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Host–guest interactions template: the synthesis of a [3]catenane

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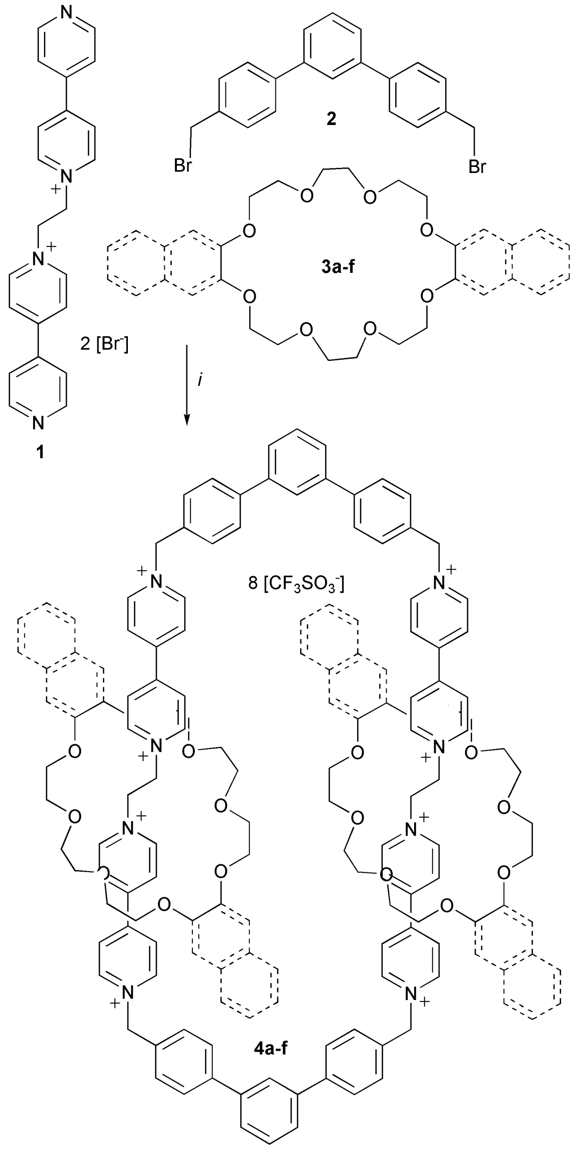
Formation of a [3]catenane containing dibenzo-24-crown ether wheels and a large dipyridiniumethane ring is templated by formation of a host–guest adduct between the [3]catenane and the external crown ether.

The synthesis of high order ($n > 2$) interlocked assemblies such as [*n*]catenanes.[1] [*n*]molecular necklaces[2] and [*n*]rotacatenanes[3] remains a considerable challenge for supramolecular chemists. One of the major problems is that, regardless of design, there is always the requirement of forming at least one large ring during the self-assembly process. A potential strategy to aid ring-closure involves the use of an external template, for example, a guest for a host catenane.

We describe herein, i) a one-step, self-assembly procedure for the preparation of [3]catenanes utilising the 1,2-bis(4,4′-bipyridinium)ethane–24C8 motif[4] and a terphenyl spacer unit,[5] ii) evidence that dibenzo-24-crown ether (DB24C8) acts as an efficient template/guest for the assembly of a [3]catenane/host and iii) the X-ray crystal structure of the [3]catenane–DB24C8 host–guest complex.

Scheme 1 outlines the preparation of a series of [3]catenanes **4a–f** from the pyridinium axle **1**[Br]$_2$, the bis(bromomethyl)terphenyl spacer **2** and crown ethers **3a–f**. ^{1}H NMR spectra showed evidence of products containing both threaded and non-threaded axles but it was not possible to quantitatively distinguish among the target [3]catenanes **4a–f**, possible [2]catenanes and the naked pyridinium ring, **5**. The efficiency of ring closure could be determined by calculating the overall yields of the cyclic products for six different crown ethers. Fig. 1 shows that the formation of products with DB24C8 is two to three times more favourable than for other crown ethers. In order to understand this anomaly, the [3]catenane **4d** was isolated by column chromatography using a 7 : 1 : 12 : 10 mixture of MeOH, MeNO$_2$, 2 M NH$_4$Cl(aq) and DMF. The ^{1}H NMR spectrum of **4d** showed evidence of a symmetrical species containing equal portions of DB24C8, 1,2-bis(4,4′-bipyridinium)ethane and terphenyl while MS data showed major peaks at 944(100) and 1491(24) for the $[M - 2CF_3SO_3]^{2+}$ and $[M - 3CF_3SO_3]^{3+}$ ion fragments verifying formation of the [3]catenane.† Attempts to grow crystals of **4d** from a variety of solvents were not successful but in the presence of excess DB24C8, orange crystals of formula [**4d**(DB24C8·2H$_2$O)·2H$_2$O] could be grown from acetone. An X-ray diffraction study‡ verified the basic [3]catenane structure but also showed this compound to be a unique three-layered host–guest adduct. The central component is an equivalent of DB24C8 which acts a host for two hydrogen-bonded water molecules (O1W–H1WA···O12′ 2.21 Å, 163.2°, O1W–H1WB···O11′ 2.11 Å, 145.8°). At the same time this adduct is also a guest bound inside the central cavity of the [3]catenane (Fig. 2) and has ion dipole (O1W···N2′ 2.88 Å) and π-stacking (centroid to centroid 3.67 Å) interactions. Additional C–H···π-interactions occur between the guest aromatic protons and one of the terphenyl aromatic rings (H···centroid 3.63 Å) while the approach of the electron-rich π-systems on the two different DB24C8 molecules is substantially larger (centroid–centroid 4.60 Å).

Dissolution of a bulk sample from the crystalline material used for X-ray crystallography provided a sample in which the host–guest ratio was by definition 1 : 1. Fig. 3 shows the DB24C8 aromatic region of the ^{1}H NMR spectra for the [3]catenane and the host–guest complex in CD$_3$CN. The upfield resonances represent the protons in the DB24C8 molecules which are part of the [3]catenane. In the host–guest complex, there are extra downfield peaks attributable to the guest DB24C8 molecule. An association constant of 2.65×10^4 M^{-1} was determined by the single-point method.[6] This relatively high value indicates that the DB24C8·(H$_2$O)$_2$ adduct is an excellent “fit” for the central cavity of the [3]catenane. The DB24C8 guest could be removed completely by repeated precipitation, and subsequent treatment of isolated **4d** with a slight excess of DB24C8 regenerated the ^{1}H NMR spectrum indicative of the host–guest complex. These results infer that



Scheme 1 *Reagents and conditions*: *i*) NaOTf(aq)–MeNO$_2$, RT, 7 days (**a**, 24C8; **b**, B24C8; **c**, N24C8; **d**, DB24C8; **e**, BN24C8; **f**, DN24C8).

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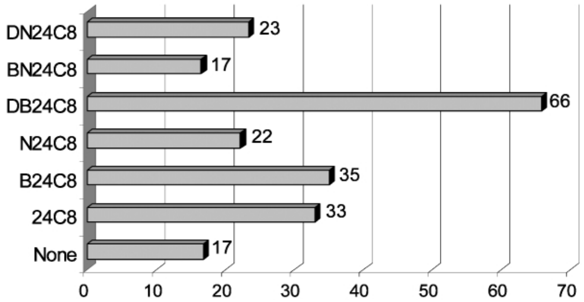

Fig. 1 Graph showing yield of cyclic products ([3]catenane, [2]catenane and “naked” ring) as a function of crown ether.

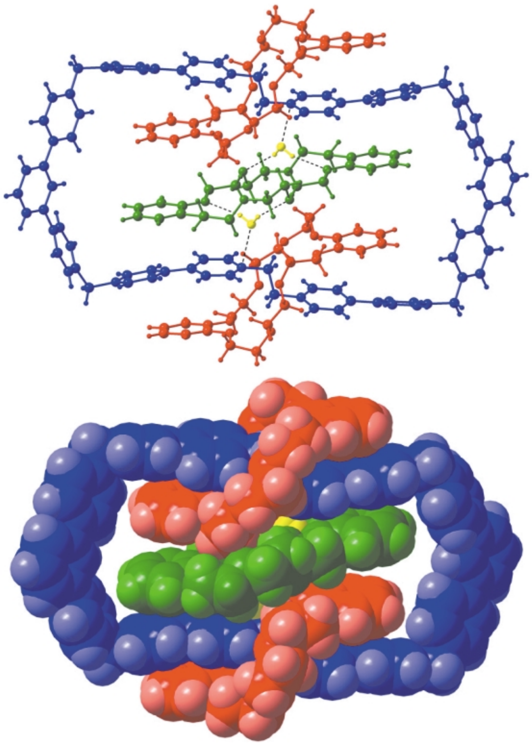

Fig. 2 Ball-and-stick (top) and space-filling (bottom) representations of the X-ray structure of **4d**, showing inclusion of the host–guest adduct DB24C8·2H2O inside the central cavity (blue = pyridinium ring, red = DB24C8 of [3]catenane, green = DB24C8 guest, yellow = water).

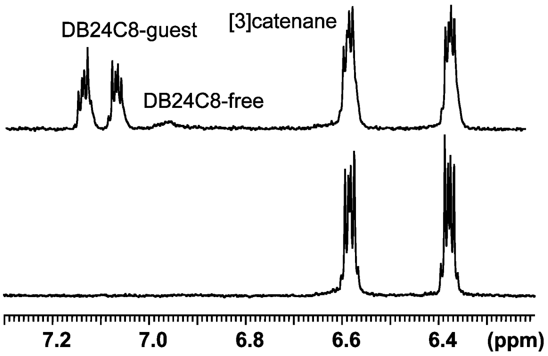

Fig. 3 ^{1}H NMR spectra of the DB24C8 aromatic region; **4d** bottom and **4d**⊂(DB24C8⊂(2H$_2$O)) top in CD$_3$CN at 2.1 × 10^{-3} M.

DB24C8 acts as an efficient template for the formation of [3]catenane **4d** by formation of the described host–guest complex. Similar interactions might allow threading of the [3]catenane to form higher order assemblies such as [$n > 3$]catenanes or [$n > 3$]rotocatenanes

Notes and references

† All preparations were carried out as described here for **4d** using various crowns for **4a–f** or no crown for **5**. [**1**]Br$_2$ (50.0 mg, 0.100 mmol) and DB24C8 (180.0 mg, 0.400 mmol) were dissolved in a two-phase NaOTf(aq)–MeNO$_2$ (3 and 7 mL) mixture. Terphenyl **2** (42.0 mg, 0.100 mol) was added and the solution stirred at RT for 7 days. The MeNO$_2$ was washed with H$_2$O (3 × 5 mL), dried over MgSO$_4$ and the solvent removed. The residue was dissolved in MeCN (10 mL) and the products were precipitated by the addition of Et$_2$O as orange solids, see Fig. 1 for yields. Catenane **4d** was purified and isolated by column chromatography using a 7 : 1 : 12 : 10 mixture of MeOH, MeNO$_2$, 2 M NH$_4$Cl(aq) and DMF. δ_H(MeCN-d$_6$, 300 K, 500 MHz): 9.26 (d, 8H, J 6.8), 8.99 (d, 8H, J 6.8), 8.20 (d, 8H, J 6.8), 8.17 (d, 8H, J 6.8), 7.89 (d, 8H, J 8.1), 7.88 (s, 2H), 7.76 (dd, 4H, J 7.6, 1.6), 7.64 (t, 2H, J 5.0), 7.62 (d, 8H, J 8.1), 6.59 (dd, 4H, J 5.9, 3.5), 6.38 (dd, 4H, J 5.9, 3.5), 5.90 (s, 4H), 5.54 (s, 4H). HRESI: (calc.) for $C_{138}H_{136}N_8F_{18}O_{34}S_6$ [M − 2OTf]$^{2+}$ m/z 1491.3593, found 1491.3535.

‡ *Crystal data*: [**4d**(DB24C8·2H$_2$O)]·(H$_2$O)$_2$: $C_{164}H_{176}F_{24}N_8O_{52}S_8$, M = 3803.61, triclinic, space group $P\bar{1}$, a = 14.531(3), b = 18.149(4), c = 19.061(4) Å, α = 63.152(3), β = 77.773(4), γ = 89.381(4)°, U = 4362.3(15) Å^3, T = 173.5(1) K, Z = 1, μ = 0.214 mm^{-1}, 13929 independent reflections (R_{int} = 0.0492). R_1 = 0.0897, wR_1 = 0.2031, (8092 reflections, $I > 2\sigma I$), R_2 = 0.1066, wR_2 = 0.2161, (all data), goodness-of-fit (F^2) = 1.115. Data were collected on a Bruker APEX CCD instrument and solutions performed using the SHELXTL 5.03 Program Library, Siemens Analytical Instrument Division, Madison, WI, USA, 1997. CCDC 221795. See http://www.rsc.org/suppdata/cc/b3/b312449e/ for crystallographic files in CIF format.[7]

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7 Ball-and-stick diagrams were prepared using DIAMOND – Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn.