Controlling Multivalent Interactions in Triply-Threaded Two-Component Superbundles

Vincenzo Balzani,*[a] Miguel Clemente-León,[a, d] Alberto Credi,*[a] James N. Lowe,[b, e] Jovica D. Badjić,[b] J. Fraser Stoddart,*[b] and David J. Williams*[c]

Abstract: We have investigated the ^{1}H NMR spectra, the absorption spectra, the fluorescence spectra and decays, and the electrochemical properties of i) a tritopic receptor in which three benzo[24]crown-8 macrorings are fused onto a triphenylene core, ii) a trifurcated trication wherein three dibenzylammonium ions are linked 1,3,5 to a central benzenoid core, and iii) their 1:1 adduct which constitutes a triply-threaded, two-component supramolecular bundle. X-Ray crystallography has established the precise geometry of this paucivalent recognition motif in the solid state. In addition to [N$^+$-H$\cdots$O] hydrogen bonding and [C-H$\cdots$O] interactions between the NH_2^+ centers on the three dibenzylammonium ion containing arms of the trication and the three crown ether rings in the tritopic receptor, there is a stabilizing [$\pi\cdots\pi$] stacking interaction between the two aromatic cores. Mass spectrometry and ^{1}H NMR spectroscopy have confirmed the integrity of the 1:1 adduct beyond the solid state, provided the solvents are relatively apolar (e.g., chloroform and acetonitrile). The intense fluorescence emissions of the two recognition components are quenched upon association with the concomitant appearance of a lower energy, broad fluorescence band originating from the $\pi-\pi$ stacking in the 1:1 adduct of the aromatic cores in the two matching components. Titration experiments, including Job plots, establish the 1:1 stoichiometry of the adduct, an observation which is also confirmed by electrochemical experiments. The electrochemical results show that, both in the tritopic receptor and in the superbundle itself, the first oxidation process is associated with the hexaalkoxytriphenylene core. The successive oxidation processes of the peripheral dioxybenzene units are affected by charge-transfer interactions in the tritopic receptor, whereas, in the superbundle, such units are not interacting. In acetonitrile solution, dethreading/rethreading of the 1:1 adduct can be controlled quantitatively by addition of base and acid. Dethreading and rethreading is also observed by ^{1}H NMR spectroscopy when dimethylsulfoxide is added to a solution of the 1:1 adduct in equal volumes of acetonitrile and chloroform. A trifurcated trication where methyl groups are located on the *para* positions of the three dibenzylammonium ions, which are linked 1,3,5 to the neutral benzenoid core, has been employed to demonstrate that dethreading of the 1:1 adduct involves doubly-threaded and singly-threaded species, that is, the paucivalent site is dismembered in a sequence of logical steps involving stable intermediates. This molecular recognition system is a rare example of a supramolecular entity based on a cooperative binding motif that can be switched on and off by chemical means.

Keywords: hydrogen bonds · luminescence · molecular machines · molecular recognition · self-assembly

---

[a] Prof. V. Balzani, Dr. A. Credi, Dr. M. Clemente-León
Dipartimento di Chimica "G. Ciamician"
Università di Bologna
Via Selmi 2, 40126 Bologna (Italy)
Fax: (+39) 051-029-9456
E-mail: vbalzani@ciam.unibo.it
acredi@ciam.unibo.it

[b] Prof. J. F. Stoddart, Dr. J. N. Lowe, Dr. J. D. Badjić
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569 (USA)
Fax: (+1) 310-206-1843
E-mail: stoddart@chem.ucla.edu

[c] Prof. D. J. Williams
Chemical Crystallography Laboratory
Department of Chemistry, Imperial College
South Kensington, London, SW7 2AY (UK)
Fax: (+44) 207-594-5835

[d] Dr. M. Clemente-León
Current address:
Instituto de Ciencia Molecular, Universitat de València
Dr. Moliner 50, 46100 Burjassot (Spain)

[e] Dr. J. N. Lowe
Current address:
Department of Chemistry, University of Pennsylvania
231 South 34th Street, Philadelphia, PA 19104-6323 (USA)

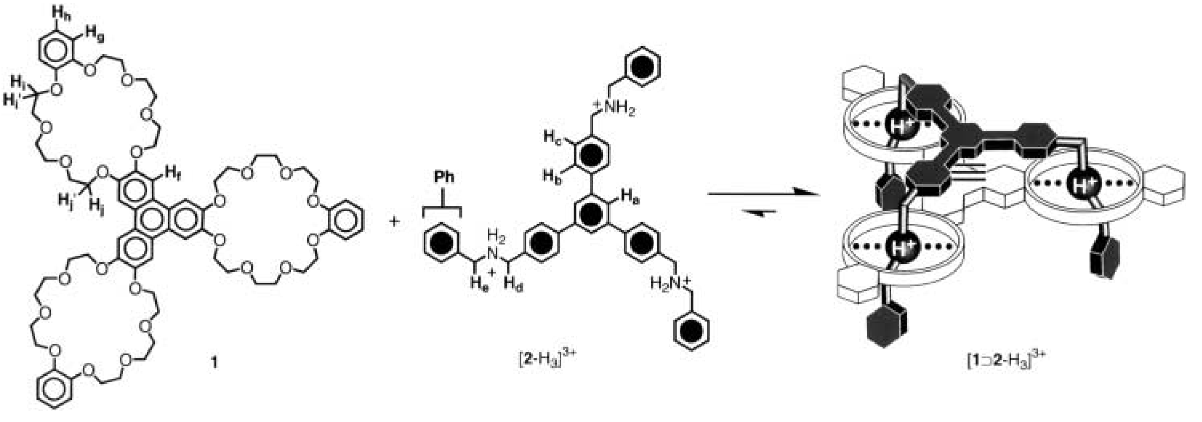
DOI: 10.1002/chem.200304979

Introduction

The concept of threading a secondary dialkylammonium ($RCH_2NH_2^+CH_2R$) ion containing an NH_2^+ center through the cavity of a macrocyclic polyether with a [24]crown ether constitution minimally was first demonstrated[1, 2] in 1995. This recognition motif, which relies primarily upon [N^+-H···O] hydrogen bonds and [C-H···O] interactions,[3] has been exploited extensively[4–6] in the noncovalent synthesis[7] of supermolecules (complexes including pseudorotaxanes) and in supramolecular assistance[7] to the covalent synthesis of interlocked molecular compounds such as catenanes and rotaxanes. These activities also led to the design of molecular-level devices and machines activated by acid–base inputs,[8–10] as well as to the modification of surfaces and to the control of the aggregation of silver nanocrystals.[11]

In an effort to achieve enhanced association using this particular recognition motif, we have recently launched an investigation[12] into the complexation properties of matching components, each containing multiple recognition sites. This clustering of weak interactions is a well known phenomenon[13] in biological systems and is variously referred to[14] as the cluster effect or multivalency. For our initial investigations on multivalency in a wholly unnatural supramolecular system, we have chosen, as the matching components, i) a tritopic receptor in the form of a tris-crown ether derivative **1**, which consists of three benzo[24]crown-8 macrorings fused onto a triphenylene core, and ii) the trifurcated trication [**2**-H_3]$^{3+}$, as its hexafluorophosphate salt,[15] wherein three dibenzylammonium ions are linked 1,3,5 to a central benzenoid core. Matching the components gives rise (Scheme 1) to the

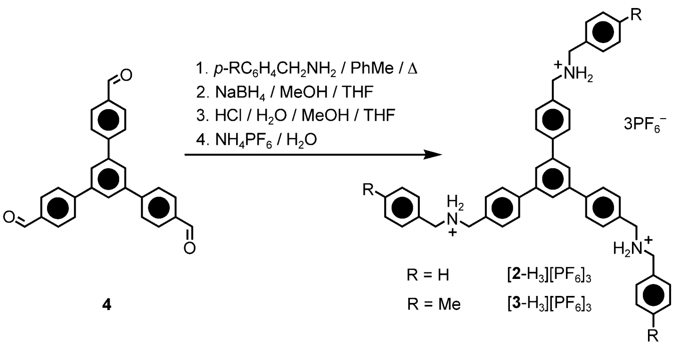
Abstract in Italian: *Sono stati studiati gli spettri ^1H NMR, gli spettri di assorbimento elettronico, gli spettri ed i decadimenti di fluorescenza e le proprietà elettrochimiche di i) un recettore tritopico formato da tre macrocicli benzo[24]corona-8 costruiti su un gruppo trifenilene centrale, ii) un tricatione ramificato in cui tre ioni dibenzilammonio sono legati ad un'unità benzenica centrale in posizione 1,3,5 e iii) il loro addotto 1:1. Quest'ultimo costituisce una sorta di "fascio" supramolecolare, in cui ciascun ramo del componente tricationico è infilato in un macrociclo del recettore tritopico. L'analisi cristallografica ai raggi X ha permesso di stabilire la geometria dell'addotto allo stato solido e di evidenziare le interazioni fra i suoi componenti. Oltre a legami a idrogeno [N^+-H···O] e [C-H···O] tra gli ioni dibenzilammonio di un componente e gli eteri corona dell'altro, si osservano interazioni di stacking [π···π] tra le due unità aromatiche centrali. L'addotto 1:1 è stabile anche in soluzione, come dimostrato da esperimenti di spettrometria di massa e di spettroscopia ^1H NMR, purché in solventi relativamente poco polari come il cloroformio o l'acetonitrile. L'intensa fluorescenza dei due componenti molecolari viene spenta in seguito alla loro associazione, con la concomitante comparsa di una banda di fluorescenza larga e a bassa energia dovuta alle interazioni [π···π] tra le due unità aromatiche centrali nell'addotto. La stechiometria 1:1 dell'addotto è confermata da titolazioni, Job plot ed esperimenti elettrochimici. I risultati di questi ultimi esperimenti mostrano che il primo processo di ossidazione osservato sia nel recettore tritopico che nell'addotto è attribuibile all'unità centrale esaossitrifenilene. I successivi processi di ossidazione delle unità diossibenzene periferiche nel recettore tritopico sono influenzati da interazioni di trasferimento di carica, mentre tali unità non interagiscono tra loro quando si trovano nell'addotto. In acetonitrile l'addotto 1:1 può essere sfilato e reinfilato in maniera quantitativa e controllata mediante l'aggiunta di acido e di base. I processi di sfilamento e reinfilamento si osservano anche aggiungendo dimetilsolfossido ad una soluzione dell'addotto in acetonitrile/cloroformio 50:50 (v/v), attraverso la spettroscopia ^1H NMR. Utilizzando un tricatione ramificato in cui si sono introdotti gruppi metilici in posizione para nelle tre unità dibenzilammonio, è stato possibile dimostrare che lo sfilamento dell'addotto 1:1 coinvolge specie doppiamente e singolarmente infilate. In altre parole, l'addotto si disassembla secondo una sequenza logica che passa attraverso specie intermedie stabili. Questo sistema di riconoscimento molecolare costituisce un raffinato esempio di architettura supramolecolare basata su interazioni che cooperano tra loro e che possono essere attivate e disattivate mediante stimoli chimici.*



Scheme 1. The equilibrium between the tris-crown ether **1** and the tris-ammonium ion [**2**-H_3]$^{3+}$ which lies very much over to the right in favor of the 1:1 adduct [**1**$\supset$**2**-H_3]$^{3+}$ in solvents such as MeCN and CH_2Cl_2. In DMSO, the 1:1 adduct becomes completely dissociated into its components. The graphical representation of the 1:1 adduct portrays the good surface-to-surface match between the two interpenetrating components. The dots indicate the [N^+-H···O] hydrogen bonds between the NH_2^+ centers (indicated by the symbol H^+ placed inside a circle) of [**2**-H_3]$^{3+}$ and the fused benzo[24]crown-8 rings in **1** and the horizontal dashes, the [π···π] stacking interactions between the central aromatic core units.

formation of a 1:1 adduct $[1 \supset 2\text{-}H_3]^{3+}$ in the shape of a triply threaded, two-component supramolecular bundle or superbundle with C_{3v} symmetry.

In this paper, we describe 1) the synthesis of **1** and a derivative [**3**-H_3][PF_6]$_3$ of the parent[14] trifurcated tricationic salt [**2**-H_3][PF_6]$_3$, 2) the characterization of the 1:1 adducts formed between **1** and [**2**-H_3]$^{3+}$, and **1** and [**3**-H_3]$^{3+}$ in solution by ^{1}H NMR spectroscopy and mass spectrometry, and 3) the solid-state superstructure of $[1 \supset 2\text{-}H_3][PF_6]_3$, obtained by X-ray crystallography on a single crystal of the 1:1 adduct. On account of their extended aromatic structures, both **1** and [**2**-H_3]$^{3+}$ are expected to be photo- and redox-active. Stimulated by the growing interest in the excited-state and redox properties of supramolecular systems,[8–10, 16–23] we have investigated the 4) photophysical and 5) electrochemical properties of the interwoven superbundle $[1 \supset 2\text{-}H_3]^{3+}$ and its free components **1** and [**2**-H_3]$^{3+}$. We have also shown that 6) assembling/disassembling of the superbundle, which involves a triple threading/dethreading process, can be reversibly and quantitatively controlled by the addition of acid and base to an acetonitrile solution. Some of the results reported in this paper have been the subject of a preliminary communication.[24, 25]

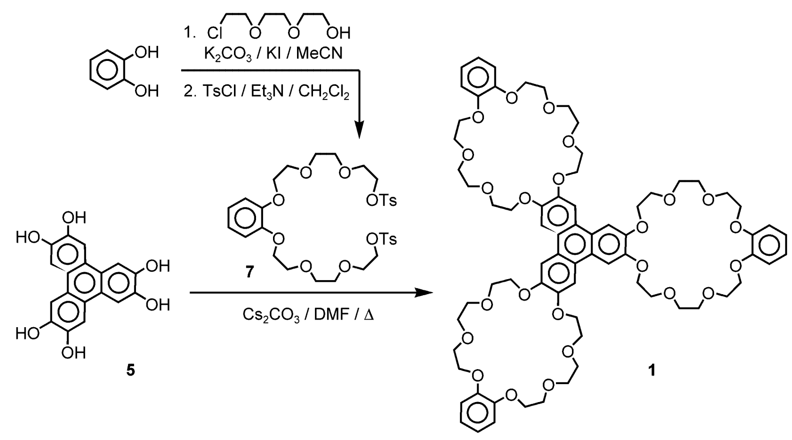


Scheme 2. The synthesis of the tris-ammonium salts [**2**-H_3][PF_6]$_3$ and [**3**-H_3][PF_6]$_3$.

Results and Discussion

Synthesis of the tritopic recognition components: Of the three components—namely **1**, [**2**-H_3][PF_6]$_3$, and [**3**-H_3][PF_6]$_3$—the synthesis of the tris-ammonium salt has been described previously,[15] starting from the known[26] trialdehyde **4** as depicted in Scheme 2. The derivative [**3**-H_3][PF_6]$_3$ of [**2**-H_3][PF_6]$_3$ with three terminal *p*-methylbenzyl groups was obtained (Scheme 2) by condensing **4** with *p*-methylbenzylamine in PhMe in a Dean–Stark apparatus to afford a trisimine, which was subsequently reduced ($NaBH_4$/THF/MeOH) to form a trisamine. The trisamine was protonated (HCl/THF/MeOH/H_2O) and the counterions were exchanged (NH_4PF_6/H_2O) to give [**3**-H_3][PF_6]$_3$.

The tris-crown ether derivative **1** was obtained (Scheme 3) in 10% yield following a triple macrocyclization (Cs_2CO_3/DMF) between 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP, **5**) and the appropriate bistosylate **7** under high dilution conditions. HHTP (**5**) was prepared according to literature procedures.[27] The bistosylate **7** was obtained[28] from catechol in two steps—its bisalkylation (K_2CO_3/KI/MeCN) with 2[2(2-chloroethoxy)ethoxy]ethanol to give a diol **6** which, on tosylation (TsCl/CH_2Cl_2), gave the desired product **7**.



Scheme 3. The synthesis of the tris-crown ether derivative **1**.

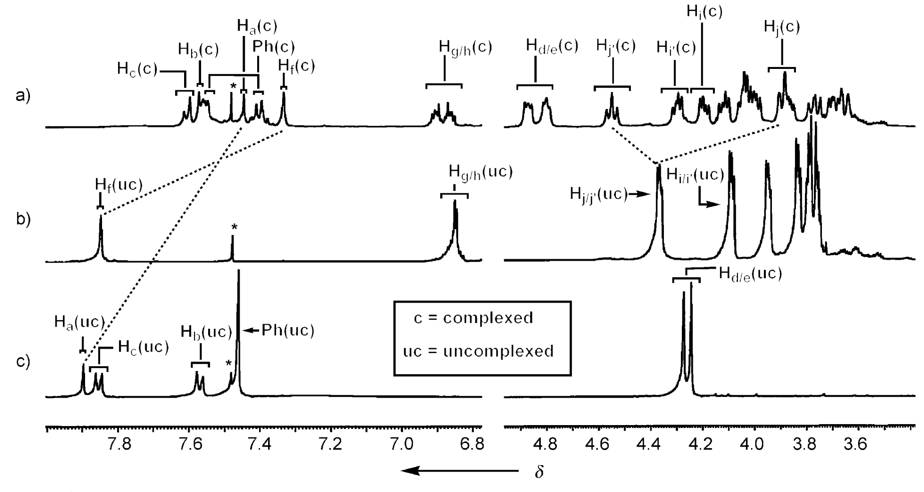


Figure 1. ^{1}H NMR Spectra [500 MHz, $CDCl_3$/CD_3CN (1:1), 7.5 mM, 300 K] recorded on a) the 1:1 adduct $[1 \supset 2\text{-}H_3][PF_6]_3$, b) the tris-crown ether **1**, and c) the tris-ammonium salt [**2**-H_3][PF_6]$_3$.

Characterization of the parent superbundle in solution: Fast atom bombardment (FAB) mass spectrometry performed on a sample obtained from an equimolar solution of the tris-crown ether derivative **1** and the tris-ammonium salt [**2**-H_3][PF_6]$_3$ revealed intense signals in the spectrum at *m*/*z* 2295, 2149, and 2004 corresponding to the [**1**+**2**-H_3+2PF_6]$^+$, [**1**+**2**-H_3+PF_6]$^+$, and [**1**+**2**-H_3]$^+$ ions, respectively. This evidence for a strong 1:1 adduct being formed in relatively apolar solvents was supported by ^1H NMR spectroscopy. A spectrum, recorded in $CDCl_3$/CD_3CN (1:1) of an equimolar mixture (7.5 mM) of **1** and [**2**-H_3][PF_6]$_3$ reveals (Figure 1a) a very highly dispersed array of almost isolated resonances. A comparison of this spectrum with those recorded under the same conditions for pure **1** (Figure 1b) and pure [**2**-H_3][PF_6]$_3$ (Figure 1c) indicates that there are *no* signals for these free species present in the ^1H NMR spectrum of the 1:1 adduct. Indeed, only when the concentration of [**1**$\supset$**2**-H_3][PF_6]$_3$ 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. With the aid of ^1H,^1H COSY (Figure 2) and 2D ^1H NMR T-ROESY (Figure 3) experiments,[29, 30] it is possible to assign the resonances as shown in Figure 1a, to a single C_{3v} symmetrical adduct—namely, the [**1**$\supset$**2**-H_3]$^{3+}$ superbundle—that is kinetically stable on the ^1H NMR timescale.[31] The large downfield shifts (Table 1) and multiplicities of the resonances for the benzylic methylene protons H_d and H_e adjacent to the NH_2^+ centers are characteristic[32] of the formation of a 1:1 complex between dibenzo[24]crown-8 (DB24C8) and the dibenzylammonium ion ([DBA]$^+$). In addition, substantial changes in the chemical shifts of the aromatic core protons—that is, H_f (−0.55 ppm) in **1** and H_a (−0.44 ppm) in [**2**-H_3]$^{3+}$—are observed, a phenomenon which suggests that these cores are [π–π] stacked with respect to each other. On complexation with the [**2**-H_3]$^{3+}$ trication, the OCH_2 protons, such as H_i/$H_{i'}$ and H_j/$H_{j'}$ in the tris-crown ether derivative separate into two different sets of signals as a consequence of **1** losing its plane of symmetry orthogonal to the principal axis in the molecule. Stated another way, the pairs of protons in each OCH_2 group that are directed toward the bound [**2**-H_3]$^{3+}$ trication become diastereotopic with respect to those which are directed away from the [**2**-H_3]$^{3+}$ trication. The diastereotopicities of the OCH_2 protons H_i/$H_{i'}$ and H_j/$H_{j'}$ in **1** can be observed (Figure 1a) in the ^1H NMR spectrum of the 1:1 adduct. In fact, for H_j/$H_{j'}$, the anisochronous effect is quite dramatic: in comparison with the free tris-crown ether derivative **1**, the resonances for one set of protons are shifted by +0.2 ppm (downfield) while those for the other set are shifted by −0.5 ppm (upfield). These observations lend further support to the conclusion that the 1:1 adduct is a highly stable supramolecular entity in $CDCl_3$/CD_3CN (1:1)—and the fact that complexation–decomplexation is slow on the ^1H NMR timescale.

Solid-state superstructure of the superbundle: A single crystal X-ray investigation[33] confirmed the formation in the solid state of a 1:1 adduct in which the three unique cationic arms of the triply charged guest are inserted through the centers of the three crown ether components of the neutral host. In contrast with the time-averaged C_{3v} symmetry observed in solution for the 1:1 adduct, here, in the solid state, a geometry that approximates more closely to C_s is adopted (Figure 4).

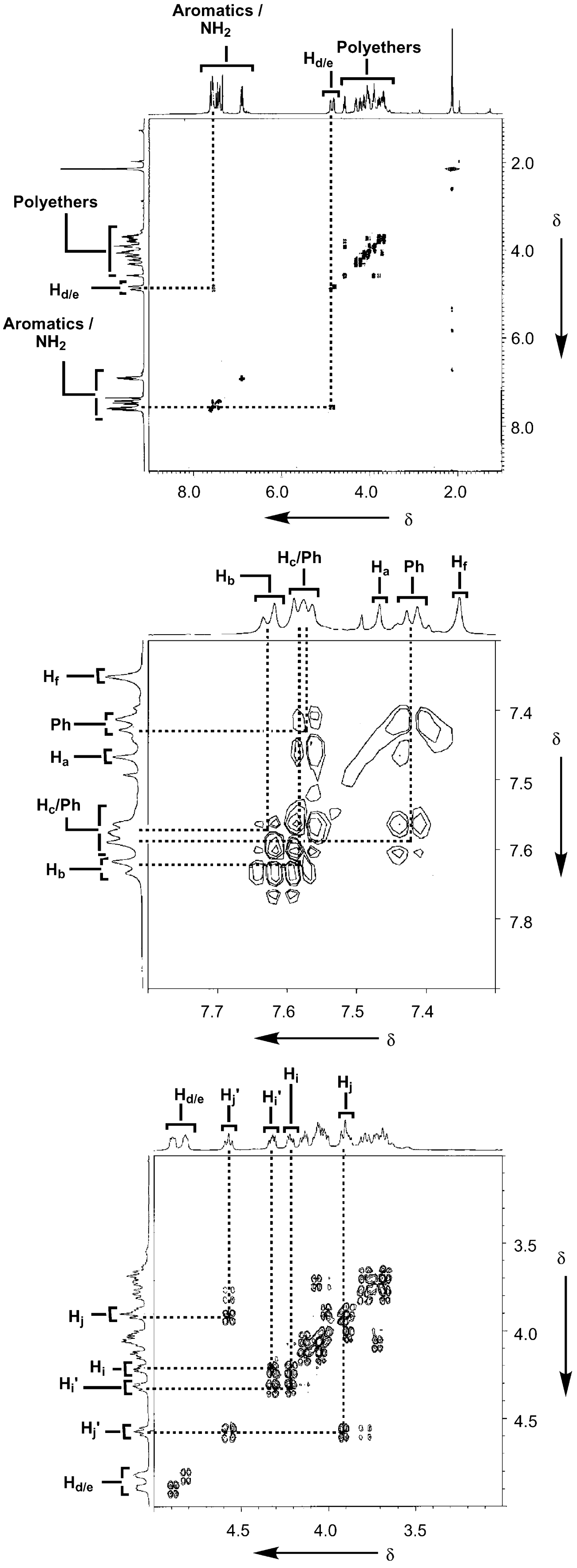


Figure 2. Selected areas of the ^1H,^1H COSY NMR spectrum [500 MHz, $CDCl_3$/CD_3CN (1:1), 7.5 mM, 300 K] of the 1:1 adduct [**1**$\supset$**2**-H_3][PF_6]$_3$.

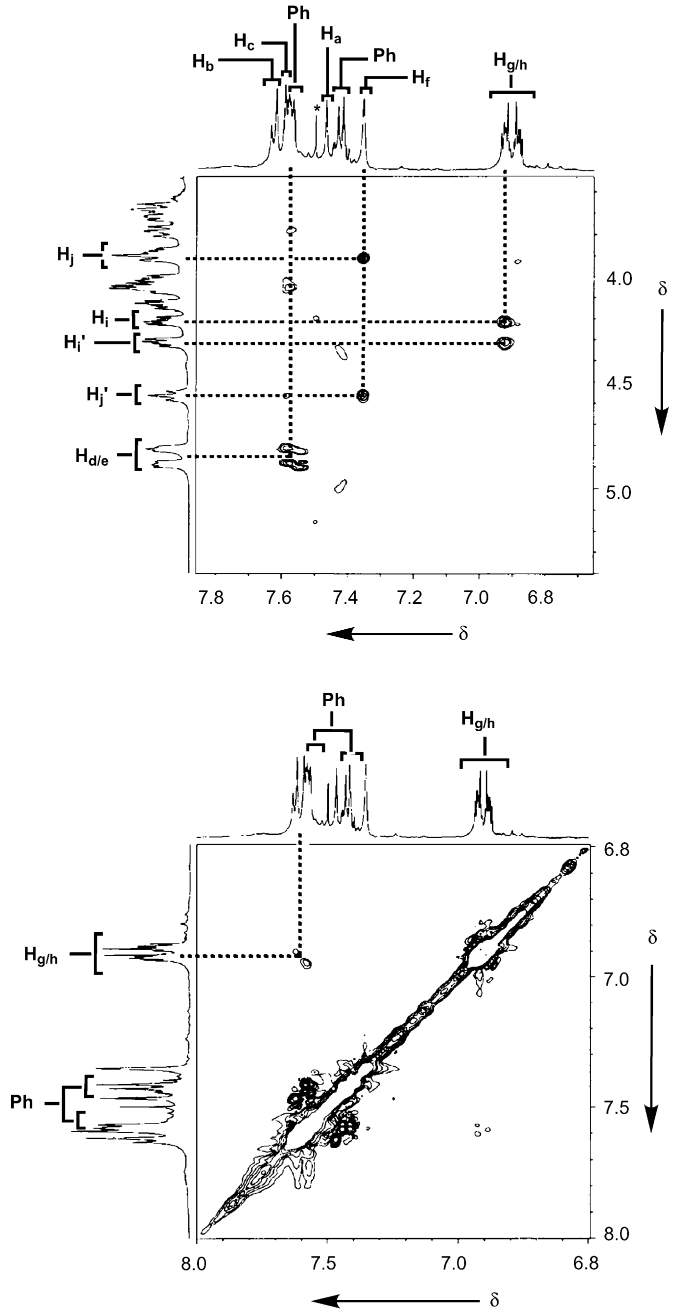


Figure 3. Selected areas of the T-ROESY NMR spectrum [500 MHz, $CDCl_3/CD_3CN$ (1:1), 7.5 mM, 300 K] of the 1:1 adduct $[\mathbf{1}\supset\mathbf{2}\text{-H}_3][PF_6]_3$.

Table 1. The chemical shifts (δ) of the protons[a] in the uncomplexed tris-crown ether **1**, the uncomplexed tris-ammonium salt $[\mathbf{2}\text{-H}_3][PF_6]_3$, and the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3][PF_6]_3$—and the change ($\Delta\delta$) in chemical shift on complexation.

Proton[b]	δ(uc)	δ(c)	$\Delta\delta$
H_a	7.89	7.45	−0.44
H_b	7.58	7.59	+0.01
H_c	7.86	7.63	−0.23
H_d/H_e	4.27	4.80–4.90	+0.5–0.6
Ph	7.46	7.58 & 7.42	–
H_f	7.86	7.35	−0.51
H_h/H_g	6.85	6.88–6.94	+0.03–0.09
H_i	4.09	4.13	+0.04
$H_{i'}$	4.09	4.20	+0.11
H_j	4.37	3.90	−0.47
$H_{j'}$	4.37	4.57	+0.20

[a] The ^1H NMR spectra were recorded at 500 MHz in $CDCl_3/CD_3CN$ (1:1) at a concentration of 7.5 mM at ambient temperature. [b] The proton designations are shown in Scheme 1.

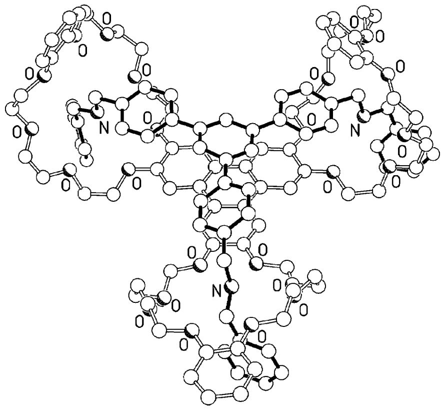


Figure 4. Ball-and-stick representation of the solid-state superstucture of the 1:1 adduct $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$.

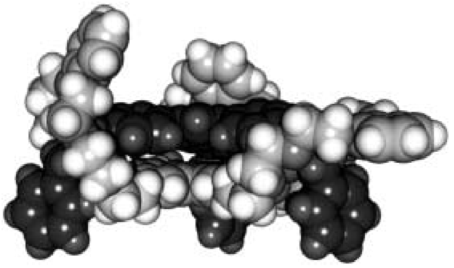


Figure 5. Space-filling representation of the solid-state superstucture of the 1:1 adduct $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$. The lighter shaded molecule is the tris-crown ether component and the darker shaded one, the tris-ammonium ion component. The discoid-shaped superbundle has a surface radius of approximately 14 Å and thickness of 16 Å, i.e., overall dimensions of ca. 2.8 × 1.6 mm.

Although the C_3 symmetry of the tri-cationic component is essentially retained, two distinctly different conformations are evident for the crown-ether components of the host: two of these macrocycles have a U-shaped conformation whereas the third adopts an extended conformation with a pseudo-C_i symmetry (Figure 5). The two-component superbundle is stabilized by a combination of [π···π], [N^+-H···O] and [C-H···O] interactions as discussed previously.[24] The two components overlay each other with the planes of their central aromatic rings nearly parallel and a centroid-centroid separation of 3.6 Å, consistent with stabilizing [π···π] interactions. A secondary conformational feature is the adoption of nonplanar conformations by the three biphenylene units of the trication. Here, the local symmetry is C_3, the planes of the three radial phenylene rings being inclined (by between ca. 15 and 23°) in a propeller-like manner with respect to the central pivotal benzenoid ring in the guest. Accompanying these twists, there is a commensurate but smaller, distortion of the triphenylene unit of the host. The only inter-superbundle interaction of note is a [π···π] stacking of one of the radial phenylene rings of the tricationic component with its C_i-related counterpart (mean interplanar separation of 3.65 Å).

Absorption and fluorescence spectra: The absorption and fluorescence data for the compounds recorded in CH_2Cl_2[34] are given in Table 2. Figure 6 shows the absorption spectra of free **1**, free $[\mathbf{2}\text{-H}_3]^{3+}$, and their 1:1 mixture, that is, of the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ in CH_2Cl_2 solution. It is evident that the formation of the superbundle causes relatively small changes in the absorption spectrum. The spectra obtained in MeCN do not differ significantly from those recorded in CH_2Cl_2.

Table 2. Absorption and fluorescence data for the compounds examined in CH_2Cl_2 at room temperature.

	Absorption		Fluorescence	
Compound	λ_{max} [nm]	ε [$\text{M}^{-1}\text{cm}^{-1}$]	λ_{max} [nm]	τ [ns]
1	278	88000	384	10
$[\mathbf{2}\text{-H}_3]^{3+}$	262	69000	356	17.5
$[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$	270	122000	410	12.5

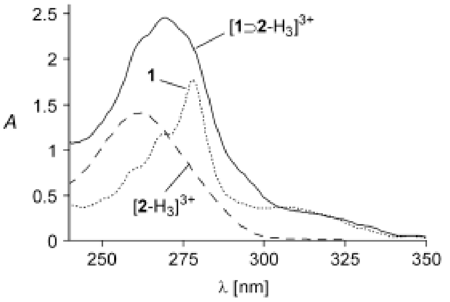


Figure 6. Absorption spectra of the 2.0×10^{-5} mol L^{-1} CH_2Cl_2 solutions of the tris-crown ether **1** (••••), the tris-ammonium ion $[\mathbf{2}\text{-H}_3]^{3+}$ (– – –) and the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ (——).

The emission spectra of free **1**, free $[\mathbf{2}\text{-H}_3]^{3+}$ and the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ in CH_2Cl_2 are illustrated in Figure 7. The tris-crown ether derivative **1** shows a relatively strong and structured emission band, quite similar to that observed[35] for its triphenylene core with $\lambda_{max} = 384$ nm and $\tau = 10$ ns. No fluorescence band typical of DB24C8 or of its 1,2-dioxybenzene subunits ($\lambda_{max} \approx 310$ nm)[10b] is observed. The $[\mathbf{2}\text{-H}_3]^{3+}$ tricationic component shows the characteristic strong fluorescence band[35] of its 1,3,5-triphenylbenzene core with $\lambda_{max} = 356$ nm and $\tau = 17.5$ ns; no emission typical ($\lambda_{max} = 337$ nm) of the $[\text{DBA}]^+$ ion is observed. In the emission spectrum of the 1:1 mixture, the fluorescence bands of the two components are no longer present, a result which is to be expected if a 1:1 adduct had been formed. The superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ exhibits a broad unstructured luminescence band at longer wavelengths ($\lambda_{max} = 410$ nm) which decays according to a single exponential with a lifetime of 12.5 ns. The excitation spectrum of $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$, recorded at $\lambda_{max} = 410$ nm, reveals that the excitation of both components leads quantitatively to the fluorescent excited state of the superbundle. By contrast, the fluorescence spectrum of DB24C8 is hardly affected[10d] by its being threaded by $[\text{DBA}]^+$ ions. The dramatic changes in the spectra observed upon titration of **1** and $[\mathbf{2}\text{-H}_3]^{3+}$ indicate that the two components are tightly connected in the resulting 1:1 adduct which, in fact, behaves as a novel fluorophoric unit. The new fluorescence emission observed in the superbundle most likely originates from a lower lying excited state, which results from the [π–π] stacking of the aromatic cores of the two components (Scheme 1). This is evident from the solid-state superstructure where the centroid–centroid separation was observed to be 3.6 Å. In MeCN solution, the fluorescence spectra and lifetimes of this tris-crown ether derivative **1** ($\tau = 9.6$ ns) and the tris-ammonium trication $[\mathbf{2}\text{-H}_3]^{3+}$ ($\tau = 17$ ns) and the 1:1 adduct ($\tau = 11.6$ ns) are very similar to those observed in CH_2Cl_2 solution.

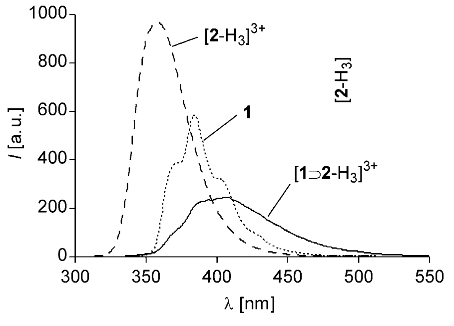


Figure 7. Emission spectra ($\lambda_{exc} = 252$ nm) of 2.0×10^{-5} mol L^{-1} CH_2Cl_2 solutions of the tris-crown ether **1** (••••), the tris-ammonium ion $[\mathbf{2}\text{-H}_3]^{3+}$ (– – –), and the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ (——).

Titration experiments: In order to establish that the association of **1** with $[\mathbf{2}\text{-H}_3]^{3+}$ is strong and also to confirm the 1:1 stoichiometry of the supramolecular species, we have carried out numerous titration experiments. Figure 8 shows the changes in the emission spectra ($\lambda_{exc} = 252$ nm) observed on the addition of small volumes of a concentrated CH_2Cl_2 solution of the tris-crown ether derivative **1** to a 2.0×10^{-5} mol L^{-1} CH_2Cl_2 solution[34] of the tris-ammonium salt $[\mathbf{2}\text{-H}_3][PF_6]_3$. A decrease in the intensity of the emission band ($\lambda_{max} = 356$ nm) of $[\mathbf{2}\text{-H}_3]^{3+}$ is accompanied by an increase in the intensity of the band ($\lambda_{max} = 410$ nm) of the superbundle.

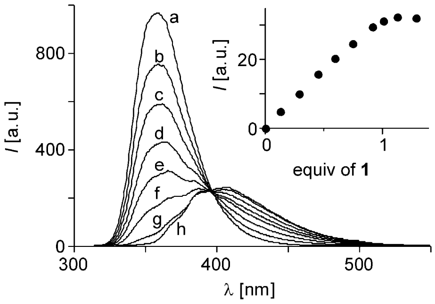


Figure 8. Changes in the emission spectra ($\lambda_{exc} = 252$ nm) of a 2.0×10^{-5} mol L^{-1} CH_2Cl_2 solution of the tris-ammonium ion $[\mathbf{2}\text{-H}_3]^{3+}$ on titration with the tris-crown ether **1**. The numbers of equivalents of tris-crown ether added are 0 (a), 0.13 (b), 0.29 (c), 0.45 (d), 0.59 (e), 0.75 (f), 0.92 (g), 1.01 (h). The inset shows the corresponding titration curve obtained by reading the luminescence intensity at 490 nm.

From the titration curve (inset in Figure 8) obtained at $\lambda_{em} = 490$ nm,[36] a K_a value in excess of 10^7 L mol^{-1} can be estimated. Titration experiments in MeCN solutions yielded a K_a value of 10^6 L mol^{-1}. Such very high association constants, compared with those[31] for the [2]pseudorotaxane formed between DB24C8 and [DBA][PF_6]—27 000 and 420 L mol^{-1} in $CHCl_3$ and MeCN, respectively—proved that association of **1** with [**2**-H_3]$^{3+}$ is strongly favored by cooperative action[37–39] between the three binding sites, emphasizing the highly complementary nature of the two components. Not surprisingly, the 1:1 adduct is even more stable[40] in CH_2Cl_2 than in MeCN.

We have also constructed Job plots for the association process by measuring the emission light intensities of the 1:1 adduct at 490 nm[36] in CH_2Cl_2 (Figure 9) and MeCN solutions containing different molar fractions of the two components. The maximum observed at $x = 0.5$ proves conclusively that the complex has 1:1 stoichiometry. Moreover, the sharpness of the curve, which is more pronounced in the CH_2Cl_2 experiment, confirms the association constant is extremely high, that is, $K_a = 1.5 \times 10^7$ L mol^{-1}.

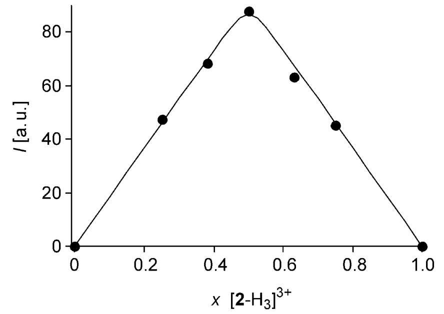


Figure 9. Job plot of the intensity of the emission at 490 nm of different mixtures of the tris-crown ether **1** and the tris-ammonium ion [**2**-H_3]$^{3+}$ as a function of the molar fraction of [**2**-H_3]$^{3+}$. Excitation was performed at 270 nm, where the two components exhibit the same molar absorption coefficient (Figure 6). The solvent was CH_2Cl_2 and the sum of the concentrations of the two components was 4.0×10^{-5} mol L^{-1} in all cases. The curve simulating the formation of a 1:1 adduct with a stability constant of 1.5×10^7 L mol^{-1} is also shown.

Electrochemical behavior: We have performed electrochemical investigations on the tris-crown ether **1**, the tris-ammonium ion [**2**-H_3]$^{3+}$ and the 1:1 adduct [**1** ⊃ **2**-H_3]$^{3+}$ both in MeCN and in CH_2Cl_2. Correlations between these species and some model compounds and complexes are shown in Figure 10. To begin with, we investigated the electrochemical behavior in MeCN of [**2**-H_3]$^{3+}$—and then of **1**. The former does not exhibit any redox processes in the potential window examined whereas the latter was found to behave in a complex manner, exhibiting three irreversible oxidation processes. The potential values, obtained from differential pulse voltammogram (DPV) measurements on **1** were +0.99, +1.29 and +1.44 V in CH_2Cl_2 and +1.00, +1.23 and +1.38 V in MeCN. The second peak is more appropriately described as a shoulder; the second and third peaks are more intense than the first one. The superbundle [**1** ⊃ **2**-H_3]$^{3+}$ exhibits only two oxidation peaks—at +1.01 and +1.44 V in CH_2Cl_2 and at +1.08 and +1.43 V in MeCN. In an attempt to assign these observed processes, and associate them with structural features, we have also examined the electrochemical behavior of some model compounds. We have found that 1) in CH_2Cl_2, 2,3,6,7,10,11-hexamethoxytriphenylene—a model compound for the central triphenylene core of the tris-crown ether **1**—reveals an irreversible process at +1.02 V, 2) in MeCN, DB24C8 exhibits two irreversible oxidation peaks at +1.32 and +1.47 V, a result that can be attributed to a donor–acceptor interaction between the two dioxybenzene subunits arising when the first one is oxidized[10e] and 3) in MeCN, the [2]pseudorotaxane formed between DB24C8 and the [DBA]$^+$ ion displays only one oxidation process at +1.46 V, an observation which can be assigned to the two equivalent dioxybenzene subunits separated by the threaded [DBA]$^+$ ion.[10e] These results allow us to assign the first oxidation process (+1.01 V) involving the superbundle [**1** ⊃ **2**-H_3]$^{3+}$ to the oxidation of the hexaoxytriphenylene core and the second one (+1.44 V) to the oxidation of the three peripheral dioxybenzene subunits. Since all the processes are irreversible,[41] it does not seem appropriate to overspeculate. We

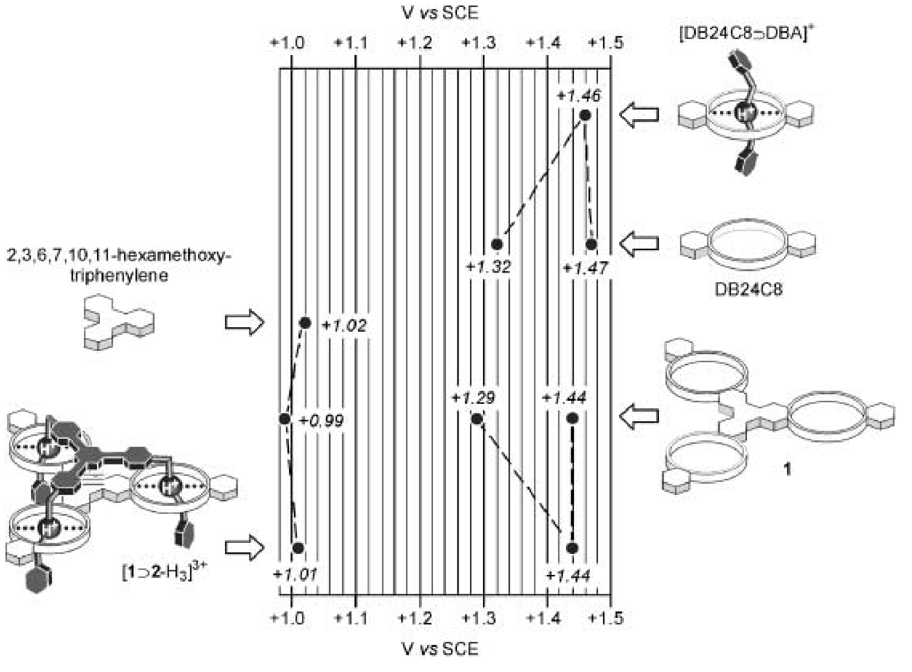


Figure 10. Correlation diagram of the potential values for the oxidation processes of the 2,3,6,7,10,11-hexamethoxytriphenylene model compound, the tris-crown ether **1** and the supramolecular bundle [**1** ⊃ **2**-H_3]$^{3+}$ in CH_2Cl_2 solution. The potential values for the oxidation processes of DB24C8 and its 1:1 complex formed with the [DBA]$^+$ ion in MeCN solution are also shown for comparison. For more details, see the text.

would only like to make the point that, after the first oxidation process, the oxidized hexaoxytriphenylene core becomes an electron acceptor. Therefore, in the free tris-crown ether **1**, the oxidized hexaoxatriphenylene core may interact with the electron-donating peripheral dioxybenzene subunits, affecting their oxidation potentials. Further donor–acceptor interactions, involving the dioxybenzene subunits may occur upon successive oxidations of these subunits as observed[10e] for DB24C8. However, donor–acceptor interactions arising from successive oxidation processes are likely to be prevented in the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ because the $[\mathbf{2}\text{-H}_3]^{3+}$ component rigidifies the superstructure and keeps the redox-active units separated from each other. Under such conditions, the three dioxybenzene peripheral units become equivalent and hence are oxidized at the same potential, just as in the case (Figure 10) of the two dioxybenzene subunits present in the [2]pseudorotaxane formed when DB24C8 binds the $[\text{DBA}]^+$ ion. The values of the peak potentials for the oxidation processes indicate that one-electron oxidation of the superbundle, which takes place on the central hexaoxytriphenylene unit, does not lead to dethreading. Such a result, unexpected at a first glance, suggests that the removal of one electron from the triphenylene unit of the tris-crown ether component does not weaken considerably the $[\text{N}^+\text{-H}\cdots\text{O}]$ hydrogen-bonding interactions that provide the principal stabilization to the superbundle.

Solvent-induced dissociation of the superbundle: Since it is known[2, 31] that DB24C8 and $[\text{DBA}][\text{PF}_6]$ do not form a complex in CD_3SOCD_3 solution, it was not surprising to us that addition of CD_3SOCD_3 to an equimolar mixture (7.5 mM) in $CDCl_3/CD_3CN$ (1:1) causes the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ to undergo complete decomplexation. This observation[42] is undoubtedly a result of the fact that CD_3SOCD_3 is a much better hydrogen-bond acceptor than $CDCl_3$ or CD_3CN. Thus, CD_3SOCD_3 competes successfully with the crown ether's oxygen atoms to hydrogen bond to the NH_2^+ centers in the tris-ammonium trication. The decomplexation was monitored by recording a series of ^{1}H NMR spectra (Figure 11), while gradually increasing the proportions of CD_3SOCD_3 present in the mixed solvent system, namely $CDCl_3/CD_3CN$ (1:1). These spectra reveal that a complete transition takes place from the fully complexed species, that is, the superbundle $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ to the completely free tris-crown ether derivative **1** and trisammonium trication $[\mathbf{2}\text{-H}_3]^{3+}$ at 33% CD_3SOCD_3. A closer inspection of the spectra leads to the identification of resonances which correspond to neither the triply-threaded 1:1 complex nor the free components. These resonances must result from the intermediate complexes on the pathway between these two extreme situations. They are probably doubly- and singly-threaded 1:1 complexes which are formed as the three arms of the $[\mathbf{2}\text{-H}_3]^{3+}$ trication dissociate progressively from the three macrocyclic polyethers present in **1**. The ^{1}H NMR spectra are exceedingly complicated, when these numerous species are all present under conditions of slow-exchange.

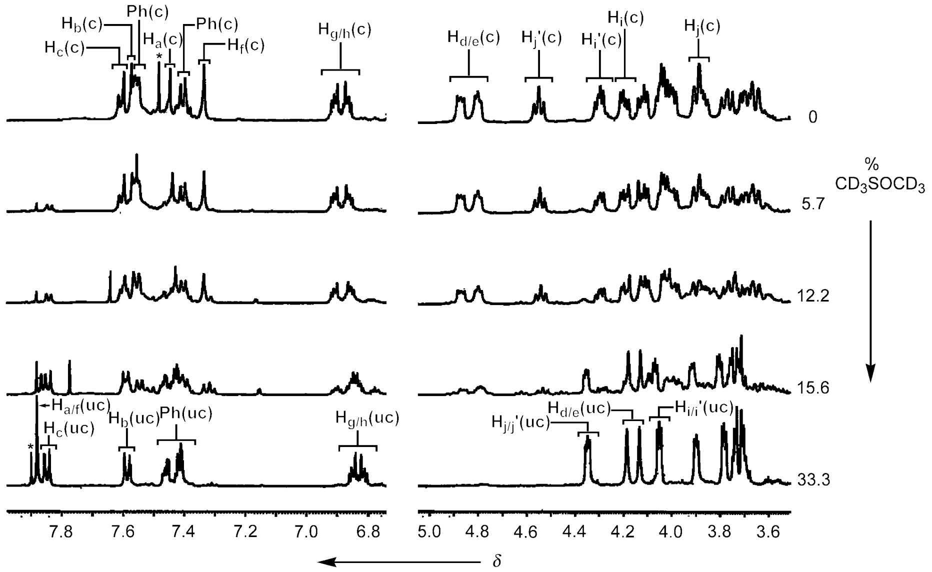


Figure 11. A series of ^{1}H NMR spectra (500 MHz, 300 K) recorded on addition of CD_3SOCD_3 to a 7.5 mM $CDCl_3/CD_3CN$ (1:1) solution of the 1:1 adduct $[\mathbf{1}\supset\mathbf{2}\text{-H}_3][\text{PF}_6]_3$ showing the progressive decomposition of the superbundle to give the tris-crown ether **1** and the tris-ammonium salt $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$.

For this reason, we decided to use a simple ^{1}H NMR probe by locating methyl groups at the *para*-positions of the three benzyl groups in $[\mathbf{2}\text{-H}_3]^{3+}$. The CD_3SOCD_3-driven decomplexation of the resulting superbundle $[\mathbf{1}\supset\mathbf{3}\text{-H}_3]^{3+}$ was followed by monitoring (Figure 12) the resonances for the different methyl groups as aliquots of CD_3SOCD_3 were added to $[\mathbf{1}\supset\mathbf{3}\text{-H}_3][\text{PF}_6]_3$ dissolved initially in $CDCl_3/CD_3CN$ (1:1). In principle, during the dissociation of $[\mathbf{1}\supset\mathbf{3}\text{-H}_3]^{3+}$ to the free species via the doubly- and singly-threaded complexes there are six different methyl environments which could possibly lead to the observation of six separate singlets in ^{1}H NMR spectra. The triply-, doubly- and singly-threaded trications each provide different "complexed methyl" environments, while the doubly-, singly-threaded and free trications each provide different "uncomplexed methyl" environments. In the event, four different singlets are observed (Figure 12) at δ 2.350 (**B**), 2.345 (**C**), 2.336 (**D**), and 2.311 (**A**) in the ^{1}H NMR spectrum recorded with 14% CD_3SOCD_3 present. It seems not unreasonable that the methyl groups located in all of the bound side arms will resonate with identical or near identical chemical shifts (**A**), irrespective of whether they are located in singly, doubly or triply threaded complexes. On this assumption, it has to be the methyl groups in the unbound arms of the free, singly and doubly threaded species that give rise (Figure 13) to the signals **C**, **B**, and **D**, respectively. It is evident from inspection of the partial spectra portrayed in Figure 12 that, as the proportion of CD_3SOCD_3 is raised, the intensity of the resonance **C** increases, while those for

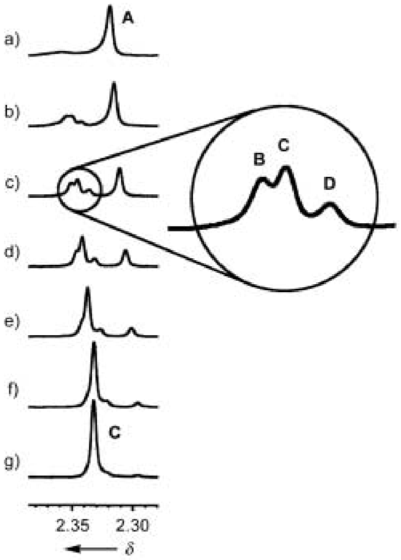


Figure 12. Partial ^{1}H NMR spectra [500 MHz, $(100-x)$% $CDCl_3/CD_3CN$ (1:1) + x% CD_3SOCD_3, x = a) 0, b) 7.4, c) 13.8, d) 19.4, e) 24.3, f) 28.6, and g) 33.3] showing the resonances corresponding to the methyl groups in an equimolar mixture of the tris-crown ether **1** and the tris-ammonium salt $[\mathbf{3}\text{-H}_3][PF_6]_3$.

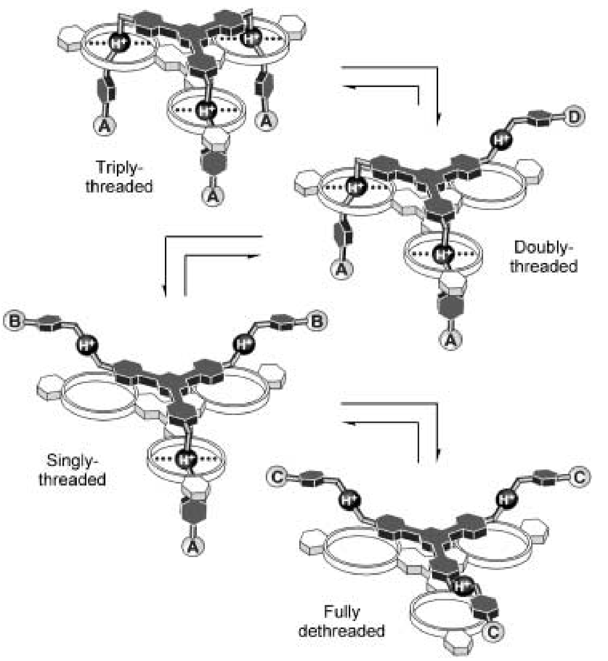


Figure 13. A schematic representation of the equilibration between the tris-crown ether **1** and the tris-ammonium ion $[\mathbf{3}\text{-H}_3]^{3+}$ involving species that are triply-, doubly-, and singly-threaded, as well as free.

resonances **B** and **D** decrease. Hence, **C** would appear to be the resonance for the free trication. Resonances **B** and **D** can only be assigned tentatively.[43] Since resonance **B**, in general, has a greater intensity than that of **D**, then resonance **B** probably corresponds to the methyl groups in the unbound arms of the singly-threaded complex, leaving resonance **D** to correspond to the methyl groups in the unbound arm of the doubly-threaded complex. One conclusion can be drawn with some certainty: the dissociation of $[\mathbf{1}\supset\mathbf{3}\text{-H}_3]^{3+}$ is a stepwise process.

Dethreading/rethreading with base/acid inputs: An important feature of pseudorotaxanes based on hydrogen-bonding interactions between crown ethers and NH_2^+ ion centers is the possibility of controlling the dethreading/rethreading processes using base/acid inputs.[8, 9, 10a,b,d,f] We have therefore investigated the possibility of dethreading the $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ superbundle in CH_2Cl_2[34] by addition of tri-*n*-butylamine (NBu_3). In an experimental foray, we examined the behavior of $[\mathbf{2}\text{-H}_3]^{3+}$ on addition of NBu_3. It is well known[44] that deprotonation of aromatic ammonium salts often causes quenching of their fluorescence because of the appearance of an n–π* excited state below the fluorescent π–π* level. We established that addition of a stoichiometric amount of NBu_3 to a solution of $[\mathbf{2}\text{-H}_3]^{3+}$ does not cause fluorescence quenching. The possibility that NBu_3 is not sufficiently strong a base to deprotonate the NH_2^+ ion centers in $[\mathbf{2}\text{-H}_3]^{3+}$ was discounted[45] by the fact that we found that addition of one equivalent of NBu_3 does cause complete quenching of the fluorescence of the $[DBA]^+$ ion ($\lambda_{max} = 337$ nm). Thus, we have to conclude that NBu_3 is strong enough to deprotonate the NH_2^+ ion centers in $[\mathbf{2}\text{-H}_3]^{3+}$ and that the fluorescence of $[\mathbf{2}\text{-H}_3]^{3+}$ is not quenched upon deprotonation because, in CH_2Cl_2 solution, the n–π* excited state of **2** is higher in energy than the emitting π–π* level. On the basis of this result, dethreading of $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ caused by deprotonation of the $[\mathbf{2}\text{-H}_3]^{3+}$ component implies the disappearance of the broad $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ emission ($\lambda_{max} = 410$ nm) and the reinstatement of both the fluorescence of the tris-crown ether ($\lambda_{max} = 384$ nm) and the (deprotonated) tris-ammonium ion ($\lambda_{max} = 356$ nm). Upon titration of $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ with NBu_3, changes in the shape and intensity of the fluorescence spectra in the expected directions were indeed observed—but to a lesser extent than expected, which indicates that dethreading was not complete. Apparently, the stabilization caused by hydrogen bonding in the $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ adduct makes deprotonation of the NH_2^+ center in the threaded compound more difficult than in the case of the free $[\mathbf{2}\text{-H}_3]^{3+}$ component. An alternative explanation would be that the deprotonation of the NH_2^+ centers in the bound $[\mathbf{2}\text{-H}_3]^{3+}$ component is not a sufficient condition for complete dethreading because of a significant contribution from the π–π stacking interaction to the stability of the 1:1 adduct. This hypothesis, however, can be rejected since no association between the tris-crown ether **1** and the deprotonated thread **2** is observed in solution.

Contrary to what happens in CH_2Cl_2 solution, addition of NBu_3 to an MeCN solution of $[\mathbf{2}\text{-H}_3]^{3+}$ causes the quenching of its fluorescence band with $\lambda_{max} = 356$ nm. The different fluorescence behavior of the deprotonated compound **2** in the two solvents is most likely related to the greater stabilization of the n–π* charge-transfer excited state in the more polar MeCN solvent. Titration experiments show that addition of one equivalent of base quenches the fluorescence of $[\mathbf{2}\text{-H}_3]^{3+}$ completely, indicating that, as expected, deprotonation of only one NH_2^+ ion center is sufficient to cause the formation of a low energy n–π* excited state. According to the above results, in MeCN solution, dethreading of $[\mathbf{1}\supset\mathbf{2}\text{-H}_3]^{3+}$ by deprotonation of the [**2**-H_3]$^{3+}$ component should lead to the disappearance of the broad emission typical of the 1:1 adduct ($\lambda_{max} = 410$ nm) and the re-instatement of the fluorescence of the tris-crown ether ($\lambda_{max} = 384$ nm). This behavior is exactly what was observed upon titration of [**1** $\supset$ **2**-H_3]$^{3+}$ with NBu_3. After addition of three equivalents of NBu_3 to [**1** $\supset$ **2**-H_3]$^{3+}$, the fluorescence spectrum was the same as that observed (Figure 14) for the tris-crown ether **1** alone and no further change was observed on addition of an excess of the amine. The occurrence of dethreading was also shown by changes in the absorption spectrum, which—at the end of the titration—matches exactly the sum of the spectra of the free components **1** and **2**. After the addition of three equivalents of NBu_3, successive addition of three equivalents of triflic acid caused the restoration of the initial absorption and emission spectra (Figure 14), indicating that the dethreading-rethreading process is fully reversible (Scheme 4).

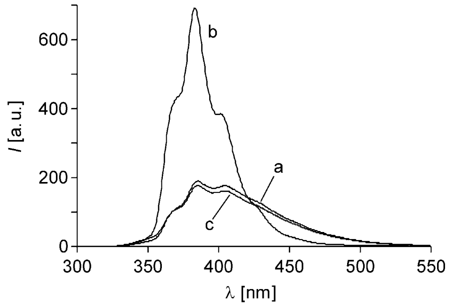


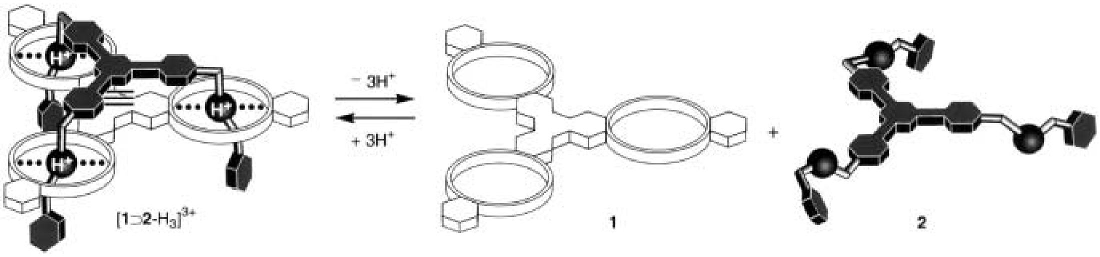
Figure 14. Fluorescence spectra ($\lambda_{exc} = 307$ nm) of a MeCN solution of [**1** $\supset$ **2**-H_3]$^{3+}$ (a), after addition of three equivalents of NBu_3 (b), and after successive addition of three equivalents of triflic acid (c).

The dethreading/rethreading process has also been investigated (Figure 15) by ^1H NMR spectroscopy. The ^1H NMR spectrum (Figure 15a) of an equimolar mixture of the tris-crown ether **1** and the tris-ammonium salt [**2**-H_3][PF_6]$_3$ in CD_3CN revealed (cf. Figure 1a) the quantitative formation of the [**1** $\supset$ **2**-H_3]$^{3+}$ superbundle. Upon addition of slightly more than three equivalents of diisopropylethylamine (NEt*i*Pr_2) to the CD_3CN solution of the superbundle, significant changes were observed in the spectrum (Figure 15b). The resonances for the benzylic methylene $H_{d/e}$ protons in [**1** $\supset$ **2**-H_3]$^{3+}$ are shifted upfield from about $\delta = 4.9$ to about $\delta = 3.8$, indicating complete deprotonation of the [**2**-H_3]$^{3+}$ trication to give the tris-amine **2**. The chemical shifts of all the other protons in both the **1** and [**2**-H_3]$^{3+}$ components of the superbundle change (Figure 15b) quite dramatically as well. In particular, resonances of the central aromatic-core protons H_a ($\delta = 7.48$ in the [**2**-H_3]$^{3+}$ component) and H_f ($\delta = 7.40$ in the **1** component), influenced by the [$\pi - \pi$] stacking interaction of the two aromatic systems, are shifted downfield to $\delta = 7.87$ and δ 7.86, respectively, clearly demonstrating the absence of any [$\pi - \pi$] stacking upon the addition of base. Moreover, the diastereotopicities of the *o*-methylene protons ($H_{i/i'}$ and $H_{j/j'}$) expressed by their pronounced anisochronous behavior in the ^1H NMR spectrum (Figure 15a) of the [**1** $\supset$ **2**-H_3]$^{3+}$ trication, are lost (Figure 15b) completely on addition of base. All of the ^1H NMR spectroscopic evidence points unambiguously to the complete dethreading of the superbundle and the presence of only two separate species—the tris-crown ether **1** and the tris-amine **2**—in the CD_3CN solution treated with NEt*i*Pr_2. Subsequent addition of a slight excess of trifluoroacetic acid compared with the previously added amine brought about complete rethreading as evidenced by the "restored" ^1H NMR spectrum (Figure 15c) of the [**1** $\supset$ **2**-H_3][PF_6]$_3$ superbundle. The results of these ^1H NMR experiments—on top of the fluorescence studies—demonstrate the reversibility of the dethreading and rethreading of [**1** $\supset$ **2**-H_3][PF_6]$_3$ and the fact that it can be controlled (Scheme 4) by inputs of base and acid, respectively.

Conclusions

An artificial recognition motif, wherein one reasonably flat and rigid component with three trigonally arranged orifices is triply penetrated by the three trigonally disposed tentacles of a slightly more flexible component has been demonstrated by numerous spectroscopic, photophysical and electrochemical experiments to be, both kinetically and thermodynamically, extremely stable in appropriate solvents.[46] More specifically, a tritopic receptor in the shape of the tris-crown ether **1** is the near-perfect match for certain trifurcated trications—namely [**2**-H_3]$^{3+}$ and [**3**-H_3]$^{3+}$—to form [2]pseudorotaxanes three times over within the same 1:1 adducts. The availability of single crystals, suitable for X-ray crystallography, of one of these adducts, that is, [**1** $\supset$ **2**-H_3][PF_6]$_3$ has established the stabilizing cooperative actions of a few key strong [N^+-H $\cdots$ O] hydrogen bonds in addition to [C-H $\cdots$ O] and [$\pi \cdots \pi$] stacking interactions, leading to the formation of a compact and efficient binding site.

While complexation can be suppressed completely in solvents such as dimethylsulfoxide, which competes favorably as a hydrogen-bond acceptor for hydrogen-bond donors, other



Scheme 4. A graphical representation of the reversible dethreading and rethreading caused by base and acid, respectively.

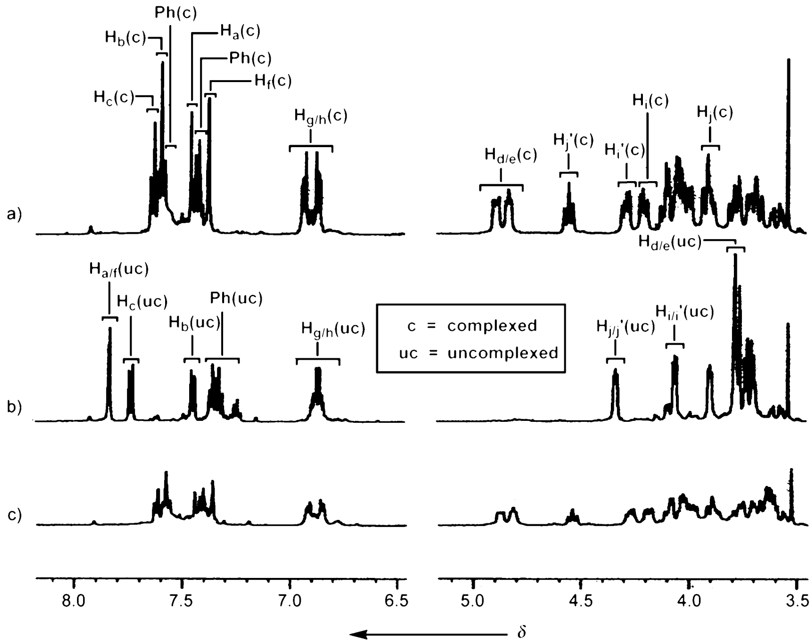


Figure 15. ^1H NMR spectra (500 MHz, CD_3CN, 148 mм, 298 K) of a) the superbundle [$\mathbf{1}\supset\mathbf{2}$-$H_3$][$PF_6$]$_3$, i.e., an equimolar mixture of **1** and [**2**-H_3][PF_6]$_3$, b) the deprotonated tris-amine **2** and the free tris-crown ether **1** upon addition of 5 μL (3.2 equiv) of diisopropylethylamine to the superbundle, and c) the rethreaded superbundle [$\mathbf{1}\supset\mathbf{2}$-$H_3$][$PF_6$]$_3$ upon addition of 2.2 μL (3.2 equiv) of trifluoroacetic acid (TFA).

organic solvents, such as dichloromethane, chloroform, and even acetonitrile, can sustain very strong superbundle formation. In the particular case of the [$\mathbf{1}\supset\mathbf{2}$-$H_3$]$^{3+}$ superbundle, the 1:1 adduct is only slightly more stable ($K_a > 10^7$ mol L^{-1}) in CH_2Cl_2 than it is ($K_a \sim 10^6$ mol L^{-1}) in the more polar MeCN. The photophysical properties of this superbundle are particularly interesting because both the separated free components exhibit characteristic fluorescent bands. These properties helped to establish beyond any doubt the 1:1 stoichiometry of the superbundle in solution. Fluorescence titration experiments have produced spectacular Job plots in support of this 1:1 adduct formation, a result which has been confirmed by both electrochemical experiments and ^1H NMR spectroscopy.

Complete and reversible dethreading/rethreading of the 1:1 adduct can be achieved in acetonitrile using base/acid inputs. This particular supramolecular species represents a prime example of a cooperative, multivalent recognition site[47] that can be switched on and off by chemical means. As such, it lends itself to the construction of molecular machines[7, 8] of nanometer-scale dimensions, as well as to the self-assembly of supramolecular polymers[48] of considerable size and stability with rigid architectures that could be extremely sensitive to pH and solvent polarities.

Experimental Section

General methods: All solvents and reagents were used as received unless stated otherwise. All solvents were dried prior to use according to standard literature procedures.[49] For the spectroscopic and electrochemical experiments, respectively, CH_2Cl_2 and MeCN were Merck Uvasol and Romil Hi-Dry and were used as received. Reactions were monitored by thin-layer chromatography on aluminum sheets coated with silica gel 60F (Merck 5554). The plates were inspected by UV light and, if required, developed in iodine vapor. Column chromatography was carried out by using silica gel 60 (Merck 9385, 230–400 mesh). Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer (at 400 MHz and 100 MHz, respectively) and on either Bruker ARX500 or Bruker Avance 500 spectrometers (at 500 MHz and 125 MHz, respectively) at ambient temperature. They were referenced using their residual signals as internal standards. The chemical shifts are expressed in ppm and the coupling constants from the ^1H NMR spectra in Hertz (Hz). Electron impact mass spectra (EI-MS) were obtained from a VB Prospec mass spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained on a VB ZAB-SE spectrometer equipped with a krypton primary atom beam using a 3-nitrobenzyl alcohol matrix. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF-MS) were recorded on an PerSeptives Biosystems instrument using a *trans*-indole acrylic acid matrix and an average of 50 laser shots per sample. The absorption spectra, fluorescence spectra and lifetimes, and electrochemical experiments were carried out[34] in CH_2Cl_2/MeCN (99:1)—hereafter referred to as CH_2Cl_2—and MeCN solutions at room temperature. The concentration of each component was 2.0×10^{-5} mol L^{-1} for the spectroscopic measurements and 5.0×10^{-4} mol L^{-1} for the electrochemical experiments. Absorption and luminescence spectra were recorded with a Perkin–Elmer λ16 spectrophotometer and a Perkin–Elmer LS-50 spectrofluorometer, respectively. Luminescence lifetimes were measured with an Edinburgh DS 199 single photon counting instrument, equipped with a deuterium-filled arclamp (excitation in the range of 250–320 nm). In the titration experiments, the luminescence data were corrected for the luminescence intensity versus absorbance instrumental response.[50] Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in argon purged solutions at room temperature with an Autolab 30 multipurpose instrument interfaced at a PC. All potentials are referred to SCE; the potential window examined was −2 to +1.5 and −2 to +2 V versus SCE in CH_2Cl_2 and MeCN, respectively. The working electrode was a glassy carbon electrode (Amel, 0.08 cm^2) and the counter electrode was a Pt spiral contained in a fine glass frit. A silver wire was employed as a quasi-reference electrode. Tetraethylammonium hexafluorophosphate (5×10^{-2} mol L^{-1}) was added as supporting electrolyte and ferrocene was used as an internal standard for the potential values. CVs were obtained at sweep rates of 20, 50, 100, 200, and 500 mV s^{-1}. DPVs were performed with scan rates of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. Experimental errors are estimated to be: wavelengths, ±1 nm; luminescence lifetimes, ±5%; redox potential values, ±10 mV.

Tris-crown ether 1: An oven-dried 2 L three-necked, round-bottomed flask, equipped with a stirrer bar, a gas inlet tube, an addition funnel, and a condenser, was purged with argon for 10 min and then charged with anhydrous DMF (300 mL). Cs_2CO_3 (30.1 g, 92 mmol) was added to the flask and the white suspension stirred vigorously and heated to 100 °C. The addition funnel was charged with a solution of 2,3,6,7,10,11-hexahydroxytriphenylene[27] (**5**) (2.5 g, 7.7 mmol) and 1,2-bis(2-(2-(2-(2-*p*-tolylsulfonyloxy)ethoxy)ethoxy)ethoxy) benzene[28] (**7**) (15.8 g, 23 mmol) in anhydrous DMF (500 mL). This solution was added dropwise during 24 h to the suspension which was heated under reflux for an additional 6 d. On cooling the reaction mixture down to room temperature, the suspension was filtered off and the residue was washed with $CHCl_3$ (250 mL). The filtrate and $CHCl_3$ washings were concentrated under reduced pressure. The resulting dark tar was dissolved in CH_2Cl_2 (500 mL) and washed with 10% aqueous K_2CO_3 (2 × 300 mL) and finally H_2O (300 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford a crude product which was subjected to column chromatography (silica gel; gradient elution $CHCl_3$/*i*PrOH 25:1 → 4:1) to yield the pure tris-crown ether **1** as an off-white solid (1.03 g, 10%). M.p. 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.87–3.94$ (m, 36 H), 4.03–4.08 (m, 12 H), 4.15–4.21 (m, 12 H), 4.39–4.42 (m, 12 H), 6.85 (m, 12 H), 7.80 (s, 6 H); ^{13}C NMR (100 MHz, $CDCL_3$): $\delta = 69.3$, 69.8, 70.0, 71.3, 71.3, 107.4, 114.1, 121.4, 123.8, 148.7, 148.9; FAB-MS: *m*/*z*: 1338 [M^+]; HRMS (MALDI-TOF): calcd for $C_{72}H_{90}O_{24}Na$: 1361.5720; found: 1361.5927.

Tris-ammonium salt [3-H$_3$][PF$_6$]$_3$: A mixture of 1,3,5-tris(4-formylphenyl)-benzene[26] (**4**) (100 mg, 0.26 mmol) and *p*-methylbenzylamine (93 mg, 0.77 mmol) in PhMe (40 mL) was heated under reflux overnight and the H_2O was collected in a Dean–Stark apparatus. The solution was allowed to cool down to room temperature and the solvent was evaporated off under reduced pressure to give 1,3,5-tris[(4-tolyliminomethyl)phenyl]benzene as an off-white solid (170 mg, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.36$ (s, 9 H), 4.84 (s, 6 H), 7.16–7.30 (m, 12 H), 7.76 (d, $J = 8$ Hz, 6 H), 7.86 (d, $J = 8$ Hz, 6 H), 7.93 (s, 3 H), 8.45 (s, 3 H). This solid was dissolved in dry THF (5 mL) and dry MeOH (5 mL). After the portionwise addition of $NaBH_4$, the reaction mixture was left to stir overnight. Aqueous 5 N HCl was added to the reaction mixture until the pH was just less than 1. This mixture was concentrated in vacuo and the residue was partitioned between aqueous 2 N NaOH solution (40 mL) and CH_2Cl_2 (40 mL). The aqueous layer was then extracted further with CH_2Cl_2 (30 mL). The combined organic extracts were washed with H_2O (30 mL) and then dried ($MgSO_4$). Filtration, followed by evaporation, gave, 1,3,5-tris[(4-tolylaminoethyl)phenyl]benzene (**3**) (134 mg, 79%) as a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.35$ (s, 9 H), 3.82 (s, 6 H), 3.86 (s, 6 H), 7.15 (d, $J = 8$ Hz, 6 H), 7.27 (d, $J = 8$ Hz, 6 H), 7.45 (d, $J = 8$ Hz, 6 H), 7.65 (d, $J = 8$ Hz, 6 H), 7.74 (s, 3 H). This oil was heated overnight under reflux in 12 N HCl. On cooling, the reaction mixture was filtered and the residue washed with H_2O (20 mL) and Me_2CO (5 mL). The resulting white solid was dissolved in hot H_2O (80 mL) and saturated aqueous NH_4PF_6 solution was added. The resulting suspension was extracted with $MeNO_2$ (2 × 50 mL). The combined extracts were washed with H_2O (2 × 100 mL), dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure to give the trisammonium salt [**3**-H$_3$][PF$_6$]$_3$ as an off-white solid (187 mg, 86%). M.p. 110 °C (decomp); ^{1}H NMR (400 MHz, CD_3CN): $\delta = 2.36$ (s, 9 H), 4.23 (m, 6 H), 4.29 (m, 6 H), 7.12 (br s, 6 H), 7.28 (d, $J = 8$ Hz, 6 H), 7.36 (d, $J = 8$ Hz, 6 H), 7.57 (d, $J = 8$ Hz, 6 H), 7.89 (d, $J = 8$ Hz, 6 H), 7.95 (s, 3 H); ^{13}C NMR (100 MHz, CD_3CN): $\delta = 20.3$, 51.0, 51.4, 125.3, 125.3, 127.9, 129.7, 130.0, 130.2, 130.8, 140.1, 141.5, 141.6; FAB-MS: *m*/*z*: 852 [$M - PF_6 - HPF_6$]$^+$.

Acknowledgement

This research was supported by the National Science Foundation (CHE-9910199 and CHE-9974928) in the United States and MURST (Supramolecular Devices Project) in Italy. The European Union is gratefully acknowledged for a Marie-Curie Fellowship (To M.C.-L.) and for support under the auspices of the Molecular-Level Devices and Machines Network (HPRN-CT-2000–00029). We thank Dr. R. Ballardini and Professors M. T. Gandolfi and M. Venturi for helpful discussions.

[1] A. G. Kolchinski, D. H. Busch, N. W. Alcock, *J. Chem. Soc. Chem. Commun.* **1995**, 1289–1291.

[2] a) P. R. Ashton, P. J. Campbell, E. J. T. Chrystal, P. T. Glink, S. Menzer, D. Philp, N. Spencer, J. F. Stoddart, P. A. Tasker, D. J. Williams, *Angew. Chem.* **1995**, *107*, 1997–2001; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1865–1869; b) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, J. F. Stoddart, P. A. Tasker, D. J. Williams, *Angew. Chem.* **1995**, *107*, 2001–2004; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1869–1871.

[3] F. M. Raymo, M. D. Bartbeger, K. N. Houk, J. F. Stoddart, *J. Am. Chem. Soc.* **2001**, *123*, 9264–9267 and references therein.

[4] For recent reviews, see: a) M. C. T. Fyfe, J. F. Stoddart, *Adv. Supramol. Chem.* **1999**, *5*, 1–53; b) T. J. Hubin, A. G. Kolchinski, A. L. Vance, D. H. Busch, *Adv. Supramol. Chem.* **1999**, *5*, 237–357; c) M. C. T. Fyfe, J. F. Stoddart, D. J. Williams, *Struct. Chem.* **1999**, *10*, 243–249; d) M. C. T. Fyfe, J. F. Stoddart, *Coord. Chem. Rev.* **1999**, *183*, 139–155; e) T. J. Hubin, D. H. Busch, *Coord. Chem. Rev.* **2000**, *200*, 5–52; f) S. J. Cantrill, A. R. Pease, J. F. Stoddart, *J. Chem. Soc. Dalton Trans.* **2000**, 3715–3734; g) T. Takata, N. Kihara, *Rev. Heteroatom. Chem.* **2000**, *22*, 197–218; h) T. Clifford, A. Abushamlen, D. H. Busch, *Proc. Natl. Acad. Sci.* **2002**, *99*, 4830–4836.

[5] S.-H. Chiu, S. J. Rowan, S. J. Cantrill, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **2002**, *8*, 5170–5183 and references therein.

[6] For miscellaneous contributions from other research laboratories see, amongst others, the following: a) N. Yamaguchi, L. M. Hamilton, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 3463–3466; *Angew. Chem. Int. Ed.* **1998**, *37*, 3275–3279; b) N. Yamaguchi, H. W. Gibson, *Chem. Commun.* **1999**, 789–790; c) T. Takata, H. Kawasaki, S. Asai, N. Kihara, Y. Furusho, *Chem. Lett.* **1999**, 111–112; d) Y. Furusho, T. Hasegawa, A. Tsuboi, N. Kihara, T. Takata, *Chem. Lett.* **2000**, 18–19; e) T. Takata, H. Kawasaki, N. Kihara, Y. Furusho, *Macromolecules* **2001**, *34*, 5449–5456; f) B. F. G. Johnson, C. M. G. Judkins, J. M. Matters, D. S. Shephard, S. Parsons, *Chem. Commun.* **2000**, 1549–1550; g) S. A. Duggan, G. Fallon, S. J. Langford, V. L. Lau, J. F. Satchell, M. N. Paddon-Row, *J. Org. Chem.* **2001**, *66*, 4419–4426; h) D. W. Zehnder II, D. B. Smithrud, *Org. Lett.* **2001**, *3*, 2485–2487; i) M. Asakawa, T. Ikeda, N. Yui, T. Shimizu, *Chem. Lett.* **2002**, 174–175; j) H. W. Gibson, N. Yamaguchi, L. Hamilton, J. W. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 4653–4665; k) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522–3533; e) H. Yamaguchi, S. Nakanishi, N. Kihara, T. Takata, *Chem. Lett.* **2003**, 410–411.

[7] M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401.

[8] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines—A Journey into the Nano World*, Wiley-VCH, Weinheim, **2003**.

[9] For recent reviews, see: a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3349–3391; b) R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi, M. Venturi, *Acc. Chem. Res.* **2001**, *34*, 445–455. For more general recent reviews on molecular-level machines, see: *Acc. Chem. Res.* **2001**, *34*, 409–522 (Special Issue on Molecular Machines, Guest Editor: J. F. Stoddart); *Struct. Bonding* **2001**, *99*, 1–291 (Special issue on Molecular Machines and Motors, Guest Editor: J.-P. Sauvage).

[10] For some of the more relevant recent papers, see: a) M. Montalti, R. Ballardini, L. Prodi, V. Balzani, *Chem. Commun.* **1996**, 2011–2012; b) P. R. Ashton, R. Ballardini, V. Balzani, M. Gómez-López, S. E. Lawrence, M. V. Martínez-Díaz, M. Montalti, A. Piersanti, L. Prodi, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 10641–10651; c) M. V. Martínez-Díaz, N. Spencer, J. F. Stoddart, *Angew. Chem.* **1997**, *109*, 1991–1994; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1904–1907; d) P. R. Ashton, R. Ballardini, V. Balzani, M. C. T. Fyfe, M. T. Gandolfi, M. V. Martínez-Díaz, M. Morosini, C. Schiavo, K. Shibata, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 2332–2341; e) P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M. V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942; f) E. Ishow, A. Credi, V. Balzani, F. Spadola, L. Mandolini, *Chem. Eur. J.* **1999**, *5*, 984–989; g) J. Cao, M. C. T. Fyfe, J. F. Stoddart, G. R. L. Cousins, P. T. Glink, *J. Org. Chem.* **2000**, *65*, 1937–1946; h) P. R. Ashton, V. Baldoni, V. Balzani, A. Credi, H. D. A. Hoffmann, M.-V. Martínez-Díaz, F. M. Raymo, J. F. Stoddart, M. Venturi, *Chem. Eur. J.* **2001**, *7*, 3482–3493; i) R. Ballardini, V. Balzani, M. Clemente-Léon, A. Credi, M. T. Gandolfi, E. Ishow, J. Perkins, J. F. Stoddart, H.-R. Tseng, S. Wenger, *J. Am. Chem. Soc.* **2002**, *124*, 12782–12795; j) A. M. Elizarov, S.-H. Chiu, J. F. Stoddart, *J. Org. Chem.* **2002**, *67*, 9175–9181.

[11] a) D. Fitzmaurice, S. N. Rao, J. A. Preece, J. F. Stoddart, S. Wenger, N. Zaccheroni, *Angew. Chem.* **1999**, *111*, 1220–1224; *Angew. Chem. Int. Ed.* **1999**, *38*, 1147–1150; b) D. Ryan, S. N. Rao, H. Rensmo, D. Fitzmaurice, J. A. Preece, S. Wenger, J. F. Stoddart, N. Zaccheroni, *J. Am. Chem. Soc.* **2000**, *122*, 6262–6257.

[12] D. A. Fulton, S. J. Cantrill, J. F. Stoddart, *J. Org. Chem.* **2002**, *67*, 7968–7981.

[13] M. Mammen, S.-K. Choi, G. M. Whitesides, *Angew. Chem.* **1998**, *110*, 2908–2953; *Angew. Chem. Int. Ed.* **1998**, *37*, 2754–2794.

[14] For a selection of examples where synthetic multivalent receptors for biological systems have been investigated, see: a) Y. Hamuro, M. C. Calama, H. S. Park, A. D. Hamilton, *Angew. Chem.* **1997**, *109*, 2797–2799; *Angew. Chem. Int. Ed.* **1997**, *36*, 2680–2683; b) M. Kanai, K. H.

Mortell, L. L. Kiessling, *J. Am. Chem. Soc.* **1997**, *119*, 9931–9932; c) K. Fujimoto, T. Miyata, Y. Aoyama, *J. Am. Chem. Soc.* **2000**, *122*, 3558–3559; d) R. Roy, F. Hernández-Mateo, F. Santoyo-González, *J. Org. Chem.* **2000**, *65*, 8743–8746; e) J. Rao, J. Lahiri, R. M. Weis, G. M. Whitesides, *J. Am. Chem. Soc.* **2000**, *122*, 2698–2710; f) P. I. Kitov, J. M. Sadawska, C. Mulvey, G. D. Armstrong, H. Ling, N. S. Pannu, R. J. Read, D. R. Bundle, *Nature* **2000**, *403*, 669–672; g) M. A. Fazal, B. C. Roy, S. Sun, S. Mallik, K. R. Rodgers, *J. Am. Chem. Soc.* **2001**, *123*, 6283–6290; h) M. Mourez, R. S. Kane, J. Mogridge, S. Metallo, P. Deschatelets, B. R. Sellman, G. M. Whitesides, R. J. Collier, *Nat. Biotechnol.* **2001**, *19*, 958–961.

[15] P. R. Ashton, A. N. Collins, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1997**, *109*, 59–62; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 59–62.

[16] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Horwood, Chichester, **1991**.

[17] A. P. De Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566.

[18] a) J.-P. Sauvage, *Acc. Chem. Res.* **1998**, *31*, 611–619; b) M.-J. Blanco, M. C. Jiménez, J.-C. Chambron, V. Heitz, M. Linke, J.-P. Sauvage, *Chem. Soc. Rev.* **1999**, *28*, 293–305.

[19] P. L. Boulas, M. Gómez-Kaifer, L. Echegoyen, *Angew. Chem.* **1998**, *110*, 226–258; *Angew. Chem. Int. Ed.* **1998**, *37*, 216–247.

[20] a) A. E. Kaifer, *Acc. Chem. Res.* **1999**, *32*, 62–71; b) A. E. Kaifer, M. Gómez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, **1999**.

[21] L. Fabbrizzi, M. Licchelli, P. Pallavicini, *Acc. Chem. Res.* **1999**, *32*, 846–853.

[22] P. Piotrowiak, *Chem. Soc. Rev.* **1999**, *28*, 143–150.

[23] *Electron Transfer in Chemistry*, *Vol. 3* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**.

[24] M. C. T. Fyfe, J. N. Lowe, J. F. Stoddart, D. J. Williams, *Org. Lett.* **2000**, *2*, 1221–1224.

[25] Previously, we have exploited our programmed approach for the noncovalent synthesis of interwoven supramolecular cages (see ref. [15]), including a supramolecular analogue of the photosynthetic special pair (M. C. Feiters, M. C. T. Fyfe, M. V. Martínez-Díaz, S. Menzer, R. J. M. Nolte, J. F. Stoddart, P. J. M. van Kan, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 8119–8120).

[26] E. Weber, M. Hecker, E. Koepp, W. Orlia, M. Czugler, I. Csöregh, *J. Chem. Soc. Perkin Trans. 2* **1988**, 1251–1257.

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

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

[29] A. Derome, M. Williamson, *J. Magn. Reson.* **1990**, *88*, 177–185.

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

[31] It has been demonstrated that the 1:1 complex formed between dibenzylammonium hexafluorophosphate and dibenzo-[24]crown-8 in $CDCl_3/CD_3CN$ (1:1) is in slow exchange on the ^1H NMR timescale with its free components at room temperature. See: P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709–728.

[32] S. Vidal, D. G. Amirsakis, T. Chang, A. R. Williams, J. F. Stoddart, A. J. P. White, D. J. Williams, unpublished results.

[33] The crystallographic data for $[\mathbf{1}\supset\mathbf{2}\text{-H}_3][\text{PF}_6]_3$ were deposited with the original communication (see ref. [24]) and have the CCDC compound code QIZMIV. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

[34] The tris-ammonium salt $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$ is insoluble in neat CH_2Cl_2. The salt was initially dissolved in the minimum amount of MeCN and then this solution was added to CH_2Cl_2. The final composition of the solution was CH_2Cl_2/MeCN (99:1 *v*/*v*). In order to explore the effect of the presence of 1% MeCN in the CH_2Cl_2 solvent in the present studies, we have measured, by fluorescence titration, the association constants for the complexation of [DBA][PF_6] by DB24C8 in CH_2Cl_2/MeCN (99:1), as well as in neat CH_2Cl_2. The K_a values obtained, namely 6×10^5 and $9\times10^5\,\text{L}\,\text{mol}^{-1}$, respectively, show that the association constant in CH_2Cl_2/MeCN (99:1) is large and indeed very close to that measured in neat CH_2Cl_2. Therefore, for the sake of simplicity, the mixed CH_2Cl_2/MeCN (99:1) solvent will be referred to hereafter as CH_2Cl_2.

[35] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, **1965**.

[36] Since light emitted in this spectral region comes exclusively from the luminescence band typical of the adduct, interference from emission of the molecular components can be safely excluded.

[37] H.-J. Schneider, A. K. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, Wiley, Chichester, **2000**, Chapter A.

[38] a) B. Perlmutter-Hayman, *Acc. Chem. Res.* **1986**, *19*, 90–96; b) A. P. Bisson, C. A. Hunter, *Chem. Commun.* **1996**, 1723–1724; c) S. Shinkai, M. Ikeda, A. Sugasaki, M. Takeuchi, *Acc. Chem. Res.* **2001**, *34*, 494–503.

[39] For an example of cooperativity based on the same recognition motifs as that described in this paper, see: J.-C. Meillon, N. Voyer, E. Biron, F. Sanschagrin, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 147–149; *Angew. Chem. Int. Ed.* **2000**, *39*, 143–145.

[40] MeCN is not only more polar than CH_2Cl_2 but it is also a much better hydrogen bond acceptor. See C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, **1988**.

[41] Chemically irreversible oxidation processes are known to occur in aromatic ethers. See, e.g., G. W. Morrow, in *Organic Electrochemistry* (Eds.: H. Lund, O. Hammerich), 4th ed., Dekker, New York, **2001**.

[42] The dissociation is not a result of diluting the sample which was diluted over the same concentration range with $CDCl_3/CD_3CN$ (1:1). No change was observed in ^1H NMR spectra recorded for increasingly dilute solutions.

[43] The doubly-threaded complex illustrated in Figure 13 has averaged C_s symmetry with an unbound arm hovering over the free crown ether in what might be described as a *syn* co-conformation which has the virtue of being stabilized by [π–π] stacking interactions. It is possible to envisage another doubly-threaded complex which also has averaged C_s symmetry but in which the unbound arm is oriented anti in a co-conformational sense from the free crown ether. This complex is likely to be more stable than the singly-threaded one. The possibility of intermediate complexes in which the stoichiometries between **1** and $[\mathbf{2}\text{-H}_3]^{3+}$ are other than 1:1 is a very real one as well, particularly at higher absolute concentrations of the host and guest. Unraveling the ins and outs of this highly dynamic supramolecular system offers a veritable maze for the contemporary physical organic chemist.

[44] R. A. Bissell, A. P. De Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, C. P. McCoy, K. R. A. S. Sandarayake, *Top. Curr. Chem.* **1993**, *168*, 223–264.

[45] The possibility that NBu_3 is not a sufficiently strong base to deprotonate the three NH_2^+ ion centers was also discounted by ^1H NMR spectroscopy. In the ^1H NMR spectrum of $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$ in CD_3COCD_3, the resonances of the benzylic methylene protons next to the NH_2^+ ion centers move upfield from $\delta = 4.71$ and 4.69 to $\delta = 3.90$ and 3.88, respectively, on the addition of 3.1 equivalents of NBu_3, confirming complete deprotonation of the $[\mathbf{2}\text{-H}_3]^{3+}$ trication to give the trisamine **2**.

[46] F. Kotzyba-Hibert, J.-M. Lehn, K. Saigo, *J. Am. Chem. Soc.* **1981**, *103*, 4266–4268.

[47] The kinetics and thermodynamics associated with this kind of multivalent recognition site are under active investigation in our laboratory. The results of these investigations will be reported in the fulness of time.

[48] *Supramolecular Polymers* (Ed.: A. Ciferri), Marcel Dekker, New York, **2000**.

[49] D. D. Perrin, W. F. L. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, **1989**.

[50] A. Credi, L Prodi, *Spectrochim. Acta A* **1998**, *54*, 159–170.

Received: March 24, 2003 [F4979]