ORGANIC LETTERS

2000
Vol. 2, No. 9
1221−1224

An Extremely Stable Interwoven Supramolecular Bundle

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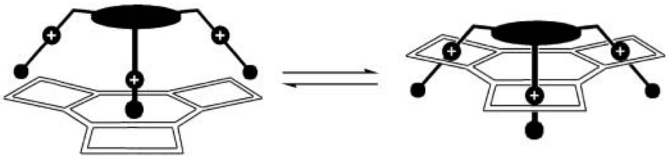
Received February 10, 2000

ABSTRACT



A tritopic receptor, in which three benzo[24]crown-8 macrorings are fused onto a triphenylene core, forms very strong supramolecular bundle-like complexes in $CDCl_3/CD_3CN$ solution with trifurcated trications wherein three dibenzylammonium ions are linked to a central benzenoid core. The triply threaded superbundles, one of which has been characterized in the solid state by X-ray crystallography, dissociate completely via doubly and singly threaded intermediates when CD_3SOCD_3 is added progressively to the $CDCl_3/CD_3CN$ solution.

Of late, a number of ingenious protocols have been developed[1] for the construction of supermolecules, i.e., chemical aggregates composed of a finite number of molecular building blocks held together by noncovalent bonds,[2] by several research groups around the world. In 1997, we reported[3] a route to the noncovalent synthesis[2] of multicomponent supermolecules with interwoven bundlelike[4,5] co-conformations.[6] This route relied on the ability of *n* molecules of the ditopic crown ether bis-*p*-phenylene[34]crown-10 (BPP34C10) to tie together two units of branched oligocations—possessing *n* dibenzylammonium ion (DBA^+) centers—by utilizing hydrogen bonding interactions. Here, we describe the noncovalent synthesis of an interwoven superbundle that is much more stable in solution than its predecessors derived from BPP34C10. This interwoven superbundle is created (Figure 1) when each of the three DBA^+ sidearms of the trication $\mathbf{1}^{3+}$ thread their way through

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(1) (a) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647−1668. (b) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469−472. (c) de Mendoza, J. *Chem. Eur. J.* **1998**, *4*, 1373−1377. (d) Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092−9093. (e) Baxter, P. N. W.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 113−120. (f) Jollife, K. A.; Timmerman, O.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 933−937. (g) Takeda, N.; Umemoto, K.; Yamagachi, K.; Fujita, M. *Nature* **1999**, *398*, 794−796. (h) Ibukuro, F.; Fujita, M.; Yamaguchi, K.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1999**, *121*, 11014−11015. (i) Olenyuk, B.; Levin, M. D.; Whiteford, J. A.; Shield, J. E.; Stang, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434−10435. (j) Albrecht, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3463−3465. (k) Schalley, C. A. *Adv. Mater.* **1999**, *11*, 1535−1537.

(2) Fyfe, M. C. T.; Stoddart, J. F. *Acc. Chem. Res.* **1997**, *30*, 393−401.

(3) (a) Ashton, P. R.; Collins, A. N.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 59−62. (b) Feiters, M. C.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Nolte, R. J. M.; Stoddart, J. F.; van Kan, P. J. M.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 8119−8120.

(4) Originally (ref 3a), we referred to these supermolecules as "interwoven supramolecular cages". However, after some reflection, we have now decided to call them "interwoven supramolecular bundles" to indicate that they do not necessarily possess internal voids that can accommodate guests.

(5) (a) Fyfe, M. C. T.; Stoddart, J. F. *Adv. Supramol. Chem.* **1999**, *5*, 1−53. (b) Fyfe, M. C. T.; Stoddart, J. F. *Coord. Chem. Rev.* **1999**, *183*, 139−155. (c) Fyfe, M. C. T.; Stoddart, J. F.; Williams, D. J. *Struct. Chem.* **1999**, *10*, 243−259. (d) Hubin, T. J.; Kolchinski, A. G.; Vance, A. L.; Busch, D. H. *Adv. Supramol. Chem.* **1999**, *5*, 237−357.

(6) We have advocated (Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *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 (a) the constituent parts of supramolecular systems and (b) the components of interlocked molecular systems.

10.1021/ol0056473 CCC: $19.00

each of the three dibenzo[24]crown-8 (DB24C8) macrorings of the triphenylene-based compound **2** as a result of, inter alia, [$N^+-H\cdots O$] hydrogen bond formation. The enhanced stability of the superbundle [**1**·**2**]$^{3+}$ arises because its noncovalent synthesis (1) employs, in a cooperative[7] manner, a stronger hydrogen bonding motif, viz., the threading[5] of DBA^+ is through the cavity of the smaller monotopic crown ether, DB24C8, and (2) involves fewer components, resulting in a smaller entropy loss when the superbundles are formed.

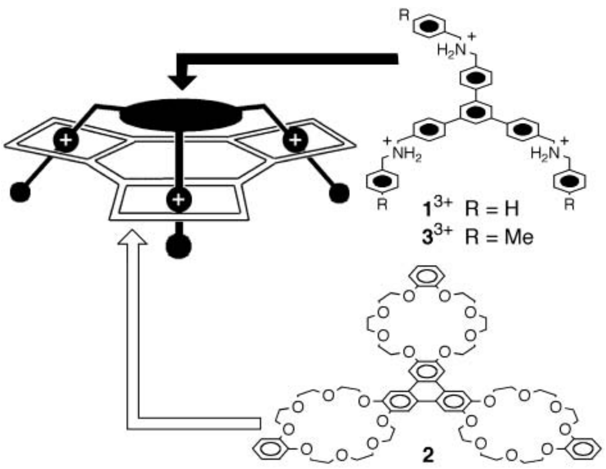

Figure 1. Noncovalent syntheses of the interwoven supramolecular bundles [**1**·**2**]$^{3+}$ and [**3**·**2**]$^{3+}$.

The preparation of **1**·$3PF_6$ has already been reported.[3a] The trimethyl analogue **3**·$3PF_6$ (Figure 1) was produced in a similar fashion except that *p*-methylbenzylamine, rather than $PhCH_2NH_2$, was condensed with 1,3,5-tris(4-formyl-phenyl)-benzene in the first step of a four-stage procedure that involves subsequent reduction, protonation, and anion-exchange steps. The triscrown **2** was obtained in 10% yield following trismacrocyclization (Cs_2CO_3/DMF) between 2,3,6,7,10,11-hexahydroxytriphenylene[8] and the appropriate ditosylate derived[9] from the diol obtained when catechol is bisalkylated with 2-[2-(2-chloroethoxy)ethoxy]ethanol.

The X-ray analysis[10] of a single crystal—obtained when an equimolar mixture of **1**·$3PF_6$ and **2** in $MeNO_2/CH_2Cl_2$ (1:1) was layered with *t*-BuOMe—reveals (Figure 2a) that the anticipated triply threaded two-component super-structure has self-assembled in accordance with the design criteria. This superstructure is almost certainly a consequence of the matching of the dimensions of the two templates and the resulting cooperativity of the hydrogen bonding and the $\pi-\pi$ stacking interactions between them. Two of the polyether macrocycles have U-shaped conformations, while the third one has an extended geometry. The central aromatic core of

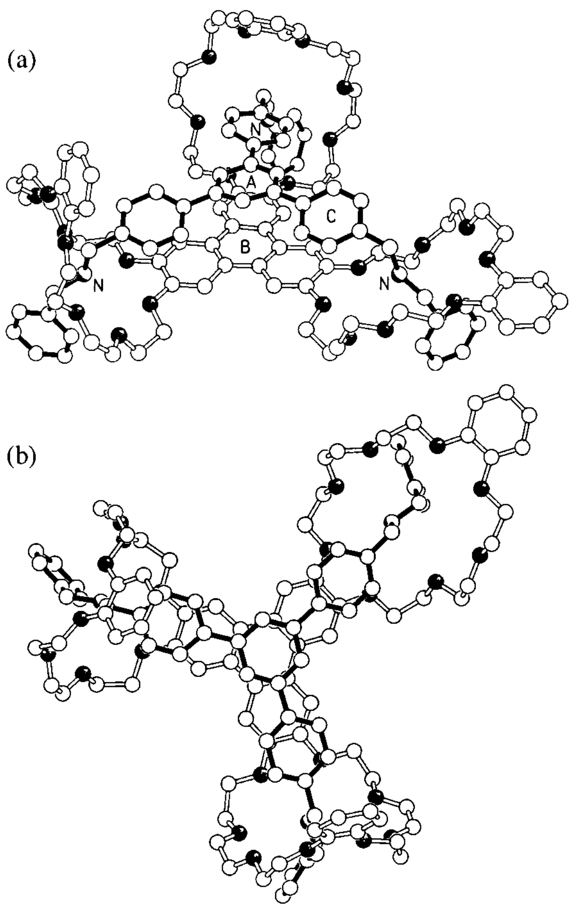

Figure 2. Solid-state superstructure of the [**1**·**2**]$^{3+}$ supermolecule: (a) elevation and (b) plan view.

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[7] Bisson, A. P.; Hunter, C. A. *Chem. Commun.* **1996**, 1723−1724.

[8] (a) Beattie, D. R.; Hindmarsh, P.; Goodby, J. W.; Haslam, S. D.; Richardson, R. M. *J. Mater. Chem.* **1992**, *2*, 1261−1266. (b) Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851−858.

[9] Ashton, P. R.; Bartsch, R. A.; Cantrill, S. J.; Hanes, Jr., R. E.; Hickingbottom, S. K.; Lowe, J. N.; Preece, J. A.; Stoddart, J. F.; Talanov, V. S.; Wang, Z.-H. *Tetrahedron Lett.* **1999**, *40*, 3661−3664.

[10] Crystal data for [**1**·**2**]·$3PF_6$: $C_{120}H_{138}N_3O_{24}\cdot 3PF_6\cdot X$ (where X represents unresolved partial occupancy and overlaying disordered solvent molecules comprising a mixture of $MeNO_2$, CH_2Cl_2, and *t*-BuOMe, allowed for as partial weight carbon atoms totaling $C_{18.5}$ and incorporated as such into the estimated molecular weight), $M = 2663.4$, monoclinic, $a = 58.624(2)$ Å, $b = 26.449(1)$ Å, $c = 19.287(1)$ Å, $\beta = 107.07(1)°$, $U = 28587(2)$ Å^3, space group $C2/c$, $Z = 8$, $D_c = 1.238$ g cm^{-3}, μ(Cu Kα) = 1.146 mm^{-1}, $T = 173(2)$ K. Data for a crystal of dimensions 0.33 × 0.67 × 0.85 mm were measured on a Siemens P4/RA diffractometer with Cu Kα radiation (graphite monochromator) using ω-scans. Of the 18 858 independent reflections measured ($\theta > 60°$), 8533 had $I_o > 2\sigma(I_o)$ and were considered to be observed. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods, and the major occupancy non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms in the 1:1 complex were idealized, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon/nitrogen atoms. Those associated with the disordered solvent molecules were not incorporated. Refinement was by blocked full-matrix least-squares methods based on F^2 and converged to give $R_1 = 0.142$, w$R_2 = 0.330$. The maximum and minimum residual electron densities in the final ΔF map were 0.48 and −0.44 e Å^{-3}. The high value of R_1 is a consequence of the extensive disorder of the structure. The central core of the 1:1 complex is well ordered, but there is evidence of disorder in the polyether arms and peripheral catechol rings of the macrocycles, as well as in the terminal benzyl groups of the trication. The PF_6^- anions are also disordered: two full and one-half anions lie in general positions the remainder in a special position. Where possible, the disorder was resolved into partial occupancy alternative orientations. Otherwise, it was compensated for by allowing large anisotropic thermal parameters. Constrained geometries were used throughout the disordered regions. The mixed overlapping solvent fragments could not be resolved. Computations were carried out using the SHELXTL program package version 5.03.

the tricationic component has a propeller-like conformation with the three radial phenylene rings rotated by between 15 and 23° out of the plane of the central A ring. There is a parallel, but smaller, deformation (twists of between 2 and 7°) in the triphenylene ring of the triscrown component. The two components overlay each other (Figure 2b) with rings A and B aligned nearly parallel (7° between their planes) with a centroid−centroid separation of 3.6 Å, consistent with stabilizing $\pi-\pi$ stacking interactions. The three NH_2^+ nitrogen atoms are all directed inward toward the center of the complex and lie within 2.9 Å of polyether oxygen atoms, indicative of $[N^+-H\cdots O]$ hydrogen bonding interactions which aid the maintenance of the three latches holding the two components of the supermolecule together. The only intercomplex interaction of note is a back-to-back $\pi-\pi$ stacking (3.65 Å interplanar separation) of rings C of C_i related pairs of supermolecules.

The ^1H NMR spectrum of an equimolar mixture (7.5 mM) of **1**·$3PF_6$ and **2**, recorded in $CDCl_3/CD_3CN$ (1:1), reveals (Figures 3a and d) a complex array of well-defined resonances. With the help of $^1H-^1H$ COSY and TROESY[11] 2-D ^1H NMR experiments, it has been possible to assign these resonances to a single C_3 symmetrical species—viz., the $[\mathbf{1}\cdot\mathbf{2}]^{3+}$ superbundle—that is believed to be kinetically stable on the ^1H NMR time scale.[12] A comparison of the ^1H NMR spectrum (Figure 3a and d) for $[\mathbf{1}\cdot\mathbf{2}]\cdot 3PF_6$ with those for **2** (Figures 3b and 3e) and **1**·$3PF_6$ (Figures 3c and 3f) indicates that there are no resonances corresponding to free species in the spectrum of the 1:1 complex. Moreover, significant changes in the chemical shifts of the aromatic core protons—namely, H_a in $\mathbf{1}^{3+}$ and H_f in **2**—and of the OCH_2 protons $H_{i/i'}$ and $H_{j/j'}$ are observed, in keeping with a co-conformation for the 1:1 complex in solution that is probably very similar to that in the solid-state superstructure (Figure 2) of $[\mathbf{1}\cdot\mathbf{2}]^{3+}$. The fact that the diastereotopicities of the OCH_2 protons $H_{i/i'}$ and $H_{j/j'}$ in **2** are so clearly evident in the ^1H NMR spectrum (Figure 3d) of $[\mathbf{1}\cdot\mathbf{2}]\cdot 3PF_6$ lends very strong support to the contention that $[\mathbf{1}\cdot\mathbf{2}]^{3+}$ is a highly stable supramolecular trication in $CDCl_3/CD_3CN$.[13] Indeed, only when the concentration of $[\mathbf{1}\cdot\mathbf{2}]\cdot 3PF_6$ is lowered from 7.5 to 0.05 mM is there any evidence of free species being present in the $CDCl_3/CD_3CN$ (1:1) solution. On the other hand, addition of CD_3SOCD_3 to the 7.5 mM $CDCl_3/CD_3CN$ (1:1) solution causes decomplexation. This observation is undoubtedly a consequence of CD_3SOCD_3 being a much better hydrogen-bond acceptor than either $CDCl_3$ or CD_3CN, and it thus competes successfully with the crown ethers' oxygen atoms for the NH_2^+ centers. Since the addition of CD_3SOCD_3 to the $CDCl_3/CD_3CN$ solution results in a mixture of triply, doubly, and singly threaded 1:1 complexes, as well as free species, under slow exchange, the ^1H NMR spectra become increasingly complicated. We sought a solution to this problem by incorporating methyl groups as ^1H NMR probes into the trication; therefore, we used **3**·$3PF_6$ instead of **1**·$3PF_6$ in subsequent investigations.[14]

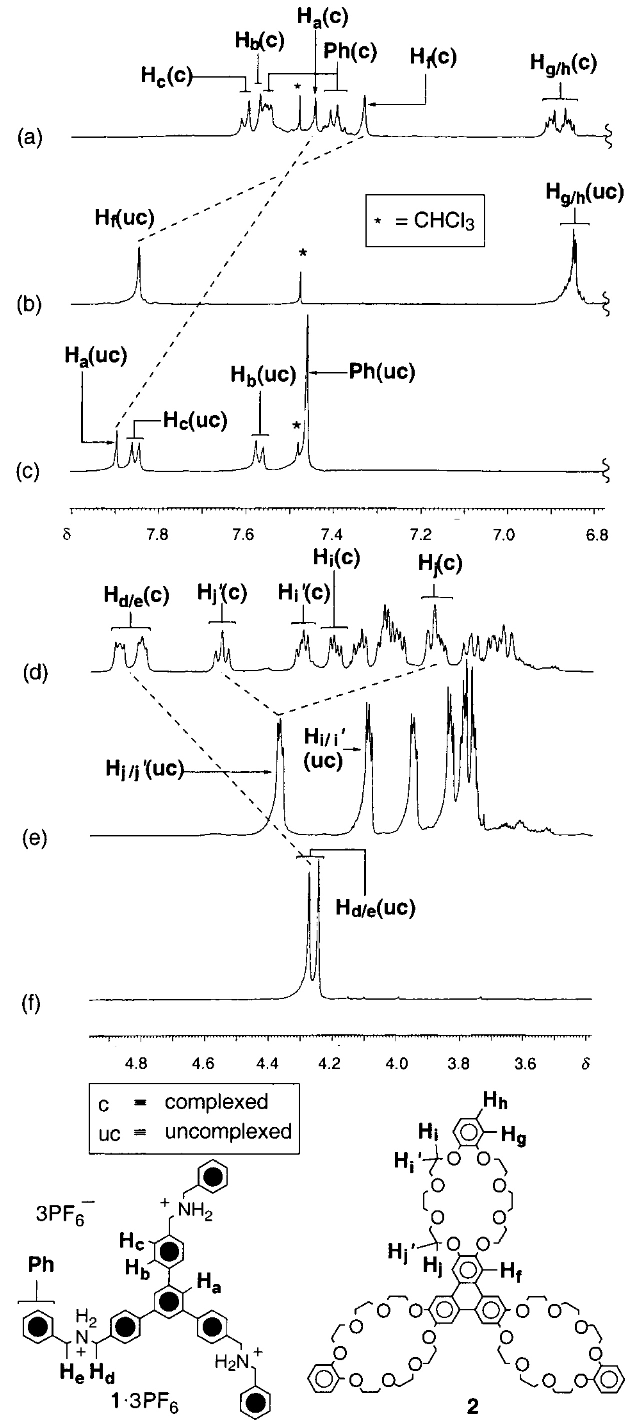

Figure 3. ^1H NMR spectra (500 MHz, $CDCl_3/CD_3CN$ (1:1), 7.5 mM, 300 K) showing the resonances in the aromatic regions for (a) an equimolar mixture of **1**·$3PF_6$ and **2**, (b) **2**, and (c) **1**·$3PF_6$ and the corresponding resonances (d), (e), and (f) in the aliphatic regions.

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[11] Hwang, T.-L.; Shaka, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 3157−3159.

[12] It has been demonstrated that the 1:1 complex formed between DBA·PF_6 and DB24C8 in $CDCl_3/CD_3CN$ (1:1) is in slow exchange on the ^1H NMR time scale with its free components at room temperature. See: Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 709−728.

[13] Note that the pairs of N^+CH_2 protons H_d and H_e in $\mathbf{1}^{3+}$ are enantiotopic and so have the same chemical shifts in the ^1H NMR spectrum of the equimolar mixture of **1**·$3PF_6$ and **2**.

Thus, decomplexation of $[\mathbf{3}\cdot\mathbf{2}]^{3+}$ was followed by adding aliquots of CD_3SOCD_3 to $[\mathbf{3}\cdot\mathbf{2}]\cdot3PF_6$ in $CDCl_3/CD_3CN$ (1:1) solution and monitoring the resonances for the different methyl groups by ^{1}H NMR spectroscopy (Figure 4). In principle, there are six different methyl groups present in these four possible species. In practice, four different signals are observed (δ 2.350 (**B**), 2.345 (**C**), 2.336 (**D**) and 2.311 (**A**)) in the spectrum (Figure 4c) recorded with 13.8% CD_3SOCD_3 present, reflecting the fact—we surmise—that the methyl groups in all of the bound sidearms resonate with identical or near-identical chemical shifts (**A**), irrespective of whether they are located in the singly, doubly, or triply threaded species, and that it is the methyl groups in the unbound arms of the free, singly, and doubly threaded species that give rise (Figure 5) to signals **C**, **B**, and **D**, respectively. It is evident from inspection of the partial spectra portrayed in Figure 4 that, as the proportion of CD_3SOCD_3 is raised, the intensity of resonance **C** increases while those of resonances **B** and **D** decrease.[15] And so it would appear that the cooperative recognition between **2** and $\mathbf{3}^{3+}$ can be reduced in a stepwise manner by changing the nature of the solvent, so that the supermolecule unlatches one latch at a time.

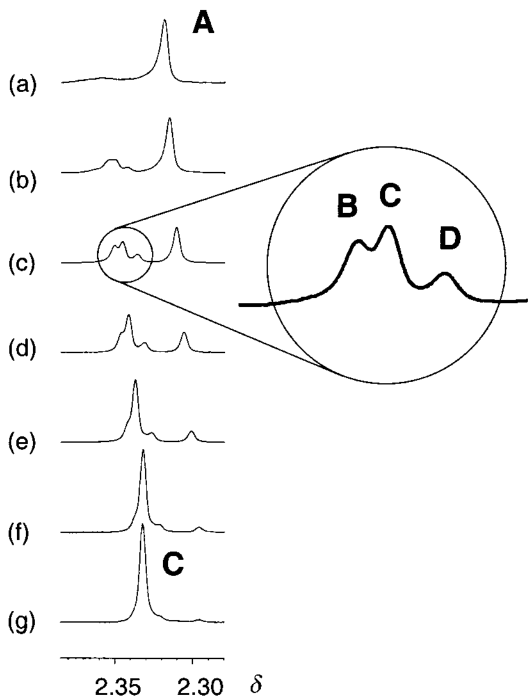

Figure 4. Partial ^{1}H NMR spectra showing the resonances corresponding to the methyl groups in an equimolar mixture of $\mathbf{3}\cdot3PF_6$ and **2** (500 MHz, $(100 - x)$ % $CDCl_3/CD_3CN$ (1:1) + x % CD_3SOCD_3, x = (a) 0, (b) 7.4, (c) 13.8, (d) 19.4, (e) 24.3, (f) 28.6, and (g) 33.3.

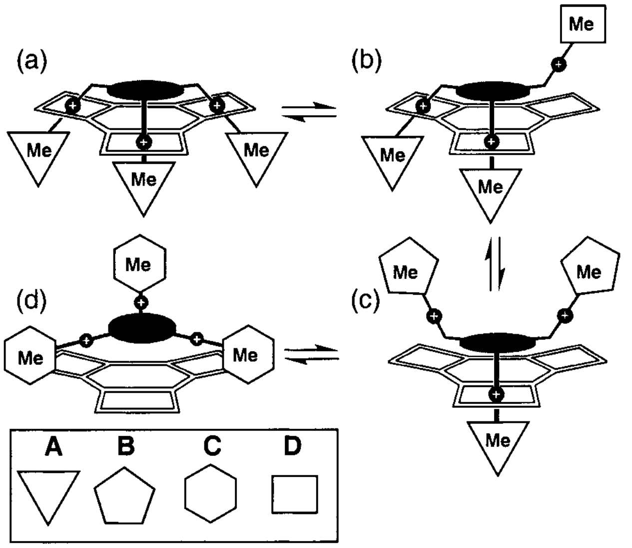

Figure 5. Schematic representation of the equilibration between **2** and $\mathbf{3}^{3+}$ involving species that are (a) triply, (b) doubly, and (c) singly threaded, as well as (d) free.

A triply cooperative,[16] stepwise, reversible binding motif, which utilizes the interpenetration of a tritopic triscrown ether by a complementary trifurcated trisammonium trication and which is extremely strong under favorable conditions, has been established. The use of this kind of binding motif in self-assembling supramolecular polymers[17] is now being pursued.

Acknowledgment. We thank UCLA for generous financial support.

Supporting Information Available: Experimental procedures for **2** and $\mathbf{3}\cdot3PF_6$ in addition to crystallographic data for $[\mathbf{1}\cdot\mathbf{2}]^{3+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) In the ^{1}H NMR spectrum ($CD_3CN/CDCl_3$) of an equimolar mixture of p-Me_2-DBA·PF_6 and DB24C8, the signals for the methyl groups in the 1:1 complex and the free p-Me_2-DBA^+ cation (which are in slow exchange) resonate at δ 2.19 and 2.35, respectively. See: Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2117−2128.

(15) Resonances **B** and **D** can be assigned speculatively. Since resonance **B**, in general, has a greater intensity than that of **D**, then resonance **B** probably corresponds to the uncomplexed methyl protons in the singly threaded species leaving resonance **D** to correspond to the uncomplexed methyl protons in the doubly threaded species.

(16) An instance of double cooperativity has been observed recently in a peptidic pseudorotaxane based on the DBA^+/DB24C8 recognition motif. See: Meillon, J.-C.; Voyer, N.; Biron, E.; Sanschagrin, F.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 143−145.

(17) For recent examples of linear supramolecular polymerizations involving the DBA^+/DB24C8 recognition motif, see (a) Yamaguchi, N.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 143−147. (b) Yamaguchi, N.; Gibson, H. W. *Chem. Commun.* **1999**, 789−790.