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Formation of ring-in-ring complexes between crown ethers and rigid TVBox⁸⁺Received 00th January 2012,
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A rigid octacationic tetraviologen-based cyclophane, TVBox⁸⁺, is reported. It possesses a highly electron-deficient rectangular cavity with a length of 23 Å and width of 6.1 Å and is capable of encapsulating either two small π-aromatic guest molecules, such as PhMe and PhCl, simultaneously, or one large molecule, e.g., bis-1,5-dinaphtho[50]crown-14.

The past several decades have witnessed a significant advance in chemistry beyond the molecule, which was pioneered by Pedersen,¹ Cram,² and Lehn.³ During this time, various synthetic macrocyclic receptors, including crown ethers,⁴ cyclodextrins,⁵ cyclophanes,⁶ cucurbiturils,⁷ calixarenes⁸ and pillararenes,⁹ have been thoroughly investigated and shown to exhibit many unique chemical and physical properties. Cyclobis(paraquat-*p*-phenylene)¹⁰ (CBPQT⁴⁺), a highly electron-deficient cyclophane, is a landmark compound because of the essential role it has played in the field of mechanically interlocked molecules¹¹ (MIMs). CBPQT⁴⁺ tends to bind strongly small π-electron-rich guest molecules, of which 1,5-dioxy-naphthalene¹² and tetrathiafulvalene¹³ derivatives are good examples. Recently, the extended versions of CBPQT⁴⁺—namely Ex^{*n*}Box⁴⁺ (*n* = 1 and 2)—have also been prepared¹⁴, exhibiting the ability to bind a wide spectrum of large polycyclic aromatic hydrocarbons^{14a} (PAHs) and even two guest molecules simultaneously.^{14c} An attempt to synthesise Ex³Box•4PF₆, however, failed on account of its limited solubility. Instead, a derivative (Fig. 1a), Me₁₂Ex²Box⁴⁺, which has 12 methyl groups attached to the central *p*-phenylene bridges, was prepared but alas it has a sterically encumbered binding pocket as a result of repulsive interactions associated with methyl substituents.^{14b} In order to avoid the solubility and steric issues, we have identified (Fig. 1b) and synthesised an octacationic tetraviologen-based analogue, namely TVBox⁸⁺, which shares similar dimensions with Ex³Box⁴⁺, yet has a much better solubility as a result of its increased charges.

In pursuit of our interest¹⁵ in the stepwise construction of a nontrivial molecular knot—namely, the Borromean rings—from three independent macrocycles, a ‘ring-in-ring’ complex is a required key intermediate. The octacationic TVBox⁸⁺, which has a

highly electron-deficient binding site spanning the length of ~2 nm, has now been explored for its ability to bind electron-rich crown ethers to form ‘ring-in-ring’ complexes. Within the context of this present investigation, three crown ethers—that is, dibenzo[24]crown-8 (DB24C8), bis-1,5-dinaphtho[38]crown-10 (DN38C10) and bis-1,5-dinaphtho[50]crown-14 (DN50C14)—were all examined and shown to form ‘ring-in-ring’ complexes in solution.

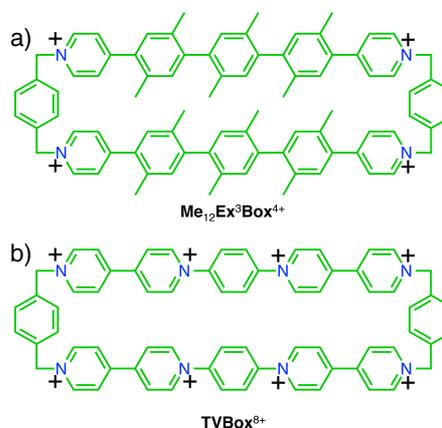
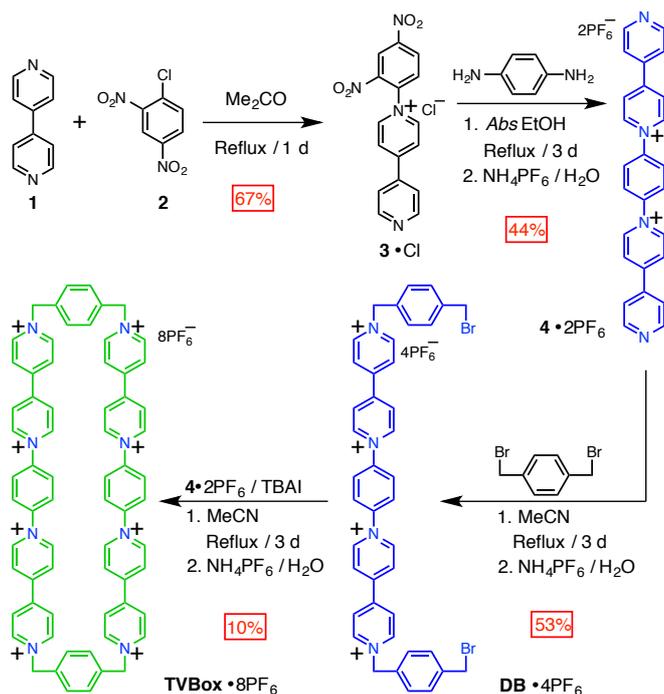


Fig. 1 Structural formulae of a) Me₁₂Ex²Box⁴⁺ and b) TVBox⁸⁺.

The synthesis (Scheme 1) of TVBox•8PF₆ begins with a Zincke reaction between the Zincke salt¹⁶ 3•Cl and an excess of 1,4-phenylenediamine, leading to the formation of 4•2PF₆, following counterion exchange. Subsequently, 4•2PF₆ is treated with an excess of 1,4-bis(bromomethyl)benzene, affording, after counterion exchange, the dibromide DB•4PF₆. Finally, the TBAI-catalysed cyclisation between DB•4PF₆ and 4•2PF₆ yields the desired product TVBox•8PF₆ in 10% yield, following counterion exchange. The relatively low yield can be attributed to the lack of a template and the lower reactivity of both DB⁴⁺ and 4²⁺. TVBox•8PF₆ was fully characterised in solution by ¹H and ¹³C NMR spectroscopies, high-resolution mass spectrometry, and

cyclic voltammetry (CV) as well as in the solid-state single-crystal X-ray diffraction. See the ESI† for the full characterization.



Scheme 1 Synthesis of the octacationic cyclophane **TVBox**• 8PF_6 .

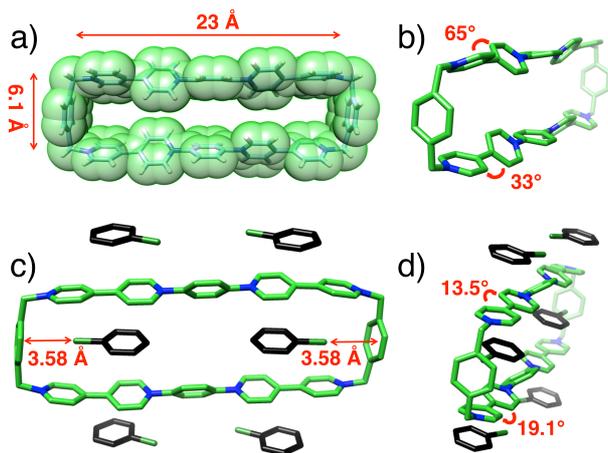


Fig. 2 a) Plan view of the **TVBox**• 8PF_6 solid-state structure illustrating the inner dimensions of the cavity (length = 23 Å, width = 6.1 Å). b) Perspective view of the **TVBox**• 8PF_6 solid-state structure showing the torsional angles (65° and 33°) between adjacent pyridinium rings.¹⁷ c) Plan view of the **[PhCl]₂•TVBox**• 8PF_6 solid-state superstructure illustrating the distance (3.58 Å) between the Cl atoms of the encapsulated PhCl molecules and *para*-xylene rings. d) Perspective view of the **[PhCl]₂•TVBox**• 8PF_6 solid-state superstructure illustrating the torsional angles (13.5° and 19.1°) between adjacent pyridinium rings. The hydrogen atoms, counterions, and solvent molecules are omitted for the sake of clarity.

Good quality single crystals of **TVBox**• 8PF_6 were obtained by slow vapour diffusion of *i*Pr₂O into a MeCN solution. The solid-state structure (Fig. 2a, b) reveals that the octacationic cyclophane possesses C_2 symmetry with a two-fold rotation axis running

orthogonally through the center of the cavity. With a length of 23 Å and a width of 6.1 Å, it shares a similar geometry to that of **Me₁₂Ex³Box⁴⁺**, and can accommodate multiple small guest molecules or potentially one guest molecule with large extended aromatic surfaces. The two torsional angles between the adjacent pyridinium units are ~33° and ~65°, respectively, which are larger than the average¹⁰ torsional angle (~20°) present in **CBPQT⁴⁺**, and are a consequence presumably of minimizing the steric repulsion arising from the pyridinium and central *p*-phenylene groups.

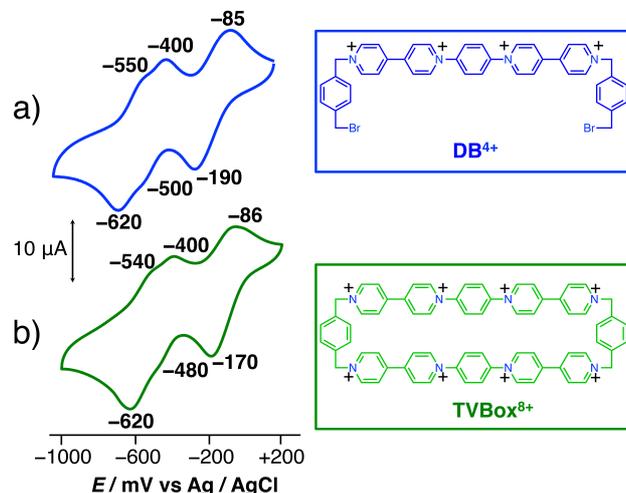


Fig. 3 Comparison of cyclic voltammograms (DMF, 0.1 M TBAPF₆, 200 mV•s⁻¹) of solutions of a) **DB⁴⁺** (1 mM) and b) **TVBox⁸⁺** (0.5 mM).

The redox properties of **DB⁴⁺** and **TVBox⁸⁺** were investigated (Fig. 3) by CV. The first reduction wave of **DB⁴⁺** is a two-electron process occurring (Fig. 3a) at a peak potential of -190 mV, in which one electron is transferred to each bipyridinium unit to yield the diradical dication **DB^{2(•+)}**, an observation which indicates that the two bipyridinium units behave independently in spite of the existence of the *p*-phenylene bridge. The second two-electron reduction occurs in two separate processes with peak potentials of -500 and -620 mV, corresponding to the reduction of the two remaining bipyridinium radical cations. The separation suggests that the redox units of the whole molecule begin to couple electronically with each other after the first reduction process, as observed¹⁸ for many organic mixed-valence compounds. The CV of **TVBox⁸⁺** exhibits (Fig. 3b) almost identical reduction processes, indicating that the two bis-(bipyridinium) units which constitute the walls of the box are not communicating in the first two-electron reduction, once again because of the nonplanarity of the *p*-phenylene bridges. The nature of the second two-electron process, however, suggests the onset of coupling between the bipyridinium radical cations through the *p*-phenylene bridges.

In the light of the fact that **Ex²Box⁴⁺** can accommodate^{14c} two aromatic molecules, the encapsulation of two aromatic guest molecules was also explored in the case of **TVBox⁸⁺**. It was found that two molecules of either PhMe or PhCl can be encapsulated, as evidenced by the solid-state superstructures obtained by performing X-ray crystallography on a single crystal following slow vapour diffusion of *i*Pr₂O into the solution of **TVBox⁸⁺** in MeCN containing 50 equiv of PhMe or PhCl. The solid-state superstructure (Fig. 2c, d) of **[PhCl]₂•TVBox⁸⁺** demonstrates that two PhCl molecules are located at each end of the cavity, leaving its centre unoccupied. The significantly decreased torsional angles (13.5° and 19.1°) and the short contacts (3.57 Å)

between Cl atoms and the centroid of the *p*-xylylene units demonstrate that the encapsulated PhCl molecules are stabilised cooperatively as a result of both aromatic π - π stacking and [Cl $\cdots\pi$] interactions.¹⁹ In addition, two more PhCl molecules are lined up in an aromatic π - π stacking motif alongside each viologen subunit of **TVBox**⁸⁺. In the case (Fig. S15) of PhMe, the encapsulated molecules are stabilised cooperatively as a result of both aromatic π - π stacking and [C-H $\cdots\pi$] interactions.

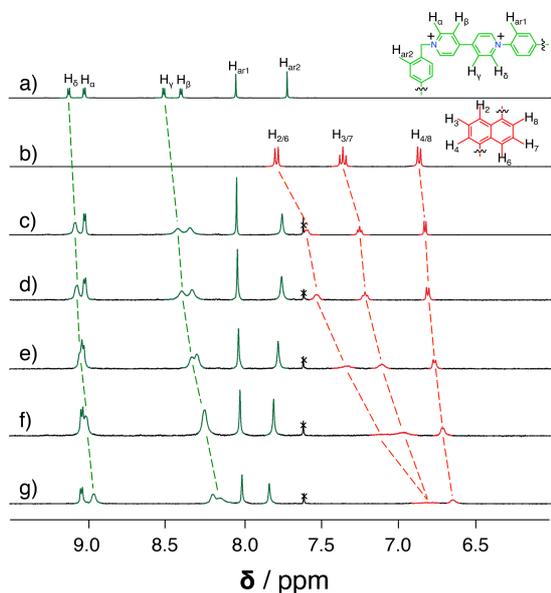


Fig. 4 Partial ¹H NMR spectra (500 MHz, CD₃CN) of a) **TVBox**•8PF₆, b) **DN50C14** and 1:1 molar mixture of **DN50C14** and **TVBox**•8PF₆ at c) 298, d) 293, e) 283, f) 273 and g) 263 K. The cross denotes CHCl₃.

Encouraged by these findings, we surmised that π -electron-rich crown ethers could potentially enter the cavity to form ‘ring-in-ring’ complexes by virtue of cooperative aromatic π - π stacking, [C-H $\cdots\pi$] interactions and possibly also [C-H \cdots O] interactions between the bipyridinium units and polyether loops. Three crown ethers—namely, **DB24C8**, **DN38C10**, and **DN50C14**—bearing π -electron-rich aromatic units with different lengths of polyether loops were investigated by ¹H NMR spectroscopy in CD₃CN. Fig. 4c shows ¹H NMR spectra recorded at 298 K for a 1:1 molar ratio of **TVBox**•8PF₆ and **DN50C14**, along with spectra (Fig. 4a, b) of the free components. The resonances for the aromatic protons in **DN50C14** are moved upfield and signals corresponding to **TVBox**⁸⁺ are also shifted and broadened. The ¹H-¹H NOESY NMR spectrum (Fig. S12) of the complex reveals that the DNP rings of **DN50C14** are located at the ends of the cavity and the polyether loops are folded and are directed top and bottom of the long sides of **TVBox**⁸⁺. All these observations indicate the complexation of **DN50C14** by **TVBox**⁸⁺ in line with previous studies.^{15b,d} The variable temperature (VT) ¹H NMR spectra (Fig. 4c-g) were also recorded on the same 1:1 molar mixture. As the sample was cooled, significant upfield shifting and broadening of the aromatic signals of **DN50C14**, in particular for H_{2/6}, occurs, illustrating that the complex becomes more stable at lower temperatures. Furthermore, since the upfield shifts originate from the mutual shielding effect of aromatic rings, those protons that are shifted most of all overlap to a greater extent with aromatic rings in the host. On the basis of these observations, it can be concluded that the 1,5-dioxynaphthalene (DNP) units of **DN50C14** adopt a perpendicular orientation inside the cavity of **TVBox**⁸⁺ with H_{2/6}

pointing towards the *p*-xylylene plane as in the energy minimized structure (Fig. 5). This co-conformation is also evidenced by the observation that the shifts of protons H_β and H_δ on **TVBox**⁸⁺ are greater than those of other signals arising from the host. All these observations support the formation of a ‘ring-in-ring’ complex, in which the crown ether resides inside of the cavity. Similar changes in chemical shifts are also observed (Fig. S7 and S9) for the equimolar mixtures involving the other two crown ethers and **TVBox**⁸⁺, implying that both **DB24C8** and **DN38C10** form similar ‘ring-in-ring’ complexes with **TVBox**⁸⁺ in solution.

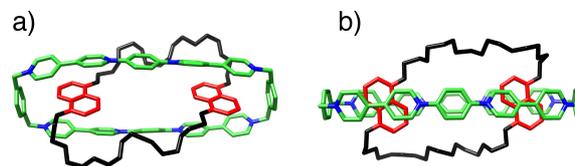


Fig. 5 Plan a) and side-on b) views of stick representations of the energy minimized structure of **DN50C14**•**TVBox**⁸⁺ by MM3.

The binding ratios between crown ethers and **TVBox**⁸⁺ were determined by Job plots (Fig. S5), revealing a 1:1 binding ratio for all three crown ethers, confirming the formation of ‘ring-in-ring’ complexes. Subsequently, ¹H NMR titrations were performed (Fig. S10) to determine the binding constants between each crown ether and **TVBox**⁸⁺. The titration of **DN50C14** into a solution of **TVBox**⁸⁺ resulted in continuous changes in the chemical shifts of the host proton resonances. By employing the software program Dynafit²⁰ with a 1:1 binding model, the binding constant between **DN50C14** and **TVBox**⁸⁺ was determined to be 1430 M⁻¹. The same experimental approach was applied (Fig. S6 and S8) to the other two crown ethers and the results are summarised in Table 1. Given the fact that **DN38C10** fits^{14c} perfectly inside **Ex²Box⁴⁺** and that **TVBox**⁸⁺ is 4 Å longer than **Ex²Box⁴⁺**, it is obvious that **DN38C10** is not large enough to occupy the cavity of **TVBox**⁸⁺ fully with maximum interactions, an outcome which leads to its lower binding affinity. The larger crown loop of **DN50C14** allows its two DNP units to position themselves close enough to both electron-deficient portions inside **TVBox**⁸⁺, thus maximising both π - π stacking and [C-H $\cdots\pi$] interactions. As a result, **DN50C14** enjoys the highest binding affinity of all. By contrast, the even shorter **DB24C8** can barely interact with both electron-deficient portions of the host simultaneously, resulting in the lowest binding affinity.

Table 1 Thermodynamic parameters for three ‘ring-in-ring’ complexes

Guest	$K_a / 10^3 (M^{-1})^a$	$\Delta G (kcal \cdot mol^{-1})$
DB24C6	0.59 ± 0.03	-3.78 ± 0.06
DN38C10	0.63 ± 0.03	-3.82 ± 0.06
DN50C14	1.43 ± 0.07	-4.30 ± 0.06

^aThe binding constant was determined by ¹H NMR titration at room temperature.

We have described the synthesis and characterisation of a novel rigid octacationic cyclophane, **TVBox**⁸⁺. This tetraviologen-based cyclophane possesses a ~2 nm long highly electron-deficient box-shaped binding pocket, which is capable of encapsulating either two π -aromatic guest molecules, such as PhMe and PhCl, concurrently, or a single aromatic crown ether with varying polyether loop lengths. The binding affinity between **TVBox**⁸⁺ and **DN50C14** in MeCN is as high as ~1400 M⁻¹, meaning that this 1:1 complex can, in principle, be used as a building block for the construction of molecular Borromean rings in a stepwise manner.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, ¹H and ¹³C NMR spectra and ¹H NMR titrations. CCDC: 1021673–1021675. See DOI: 10.1039/c000000x/

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