

temperature (575–875 K) and annealing times did not give significant improvements. However, the diffraction pattern is in all cases reproducible. The Raman spectra are very similar to those of the decomposition products. The band at  $386\text{ cm}^{-1}$  ( $\text{Si}_3^{4-}$ ) is distinctly recognizable. The other bands found at 475 and/or  $480\text{ cm}^{-1}$ , and at 353, 334, and  $278\text{ cm}^{-1}$  and/or  $519\text{ cm}^{-1}$ , may be assigned to the anion  $\text{Si}_4^{4-}$  and to elemental silicon. Even though no new products that exhibit only the spectrum of the anion  $\text{Si}_3^{4-}$  were obtained by this route, the synthesis from the elements Cs and Si does clearly produce compounds with this anion.

Meanwhile, our results have been confirmed by the investigations of Quéneau et al.<sup>[16]</sup> who isolated the compound  $\text{Rb}_{12}\text{Si}_{17}$  and elucidated its crystal structure. In full accordance with our predictions,<sup>[5]</sup> this structure contains the clusters  $\text{Si}_4^{4-}$  and  $\text{Si}_3^{4-}$ . The bond lengths obtained from the structural analysis ( $d(\text{Si}-\text{Si}) = 2.40, 2.64, 2.37, 2.38\text{ Å}$ ) largely agree with our values (Figure 3 a), but are generally somewhat smaller. This might be due to the quality of the experimental data ( $R_F = 0.176$ ;  $I > 2\sigma(I)$ ). In any case, it is clear that a combination of structural analyses, quantum chemical methods, and quantitative analyses of the vibrational spectra can prove,<sup>[5]</sup> and allow more than to suggest,<sup>[17]</sup> the existence of new cluster compounds.

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## Self-Organization of a Heteroditopic Molecule to Linear Polymolecular Arrays in Solution\*\*

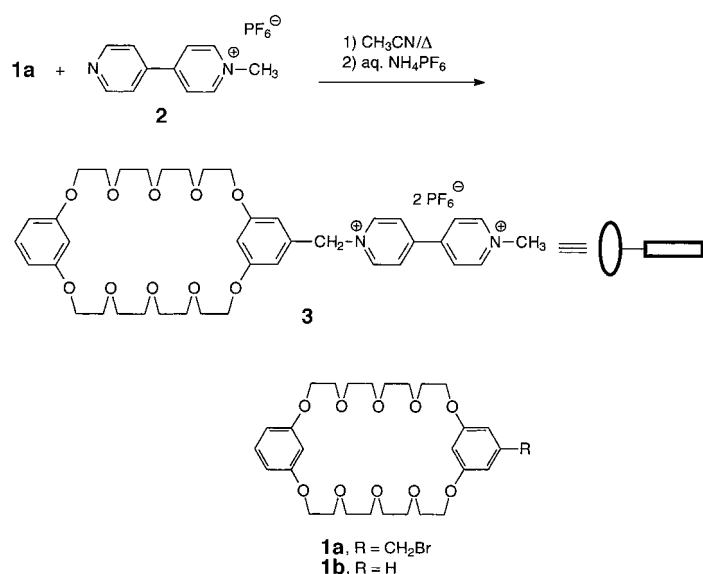
Nori Yamaguchi, Devdatt S. Nagvekar, and Harry W. Gibson\*

Nature displays a variety of supramolecular structures within a scale of 1 to 100 nm, beautifully put together with relatively simple building blocks by means of self-organization.<sup>[1]</sup> Over the last few decades chemists have elegantly adopted a variety of noncovalent bonding interactions to construct supramolecular architectures in the way that Nature does it.<sup>[2]</sup> The versatility and efficiency of utilizing such noncovalent forces<sup>[3]</sup> inspired us to design and to prepare a heteroditopic molecule to create linear oligo- and polymolecular arrays self-organized in solution by host–guest complexation.<sup>[4]</sup>

The synthetic methodology employed for **3** from **1a**<sup>[5]</sup> is depicted in Scheme 1. According to CPK models, the

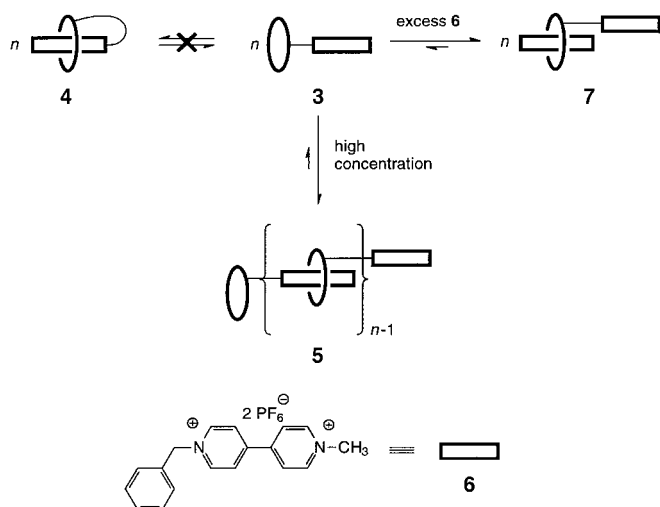
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Scheme 1. The synthesis of the heteroditopic molecule **3**.

existence of the complex **4** was disregarded based on the stiffness of the molecule, which effectively prevents the paraquat unit from curling around to complex intramolecularly with the macrocyclic unit (Scheme 2). In contrast, intermolecular complexation of **3** can lead to the formation of linearly chained, pseudo-polymeric supramolecules **5**.



Scheme 2. Schematic illustration of the formation of the linear oligo- and polymolecular arrays **5** by self-organization of **3**.

The  $^1\text{H}$  NMR spectra of **3** in  $[\text{D}_6]\text{acetone}$  at  $22^\circ\text{C}$  (Figure 1) are concentration-dependent, which reflects the involvement of rapidly exchanging noncovalent bonding interaction(s) in solution. The chemical shift of a proton located in the cavity of the crown ether binding site  $\text{H}_g$  was monitored by  $^1\text{H}$  NMR spectroscopy. The observed time-averaged chemical shifts  $\delta_o$  can be defined according to Equation (1) by using the

$$\delta_o = \delta_c p + \delta_u (1 - p) \quad (1)$$

chemical shifts obtained for totally complexed and free crown ether.  $\delta_c$  is the chemical shift in a solution in which the crown

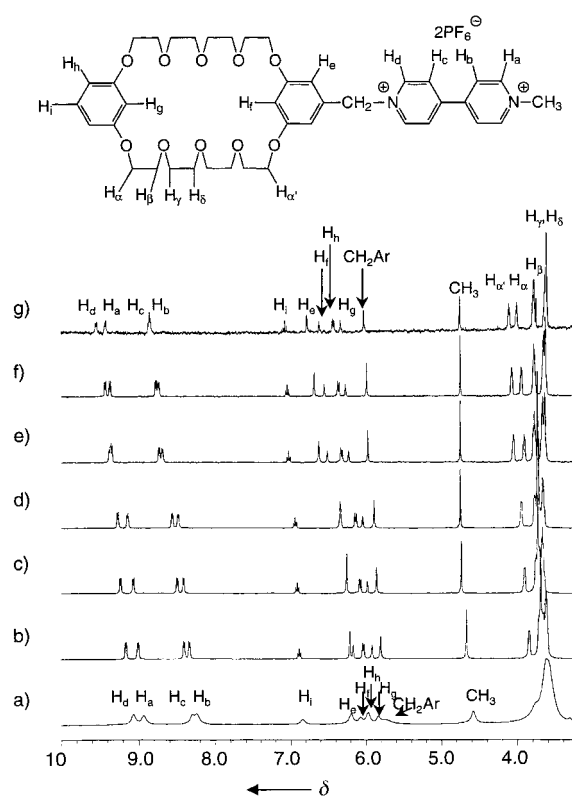


Figure 1. The  $^1\text{H}$  NMR spectra (400 MHz,  $[\text{D}_6]\text{acetone}$ ,  $22^\circ\text{C}$ ) of **3** at different concentrations: a) 2.0 M, b)  $5.0 \times 10^{-1}\text{M}$ , c)  $5.0 \times 10^{-2}\text{M}$ , d)  $1.0 \times 10^{-2}\text{M}$ , e)  $1.0 \times 10^{-3}\text{M}$ , f)  $5.0 \times 10^{-4}\text{M}$ ; g)  $6.3 \times 10^{-5}\text{M}$ .

ether is 100% complexed and  $\delta_u$  is that of the free crown ether, and  $p$  is the fraction of the complexed crown ether.<sup>[6, 7]</sup> From  $p$  the average number  $n$  of monomeric units in the aggregate **5** can be estimated according to Equation (2). The

$$n = 1/(1 - p) \quad (2)$$

$n$  values calculated in this manner are given in Table 1.<sup>[8]</sup> As concentration increases the size of the aggregates increases to truly large values and noncovalently bonded polymers are formed.<sup>[9]</sup> Since the molecular weight of **3** is 1010 g mol<sup>-1</sup>, for  $n = 50$  the total molar mass is 50 500 g mol<sup>-1</sup>.

The  $^1\text{H}$  NMR spectrum of **3** at 2.0M (Figure 1a) clearly reveals signals substantially broadened with respect to the

Table 1. Dependence of the degree of aggregation  $n$  of **5** on the concentration of **3**, calculated from the chemical shift  $\delta_0$  of the NMR signal<sup>[a]</sup> of H<sub>g</sub>.

$c_0(\mathbf{3})[\text{M}]$	$\delta_0$	$p$	$n$
2.0	5.839	0.98	50
1.4	5.862	0.93	14
1.0	5.881	0.89	9.1
$5.0 \times 10^{-1}$	5.918	0.82	5.6
$1.0 \times 10^{-1}$	5.964	0.73	3.7
$6.7 \times 10^{-2}$	5.974	0.71	3.4
$5.0 \times 10^{-2}$	5.977	0.70	3.3
$1.0 \times 10^{-2}$	6.041	0.58	2.4
$1.0 \times 10^{-3}$	6.227	0.21	1.3
$5.0 \times 10^{-4}$	6.268	0.13	1.1

[a] 400 MHz, [D<sub>6</sub>]acetone, 22 °C.

spectra recorded at lower concentrations. This can be understood in terms of the formation of larger pseudo-polymeric aggregates **5** at higher concentration; as a result the solution viscosity is increased (see below), and the mobility of the polymeric chain is restricted, thus causing the signal broadening in the NMR spectra. In contrast, the  $^1\text{H}$  NMR spectrum of a 1:1 solution of monotopic components **1b** and **6** in acetone maintains sharp and well-resolved signals even at the highest concentration we investigated (2.0 M/2.0 M). This observation, therefore, rules out non-ideality of highly concentrated solutions per se as a cause for the signal broadening.

The 2D-NMR spectra (NOESY) were consistent with the pseudorotaxane geometry formed between the two complementary functionalities of adjacent units. As expected, the ethyleneoxy protons  $\text{H}_\alpha$ ,  $\text{H}_\beta$ , and  $\text{H}_\gamma$  strongly interact through space with the protons of the paraquat unit ( $\text{H}_\text{a} - \text{H}_\text{d}$ ) and also with the benzylic methylene protons. Most importantly, the protons  $\text{H}_\text{b}$  and  $\text{H}_\text{c}$  of the paraquat moiety experience through-space interactions with the aromatic protons residing inside the crown ether cavity,  $\text{H}_\text{f}$  and  $\text{H}_\text{g}$ , but not with those outside the cavity,  $\text{H}_\text{e}$ ,  $\text{H}_\text{h}$ , and  $\text{H}_\text{i}$ .

High solution viscosity is characteristic of linear polymeric structures.<sup>[10]</sup> Indeed, the reduced viscosity of solutions of **3** in acetone increased in nonlinear fashion with concentration due to the formation of **5** (Figure 2a), while that of equimolar solutions of **1b** and **6** in acetone increased only slightly with concentration (Figure 2b), thus ruling out the polyelectrolyte effect as the major cause of the viscosity change observed with

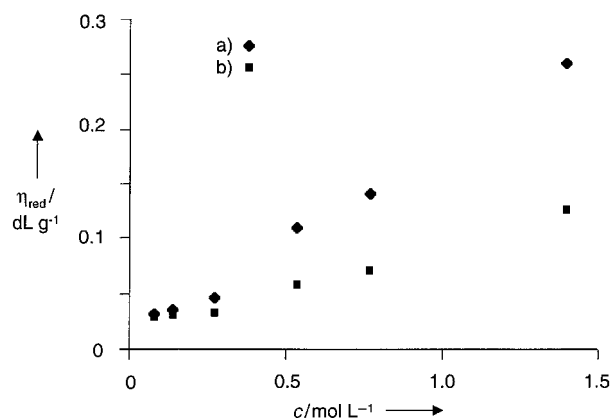


Figure 2. Reduced viscosity as a function of concentration (solutions in acetone at 22 °C): a) **3**, b) **1b** and **6** (1:1).

**5**. The high viscosity observed for **5** at 1.4 M ( $n = 14$ , Table 1),  $\eta_{\text{red}} = 0.26$  vs.  $0.13 \text{ dL g}^{-1}$  for solutions of **1b** and **6** (1:1), and the fact that a 2.0 M solution of **3** in acetone was too viscous to flow through the viscometer<sup>[11]</sup> argue against the presence of significant amounts of small cyclic species, since it is well known that cyclic molecules have smaller hydrodynamic volumes and hence lower viscosities than their linear counterparts.<sup>[12]</sup>

Two red-orange samples of amorphous **5**, prepared by freeze-drying<sup>[13]</sup> 0.1 and 1.0 M solutions of the heteroditopic molecule **3** in acetone, were studied by differential scanning calorimetry (DSC). The glass transitions ( $T_g$ ) occurred at 42.1 and 58.3 °C, respectively. On the other hand, samples of **3**

recrystallized from water (in which self-organization does not occur) are crystalline, and display a melting transition at 80.3 °C. The amorphous nature of the samples prepared in acetone is indicative of linear polymers. Furthermore, the higher  $T_g$  value of **5**, which was obtained from the more concentrated solution, is consistent with a higher extent of self-organization  $n$ , as demonstrated by the  $^1\text{H}$  NMR and viscosity experiments.

Mass spectrometric studies of **5** provided support for the existence of the self-organized linear arrays. The FAB mass spectrum<sup>[14]</sup> (Figure 3) reveals peaks at  $m/z = 3896$  and 3751,

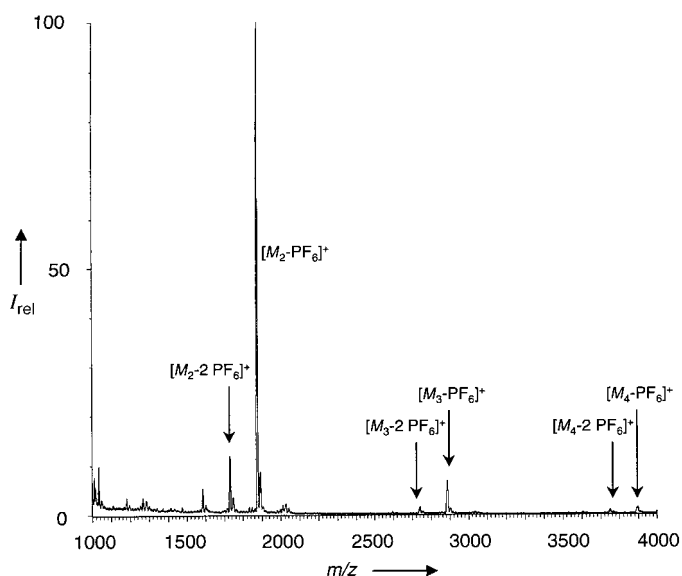


Figure 3. The FAB mass spectrum of the self-organized pseudo-oligomeric material **5**.

which can be attributed to the tetramer ( $n = 4$ ,  $[\text{M}_4 - \text{PF}_6]^+$  and  $[\text{M}_4 - 2 \text{PF}_6]^+$ ). The peaks at  $m/z = 2886$  and 2741 indicate the existence of trimeric oligomer ( $n = 3$   $[\text{M}_3 - \text{PF}_6]^+$  and  $[\text{M}_3 - 2 \text{PF}_6]^+$ ). In addition, we detected the  $[\text{M}_2 - \text{PF}_6]^+$ ,  $[\text{M}_2 - 2 \text{PF}_6]^+$ ,  $[\text{M} - \text{PF}_6]^+$  and  $[\text{M} - 2 \text{PF}_6]^+$  peaks, corresponding to the dimeric and monomeric species.

We have demonstrated that the heteroditopic molecule **3** instantaneously “self-associated” to form pseudo-oligomeric and pseudo-polymeric rotaxane types of linear arrays in solution. The trapping of the crown ether moieties in such linear arrays **5** by the use of blocking chemistry will lead to mechanically “locked-in” linear arrays which may ultimately be studied by using other characterization techniques available in polymer science. This exciting concept of utilizing noncovalent bonding interactions can potentially be expanded to achieve other novel self-organizing nanoscopic structures; we are pursuing such objectives.

#### Experimental Section

**3**: In a 50-mL round-bottomed flask equipped with a magnetic stirrer **1a**<sup>[5]</sup> (0.35 g, 0.56 mmol), **2** (0.18 g, 0.57 mmol), and MeCN (20 mL) were refluxed for 24 h. The orange solution was precipitated in diethyl ether to afford a yellow solid, which was dissolved in  $\text{H}_2\text{O}$ , and aqueous  $\text{NH}_4\text{PF}_6$  was added until no further precipitation was observed. The product was recrystallized from  $\text{H}_2\text{O}$  to give a yellow solid (0.50 g, 89% yield), m.p. 79–

80 °C. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, 22 °C): δ = 3.55 (16 H, m), 3.70 (8 H, t, *J* = 3.2 Hz), 4.00 (4 H, t, *J* = 3.2 Hz), 4.07 (4 H, t, *J* = 3.2 Hz), 4.21 (3 H, s), 5.77 (2 H, s), 6.44–6.47 (3 H, m), 6.60 (1 H, s), 6.80 (2 H, s), 7.10 (1 H, t, *J* = 3.6 Hz), 8.69 (2 H, d, *J* = 6.4 Hz), 8.72 (2 H, d, *J* = 6.4 Hz), 9.25 (2 H, d, *J* = 6.4 Hz), 9.48 (2 H, d, *J* = 6.4 Hz); elemental analysis calcd for C<sub>40</sub>H<sub>52</sub>N<sub>2</sub>O<sub>10</sub>P<sub>2</sub>F<sub>12</sub>: C 47.63, H 5.00; found: C 47.35, H 5.02.

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- [7] The signal corresponding to the methyl group of the heteroditopic molecule in **5** is strongly shifted upfield (δ ≈ 0.2) at higher concentration (2.0 M in Figure 1). Similarly, a significant upfield chemical shift is observed for the methyl group of **6** in the <sup>1</sup>H NMR spectrum of a 1:1 solution of monotopic components **1b** and **6** ([D<sub>6</sub>]acetone) at higher concentration (e.g., 2.0 M each). These observations can be explained by the increased concentration of PF<sub>6</sub><sup>−</sup> in solution. To demonstrate this experimentally, a solution of **6** in acetone (1.0 × 10<sup>−2</sup> M) was mixed with various concentrations of tetrabutylammonium hexafluorophosphate solutions (from 0.1 to 2.0 M) and the <sup>1</sup>H NMR spectra were recorded. The higher the concentration of PF<sub>6</sub><sup>−</sup>, the greater the upfield chemical shift of the methyl group. On the other hand, the chemical shift of the phenyl group of **6** is independent of the PF<sub>6</sub><sup>−</sup> concentration. Therefore, the chemical shifts of H<sub>g</sub> (Figure 1) are influenced by complexation, not by the changes of PF<sub>6</sub><sup>−</sup> concentration, validating the calculation of *p* based on the <sup>1</sup>H NMR data.
- [8] Nearly identical results were obtained by analysis of the NMR signal for H<sub>i</sub>.
- [9] The expression *n* = 1/(1 − *p*) assumes that the cyclic species do not contribute to consumption of host and guest sites. In covalent polymer chemistry it is well understood that the percentage of cyclic molecules of any size formed at high concentrations (e.g., 1.0 M) is very small indeed (< 3%) and that linear macromolecules are preferentially formed. For reviews on cyclization versus linear polymerization, see: a) G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**, p. 73; b) S. C. Hamilton, J. A. Semlyen, *Polymer*, **1997**, *38*, 1685–1691. Therefore, the assumption that the absence of cyclic complexes dramatically increases with concentration is validated.
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- [13] The solutions were slowly cooled to −95 °C and frozen with an acetone-ethanol/liquid nitrogen bath. The solvent was then removed under high vacuum to obtain red-orange solids. The <sup>1</sup>H NMR spectra of 0.1 and 1.0 M solutions in acetone at lower temperatures revealed that the chemical shifts of H<sub>g</sub> observed at −20 °C down to slightly above the freezing temperature of the solvent (−94 °C) were unchanged at δ = 5.944 and 5.862, which correspond to *n* values of 4.3 and 14, respectively.
- [14] A 5.0 × 10<sup>−1</sup> M solution of **3** in acetone (*n* = 5.6 Table 1) was mixed with the matrix (3-nitrobenzyl alcohol) on the probe. The spectrum was immediately recorded in the positive-ion mode. The relative intensities for the [M<sub>1</sub> − PF<sub>6</sub>]<sup>+</sup>, [M<sub>3</sub> − PF<sub>6</sub>]<sup>+</sup>, and [M<sub>2</sub> − PF<sub>6</sub>]<sup>+</sup> peaks were 0.29, 1.4, and 22% of the base peak [M − PF<sub>6</sub>]<sup>+</sup>, respectively.

## Toposelective and Chiroselective Self-Assembly of [2 × 2] Grid-Type Inorganic Arrays Containing Different Octahedral Metallic Centers

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The self-assembly of specific supramolecular architectures from a set of organic ligands and metal ions results from the processing of the structural information stored in the ligands by metal ions operating through the algorithm defined by their coordination geometry.<sup>[1]</sup> It implies the design of ligands presenting suitable features (such as nature, number, and disposition of binding sites) and the choice of appropriate metal ions.

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