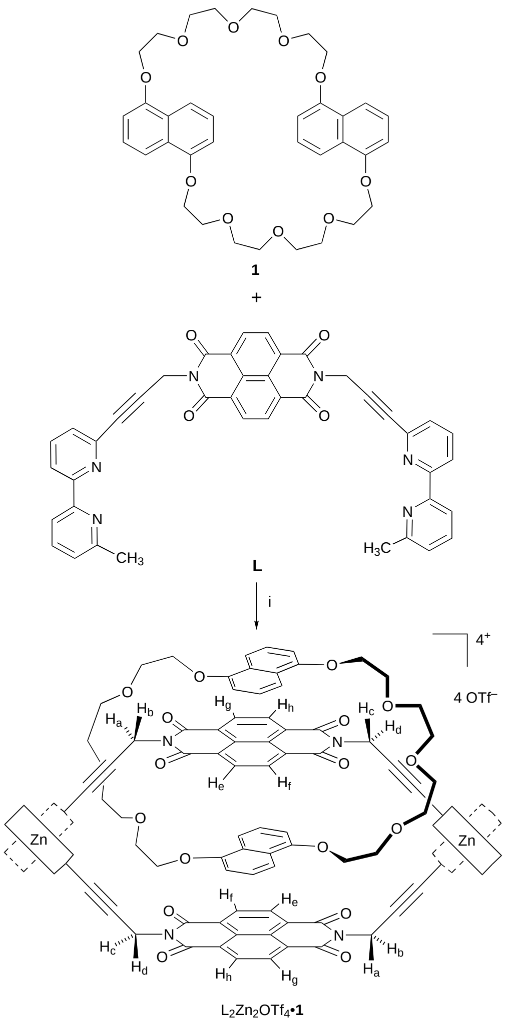
Addition of a dinaphtho-crown ether to the components of a chiral metallomacrocycle affords a [2]catenane as the exclusive thermodynamic product; the reversible assembly process is driven by a combination of zinc(II)–bipyridyl ligation and π-donor/π-acceptor interactions between the electronically complementary aromatic components.

In recent years a range of non-covalent interactions have been employed in the template directed kinetically controlled syntheses of wholly organic catenated structures, including π-association of aromatic rings,[1] metal–ligand coordination[2] and hydrogen-bonding interactions.[3–5] The application of these strategies results in mechanically interlocked ring systems, whose separation would require the cleavage of a covalent bond.[6] Catenanes incorporating an organic ring and a magnesium metallomacrocycle,[7] as well as interlocked metallomacrocyclic structures,[8,9] have also been reported: incorporation of labile metal coordination sites into the ring introduces the possibility of reversibility into the threading process, although this feature has not hitherto been fully explored.[10] We now report the use of both metal ligation and donor–acceptor interactions to achieve quantitative catenane synthesis under reversible, thermodynamically controlled conditions.

We reported the design and synthesis of ligand L which assembles exclusively into a helical [2 + 2] metallomacrocycle in the presence of zinc(II) ions and a complementary aromatic substrate.[11,12] The π-electron rich aromatic guest plays a crucial role in the assembly process, effecting the selection of its optimal metallomacrocycle host from the range of geometries and oligomers present in solutions containing only L and Zn^{II}. The driving force for the formation of the supramolecular complex is provided by the π-donor/π-acceptor stacking interactions present in the final complex. Similar programmed recognition features between π-electron deficient aromatic diimides and the π-electron rich dinaphtho-crown ether **1** have been used to prepare neutral [2]catenanes in good yield *via* irreversible acetylenic couplings.[13–15] In light of these results we have utilised the electron-deficient diimide present in L and the electron-rich diethers of crown **1** to promote the assembly of a chiral [2]catenane in a thermodynamically controlled association process.

Titration of a solution of **1** into a CD_3CN solution of $L_2Zn_2OTf_4$ (in equilibrium with other oligomers)[11,12] resulted in a change from pale yellow to purple–maroon, indicative of the formation of a π-donor/π-acceptor complex (Scheme 1). Electrospray mass spectrometry of the complex was consistent with formation of the catenane, with peaks at *m/z* 530.8 $[L_2Zn_2\cdot\mathbf{1}]^{4+}$, 757.8 $[L_2Zn_2OTf\cdot\mathbf{1}]^{3+}$ and 1210.8 $[L_2Zn_2OTf_2\cdot\mathbf{1}]^{2+}$; no peaks corresponding to the individual components were detected.

Unambiguous evidence for formation of the catenane‡ was obtained by analysis of the ^1H NMR spectra obtained on titration of **1** into a solution of L and zinc(II) triflate. The resulting spectrum exhibits a new set of sharp signals [Fig. 1(*b*)]; an identical spectrum was also obtained upon dissolution of equimolar amounts of L, zinc(II) triflate and 0.5 equiv. of **1** in CD_3CN. Two distinct environments for the 'inner' and 'outer' naphthyl protons of **1** were detected,‡ both sets of signals resonating at higher field to those of 'free' **1**, an observation consistent with slow exchange of the crown naphthyl rings on the NMR chemical shift timescale. In the methylene region of the spectrum the predominant AB system of the $L_2Zn_2OTf_4$ host [Fig. 1(*a*)] is split into two AB systems upon interlocking with **1** [Fig. 1(*b*)], consistent with the helical catenated structure§ being templated out of the equilibrating mixture of complexes. Similar distinct changes were observed in the aromatic region of the spectrum where the protons of the naphthalenediimide spacer evolved from a singlet in the equilibrating pre-complexation mixture [Fig. 1(*a*)] to four doublets in the interlocked complex [Fig. 1(*b*)]. These observations taken in isolation suggest that the two diimide units of $L_2Zn_2OTf_4\cdot\mathbf{1}$, like the crown naphthyl rings, exist in 'inner' and



Scheme 1 *Reagents and conditions*: i, $Zn(OTf)_2$, acetonitrile

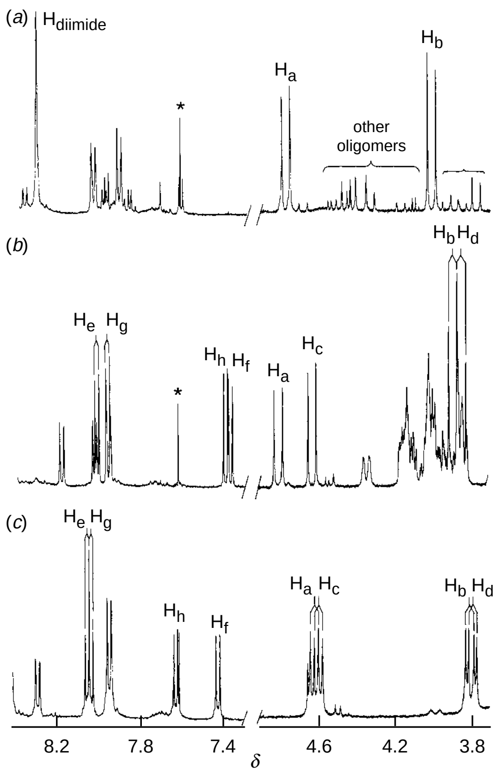


Fig. 1 ^{1}H NMR spectra (400 MHz, CD_3CN) of the methylene and aromatic regions of (*a*) $L_2Zn_2OTf_4$ (in equilibrium with oligomers) at 300 K, (*b*) $L_2Zn_2OTf_4 \cdot \mathbf{1}$ at 300 K and (*c*) $L_2Zn_2OTf_4 \cdot \mathbf{2}$ at 235 K; * impurity

'outer' environments (with respect to **1**). However, the appearance of similar splitting patterns in the complex formed between $L_2Zn_2OTf_4$ host and 1,5-dimethoxynaphthalene **2** at 235 K [Fig. 1(*c*)] indicates that the two diimide units of $L_2Zn_2OTf_4 \cdot \mathbf{1}$ are in the same environment (assigned as shown in Scheme 1).¶|| This observation is consistent with an exchange process in which the 'outer' naphthyl ring of **1** is able to sweep around the periphery of $L_2Zn_2OTf_4$, rendering the two diimide components equivalent. This behaviour parallels that displayed by our recently reported neutral [2]catenanes.[13,14]

The catenane is remarkably stable: up to 350 K the maroon colour of the interlocked complex is retained and no signal coalescence is observed in the NMR spectrum. For comparison, the analogous complex formed with **2** contained exchange broadened resonances at room temperature; these coalesce on heating to 350 K to give two methylene doublets and a broad signal for the diimide protons, while at 235 K sharp, slowly-exchanging multiple resonances are observed [Fig. 1(*c*)]. Although the exact orientation of the bound naphthyl rings between the two aromatic diimide spacers is unknown, the optimal stacking of **1**, and also **2** (at 235 K), with $L_2Zn_2OTf_4$ results in overall asymmetry in this system.

We have shown that a stable [2]catenane can be non-covalently assembled from five components using pre-programmed recognition sites. The lability of the zinc(II)–bipyridyl coordination complex is an important feature of this system as it facilitates opening of the [2 + 2] metallomacrocycle to allow the thermodynamically favourable interlocking process in the presence of the crown. The access to a range of coordination geometries for zinc(II) is probably also important in optimising the electrostatic interactions between the π-complementary components. The principles embodied in the reversible nature of this assembly process should facilitate template-directed syntheses of more complex organic and supramolecular structures that would otherwise be difficult to obtain, and dynamic combinatorial libraries of mechanically interlocked structures.[16]

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Notes and References

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‡ *Selected data* for $L_2Zn_2OTf_4 \cdot \mathbf{1}$: ^{1}H NMR ($CD_3CN$, 300 K): $L_2Zn_2OTf_4$ resonances, δ 2.51 (6 H, s, 2 × CH_3), 2.63 (6 H, s, 2 × CH_3), 3.82 and 4.62 (4 H, AB system, *J* 17.3 Hz, H_a and H_b), 3.87 and 4.79 (4 H, AB system, *J* 17.2 Hz, H_c and H_d), 7.37 (2 H, d, *J* 7.6 Hz, H_f), 7.40 (2 H, d, *J* 7.6 Hz, H_h), 7.96 (2 H, d, *J* 7.8 Hz, 2 × $H^{5''}$), 7.97 (2 H, d, *J* 7.6 Hz, H_g), 8.02 (2 H, d, *J* 7.6 Hz, H_e), 8.03 (2 H, d, *J* 7.8 Hz, 2 × $H^{5''}$), 8.19 (2 H, d, *J* 8.1 Hz, 2 × $H^{5'}$), 8.42 (2 H, d, *J* 8.1 Hz, 2 × $H^{5'}$), 8.52 (2 H, app t, 2 × $H^{4''}$), 8.62 (2 H, app t, 2 × $H^{4''}$), 8.76 (2 H, d, *J* 7.9 Hz, 2 × $H^{3''}$), 8.81–8.85 (4 H, m, 2 × $H^{3''}$ and 2 × $H^{4'}$), 8.98–9.04 (4 H, app t, 4 × $H^{3'}$), 9.14 (2 H, app t, 2 × $H^{4'}$). **1**, δ 3.54–3.60 (2 H, m, CH_2), 3.63–3.70 (2 H, m, CH_2), 3.80–4.18 (26 H, m, 13 × CH_2), 5.29 [2 H, dd, *J* 2.3, 6.1 Hz, H^2 and H^6 (inner)], 5.68–5.73 [4 H, m, H^3, H^4, H^7 and H^8 (inner)], 5.94 [2 H, d, *J* 7.6 Hz, H^2 and H^6 (outer)], 6.42 [2 H, app t, H^3 and H^7 (outer)], 6.52 [2 H, d, *J* 8.4 Hz, H^4 and H^8 (outer)]; *m/z* 530.8 ($L_2Zn_2 \cdot \mathbf{1}$, $C_{120}H_{96}N_{12}O_{18}Zn_2$, M^{4+}), 758.7 ($L_2Zn_2OTf \cdot \mathbf{1}$, $C_{121}H_{96}F_3N_{12}O_{21}SZn_2$, M^{3+}) 1210.8 ($L_2Zn_2OTf_2 \cdot \mathbf{1}$, $C_{122}H_{96}F_6N_{12}O_{24}S_2Zn_2$, M^{2+}).

§ The helical configuration was assigned by comparison with our previous studies in which the metallomacrocycle host was characterised in both solution and the solid state.[11,12]

¶ The labelling of spin systems in Scheme 1 is arbitrary; unequivocal assignment of $H_{a,b}$ and $H_{c,d}$ was not possible as NOE crosspeaks to $H_{e,f,g,h}$ were not detected.

|| Two-dimensional NOESY spectra of the catenane complex revealed the expected proton connectivities and additional cross-peaks from the inner naphthyl protons to the two bipyridyl $H^{5'}$ environments as well as to some of the naphthalene diimide protons.

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