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A Ring-in-Ring Complex**

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David J. Williams*

Over the past two decades a vast array of interlocked and intertwined molecular compounds—specifically, catenanes, rotaxanes, and knots[1]—have been assembled using supramolecular assistance (templation[2]) as the key element in their synthesis[3] under either kinetic[4] or thermodynamic[5] control. Although these synthetic protocols have been implemented more recently for the construction of more intricate variants, such as oligocatenanes,[6] molecular necklaces,[7] and cyclic daisy chains[8] to name but a few, the topological challenge of the de novo synthesis of Borromean ring compounds[9] still presents a considerable hurdle to be overcome. Our way of addressing this challenge is to employ recognition motifs to create initially stable ring-in-ring superstructures[10] which could serve as templates for subsequent catenation. Here, we report 1) the design and noncovalent synthesis of a prototype, mutually orthogonal, partially preorganized, ring-in-ring complex, together with 2) the solid-state characterization of the 1:1 complex in the context of the X-ray crystal structures of its two separate ring components, and 3) the solution-state behavior of the 1:1 complex.

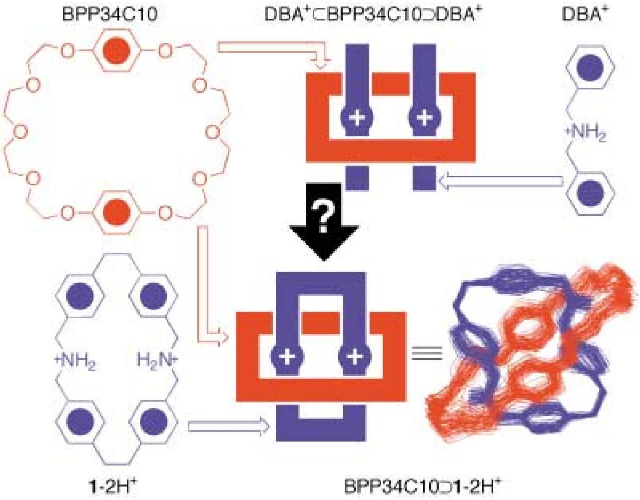

Figure 1. Employing precedent in the design and synthesis of a proposed 1:1 complex formed between BPP34C10 and $\mathbf{1}\text{-}2\,\mathrm{H}^{2+}$, together with an overlaid set of 70 co-conformations of BPP34C10 · $\mathbf{1}\text{-}2\,\mathrm{H}^{2+}$ sampled from the last 70 ps of a 100-ps MD experiment.

Previously, we have shown[11] that bisparaphenylene[34]-crown-10 (BPP34C10) can encircle two dibenzylammonium (DBA$^+$) ions simultaneously by locating the two NH$_2^+$ centers 6.9 Å apart in the polyether loops of BPP34C10 and relying upon N$^+$–H ··· O hydrogen bonds to form a stable 1:2 (DBA$^+$ ⊂ BPP34C10 ⊃ DBA$^+$) complex. Thus, it seemed not unreasonable to us that BPP34C10 might also be able to complex (Figure 1) with a suitably proportioned dicationic macrocycle containing two NH$_2^+$ centers. After inspection of the solid-state superstructure[11] of the 1:2 complex formed between BPP34C10 and DBA$^+$, and construction of CPK space-filling molecular models, we concluded that the macrocycle $\mathbf{1}\text{-}2\,\mathrm{H}^{2+}$ was a suitable candidate for further investigation. Our intuition was given a considerable boost by the results of the molecular dynamics (MD) calculations.[12] They predicted the existence of a stable co-conformation[13] in which the BPP34C10 ring encircles the dicationic macrocycle, such that the polyether loops surround the NH$_2^+$ centers, namely, the 1:1 (BPP34C10 ⊃ $\mathbf{1}\text{-}2\,\mathrm{H}^{2+}$) complex (illustrated in Figure 1) might constitute a discrete supermolecule.

The synthesis (Scheme 1) of the dicationic macrocycle $\mathbf{1}\text{-}2\,\mathrm{H}\cdot 2\,\mathrm{PF}_6$ was achieved by employing a bis-Wittig reaction in the key cyclization step. The bisphosphonium salt[14] $\mathbf{2}\text{-}\mathrm{H}\cdot 3\,\mathrm{PF}_6$ was protected ($\mathrm{Boc_2O/Et_3N/MeOH}$) to give $\mathbf{3}\cdot 2\,\mathrm{PF}_6$

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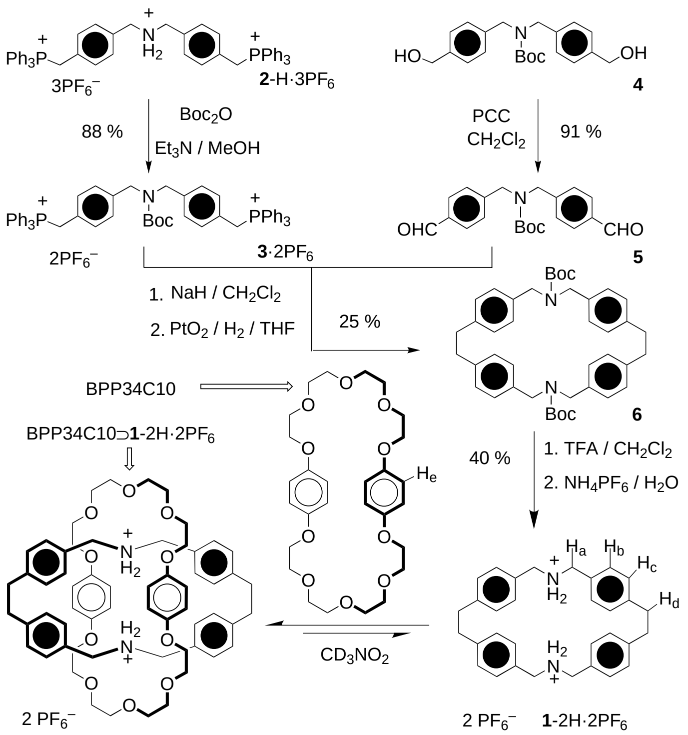

Scheme 1. The covalent synthesis of $\mathbf{1}\text{-}2\,H\cdot 2\,PF_6$ followed by the non-covalent synthesis of BPP34C10 ⊃ $\mathbf{1}\text{-}2\,H\cdot 2\,PF_6$. Boc = *tert*-butoxycarbonyl, PCC = pyridinium chlorochromate, TFA = trifluoroacetic acid.

while the Boc-protected diol[15] **4** was converted (PCC/CH_2Cl_2) into the appropriate dialdehyde[16] **5**. Heating of $\mathbf{3}\cdot 2\,PF_6$ with **5** in CH_2Cl_2 under reflux in the presence of an excess of NaH for four days afforded the unsaturated [1+1] macrocycle as the major product following chromatography on silica gel. The macrocycle was hydrogenated immediately using a catalytic amount of Adam's catalyst in THF under an atmosphere of hydrogen to produce the di-Boc-protected macrocycle **6**. Deprotection (TFA/CH_2Cl_2), followed by counterion exchange (NH_4PF_6/H_2O), gave $\mathbf{1}\text{-}2\,H\cdot 2\,PF_6$ as a white solid from which good quality single crystals were grown by liquid diffusion of iPr$_2$O into a solution of the salt in MeCN. X-Ray crystallography[17, 18] revealed (Figure 2) that this dicationic macrocycle has a semi-open conformation possessing crystallographic C_{2h} symmetry with the two NH_2^+ centers directed in toward the center of the macroring. Although the two bismethylene linkages have pseudo-*gauche* (46°) conformations, the paraxylyl ring systems are oriented so as to form the parallel-sided diamond-shaped box illustrated in Figure 2a. The separations between the two N atoms and between the centers of the two bismethylene linkages are 5.6 and 12.4 Å, respectively. The two PF_6^- counterions are located (Figure 2b) symmetrically above and below the macroring center and are held in position by a pair of $N^+\text{–}H\cdots F$ hydrogen bonds. There are no intermolecular π–π stacking interactions.

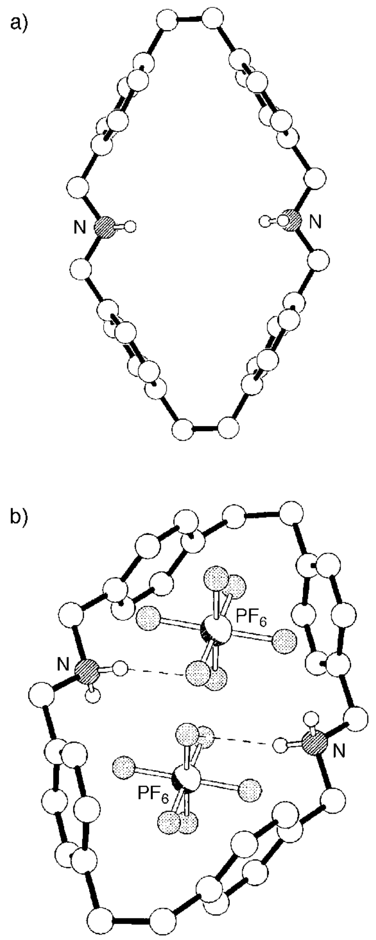

Figure 2. The solid-state structure of $\mathbf{1}\text{-}2\,H^{2+}$ viewed normal to the C_2 axis and edge on to the horizontal mirror plane (a) and the solid-state superstructure of $\mathbf{1}\text{-}2\,H\cdot 2\,PF_6$ showing the positioning above and below the ring center of the pair of $N^+\text{–}H\cdots F$ hydrogen-bonded PF_6^- ions (b). The $N^+\cdots F$ and $H\cdots F$ distances are 3.32 and 2.44 Å, respectively, and the $N^+\text{–}H\cdots F$ angle is 169°.

The fast-atom bombardment (FAB) mass spectrum recorded on an equimolar mixture of $\mathbf{1}\text{-}2\,H\cdot 2\,PF_6$ and BPP34C10 reveals a peak at m/z 983 corresponding to a 1:1 complex with loss of one HPF_6 and one PF_6^- ion. When equimolar amounts of the same two components (10 mM each) are dissolved in CD_3NO_2 at room temperature, dramatic changes in the ^1H NMR spectrum are observed (Figure 3) relative to the spectra for the free host and free guest. Particularly worthy of note are the observations[19] that 1) the singlet for the hydroquinone ring protons (H_e) of the BPP34C10 unit is shifted upfield by 0.2 ppm, 2) the signals for the α-, β-, γ-, and δ-OCH_2 protons are shifted by −0.1, +0.05, +0.10, and +0.13 ppm, respectively, 3) one of the two "doublets" belonging to the AA′BB′ pattern of the macrocycle's aromatic protons (H_b, H_c) is transformed from a sharp signal centered on $\delta = 7.13$ into a broad one resonating at $\delta = 6.88$, and 4) the singlet corresponding to the methylene protons (H_a) adjacent to the NH_2^+ center at $\delta = 4.17$ is shifted upfield by about 0.34 ppm and broadened. The considerable changes ($\Delta\delta$) in the chemical shifts of the signals for the CH_2N^+ protons (H_a) and their proximal aromatic protons (H_b)—in contrast with the negligible $\Delta\delta$ values for the bismethylene protons (H_d) and their proximal aromatic protons (H_c)—in the macrocyclic dication upon complexation suggests that the crown ether encircles and hydrogen bonds to the NH_2^+ centers such that the mean plane of the BPP34C10 ring is approximately orthogonal to that of $\mathbf{1}\text{-}2\,H^{2+}$. Moreover, TROSEY experi-

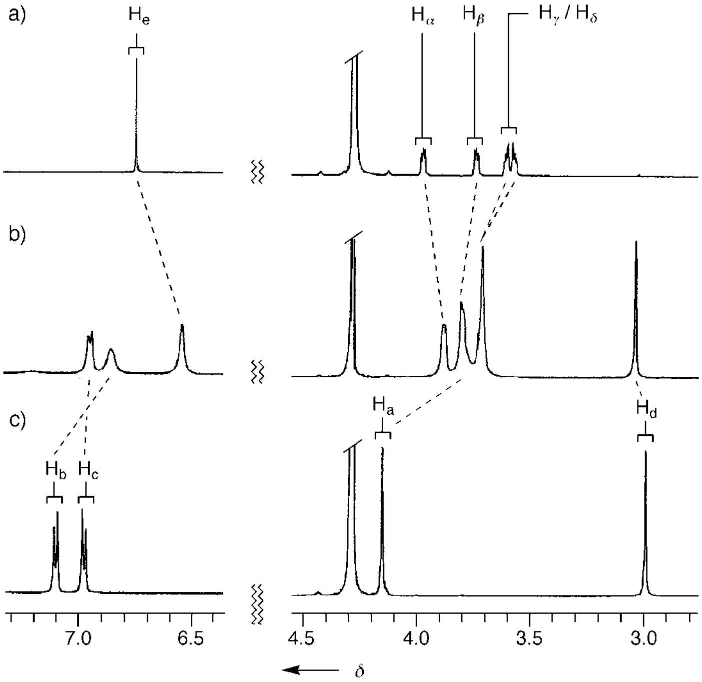

Figure 3. Partial ^{1}H NMR spectra (500 MHz, CD_3NO_2, 298 K) of BPP34C10 (a), an equimolar mixture (10 mM) of BPP34C10 and **1**-2H·2PF_6 (b), and **1**-2H·2PF_6 (c). See Scheme 1 for the labeling of the protons.

ments,[20] using the equimolar (10 mM) mixture of **1**-2H^{2+} and BPP34C10 in CD_3NO_2 at 298 K, show (Figure 4) cross-peaks between the signals for the hydroquinone ring protons (H_e) in the crown ether and both the CH_2N^+ protons (H_a) and the aromatic protons (H_b, H_c) in the macrocyclic dication. These experimental observations were supported by the results of a further MD study in which the relative intercomponent H···H distances were scrutinized over the course of a 1-ns MD experiment.[12] In all cases, each of the eight H_e atoms on the two hydroquinone rings of the BPP34C10 component had their distances measured to their closest corresponding H_a, H_b, and H_c atoms in the **1**-2H^{2+} component. The mean interatomic distances for each pair of H atoms were then averaged in co-conformational space to give[21] 4.9, 3.3, and 3.4 Å for $H_e \cdots H_a$, $H_e \cdots H_b$, and $H_e \cdots H_c$, respectively.

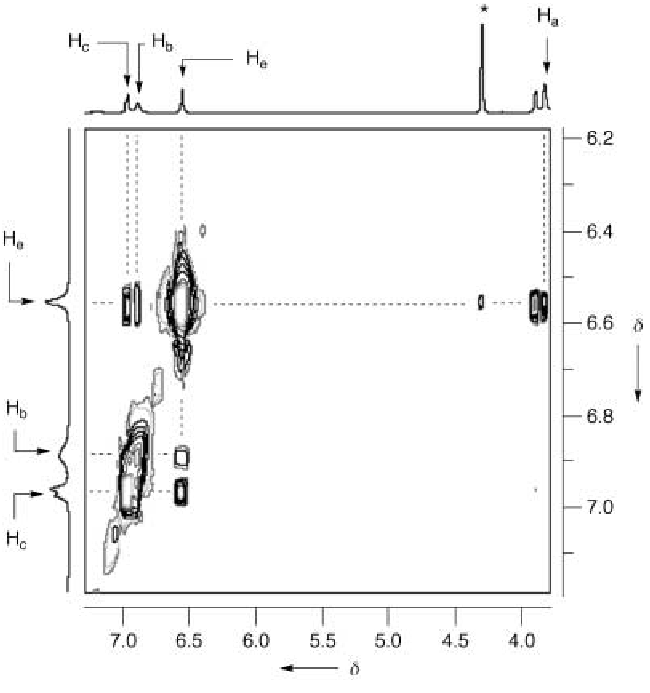

Figure 4. Partial T-ROSEY NMR spectrum (500 MHz, CD_3NO_2, 298 K) of an equimolar mixture (10 mM) of BPP34C10 and **1**-2H·2PF_6.

By using the method[22] of continuous variations (Job plot) with both the H_b atom in **1**-2H·2PF_6 and the H_e atom in BPP34C10 as ^{1}H NMR probes in a mixed solvent of CD_3CN and CD_2Cl_2 (1:1),[23] convincing evidence for 1:1 stoichiometry in the complexation of **1**-2H^{2+} by BPP34C10 was observed. K_a Values in CD_3NO_2 for the 1:1 complex were found to be 4000 ± 900 and 3100 ± 500 M^{-1}, using these two protons (H_b and H_e, respectively) in ^{1}H NMR dilution experiments.[22]

Single crystals of the 1:1 complex, suitable for X-ray analysis,[18, 24] were grown by vapor diffusion of iPr$_2$O into an equimolar solution of **1**-2H·2PF_6 and BPP34C10 in a solution mixture of MeCN, $MeNO_2$, and CH_2Cl_2. The solid-state superstructure of BPP34C10 $\supset$ **1**-2H·2PF_6 shows (Figure 5) the dicationic guest to be threaded, as anticipated, through the center of the crown ether host. The complex has crystallographic C_i symmetry and the BPP34C10 component has a conformation remarkably similar to that already reported[11] for the DBA·PF_6 $\subset$ BPP34C10 $\supset$ DBA·PF_6 complex (Figure 1), though with an increased separation between its two hydroquinone rings of 7.68 Å (centroid–centroid) compared with 6.99 Å in the 2:1 complex. The guest dication is seen to have undergone a significant change in conformation (relative to that for the free dication depicted in Figure 2), with its two NH_2^+ centers now directed outwards and away from the macroring center so that they can form strong $N^+{-}H \cdots O$ hydrogen bonds to the central oxygen atoms in the two polyether loops of the BPP34C10 host. The two bismethylene linkages still retain a pseudo-*gauche* geometry but the para-xylyl ring systems are each tilted in toward their macroring center. The separations between the two N atoms and the centers of the bismethylene bridges are now 7.9 and 11.1 Å, respectively. The [1+1] supermolecules form continuous stacks through $\pi-\pi$ stacking of the exterior benzenoid rings in the macrocyclic dication.

Herein we have shown that the recognition motif involving NH_2^+ centers and polyether loops[11] can be employed in the noncovalent assembly of a ring-in-ring superstructure that exists, not only in the solid state, but also in solution. The control over the superstructure achieved with this particular recognition motif[25] bodes well for the covalent syntheses of Borromean ring compounds by supramolecular assistance under kinetic control.

Experimental Section

3·2PF_6: Et_3N (2.2 mL, 1.6 mmol) was added slowly by syringe over 30 min to a solution of the bisphosphonium salt[14] **2**-H·3PF_6 (1.0 g, 0.8 mmol) and Boc_2O (3.48 g, 1.6 mmol) in MeOH (50 mL), and the reaction mixture was stirred at room temperature for 12 h. After removal of the solvent, the residue was dissolved in MeCN (10 mL) and a solution of NH_4PF_6 (2 g) in H_2O (20 mL) was added. Most of the MeCN was evaporated off under reduced pressure before the aqueous solution was extracted with CH_2Cl_2

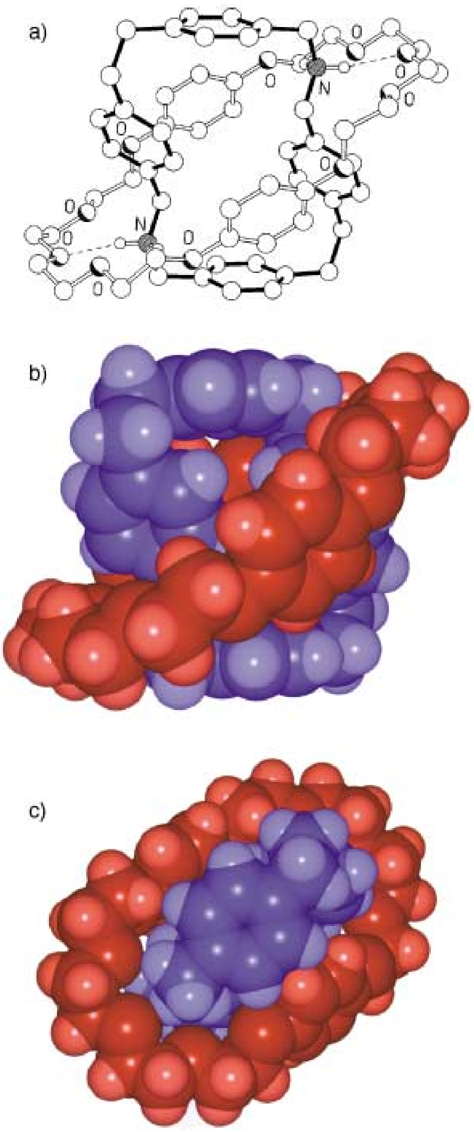

Figure 5. The ball-and-stick representation (a) of the ring-in-ring superstructure formed between BPP34C10 and **1**-2 H^{2+}. The N^+–H ··· O hydrogen bond has N^+ ··· O and H ··· O distances of 2.91 and 2.04 Å, respectively, and a N^+–H ··· O angle of 161°. Elevation (b) and plan space-filling (c) representations of the 1:1 complex.

(2 × 50 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), concentrated, and the residue was purified by column chromatography (SiO_2; MeCN:CH_2Cl_2 (3:17)) to yield **3** · 2 PF_6 as a white solid (0.8 g, 88 %); ^1H NMR (360 MHz, CD_2Cl_2): δ = 1.42 (s, 9 H), 4.20 – 4.40 (br s, 4 H), 4.46 (d, J_{PH} = 14 Hz, 4 H), 6.75 – 6.78 (m, 4 H), 6.94 (br s, 4 H), 7.45 – 7.51 (m, 12 H), 7.63 – 7.69 (m, 12 H), 7.83 – 7.87 (m, 6 H); ^{13}C NMR (90 MHz, CD_2Cl_2): δ = 28.7, 31.0 (d, J_{PC} = 48.6 Hz), 50.1, 80.8, 117.5 (d, J_{PC} = 85.6 Hz), 125.6, 129.1, 131.0 (d, J_{PC} = 12.5 Hz), 131.5 (d, J_{PC} = 5.4 Hz), 134.5 (d, J_{PC} = 9.6 Hz), 136.1, 139.9, 156.2; MS (FAB): *m/z*: 992 [*M* – PF_6]$^+$, 846 [*M* – H – 2 PF_6]$^+$.

1-2 H · 2 PF_6: CH_2Cl_2 (500 mL) was added to a round-bottom flask charged with **3** · 2 PF_6 (1.35 g, 1.19 mmol) and NaH (150 mg, 6.3 mmol). The dialdehyde[15] **5** (42 mg, 1.19 mmol), dissolved in CH_2Cl_2 (100 mL), was added slowly by syringe over 12 h to the reaction flask and the mixture was heated under reflux for 4 days before the reaction was quenched by the slow addition of MeOH (10 mL) and the mixture concentrated to afford a residue. Chromatographic purification (SiO_2; MeCN:CH_2Cl_2 (3:97)) removed the Ph_3PO and afforded the crude bis-Wittig product which was dissolved in THF (10 mL). PtO_2 (50 mg) was added and H_2 gas was bubbled through the solution for 10 min. The mixture was then stirred under H_2 (balloon) for 3 h, before being concentrated to give a residue that was subjected to column chromatography (SiO_2; hexane:CH_2Cl_2:EtOAc (16:3:1)) to yield **6** as a white solid (380 mg, 25 %); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.53 (s, 18 H), 2.83 (s, 8 H), 4.20 – 4.40 (br s, 8 H), 6.65 (d, *J* = 7 Hz, 8 H), 6.70 – 6.90 (br s, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.5, 38.1, 48.3, 80.0, 127.6, 127.9, 129.5, 134.6, 139.5, 156.2; MS (FAB): *m/z*: 1293.6 [*M*+H]$^+$. This Boc-protected diamine (100 mg, 0.08 mmol) was dissolved in a mixture of TFA (0.75 mL) and CH_2Cl_2 (0.75 mL) and stirred at room temperature for 12 h. A solution of NH_4PF_6 (300 mg) in H_2O (3 mL) was added to the reaction mixture. On removal of the volatile solvents, a white precipitate was formed which was filtered off and dissolved in MeCN (2 mL). Following an identical repeat treatment with aqueous NH_4PF_6 solution, a white precipitate was isolated and washed with Et_2O (5 mL) to yield **1**-2 H · 2 PF_6 as a white solid (57 mg, 40 %); ^1H NMR (500 MHz, CD_3NO_2): δ = 3.05 (s, 8 H), 4.17 (s, 8 H), 7.00 (d, *J* = 8 Hz, 8 H), 7.13 (d, *J* = 8 Hz, 8 H); ^{13}C NMR (125 MHz, CD_3NO_2): δ = 37.5, 51.8, 128.5, 130.9, 131.6, 144.7; electrospray MS: *m/z*: 593.4 [*M* – PF_6]$^+$, 447.3 [*M* – H – 2 PF_6]$^+$.

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[8] The term "daisy chain" is used to describe an interwoven chain, usually made of flowers, in which each monomer unit acts as a donor and an acceptor for a threading interaction, see a) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1344–1347; *Angew. Chem. Int. Ed.* **1998**, *37*, 1294–1297; b) P. R. Ashton, I. W. Parsons, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams, R. Wolf, *Angew. Chem.* **1998**, *110*, 2016–2019; *Angew. Chem. Int. Ed.* **1998**, *37*, 1913–1916; c) N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518–2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361–2364; d) A. Mirzoian, A. E. Kaifer, *Chem. Commun.* **1999**, 1603–1604; e) J. Bügler, N. A. J. M. Sommerdijk, A. J. W. G. Visser, A. van Hoek, R. J. M. Nolte, J. F. J. Engbersen, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1999**, *121*, 28–33; f) M. B. Nielsen, J. G. Hansen, J. Becher, *Eur. J. Org. Chem.* **1999**, 2807–2815; g) M. C. Jiménez, C. Dietrich-Buchecker, J.-P. Sauvage, A. De Cian, *Angew. Chem.* **2000**, *112*, 1351–1354; *Angew. Chem. Int. Ed.* **2000**, *39*, 1295–1298; h) S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, D. J. Williams, *Org. Lett.* **2000**, *2*, 759–762; i) T. Fujimoto, Y. Sakata, T. Kaneda, *Chem. Commun.* **2000**, 2143–2144; j) T. Hoshino, M. Miyauchi, Y. Kawaguchi, H. Yamaguchi, A. Harada, *J. Am. Chem. Soc.* **2000**, *122*, 9876–9877; k) H. Onagi, C. J. Easton, S. F. Lincoln, *Org. Lett.* **2001**, *3*, 1041–1044; l) S. J. Cantrill, G. J. Youn, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **2001**, *66*, 6857–6872.

[9] The Borromean rings, named after the coat of arms of the Borromeo family of the Renaissance era in Italy, is a unique topological knot that is composed of three interlocked rings in which no two of these individual rings is catenated. Consequently, if any one ring is cleaved, disassembly of the entire knot will ensue. So far, their synthesis has been achieved only by the ingenious use of DNA strands and biochemical techniques, see a) N. C. Seeman, *Acc. Chem. Res.* **1997**, *30*, 357–363; b) C. Mao, W. Sun, N. C. Seeman, *Nature* **1997**, *386*, 137–138; c) N. C. Seeman, H. Wang, X. Yang, C. Mao, W. Sun, L. Wenzler, Z. Shen, R. Sha, H. Yan, M. H. Wong, P. Sa-Ardyen, B. Liu, H. Qiu, X. Li, J. Qi, S. M. Du, Y. Zhang, J. E. Mueller, T.-J. Fu, Y. Wang, J. Chen, *Nanotechnology* **1998**, *9*, 257–273. Microscale metallic Borromean rings have been constructed by a fabrication technique, see H. Wu, S. Brittain, J. Anderson, B. Grzybowski, S. Whitesides, G. M. Whitesides, *J. Am. Chem. Soc.* **2000**, *122*, 12691–12699.

[10] Herein we use the term "ring-in-ring" to describe the relative (supramolecular) geometry in which one macrocycle is located inside another such that their mean planes are more or less perpendicular to each other in order to differentiate them from the more familiar "macrocycle-within-macrocycle" situation (S.-Y. Kim, L.-S. Jung, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim, *Angew. Chem.* **2001**, *113*, 2177–2179; *Angew. Chem. Int. Ed.* **2001**, *40*, 2119–2121) wherein the mean planes of the macrocycles are roughly coincident. For other examples of the "macrocycle-within-macrocycle" superstructure, see a) F. Vögtle, W. M. Müller, *Angew. Chem.* **1979**, *91*, 676–677; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 623–624; b) S. Kamitori, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1987**, *109*, 2409–2414.

[11] P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709–728.

[12] After construction of the complex BPP34C10 ⊃ **1**-$2H^{2+}$ within the input submode of MacroModel v5.5 (F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, M. Lipton, C. Caulfield, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem.* **1990**, *11*, 440–467), the ring-in-ring co-conformation was optimized using the PRCG algorithm (E. Polak, G. Ribière, *Rev. Fr. Inf. Rech. Oper.* **1969**, *16*, 35), considering solvation in the form of the GB/SA model (W. C. Still, A. Tempczyk, R. C. Hawley, T. Hendrickson, *J. Am. Chem. Soc.* **1990**, *112*, 6127–6129) for $CHCl_3$ and the AMBER* force field (S. J. Weiner, P. A. Kollman, D. A. Case, U. C. Singh, C. Ghio, G. Alagona, S. Profeta, P. Weiner, *J. Am. Chem. Soc.* **1984**, *106*, 765–784). 100 Co-conformations were sampled during the course of a 100-ps MD simulation (1.5-fs timestep) at 300 K.

[13] We have advocated (M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **1997**, *109*, 2158–2160; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2068–2070) the use of the term "co-conformation" to designate the different three-dimensional spatial arrangements of the constituent parts in supramolecular systems.

[14] S. J. Rowan, S. J. Cantrill, J. F. Stoddart, *Org. Lett.* **1999**, *1*, 129–132.

[15] P. R. Ashton, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 729–736.

[16] P. R. Ashton, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 12514–12524.

[17] Crystal data for **1**-$2H\cdot 2PF_6$: $[C_{32}H_{36}N_2][PF_6]_2$, $M_r = 738.6$, orthorhombic, space group *Pnnm* (no. 58), $a = 8.360(2)$, $b = 9.180(1)$, $c = 21.516(3)$ Å, $V = 1651.3(5)$ Å^3, $Z = 2$ (C_{2h} symmetry), $\rho_{calcd} = 1.485\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 2.26\ cm^{-1}$, $T = 203$ K, colorless plates; 1494 independent measured reflections, F^2 refinement, $R_1 = 0.037$, $wR_2 = 0.091$, 1130 independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leqslant 50°]$, 140 parameters.

[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-170077 (**1**-$2H\cdot 2PF_6$) and -170078 (BPP34C10 ⊃ **1**-$2H\cdot 2PF_6$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[19] These peak assignments were confirmed by variable-temperature ^1H NMR spectroscopic studies. When the temperature of the ^1H NMR probe is raised to 373 K, the signals evident in Figure 2b that arise from both the guest and host components move close to the chemical shifts observed for them in their free states at ambient temperature. Such a pattern of behavior implies that, not only is the complexation between **1**-$2H\cdot 2PF_6$ and BPP34C10 negligible at +100 °C in CD_3NO_2, but also that the binding between the guest and host is enthalpy driven.

[20] T.-L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* **1992**, *114*, 3157–3159.

[21] When analogous averages are calculated from the X-ray crystal data for BPP34C10 ⊃ **1**-$2H\cdot 2PF_6$, the corresponding interatomic distances are 4.8, 3.2, and 3.4 Å, respectively.

[22] K. A. Connors, *Binding Constants*, Wiley, New York, **1987**.

[23] The mixed solvent system was used to obtain Job plots since BPP34C10 is soluble in CD_2Cl_2 but not very soluble in CD_3CN whereas **1**-$2H\cdot 2PF_6$ is soluble in CD_3CN but not in CD_2Cl_2. Free (or excess) BPP34C10 is not very soluble in CD_3NO_2 and so experiments to establish the stoichiometry of the complex in this solvent are difficult.

[24] Crystal data for BPP34C10 ⊃ **1**-$2H\cdot 2PF_6$: $[C_{60}H_{76}N_2O_{10}][PF_6]_2\cdot 2MeCN$, $M_r = 1357.3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.913(1)$, $b = 13.460(1)$, $c = 20.118(1)$ Å, $\beta = 103.26(1)°$, $V = 3403.5(3)$ Å^3, $Z = 2$ (C_i symmetry), $\rho_{calcd} = 1.324\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 13.7\ cm^{-1}$, $T = 293$ K, colorless cubes; 5053 independent measured reflections, F^2 refinement, $R_1 = 0.059$, $wR_2 = 0.157$, 3723 independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leqslant 120°]$, 440 parameters.

[25] There has been some speculation in the literature about the use of this recognition motif in a Borromean ring synthesis, see T. J. Hubin, A. G. Kolchinski, A. L. Vance, D. H. Busch, *Adv. Supramol. Chem.* **1999**, *5*, 237–357.