

## A Mechanically Interlocked Bundle

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**Abstract:** The prototype of an artificial molecular machine consisting of a tris-ammonium tricationic component interlocked with a tris(crown ether) component to form a molecular bundle with averaged  $C_{3v}$  symmetry has been designed and synthesized. The system is based on noncovalent interactions, which include 1)  $N^+-H\cdots O$  hydrogen bonds; 2)  $C-H\cdots O$  interactions between the  $CH_2NH_2^+CH_2$  protons on three dibenzylammonium-ion-containing arms, which are attached symmetrically to a benzenoid core, and three dibenzo[24]crown-8 macrorings fused onto a triphenylene core; and 3)  $\pi\cdots\pi$  stacking interactions between the aromatic cores. The template-directed synthesis of the mechanically interlocked, triply threaded bundle involves post-assembly covalent modification, that is, the efficient conversion of three azide

functions at the ends of the arms of the bound and threaded trication into bulky triazole stoppers, after 1,3-dipolar cycloaddition with di-*tert*-butylacetylenedicarboxylate to the extremely strong 1:1 adduct that is formed in dichloromethane/acetonitrile (3:2), on account of a cluster effect associated with the paucivalent adduct. Evidence for the averaged  $C_{3v}$  symmetry of the molecular bundle comes from absorption and luminescence data, as well as from electrochemical experiments,  $^1H$  NMR spectroscopy, and mass spectrometry. The photophysical properties of the mechanically interlocked bundle are very similar to those of the super-

bundle that precedes the formation of the bundle in the process of supramolecular assistance to covalent synthesis. Although weak non-nucleophilic bases (e.g., *n*Bu<sub>3</sub>N and *i*Pr<sub>2</sub>NEt) fail to deprotonate the bundle, the strong *t*BuOK does, as indicated by both luminescence and  $^1H$  NMR spectroscopy. While deprotonation undoubtedly loosens up the interlocked structure of the molecular bundle by replacing relatively strong  $N^+-H\cdots O$  hydrogen bonds by much weaker  $N-H\cdots O$  ones, the  $\pi\cdots\pi$  stacking interactions ensure that any structural changes are inconsequential, particularly when the temperature of the solution of the neutral molecular bundle in dichloromethane is cooled down to considerably below room temperature.

**Keywords:** hydrogen bonds • luminescence • molecular recognition • multivalency • self-assembly

### Introduction

Nowadays, there seems to be an almost inexhaustible collection of complex supramolecular assemblies known<sup>[1]</sup> that utilize hydrogen bonding as their main source of noncovalent interactions to hold together, often in highly cooperative ways, a number of molecular building blocks or tectons<sup>[2]</sup>

with a remarkable degree of architectural control and precision. The discovery<sup>[3]</sup> in the mid-90s that suitably sized crown ether macrocycles will thread spontaneously onto secondary dialkylammonium ions, forming interpenetrating complexes called pseudorotaxanes,<sup>[4]</sup> primarily as a result of  $N^+-H\cdots O$  hydrogen bonds and  $C-H\cdots O$  interactions,<sup>[5]</sup> has evolved<sup>[6]</sup> from these early beginnings, where only *one* monotopic crown ether macrocycle was threaded onto *one* dialkylammonium ion center, to the construction of much more elaborate multiply threaded superstructures. This very simple recognition motif, in which the sources of the noncovalent interactions are primarily hydrogen bonds, is augmented, not only by multivalency,<sup>[8]</sup> but also by the fact that one molecular structure (the cationic component) interpenetrates the other molecular structure.<sup>[9]</sup> In the limit, of course, post-assembly covalent modification can be employed to transport the multivalent supramolecular assembly into a mechanically interlocked molecular domain. It is this limit that will be addressed in this paper.

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We have described quite recently an example<sup>[10]</sup> of multivalency at work in which a tritopic crown ether, in which three benzo[24]crown-8 rings are fused onto a triphenylene core, forms an extremely stable ( $K_a > 10^7 \text{ mol L}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) triply threaded, two-component superbundle with a trifurcated trication, wherein three dibenzylammonium ions are linked to a central benzenoid core. The assembly and disassembly of this superbundle can be reversibly and quantitatively controlled by an acid–base input.<sup>[10]</sup> As such, it lends itself conceptually to the construction of molecular machines<sup>[12,13]</sup> of nanometer-scale dimensions, as well as to the self-assembly of supramolecular polymers<sup>[14]</sup> of considerable size and stability with rigid architectures, but whose superstructures could be sensitive to pH and solvent polarity. Against this background, we report here 1) the template-directed synthesis<sup>[15]</sup> of a mechanically interlocked, triply threaded tricationic bundle  $[\mathbf{3}\text{-H}_3]^{3+}$  with averaged  $C_{3v}$  symmetry by treating the trifurcated trisammonium ion  $[\mathbf{2}\text{-H}_3]^{3+}$ , which carries azide functions on the *para*-positions of its three benzyl groups, with di-*tert*-butylacetylenedicarboxylate in the presence of the tritopic crown ether **1** (Scheme 1) and 2) the full characterization of the  $[\mathbf{3}\text{-H}_3]^{3+}$  species by  $^1\text{H}$  NMR spectroscopy and mass spectrometry. Inspired by the rapidly growing interest<sup>[16]</sup> in the construction of redox-controllable molecular electronic devices for possible applications to nanoelectronics,<sup>[17]</sup> we have also investigated 3) the photophysical and electrochemical properties of the me-

chanically interlocked bundle and 4) the reversible co-conformational changes<sup>[18]</sup> undergone by the superbundle upon acid–base treatment using (variable temperature)  $^1\text{H}$  NMR spectroscopy as the probe.

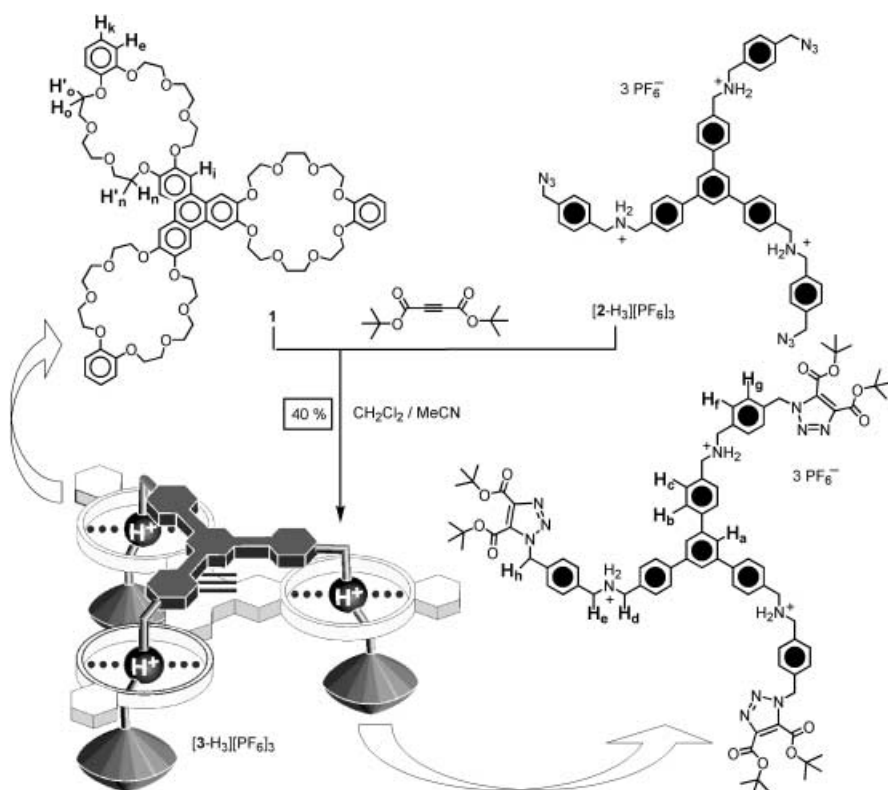
## Results and Discussion

### Template-directed synthesis of the mechanically interlocked bundle:

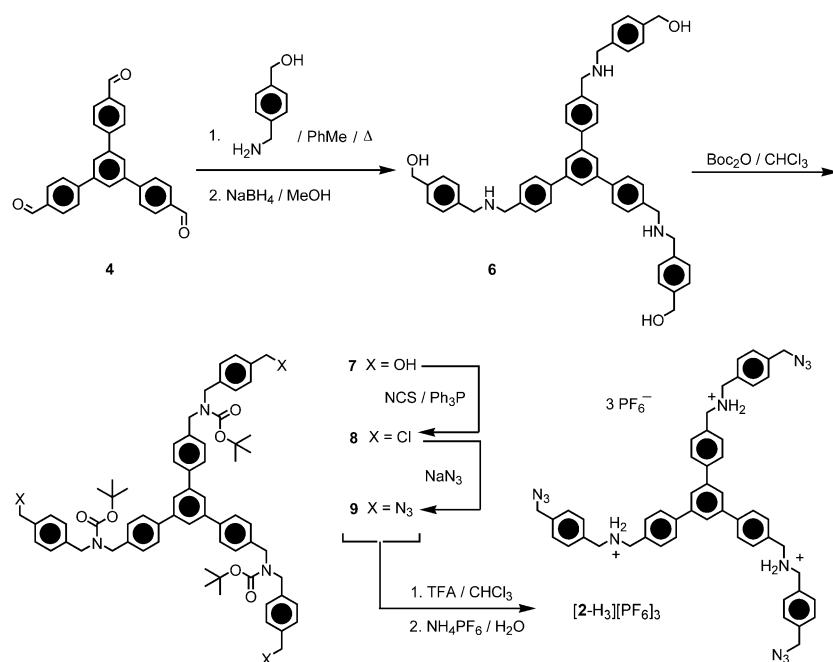
The syntheses of 1,3,5-tris(*p*-formylphenyl)benzene (**4**) and the tris(crown ether) have already been reported in an earlier paper.<sup>[10b]</sup> The preparation of the trifurcated trisammonium salt  $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$  is outlined in Scheme 2. 1,3,5-Tris(*p*-formylphenyl)benzene (**4**) was condensed with 4-(aminoethyl)benzyl alcohol<sup>[19]</sup> to give the trisimine **5**, which was reduced ( $\text{NaBH}_4/\text{MeOH}$ ) to the trisamine **6**. Trisamine **6** was then Boc-protected to afford the triol **7**, which was converted subsequently ( $\text{NCS}/\text{Ph}_3\text{P}/\text{THF}$ ) to the trischloride **8** and then ( $\text{NaN}_3/18\text{C6}/\text{MeCOEt}$ ) to the trisazide **9**. Following TFA deprotection of **9** in  $\text{CHCl}_3$  and counterion exchange ( $\text{NH}_4\text{PF}_6/\text{MeOH}/\text{H}_2\text{O}$ ), the trifurcated trisammonium salt  $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$  was obtained. The mechanically interlocked bundle  $[\mathbf{3}\text{-H}_3][\text{PF}_6]_3$  was obtained by using a template-directed threading approach, followed by post-assembly covalent modification whereby a 1,3-dipolar cycloaddition<sup>[20]</sup> is repeated three times over within the 1:1 adduct formed between the tris(crown ether) **1** and the trisammonium ion  $[\mathbf{2}\text{-H}_3]^{3+}$ .

The 1:1 triply threaded superbundle was assembled initially in  $\text{CH}_2\text{Cl}_2/\text{MeCN}$  (3:2) containing **1** and  $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$  (Scheme 1). The azidomethyl groups on the three *para*-positions of the three terminal benzyl groups of the  $[\mathbf{2}\text{-H}_3]^{3+}$  ion, each threaded through one of the three macrocyclic rings associated with the tris(crown ether) **1**, were then treated<sup>[21]</sup> with di-*tert*-butylacetylenedicarboxylate, affording  $[\mathbf{3}\text{-H}_3][\text{PF}_6]_3$  in 40% yield.<sup>[22]</sup> The fact that the product survived the purification by column chromatography provides circumstantial evidence that it is mechanically interlocked, and also that the triazole stoppers are large enough to ensure that the molecular components cannot dissociate.<sup>[20]</sup>

**Spectrometric and NMR spectroscopic characterization of the bundle:** Fast atom bombardment (FAB) mass spectrometry of  $[\mathbf{3}\text{-H}_3][\text{PF}_6]_3$  strongly supports the structural as-



Scheme 1. The template-directed synthesis of the mechanically interlocked bundle  $[\mathbf{3}\text{-H}_3][\text{PF}_6]_3$  by means of kinetically controlled, [1,3]-dipolar cycloadditions to trap the superbundle formed in  $\text{CH}_2\text{Cl}_2/\text{MeCN}$  (3:2) at  $40^\circ\text{C}$  between the tritopic tris(crown ether) **1** and the trifurcated trisammonium salt  $[\mathbf{2}\text{-H}_3][\text{PF}_6]_3$ . The labeled protons on the two structural components of the bundle are referred to in a range of  $^1\text{H}$  NMR spectra, illustrated in Figures 2–4.



Scheme 2. The synthesis of the trisammonium salt  $[2-H_3][PF_6]_3$  carrying three azide functions for reaction (Scheme 1) with di-*tert*-butylacetylenedicarboxylate to form bulky triazole stoppers.

segment of the mechanically interlocked bundle made in Scheme 1. The FAB mass spectrum revealed peaks at  $m/z = 3283$ ,  $3140$ ,  $2993$ ,  $2850$ , and  $1497$  corresponding to the  $[M]^+$ ,  $[M-PF_6]^+$ ,  $[M-2PF_6]^+$ ,  $[M-3PF_6]^+$ , and  $[M-2PF_6]^{2+}$  ions, respectively. Furthermore, high-resolution electron spray (HR-ESI) mass spectrometry of  $[3-H_3][PF_6]_3$  revealed (Figure 1) that the most intense peak in the spectrum occurred at  $m/z = 1496.6814$  with an isotope distribution corresponding to the  $[M-2PF_6]^+$  ion.

The  $^1H$  NMR spectrum of  $[3-H_3][PF_6]_3$  recorded in  $CD_2Cl_2$  reveals a complex array of well-defined resonances (Figure 2a). The peak assignments (see Scheme 1 for proton labels) to these resonances produced by the bundle  $[3-H_3]^{3+}$  were made with the aid of  $^1H$ - $^1H$  COSY

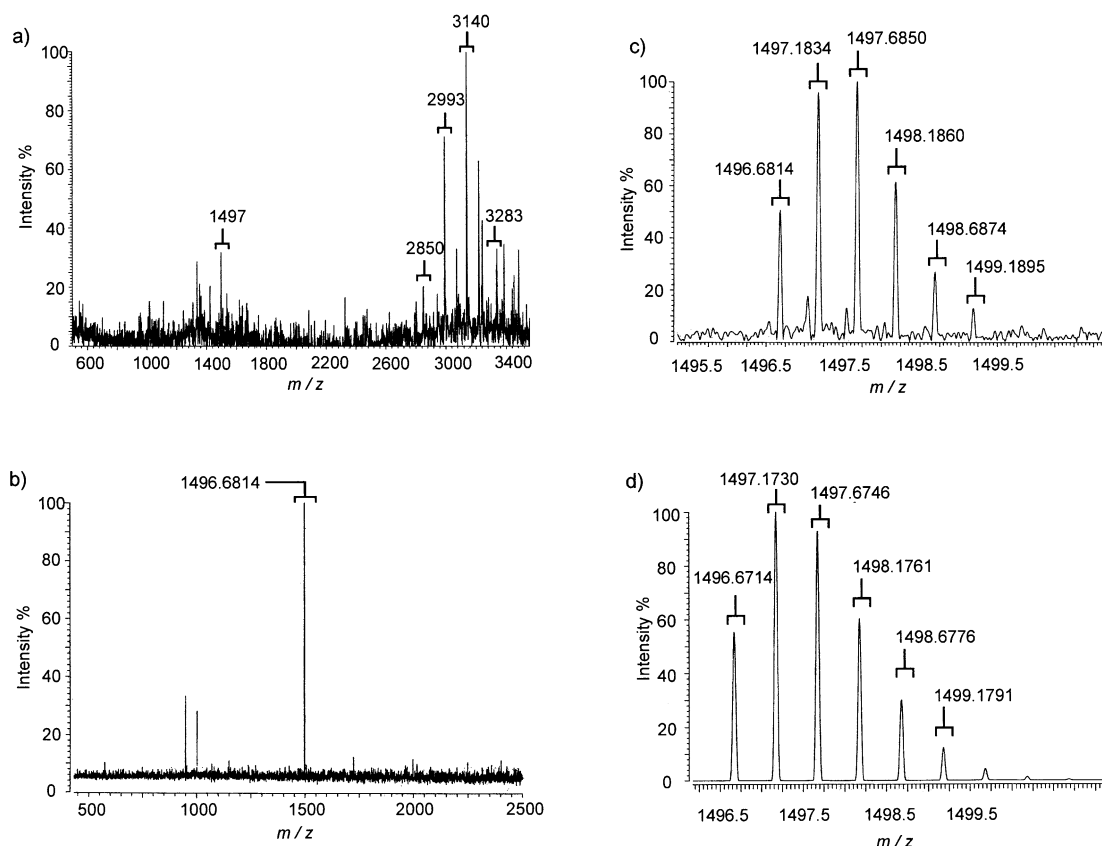


Figure 1. a) Low-resolution fast atom bombardment (FAB) mass spectrum of  $[3-H_3][PF_6]_3$  with peaks at  $m/z$  3283, 3140, 2993, 2850, and 1497 corresponding to the  $[M]^+$ ,  $[M-PF_6]^+$ ,  $[M-2PF_6]^+$ ,  $[M-3PF_6]^+$ , and  $[M-2PF_6]^{2+}$  ions, respectively. b) High-resolution electrospray ionization (HR-ESI) mass spectrum of  $[3-H_3][PF_6]_3$  with a major peak at  $m/z$  1496.6814 corresponding to the  $[M-2PF_6]^{2+}$  ion. Experimental (c) and calculated (d) isotope distributions for the peak at  $m/z$  1496.6814 in the HR-ESI mass spectrum.

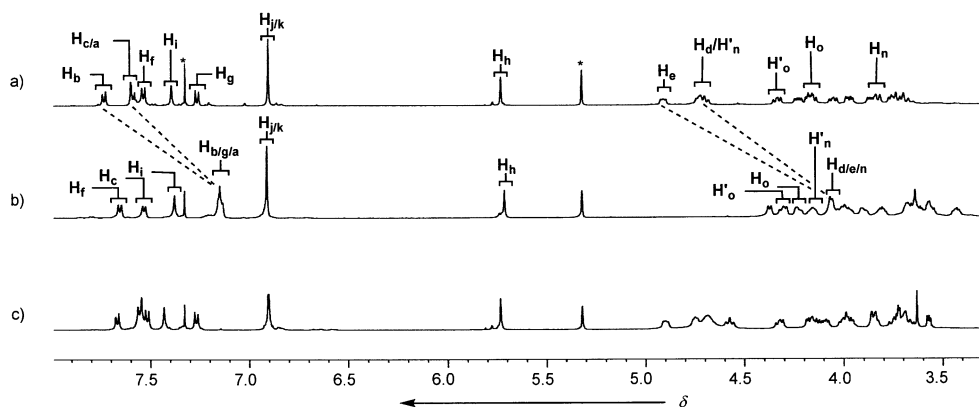


Figure 2. The  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 9.8 mm, 298 K) of a)  $[3\text{-H}_3][\text{PF}_6]_3$ , b) the deprotonated mechanically interlocked bundle, namely **3**, after addition of slightly more than three equivalents of solid  $t\text{BuOK}$  to  $[3\text{-H}_3][\text{PF}_6]_3$ , and c) the reprotonated bundle, that is,  $[3\text{-H}_3]^{3+}$ , after the subsequent addition of a slight excess ( $>3$  equiv) of trifluoroacetic acid (TFA).

(Figure 3 a and b) and TROESY (Figure 4) two-dimensional  $^1\text{H}$  NMR experiments. They are completely in accordance with molecules that have averaged  $\text{C}_{3v}$  symmetry. The methylene protons,  $\text{H}_{\text{e}}$  and  $\text{H}_{\text{d}}$ , adjacent to the secondary dialkylammonium ( $-\text{NH}_2^+-$ ) centers resonate (Figure 2a) at  $\delta = 4.91$  and  $4.72$  ppm, respectively; chemical shifts that are not

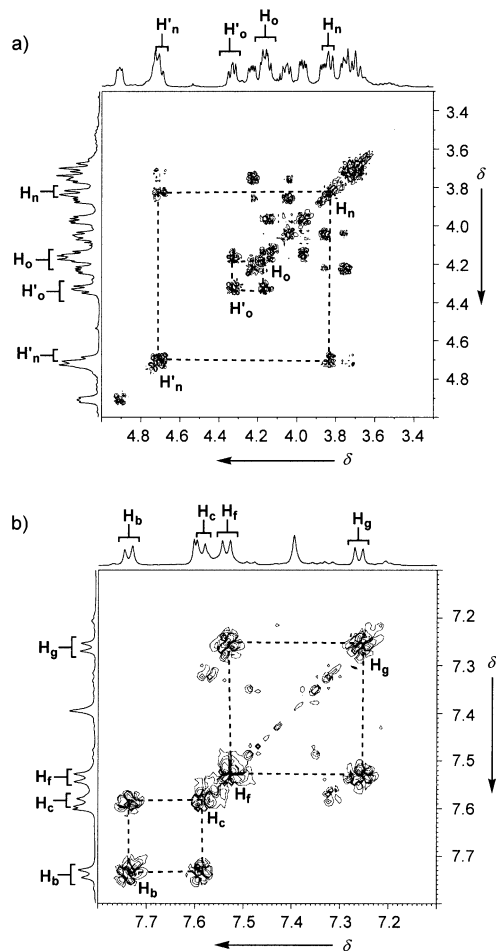


Figure 3. Selected regions (a and b) of the  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 9.8 mm, 298 K) of  $[3\text{-H}_3][\text{PF}_6]_3$ .

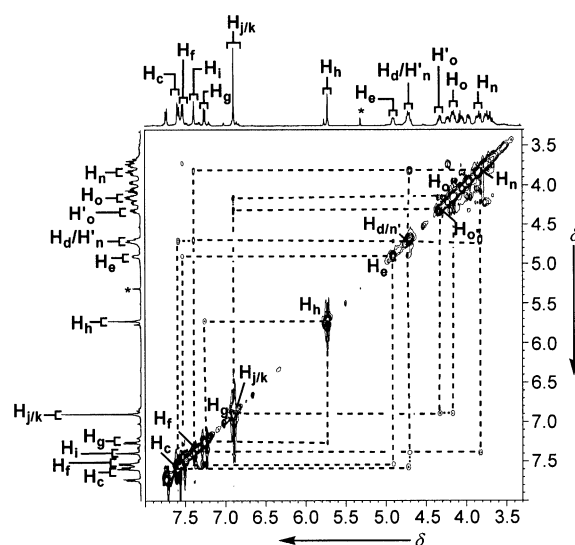
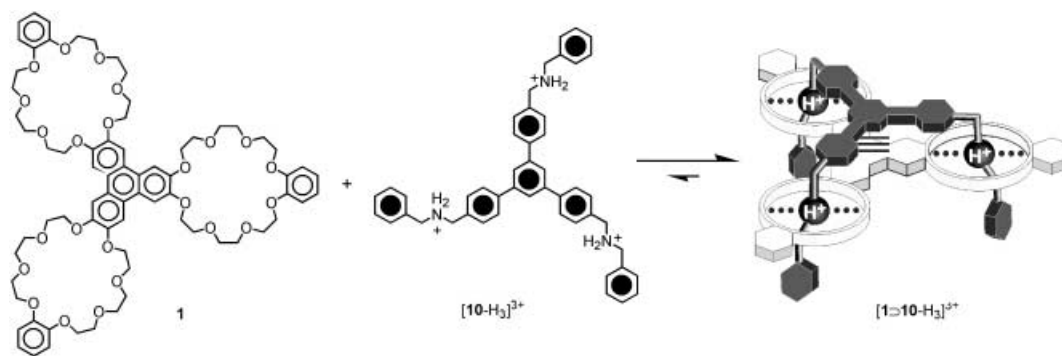


Figure 4. Selected regions of the  $^1\text{H}$ - $^1\text{H}$  TROESY NMR spectrum (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 9.8 mm, 298 K) of the mechanically interlocked superbundle  $[3\text{-H}_3][\text{PF}_6]_3$ .

all that dissimilar from those ( $\delta = 4.87$  and  $4.80$  ppm, respectively) for the analogous methylene protons in the kinetically-stable, triply threaded interwoven superbundle (Scheme 3) lacking the triazole stoppers.<sup>[10]</sup> Relative to  $[10\text{-H}_3]^{3+}$ , in which the  $\text{CH}_2\text{NH}_2^+\text{CH}_2$  protons resonate at  $\delta = 4.29$  and  $4.25$  ppm, the downfield shifts and multiplicities exhibited by  $\text{H}_{\text{e}}$  and  $\text{H}_{\text{d}}$  in  $[3\text{-H}_3]^{3+}$  are diagnostic<sup>[3]</sup> of the threading of dibenzylammonium ions through dibenzo[24]-crown-8 (DB24C8) rings. They demonstrate the interlocked nature of the two components in the mechanically interlocked bundle  $[3\text{-H}_3]^{3+}$ . The resonances for aromatic core protons ( $\text{H}_{\text{a}}$  and  $\text{H}_{\text{i}}$  at  $\delta = 7.60$  and  $7.40$  ppm, respectively) of the two components are shifted upfield significantly relative to the chemical shifts ( $\delta = 7.97$  and  $7.83$  ppm, respectively) of the analogous protons in the separate components—namely, **1** and  $[10\text{-H}_3]^{3+}$  of the superbundle  $[1\text{-}10\text{-H}_3]^{3+}$  shown in Scheme 3—indicating  $\pi\cdots\pi$  stacking of the central aromatic cores of the components with respect to one another. Inspection of the region between  $\delta = 3.6$  and  $4.4$  ppm in



Scheme 3. The equilibrium between the tris(crown ether) **1** and the trisammonium ion  $[10-H_3]^{3+}$ , which lies very much to the right in favor of the superbundle in solvents such as acetonitrile and dichloromethane. The graphical representation of the superbundle portrays the good surface-to-surface match between the two interpenetrating components. The dots indicate the  $N^+-H\cdots O$  hydrogen bonds between the  $-NH_2^+$  centers of  $[10-H_3]^{3+}$  and the fused DB24C8 rings in **1**, and the horizontal dashes indicate the  $\pi\cdots\pi$  stacking interactions between the central aromatic cores. The superbundle can be disassembled by addition of base (e.g.,  $nBu_3N$ ) and reassembled by addition of acid (e.g.,  $CF_3CO_2H$ ).

the  $^1H$  NMR spectrum (Figure 2a) reveals that all the pairs of *O*-methylene protons are anisochronous in the tris(crown ether) component of  $[3-H_3]^{3+}$ , since these protons are diastereotopic on account of the fact that the plane of symmetry in the plane of the 'free' tris(crown ether) **1** is no longer present in the mechanically interlocked bundle. Thus, all the  $^1H$  NMR spectroscopic evidence supports the mechanically interlocked, triply threaded structure proposed in Scheme 1 for the tricationic bundle  $[3-H_3]^{3+}$ .

**Absorption, luminescence, and electrochemical properties of the bundle:** Absorption and luminescence data, obtained in air-equilibrated MeCN at room temperature, for the mechanically interlocked bundle  $[3-H_3]^{3+}$  and the tris(crown ether) **1** are gathered together in Table 1, along with the

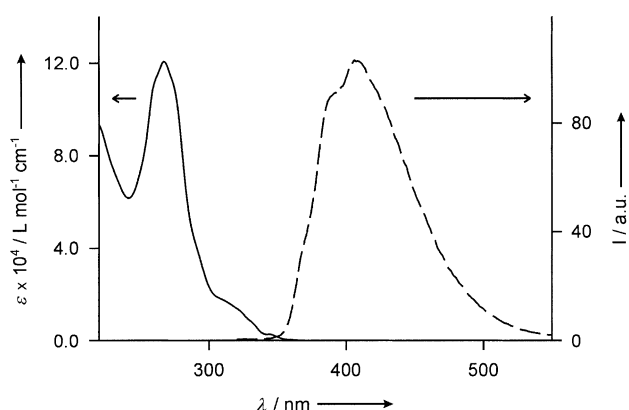


Figure 5. Absorption (full line) and luminescence (dashed line;  $\lambda_{\text{ex}} = 280$  nm) spectra recorded at room temperature of  $[3-H_3]^{3+}$  in an air-equilibrated MeCN.

Table 1. Spectroscopic and electrochemical data obtained in MeCN at room temperature

|                   | Absorption            |                                         | Luminescence          |             | Electrochemistry<br>$E_p$ [V vs SCE] <sup>[a]</sup> |
|-------------------|-----------------------|-----------------------------------------|-----------------------|-------------|-----------------------------------------------------|
|                   | $\lambda_{\max}$ [nm] | $\epsilon$ [ $M^{-1} \text{ cm}^{-1}$ ] | $\lambda_{\max}$ [nm] | $\tau$ [ns] |                                                     |
| <b>1</b>          | 276                   | 100 000                                 | 383                   | 9.6         | +1.00, +1.23, +1.38                                 |
| $[10-H_3]^{3+}$   | 260                   | 66 000                                  | 359                   | 17.0        | —                                                   |
| $[1>10-H_3]^{3+}$ | 267 <sup>[b]</sup>    | 130 000 <sup>[b]</sup>                  | 410 <sup>[b]</sup>    | 11.6        | +1.08 <sup>[c]</sup> , +1.43 <sup>[c]</sup>         |
| $[3-H_3]^{3+}$    | 267                   | 121 000                                 | 408                   | 4.6         | +1.07, +1.43                                        |

[a] Irreversible processes; potential values estimated from DPV peaks. [b] Obtained on a  $2 \times 10^{-5} \text{ mol L}^{-1}$  1:1 mixture of **1** and  $[10-H_3]^{3+}$  in which about 80% of the components are associated to give the superbundle after subtraction of the bands arising from the uncomplexed components. [c] Obtained on  $5 \times 10^{-4} \text{ mol L}^{-1}$  1:1 mixture of **1** and  $[10-H_3]^{3+}$  in which >95% of the components are associated to give the superbundle.

data for the trisammonium ion  $[10-H_3]^{3+}$ , which can be regarded as a model for the dumbbell component of the bundle, and its 1:1 adduct  $[1>10-H_3]^{3+}$  with **1**. The absorption and luminescence spectra of  $[3-H_3]^{3+}$  are shown in Figure 5.

The absorption spectrum of the mechanically interlocked bundle does not differ significantly from that expected on the basis of the spectra obtained for its components. The intense luminescence bands arising from the triphenylene unit

of **1** ( $\lambda_{\max} = 383$  nm) and from 1,3,5-triphenylbenzene unit of  $[10-H_3]^{3+}$  ( $\lambda_{\max} = 359$  nm) are no longer present in the mechanically interlocked bundle; however, the interlocked bundle shows a weaker and broad luminescence band with  $\lambda_{\max} = 408$  nm and  $\tau = 4.6$  ns. This new fluorescence band most likely originates from a lower lying excited state that arises from the  $\pi\cdots\pi$  stacking of the aromatic cores of the two components. Interestingly, this band exhibits a structure somewhat reminiscent of that observed for **1**. The excitation spectrum of  $[3-H_3]^{3+}$ , recorded at  $\lambda_{\text{em}} = 408$  nm, matches exactly its absorption spectrum, showing that light irradiation leads to the fluorescence excited state of the mechanically interlocked bundle, irrespective of which component is excited. In summary, the photophysical properties of  $[3-H_3]^{3+}$  are very similar to those<sup>[10b]</sup> of the triply threaded, two-component superbundle  $[1>10-H_3]^{3+}$ , illustrated in Scheme 3.

In contrast to what happens with  $[1>10-H_3]^{3+}$ , deprotonation of the three  $-NH_2^+$  centers of the mechanically interlocked bundle cannot possibly lead to the disassembly of its two components, since they are mechanically interlocked on account of the bulky stoppers located at the three extremities of the trisammonium ion component. Therefore, this

bundle offers the interesting possibility of disabling the template employed for its preparation. It has been observed<sup>[23]</sup> that removal of the Cu<sup>I</sup> template in transition-metal-assembled catenates leads to a substantial rearrangement of the mechanically interlocked structure for the derived catenane. The triply threaded architecture of the [3-H<sub>3</sub>]<sup>3+</sup> bundle, together with the size and shape of its two components, suggests that disruption of the hydrogen-bonding interaction between them should not lead to substantial structural rearrangements.

Non-nucleophilic tertiary amines, such as *n*Bu<sub>3</sub>N or *i*Pr<sub>2</sub>NEt, have been employed<sup>[13c-e,24]</sup> routinely to deprotonate –NH<sub>2</sub><sup>+</sup>– centers. Indeed, in MeCN, the trisammonium ion [10-H<sub>3</sub>]<sup>3+</sup> is fully deprotonated<sup>[10b]</sup> on addition of three equivalents of *n*Bu<sub>3</sub>N. Addition of *n*Bu<sub>3</sub>N (up to a large excess) to a solution of [3-H<sub>3</sub>]<sup>3+</sup> in MeCN did not result in any appreciable changes in the absorption and luminescence spectra, suggesting that deprotonation does not take place. The result could be related to the large stabilization of the protonated form of the mechanically interlocked bundle as a consequence of multiple hydrogen-bonding interactions.<sup>[25]</sup> Deprotonation, however, does take place in the case of the superbundle [1⊃10-H<sub>3</sub>]<sup>3+</sup>.<sup>[10b]</sup> The different behavior between the mechanically interlocked and supramolecular bundles can be attributed<sup>[26]</sup> to entropic factors related to the possibility for [1⊃10-H<sub>3</sub>]<sup>3+</sup> to disassemble into its molecular components—a possibility which is precluded to [3-H<sub>3</sub>]<sup>3+</sup>. Such a disassembly process implies a substantial increase in entropy, because 1) the number of species increases and 2) the “disassembled” molecular components are characterized by much larger conformational freedom.

Upon addition of three equivalents of *t*BuOK—a very much stronger proton acceptor compared to tertiary amines—to [3-H<sub>3</sub>]<sup>3+</sup>, changes were observed in the absorption and emission spectra. In particular, the shape of the luminescence band with λ<sub>max</sub> = 408 nm is slightly modified and its intensity diminishes to ca. 40% of its initial value. Such a quenching phenomenon could be supported by the appearance of lower lying n–π\* excited states, arising from the presence of amino groups.<sup>[27]</sup> It is important to note that these spectroscopic changes are reversed after addition of an acid in an amount equivalent to that of the previously added base.

The electrochemical data for the bundle [3-H<sub>3</sub>]<sup>3+</sup>, tris(crown ether) **1**, the trisammonium ion [10-H<sub>3</sub>]<sup>3+</sup>, and the 1:1 adduct [1⊃10-H<sub>3</sub>]<sup>3+</sup> in MeCN (Scheme 3) are reported in Table 1. In the potential window examined (from +2 to –1.2 V vs SCE), [10-H<sub>3</sub>]<sup>3+</sup> is not electroactive, and **1** and [3-H<sub>3</sub>]<sup>3+</sup> exhibit only oxidation processes. The tris(crown ether) **1** shows three irreversible oxidation peaks at potentials (obtained from DPV measurements) of +1.00, +1.23, and +1.38 V. The bundle undergoes only two irreversible oxidation processes at +1.07 and +1.43 V, a behavior quite similar to that of [1⊃10-H<sub>3</sub>]<sup>3+</sup>. On the basis of the results of a previous investigation,<sup>[10b]</sup> the first oxidation peak (+1.07 V) can be assigned to the hexaoxytriphenylene core, and the second one (+1.43 V) to oxidation of the three peripheral catechol units. Given the irreversible nature of the

three processes, it would be inappropriate to enter into any further speculation.

**Deprotonation/reprotonation of the mechanically interlocked bundle:** One of the reasons for assembling mechanically interlocked molecular compounds like [3-H<sub>3</sub>]<sup>3+</sup> is to develop machines on the nanoscale level which can be pH-driven. Since the bundle [3-H<sub>3</sub>]<sup>3+</sup> can be looked upon as a prototype of a new class of artificial molecular machines, we were motivated to subject it to deprotonation and subsequent reprotonation, that is, to demonstrate a reversible cycle.

Addition of slightly more than a threefold excess of *t*BuOK to a CD<sub>2</sub>Cl<sub>2</sub> solution of [3-H<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> results in a dramatic change in its <sup>1</sup>H NMR spectrum (Figure 2b). The resonances for the methylene protons H<sub>d</sub> and H<sub>e</sub> in [3-H<sub>3</sub>]<sup>3+</sup> are shifted upfield from δ = 4.72 and 4.91 ppm, respectively, to δ = 4.12 ppm in **3**, indicating complete deprotonation of all three –NH<sub>2</sub><sup>+</sup>– centers. The resonance for the central aromatic core protons (H<sub>a</sub>) in the trisammonium ion component is shifted upfield from δ = 7.60 ppm in [3-H<sub>3</sub>]<sup>3+</sup> to δ = 7.19 ppm in **3**, implying either some conformational change in the component itself or a relative movement with respect to the hexaoxytriphenylene core of the trisammonium ion component. While the resonance for the nearby H<sub>b</sub> protons in the trisammonium ion component experiences an equally dramatic shift from δ = 7.70 ppm in [3-H<sub>3</sub>]<sup>3+</sup> to δ = 7.10 ppm in **3**, the adjacent H<sub>c</sub> protons on the same phenylene rings change very little chemical shiftwise. The same is true for the protons H<sub>f</sub>, H<sub>g</sub>, and H<sub>h</sub> in the trisammonium ion component in the vicinity of the three triazole stoppers. In the tris(crown ether), the *O*-methylene protons retain their diastereotopicities, indicating that the two components are still interacting intimately with each other. This conclusion is further vindicated by the fact that the resonances for the aromatic protons H<sub>i</sub> on the central hexaoxytriphenylene core of the tris(crown ether) component undergo no change in their chemical shifts whatsoever. We are drawn to the conclusion that there is no substantial change in the relative geometries of the two components in the bundle in going from the tricationic to the neutral form. It is not unlikely that a combination of strong N<sup>+</sup>–H···O hydrogen bonds and weak C–H···O interactions in [3-H<sub>3</sub>]<sup>3+</sup> are replaced in **3** by weak N–H···O hydrogen bonds and even weaker C–H···O interactions, with the π···π stacking interactions remaining essentially intact, albeit that the relative geometry between the two aromatic cores has most likely altered somewhat. This interpretation of the structural changes undergone in going from [3-H<sub>3</sub>]<sup>3+</sup> to **3** has some precedence<sup>[28]</sup> in a model [2]ro-taxane, for which the X-ray crystal structures are available (Figure 6) for both the charged and neutral forms. They reveal that the macrorings encircle and interact with the heteroatomic centers in the dumbbell components, whether they are charged or neutral.

Variable temperature <sup>1</sup>H NMR spectra were recorded for both [3-H<sub>3</sub>]<sup>3+</sup> and **3** in CD<sub>2</sub>Cl<sub>2</sub>. In the case of the tricationic bundle [3-H<sub>3</sub>]<sup>3+</sup>, as the solution was cooled down from 298 to 208 K, no significant changes in chemical shifts were observed, indicating that the two components are tightly inter-

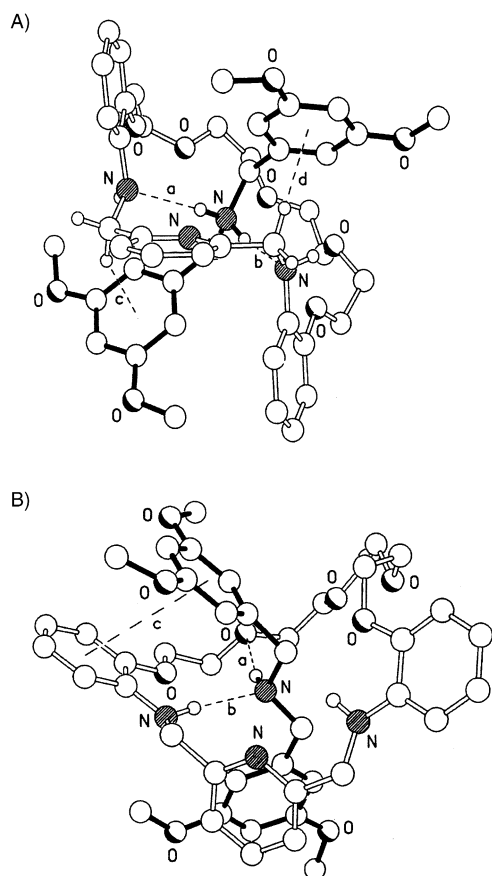


Figure 6. Ball-and-stick representations of the solid-state structures of A) a charged [2]rotaxane stabilized by two  $N^+H\cdots N$  hydrogen bonds (a and b) and two  $C-H\cdots\pi$  interactions (c and d), and B) a neutral [2]rotaxane stabilized by one  $N-H\cdots O$  (a) and one  $N-H\cdots N$  (b) hydrogen bond and a  $\pi\cdots\pi$  stacking interaction (c).

locked with little freedom to undergo co-conformational changes. By contrast, when a solution of **3** was cooled down, there were notable changes in chemical shifts (Figure 7), indicative of alterations in co-conformations within the neutral bundle commensurate with its containing much weaker non-covalent bonds between its two components. We have also noted that the resonances for protons  $H_c$ ,  $H_f$ , and  $H_g$  in **3** undergo a pattern of chemical shifts changes that leave them, at low temperatures, with  $\delta$  values reminiscent of those for the same protons in  $[3-H_3]^{3+}$ . This phenomenon supports the contention that deprotonation/reprotonation of  $[3-H_3]^{3+}/\mathbf{3}$  is associated by only relatively small differences in the overall structure of the mechanically interlocked bundle, whether it be tricationic or neutral.

## Conclusion

The fact that we have been able to harness the cluster effect, associated with paucivalency, to assemble a supramolecular bundle and then convert it into its triply locked counterpart in a kinetically fast and efficient manner has demonstrated that the realm of interlocked molecules can be extended beyond merely simple catenanes and rotaxanes.

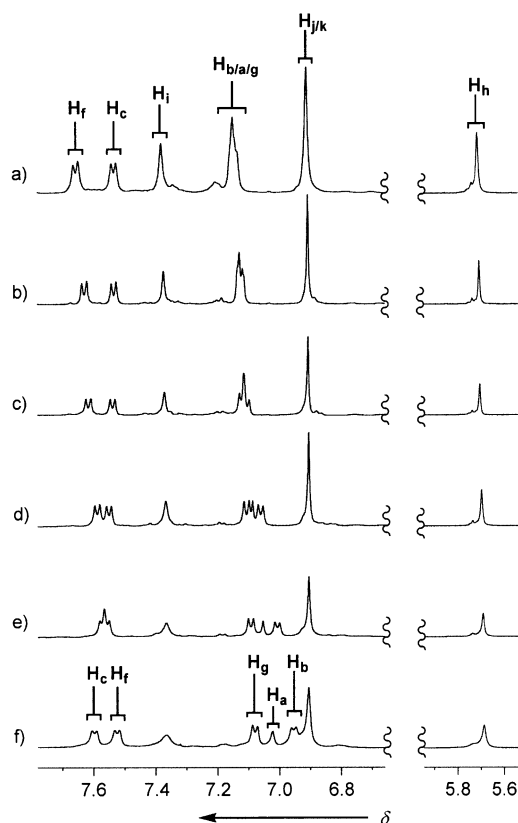


Figure 7. A series of  $^1H$  NMR spectra (500 MHz,  $CD_2Cl_2$ , 9.8 mm) of the deprotonated mechanically interlocked bundle, namely **3**, recorded at various temperatures: a) 298 K, b) 278 K, c) 268 K, d) 248 K, e) 228 K, f) 208 K.

Our observation that the three trigonally disposed  $-NH_2^+$ -centers, encircled by three trigonally oriented DB24C8 rings, can all be deprotonated and reprotonated lends authority to our belief that artificial molecular machines,<sup>[12,13]</sup> whereby chemical input induces mechanical output, can be constructed with a view to making them run in a cyclical manner. This goal is one which is now being pursued jointly with some gusto in our two different laboratories.

## Experimental Section

**General:** All chemicals were purchased from Aldrich and were used without further purification. Column chromatography was performed on silica gel 60 (Merck 40–60 nm, 230–400 mesh). Melting points were determined on an Electrothermal 9200 apparatus and reported uncorrected.  $^1H$  and  $^{13}C$  NMR spectra were recorded on Bruker Avance-500 at 500 and 125 MHz spectrometers, respectively. The chemical shift values are expressed as  $\delta$  values and the coupling constants values ( $J$ ) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; and m, multiplet. Fast atom bombardment mass spectrometry (FABMS) was performed on a VG ZAB-SE mass spectrometer, equipped with a krypton primary atom beam and with a 3-nitrobenzyl alcohol matrix. Both high-resolution matrix-assisted laser desorption ionization spectra (HR-MALDI) and electron-spray mass spectra (HR-ESI) were measured on an IonSpec Fourier transform mass spectrometer. The experimental setup for the photophysical and electrochemical experiments was described in detail in ref. [10b].

**Compound 6:** A mixture of 4-(aminomethyl)benzylalcohol (3.2 g, 23.3 mmol) and **4**<sup>[10b]</sup> (3.0 g, 7.7 mmol) was heated in PhMe (100 mL)

under reflux overnight, while H<sub>2</sub>O was removed through a Dean–Stark trap. The reaction mixture was cooled down in a freezer to –10 °C and the resulting suspension filtered to give the trisimine **5** as a white solid (4.02 g, 74 %). M.p. 166–168 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>SOCD<sub>3</sub>, 25 °C): δ = 4.50 (d, *J* = 4.5 Hz, 6H), 4.81 (s, 6H), 5.17 (br, 3H), 7.32 (m, 12H), 7.92 (d, *J* = 8.0 Hz, 6H), 8.01 (m, 9H), 8.58 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 64.7, 65.0, 125.4, 127.1, 127.4, 128.1, 128.8, 135.4, 138.6, 139.6, 141.7, 143.0, 161.5 ppm; HRMS (MALDI): *m/z* calcd for C<sub>51</sub>H<sub>46</sub>N<sub>3</sub>O<sub>3</sub>: 748.3534 [*M*+H]<sup>+</sup>; found: 748.3578.

NaBH<sub>4</sub> (1.02 g, 26.8 mmol) was added portionwise to a solution of **5** (white solid) in dry MeOH (100 mL) and dry THF (100 mL). After the reaction had been left to stir overnight the solvent was removed in vacuo. The resulting solid was partitioned between THF (150 mL) and brine (100 mL). The aqueous phase was washed with THF (100 mL). The organic phases were combined and dried (MgSO<sub>4</sub>), and the solvent was removed in vacuo to give **6** as a yellow liquid (3.6 g, 90 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 3.74 (s, 6H), 3.77 (s, 6H), 4.50 (s, 6H), 7.22 (d, *J* = 8 Hz, 6H), 7.43 (d, *J* = 8 Hz, 6H), 7.67 (d, *J* = 8 Hz, 6H), 7.80 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 50.7, 50.9, 61.9, 123.3, 124.2, 124.9, 125.7, 126.5, 129.1, 137.6, 138.6, 139.4, 140.2 ppm; HRMS (MALDI): *m/z* calcd for C<sub>51</sub>H<sub>52</sub>N<sub>3</sub>O<sub>3</sub>: 754.4003 [*M*+H]<sup>+</sup>; found: 754.3147.

**Compound 7:** The trisamine **6** (2.7 g, 3.6 mmol) was dissolved in CHCl<sub>3</sub> (450 mL) and then di-*tert*-butyl dicarbonate (7.9 g, 36.1 mmol) was added. The reaction mixture was left to stir for 24 h, before being washed with 2 M HCl aqueous solution (2 × 200 mL) and H<sub>2</sub>O (200 mL). The organic phase was dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to yield the crude product, which was subsequently purified by column chromatography (SiO<sub>2</sub>: CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 95:5) to yield **7** (2.3 g, 60 %). M.p. 68–70 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.52 (s, 27H), 4.45 (br, 12H), 4.71 (s, 6H), 7.20–7.34 (m, 6H), 7.35 (d, *J* = 8 Hz, 6H), 7.66 (d, *J* = 8 Hz, 6H), 7.77 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.4, 48.7, 48.9, 65.0, 80.2, 124.8, 127.2, 127.4, 127.6, 127.9, 128.2, 128.4, 137.2, 139.9, 141.9, 155.9 ppm; HRMS (MALDI): *m/z* calcd for C<sub>66</sub>H<sub>75</sub>N<sub>3</sub>O<sub>3</sub>Na<sup>+</sup>: 1076.5401 [*M*+Na]<sup>+</sup>; found: 1076.5425.

**Compound 8:** Triphenylphosphine (4.1 g, 15.8 mmol) in THF (100 mL) was added to *N*-chlorosuccinimide (2.4 g, 18.1 mmol) in THF (100 mL) under an argon atmosphere, to form a white suspension. The triol **7** (2.0 g, 1.9 mmol), dissolved in THF (40 mL), was then slowly added and the reaction mixture was left to stir overnight. The solvent was evaporated and the product purified by column chromatography (SiO<sub>2</sub>: hexanes/EtOAc, 7:3). The product **8** was obtained as an off-white solid (2.0 g, 95 %). M.p. 62–64 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.57 (s, 27H), 4.45 (s, 6H), 4.52 (s, 6H), 4.65 (s, 6H), 7.22–7.40 (m, 12H), 7.42 (d, *J* = 8 Hz, 6H), 7.71 (d, *J* = 8 Hz, 6H), 7.82 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.5, 46.0, 48.9, 49.2, 80.3, 125.0, 127.5, 127.8, 128.5, 128.9, 136.6, 137.4, 138.4, 140.1, 142.0, 156.0 ppm; HRMS (MALDI): *m/z* calcd for C<sub>66</sub>H<sub>72</sub>N<sub>3</sub>O<sub>6</sub>Cl<sub>3</sub>Na<sup>+</sup>: 1130.4384 [*M*+Na]<sup>+</sup>; found: 1130.4398.

**Compound 9:** Sodium azide (1.1 g, 18.1 mmol) was added to the trischloride **8** (1.0 g, 0.9 mmol) in 2-butanone (80 mL), followed by a few crystals of [18]crown-6, and the suspension was heated under reflux for 18 h. Evaporation of the solvent, followed by filtration through a thin silica pad (SiO<sub>2</sub>, hexanes/EtOAc, 7:3) yielded **9** (0.93 g, 91 %) as a white solid. M.p. 50–52 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 1.57 (s, 27H), 4.39 (s, 6H), 4.46 (s, 6H), 4.55 (s, 6H), 7.34 (m, 18H), 7.12 (d, *J* = 8 Hz, 6H), 7.83 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 28.4, 48.9, 49.2, 54.4, 80.2, 124.9, 127.4, 127.8, 128.4, 134.3, 137.3, 138.2, 140.0, 142.0, 155.9 ppm; HRMS (MALDI): *m/z* calcd for C<sub>66</sub>H<sub>72</sub>N<sub>12</sub>O<sub>6</sub>Na<sup>+</sup>: 1151.5595 [*M*+Na]<sup>+</sup>; found: 1151.5684.

**Salt [2-H<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub>:** Trifluoroacetic acid (ca. 20 mL) was added to the *t*Boc-protected trisamine **9** (0.9 g, 0.8 mmol) in CHCl<sub>3</sub> (120 mL), and the reaction mixture was stirred at room temperature for 16 h. The solvent was evaporated, and the residue dissolved in MeOH (15 mL). A saturated solution of NH<sub>4</sub>PF<sub>6</sub> in H<sub>2</sub>O was added dropwise, followed by H<sub>2</sub>O (50 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>/MeNO<sub>2</sub> (100 mL, 5:2), and the organic phase washed with water (3 × 100 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to yield [2-H<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> (0.75 g, 74 %) as a yellow solid. M.p. 156–158 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 25 °C): δ = 4.31 (s, 6H), 4.33 (s, 6H), 4.46 (s, 6H), 7.46 (d, *J* = 8 Hz, 6H), 7.53 (d, *J* = 8 Hz,

6H), 7.60 (d, *J* = 8 Hz, 6H), 7.91 (d, *J* = 8 Hz, 6H), 7.97 ppm (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C): δ = 51.0, 51.1, 53.5, 125.2, 127.8, 128.8, 129.8, 130.1, 130.6, 130.7, 137.6, 141.3, 141.5 ppm; HRMS (MALDI): *m/z* calcd for C<sub>51</sub>H<sub>49</sub>N<sub>12</sub><sup>+</sup>: 829.4198 [*M*–2HPF<sub>6</sub>–PF<sub>6</sub>]<sup>+</sup>; found: 829.4231.

**Salt [3-H<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub>:** The trisammonium salt [2-H<sub>3</sub>][PF]<sub>6</sub> (0.06 g, 0.005 mmol) and the tris(crown ether) **1** (0.06 g, 0.005 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/MeCN (2.5 mL, 3:2). Di-*tert*-butylacetylenedicarboxylate (0.27 g, 1.194 mmol) was then added to the reaction mixture, which was subsequently heated at 40 °C under an argon atmosphere for 24 h. The solution was cooled down to room temperature, evaporated in vacuo, and the residue purified by column chromatography (SiO<sub>2</sub>: CHCl<sub>3</sub>/MeCN, 8:2) to yield [3-H<sub>3</sub>][PF<sub>6</sub>]<sub>3</sub> (0.06 g, 40 %) as a white solid. M.p. 189 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 25 °C): δ = 1.43 (s, 27H), 1.53 (s, 27H), 3.60–4.20 (m, 60H), 4.22–4.30 (m, 6H), 4.50–4.54 (m, 6H), 4.79–4.82 (m, 6H), 4.86–4.90 (m, 6H), 5.72 (s, 6H), 6.84–6.92 (m, 12H), 7.23 (d, *J* = 8 Hz, 6H), 7.35 (s, 6H), 7.42 (s, 3H), 7.54 (br, 6H), 7.56–7.62 (m, 18H); <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 25 °C): δ = 26.9, 27.2, 51.1, 52.1, 52.8, 67.3, 67.4, 70.4, 70.5, 71.8, 82.7, 85.0, 104.5, 112.2, 121.0, 122.7, 125.7, 127.9, 129.2, 129.6, 129.9, 130.4, 131.0, 132.9, 135.9, 137.2, 138.1, 141.0, 146.2, 147.6, 157.2, 159.4 ppm; HRMS (ESI): *m/z* calcd for C<sub>159</sub>H<sub>195</sub>O<sub>36</sub>N<sub>12</sub>F<sub>6</sub>P<sub>3</sub><sup>+</sup>: 1496.6714 [*M*–2PF<sub>6</sub>]<sup>2+</sup>; found: 1496.6814.

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