

Kinetically Controlled Self-Assembly of  
Pseudorotaxanes on Crystallization

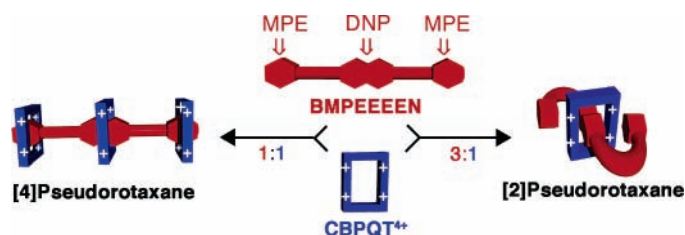
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## ABSTRACT



Mixing of equimolar amounts of cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) with a bis-4-methylphenyl ether (MPE twice) of a 1,5-dioxynaphthalene (DNP) derivative in MeCN/CH<sub>2</sub>Cl<sub>2</sub> (3:1) results in the formation of a [2]pseudorotaxane which, on crystallization, yields a [4]pseudorotaxane in the solid state that is stabilized by multiple [C–H···F] interactions: a mixture of the same components in a 1:3 ratio affords a crystalline [2]pseudorotaxane after vapor diffusion of methyl-*tert*-butyl ether into a solution of these components in MeCN/CH<sub>2</sub>Cl<sub>2</sub> (3:1).

The ability to control the self-assembly of different molecules in the solid state is an often sought-after goal of solid-state chemists. The practice has been referred to as crystal engineering.<sup>1</sup> Toward this uncertain goal, care must be taken in the understanding and design of the important noncovalent and supramolecular interactions<sup>2</sup> that largely determine the superstructures of molecules in crystalline solids. Much

progress has been made in exploiting the molecular recognition information<sup>3</sup> stored within molecules to orchestrate specific packing arrangements on molecules in crystals. Appropriately designed organic crystals have also been shown to exhibit control of chemical reactivity<sup>4</sup> in the solid state and have also led to crystalline materials with promising electronic<sup>5</sup> and photonic<sup>6</sup> properties. In addition, noncovalent intermolecular forces that may be too weak to be observed between molecules in the solution state may end up having subtle and dramatic effects on packing arrangements in the solid state and may lead to superstructures that could not be

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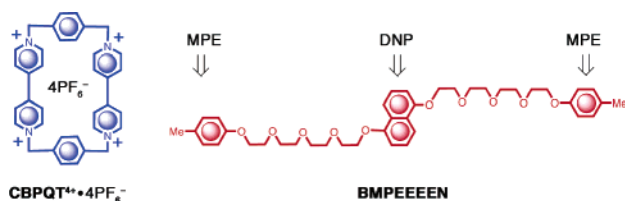
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predicted a priori. Here, we describe the formation, under slightly different conditions, of both a [2]- and [4]pseudorotaxane in the solid state from the same cyclophane host and threadlike guest, despite the fact that only the [2]pseudorotaxane can be detected in solution by  $^1\text{H}$  NMR spectroscopy.

The known self-assembly that takes place between the  $\pi$ -electron-deficient host, cyclobis(paraquat-*p*-phenylene) $^7$  (**CBPQT** $^{4+}$ ), and various  $\pi$ -electron-rich guests, such as hydroquinone and resorcinol derivatives, $^{7a,8}$  2,6- as well as 1,5-dioxynaphthalene derivatives, $^9$  indole and its derivatives, $^{10}$  neurotransmitters, $^{11}$  biphenyl derivatives, $^{12}$  tetrathiafulvalene, $^{13}$  and mono- and bispyrrolotetrathiafulvalenes, $^{14}$  to give [2]pseudorotaxanes is a result of  $[\pi\cdots\pi]$ ,  $[\text{C}-\text{H}\cdots\pi]$ , and  $[\text{C}-\text{H}\cdots\text{O}]$  interactions.

Upon mixing equimolar amounts of **CBPQT** $\cdot 4\text{PF}_6$  and a 1,5-dioxynaphthalene (DNP) derivatized thread (**BMPEEEEN**) (Figure 1) with 4-methylphenyl ether (MPE) appendages in



**Figure 1.** Structural formulas of **CBPQT** $^{4+}\cdot 4\text{PF}_6^-$  and **BMPEEEEN**.

$\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$  (3:1) at 25 °C, a deep violet color was observed immediately, indicating the formation of a charge-transfer (CT) complex. $^{15}$  The  $^1\text{H}$  NMR spectrum recorded at +25 °C revealed noticeable line broadening of all the resonances, indicative of exchange occurring on the  $^1\text{H}$  NMR

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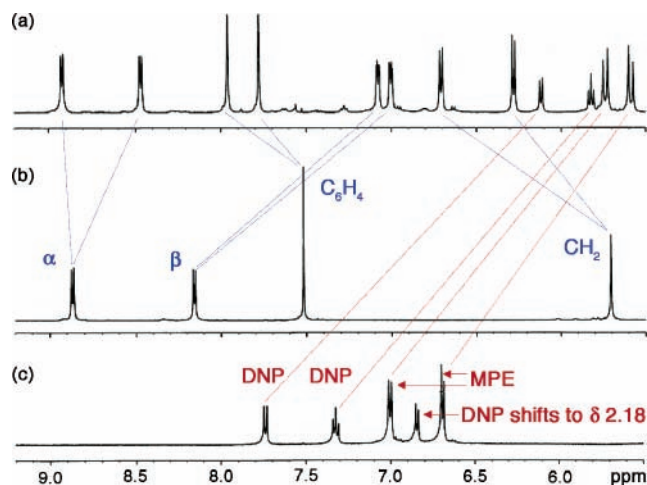
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time scale between the [2]pseudorotaxane and free species. Cooling the sample to  $-15$  °C resulted (Figure 2) in well-



**Figure 2.**  $^1\text{H}$  NMR spectra showing the aromatic region of (a) the 1:1 complex between **CBPQT** $^{4+}$  and **BMPEEEEN**, (b) **CBPQT** $^{4+}$ , and (c) **BMPEEEEN** recorded at  $-15$  °C in 3:1  $\text{CD}_3\text{CN}/\text{CD}_2\text{Cl}_2$ . Blue and red lines indicate the upfield or downfield shifts of proton signals for **CBPQT** $^{4+}$  and **BMPEEEEN**, respectively.

resolved signals and revealed the [2]pseudorotaxane to be the dominant species ( $>98\%$  by integration). Large upfield shifts for the DNP and MPE protons in the [2]pseudorotaxane were observed, along with the separation of all the signals for the **CBPQT** $^{4+}$  protons into two resonances, in accordance with a DNP unit threading a ring and imposing its local  $C_{2h}$  symmetry upon the **CBPQT** $^{4+}$  ring. $^{16}$  The large upfield shifts of the resonances for the MPE protons (1.15 and 1.35 ppm for those at the 2- and 3-positions, respectively) are the result of  $[\pi\cdots\pi]$  stacking interactions of the MPE appendages to the exterior surfaces of the bipyridinium units in the **CBPQT** $^{4+}$  ring. This type of interaction has been observed before in solution and in the solid state in similar [2]-pseudorotaxanes where the appendages to the threadlike guest are hydroquinone, $^{17}$  1,5-dioxynaphthalene, $^{18}$  anthracene, $^{19}$  and 4-*tert*-butylaniline $^{20}$  units. There is no doubt that the additional  $[\pi\cdots\pi]$  stacking interactions to the exterior of the **CBPQT** $^{4+}$  ring confer increased stability upon the 1:1 complex.

(15) UV/vis spectroscopic studies in  $\text{MeCN}/\text{CH}_2\text{Cl}_2$  (3:1) revealed a strong CT band with a  $\lambda_{\text{max}} = 527$  nm. Isothermal titration microcalorimetry measurements afforded a  $K_a$  value of  $27\,000\text{ M}^{-1}$  ( $\Delta G^\circ = -6.04$  kcal  $\text{mol}^{-1}$ ) in this mixed solvent system. The ITC measurements were consistent with a 1:1 complex being formed between **CBPQT** $\cdot 4\text{PF}_6$  and **BMPEEEEN**.

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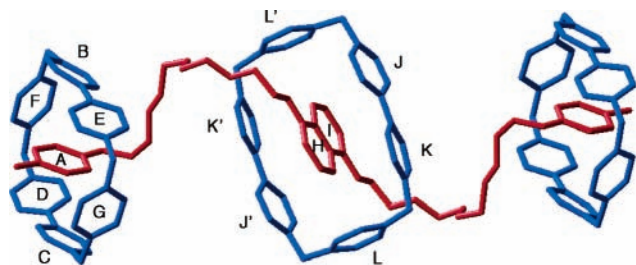
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Large violet single crystals, suitable for X-ray crystallography,<sup>21</sup> were grown by vapor diffusion of methyl-*tert*-butyl ether (MTBE) into MeCN/CH<sub>2</sub>Cl<sub>2</sub> (3:1) containing equimolar amounts of **CBPQT**·4PF<sub>6</sub> and **BMPEEEEEEN**. Surprisingly, the solid-state superstructure<sup>22</sup> revealed not the presence of the [2]pseudorotaxane but rather a [4]pseudorotaxane in which **CBPQT**<sup>4+</sup> rings encircle not only the central DNP unit but also both terminal MPE units (Figure 3). The



**Figure 3.** X-ray superstructure of the [4]pseudorotaxane formed from a 1:1 mixture of **CBPQT**<sup>4+</sup> and **BMPEEEEEEN** (hydrogen atoms, MeCN, and PF<sub>6</sub><sup>-</sup> anions have been omitted for clarity).

formation of a [4]pseudorotaxane, on crystallization, is surprising.<sup>23</sup> It requires that the complexation of the MPE units by the **CBPQT**<sup>4+</sup> rings occurs at the expense of stabilizing [C–H···O] interactions<sup>24</sup> that normally exist when **BMPEEEEEEN** threads through a **CBPQT**<sup>4+</sup> ring to form a [2]pseudorotaxane. Although we suspect<sup>25</sup> that the MPE units will be bound extremely weakly by **CBPQT**<sup>4+</sup>, we decided to explore whether the presence of the [4]pseudorotaxane could be detected in solution. <sup>1</sup>H NMR spectroscopic studies of a 3:1 (as well as a 1:3) mixture of **CBPQT**·4PF<sub>6</sub> and **BMPEEEEEEN** in CD<sub>3</sub>CN/CD<sub>2</sub>Cl<sub>2</sub> (3:1) showed no evidence for [4]pseudorotaxane formation. Peaks associated with the [2]pseudorotaxane were observed with no noticeable shifts of any signals compared with the equimolar mixture plus

(21) Crystals were analyzed with a Bruker Smart 1000 CCD-based diffractometer. Narrow-frame integration used the Bruker SAINT program system. Crystallographic data (excluding structure factors) for the superstructures of the [4]- and [2]pseudorotaxanes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-602067 and CCDC-602068, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EK, U.K. (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

(22) Empirical formula C<sub>168</sub>H<sub>178</sub>F<sub>72</sub>N<sub>2</sub>O<sub>10</sub>P<sub>12</sub>, *M* = 4404.96, triclinic, space group *P*1; *a* = 12.0701(10), *b* = 13.3831(12), *c* = 31.737(3) Å; α = 92.674(2)°, β = 92.3480(10)°, γ = 113.6250(10)°, *V* = 4681.9(7) Å<sup>3</sup>, *Z* = 1, ρ<sub>c</sub> = 1.562 g cm<sup>-3</sup>, μ(Mo Kα) = 0.244 mm<sup>-1</sup>, *F*(000) = 2248, *T* = 110 K; orange prisms, 0.30 × 0.20 × 0.10 mm<sup>3</sup>, 21 940 independent observed reflections, *R*<sup>2</sup> using SHELXTL software package, 1348 parameters, *R*<sub>1</sub>/*wR*<sub>2</sub> [*I* > 2σ(*I*)] = 0.085/0.196. Three of the six independent PF<sub>6</sub><sup>-</sup> anions were disordered. In each case, only the major occupancy orientation was refined anisotropically. Disorder was also present in three of the five included independent acetonitrile solvent molecules.

(23) A previously reported solid-state superstructure between **CBPQT**<sup>4+</sup> and a hydroquinone-based thread terminated by 4-*tert*-butylaniline residues revealed it to be a [2]pseudorotaxane. See ref 20.

(24) Houk, K. N.; Menzer, S.; Newton, S. P.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 1497–1487 and references therein.

(25) The binding between **CBPQT**·4PF<sub>6</sub> and 1,4-dimethoxybenzene is very weak (*K*<sub>a</sub> = 17 M<sup>-1</sup> in MeCN). See ref 8.

resonances corresponding to an excess of free host in the former instance and an excess of free guest in the latter instance. The CT band (λ<sub>max</sub> = 527 nm) for a 3:1 mixture of **CBPQT**·4PF<sub>6</sub> and **BMPEEEEEEN** MeCN/CH<sub>2</sub>Cl<sub>2</sub> (3:1) was identical to that of a 1:1 mixture of the two components, indicating that further complexation of the terminal MPE units by **CBPQT**<sup>4+</sup> is not favored in solution.

It follows that formation of a [4]pseudorotaxane from a 1:1 (host/guest) mixture must be the result of additional noncovalent interactions<sup>2</sup> that are absent in solution but present in the crystal. These interactions involve the PF<sub>6</sub><sup>-</sup> anions in the form of short [F···H] contacts of 2.6 Å or less (Table 1) between the anions and hydrogen bond donors on

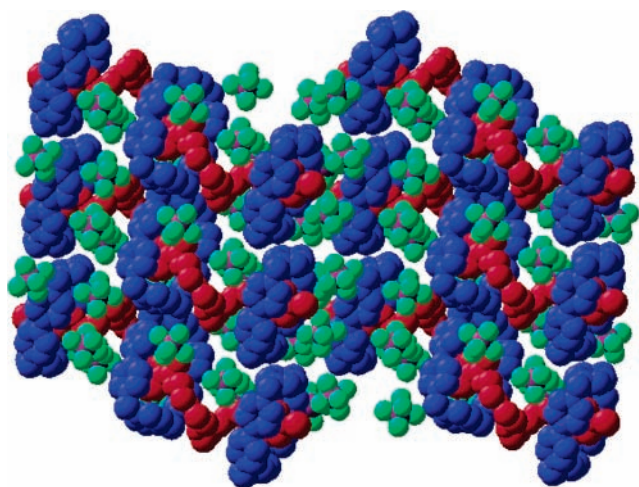
**Table 1.** Hydrogen Bond Lengths (Å) for the Interactions between the F Atoms of the PF<sub>6</sub><sup>-</sup> Anions and the H Atoms of Either **BMPEEEEEEN** or **CBPQT**<sup>4+</sup> in the Solid-State Superstructure of the [4]Pseudorotaxane

interaction <sup>a</sup>	no. of H bonds	range <sup>b</sup> (Å)
[F···H(B)]	2	2.56–2.58
[F···H(C)]	4	2.47–2.50
[F···H(D)]	3	2.50–2.59
[F···H(E)]	3	2.28–2.53
[F···H(F)]	1	2.58
[F···H(G)]	2	2.46–2.59
[F···H(J)]	3	2.12–2.45
[F···H(K)]	2	2.32–2.47
[F···H(L)]	2	2.36–2.55
[F···H(PEG)]	7	2.28–2.60

<sup>a</sup> Aromatic rings B–D and J–L are labeled as indicated in Figure 3. The polyether chains of **BMPEEEEEEN** have been assigned the descriptor PEG. <sup>b</sup> The range indicates the shortest and longest [C–H···F] bond lengths for the interactions specified in column 1.

both the **CBPQT**<sup>4+</sup> ring and the polyether chains of **BMPEEEEEEN**. A multitude of [C–H···F] contacts are revealed on inspection of the space-filling representation (Figure 4) of the packing of the [4]pseudorotaxane supermolecules. In addition to the [C–H···F] interactions, stabilizing noncovalent [π···π] and [C–H···π] interactions exist (see Supporting Information) between the MPE terminal units of the guest and the **CBPQT**<sup>4+</sup> host. However, it is the multitude of [C–H···F] contacts which are the dominating interactions and which promote<sup>26</sup> the kinetically controlled self-assembly<sup>27</sup> of the [4]pseudorotaxane. Yet, the question

(26) In the area of crown ether/dialkylammonium ion recognition, we have observed previously the PF<sub>6</sub><sup>-</sup> anion-assisted formation in the solid state of *discrete supermolecules* with pseudorotaxane geometries which are stabilized by complementary [C–H···F] hydrogen bond interactions. See: (a) Ashton, P. R.; Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 12514–12524. (b) Ashton, P. R.; Fyfe, M. C. T.; Hickingbottom, S. K.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem.–Eur. J.* **1998**, *4*, 577–589. (c) Ashton, P. R.; Fyfe, M. C. T.; Martínez-Díaz, M.-V.; Menzer, S.; Schiavo, C.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem.–Eur. J.* **1998**, *4*, 1523–1534. (d) Fyfe, M. C. T.; Stoddart, J. F.; Williams, D. J. *Struct. Chem.* **1999**, *10*, 243–259. (e) Amirsakis, D. G.; Garcia-Garibay, M. A.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4256–4261.



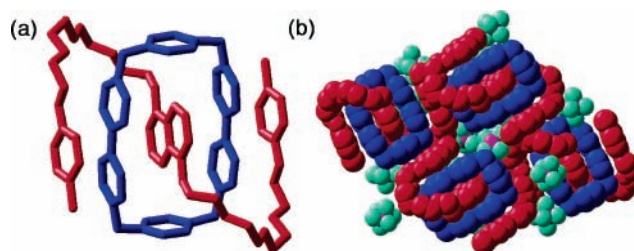
**Figure 4.** Crystal packing of [4]pseudorotaxanes showing the channel arrangement of  $\text{PF}_6^-$  anions (hydrogen atoms and MeCN omitted for clarity).

still remains as to the origin of the upfield shifts in the  $^1\text{H}$  NMR spectrum (Figure 2) of the [2]pseudorotaxane in solution.

In a determined attempt to produce crystals of the [2]pseudorotaxane, single crystals,<sup>28</sup> suitable for X-ray analysis,<sup>22</sup> were obtained by vapor diffusion of MTBE into a MeCN/ $\text{CH}_2\text{Cl}_2$  (3:1) solution of a 3:1 (guest/host) mixture of **BMPEEEEN** and **CBPQT** $\cdot 4\text{PF}_6$ . These crystals turned out to contain the [2]pseudorotaxane, as shown by the solid-state superstructure (Figure 5a) wherein the threadlike guest wraps itself around the host such that the terminal MPE units

(27) A dramatic example of a kinetically controlled self-assembly process has been witnessed when, on crystallization from the appropriate solvent mix, tetrabenzocrown-8 and dibenzylammonium hexafluoro-phosphate form an array of [2]pseudorotaxanes stabilized by  $[\text{C}\cdots\text{H}\cdots\text{F}]$  hydrogen bonds to highly ordered, interstitially located  $\text{PF}_6^-$  anions. When the crystals of the [2]pseudorotaxane are dissolved in  $\text{CD}_3\text{COCD}_3$ , the 1:1 complex disassembles spontaneously at 25 °C with a half-life of 15.5 days, i.e.,  $\Delta G^\ddagger = 26 \text{ kcal mol}^{-1}$ . See: (a) Ashton, P. R.; Cantrill, S. J.; Preece, J. A.; Stoddart, J. F.; Wang, Z.-H.; White, A. J. P.; Williams, D. J. *Org. Lett.* **1999**, *1*, 1917–1920. (b) Cantrill, S. J.; Preece, J. A.; Stoddart, J. F.; Wang, Z.-H.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 6675–6681.

(28) Empirical formula  $\text{C}_{84}\text{H}_{96}\text{F}_{24}\text{N}_8\text{O}_{10}\text{P}_4$ ,  $M = 1957.57$ , triclinic, space group  $P\bar{1}$ ;  $a = 10.6205(15)$ ,  $b = 15.682(2)$ ,  $c = 26.990(4) \text{ \AA}$ ;  $\alpha = 89.915(2)^\circ$ ,  $\beta = 98.958(2)^\circ$ ,  $\gamma = 90.134(2)^\circ$ ,  $V = 4440.2(11) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_c = 1.464 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 0.197 \text{ mm}^{-1}$ ,  $F(000) = 2024$ ,  $T = 100 \text{ K}$ ; red tablet  $0.40 \times 0.40 \times 0.20 \text{ mm}^3$ , for 20 722 independent observed reflections,  $F^2$  refinement, 1183 parameters,  $R1/wR2 [I > 2\sigma(I)] = 0.055/0.124$ . The crystals of the compound were found to be twin, and the two twin domains were refined using a transformation matrix. The twin population refined to 38%. There were two one-half independent molecules per asymmetric unit, located on a crystallographic inversion center. Disorder was found in one of the four crystallographically independent  $\text{PF}_6^-$  anions molecules. Two partial occupancies were identified, and only the major occupancy was refined anisotropically.



**Figure 5.** X-ray crystal superstructure (a) and packing (b) obtained from a mixture of **CBPQT** $^{4+}$  and **BMPEEEEN** in a 3:1 molar ratio showing the exclusive formation of the [2]pseudorotaxane (hydrogen atoms and MeCN omitted for clarity). Some of the  $\text{PF}_6^-$  anions are shown in the packing diagram.

in **BMPEEEEN** are  $[\pi\cdots\pi]$  stacked alongside the outer faces of the **CBPQT** $^{4+}$  bipyridinium units. This kind of interaction, which has been noted<sup>8,9</sup> previously in similar 1:1 complexes, persists in solution and so accounts for the upfield shifts of the MPE protons in the  $^1\text{H}$  NMR spectrum (Figure 2) of the [2]pseudorotaxane. The packing (Figure 5b) of these supermolecules is also highly ordered in the crystal where MPE units are found to be in a  $[\pi\cdots\pi]$  stacking interaction mode<sup>29</sup> with the *p*-xylyl units of the **CBPQT** $^{4+}$  rings in neighboring supermolecules.

The results reported here highlight the vagaries that surround crystal engineering, even with a relatively simple duo of organic substrates in the shape of a neutral one and a tetracationic one. Given half a chance, the supporting anions can intervene quite dramatically and dictate the solid-state superstructure obtained on crystallization in a profound manner.

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**Supporting Information Available:** Synthetic procedure for the synthesis of **BMPEEEEN**, isothermal titration microcalorimetry, UV/vis, mass spectrometric, and room temperature  $^1\text{H}$  NMR spectroscopic data, as well as distance and angle measurements for all noncovalent bonding interactions present in both the [2]- and [4]pseudorotaxane superstructures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(29) The self-organization of arrays of [2]pseudorotaxanes to form infinite two-dimensional sheets has been observed previously. See refs 3a and 18.