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First supramolecular poly(taco complex)†

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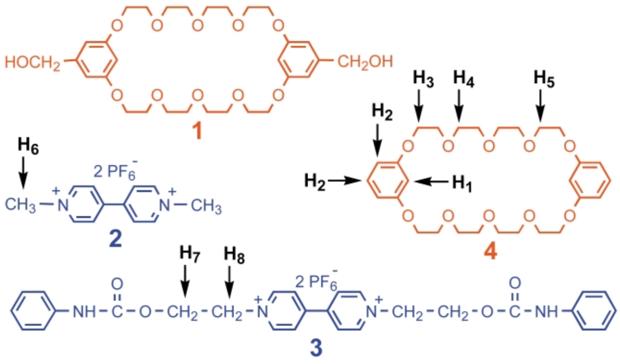
Received (in Columbia, SC, USA) 7th March 2003, Accepted 25th April 2003
First published as an Advance Article on the web 20th May 2003

The first supramolecular poly(taco complex) was formed in the solid state as shown by X-ray analysis.

The field of non-covalent polymers or supramolecular polymers, a topic of great current interest, is being explored by scientists all over the world.[1] Among reported non-covalent polymers, many have been based on host–guest complexations, especially pseudorotaxane-type complexations.[1a,1g,1j] In 1999, we first reported that bis(5-hydroxymethyl-1,3-phenylene)-32-crown-10 (**1**) formed a taco (or folded sandwich-type) complex with *N*,*N*′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate) (**2**) in the solid state.[2] However up to now, no non-covalent polymers based on taco complex-type structures have been published. Here we report the first non-covalent poly(taco complex).

2 and its derivatives have been used to construct many host–guest complexes.[2,3] Recently we made its novel urethane derivative, *N*,*N*′-bis[β-(phenyliminocarbonyloxy)ethyl]-4,4′-bipyridinium bis(hexafluorophosphate) (**3**). Acetone solutions of **2** with bis(*m*-phenylene)-32-crown-10 (**4**)[4] and **3** with **4** are yellow because of the charge transfer between the electron-rich aromatic rings of the crown ethers and the electron-poor pyridinium rings of the guests. A Job plot[5] (Fig. 1) based on proton NMR data demonstrated that the complex between **3** and **4** was of 1 : 1 stoichiometry in acetone solution. Our previous study showed that the complex between **2** and **4** also has 1 : 1 stoichiometry.[2] Two solutions containing **2** and **3**, respectively, with **4** were characterized by proton NMR (Fig. 2). It was found that the chemical shift changes of hydrogens on crown ether **4** were the same for the two complexations, yielding the same apparent association constant, 5.5 (± 0.8) × 10^2 M^{-1} at 1.00 mM initial concentrations of host and guest.‡

Single crystals of **3·4** for X-ray analysis were grown from an equimolar solution of **3** and **4** in a mixture of acetone and chloroform (2.5 : 1). As shown by its crystal structure (Fig. 3),§ just like **2·1**,[2] **3·4** is stabilized by C–H···O and face-to-face π-stacking interactions between both phenylene rings of **4** and the pyridinium rings of **3**. However there are some apparent differences. Firstly, **2·1** is stabilized by three hydrogen bonds between the guest and host, while **3·4** has six hydrogen bonds between the guest and host. What is more important is that four of six hydrogen bonds of **3·4** involve *N*-methylene hydrogens, which usually are not involved in hydrogen bonding with the host. One example reported up to now is the pseudorotaxane based on bis(*p*-phenylene)-34-crown-10.[7] Secondly, face-to-face π-stacking interactions are different in **2·1** and **3·4**; the dihedral angle and the centroid–centroid distance between two crown aromatic rings change from 6.9° and 7.39 Å to 3.2° and 6.898 Å, respectively. This latter distance is very short. Even in a pseudorotaxane-like complex based on a cryptand and **2**, the corresponding value is 6.94 Å.[2]



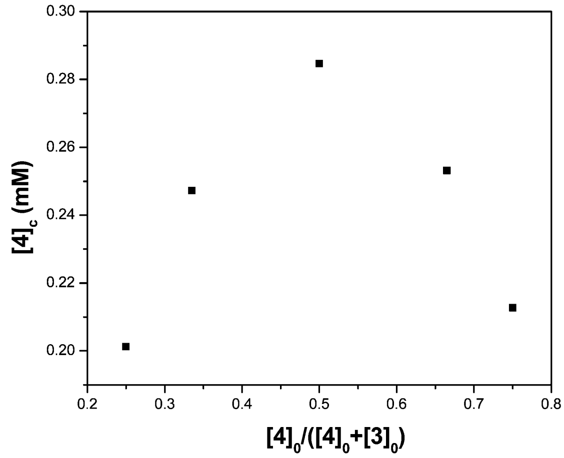


Fig. 1 Job plot: the stoichiometry of the complex between **3** and **4** in CD_3COCD_3 solution using data for H_2 of **4**. $[\mathbf{4}]_c$ is the concentration of complexed **4**. $[\mathbf{3}]_0 + [\mathbf{4}]_0$ = 2.00 mM.

In the solid state, the complex is arranged linearly to form a non-covalent taco complex supramolecular polymer (Fig. 4). The stabilization forces between complex monomers are two direct hydrogen bonds, eight indirect hydrogen bonds, and face-to-face π-stacking interactions. Each PF_6^- counterion acts as a hydrogen bonding bridge to stabilize the non-covalent polymer

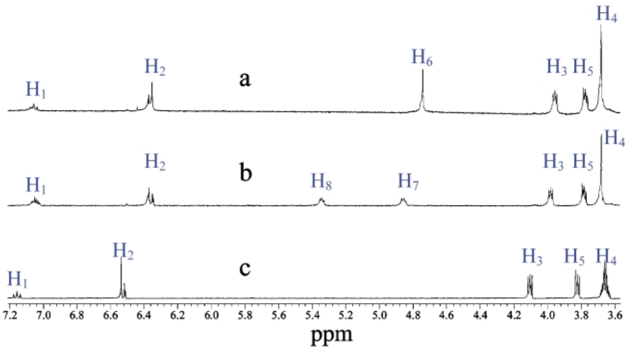


Fig. 2 ^1H NMR spectra (400 MHz, CD_3COCD_3, 22 °C) of (a) 1.00 mM **2** and 1.00 mM **4**, (b) 1.00 mM **3** and 1.00 mM **4**, (c) 1.00 mM **4**.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b302682e/

DOI: 10.1039/b302682e

by connecting one guest by three hydrogen bonds and the next one by one hydrogen bond. The N–Hs of the urethane moiety are involved in bifurcated H-bonds with the PF_6^-, which also H-bonds with the α-pyridyl protons of **3**. The dihedral angle and centroid–centroid distance between neighbouring crown ether aromatic rings are 3.2° and 3.765 Å.

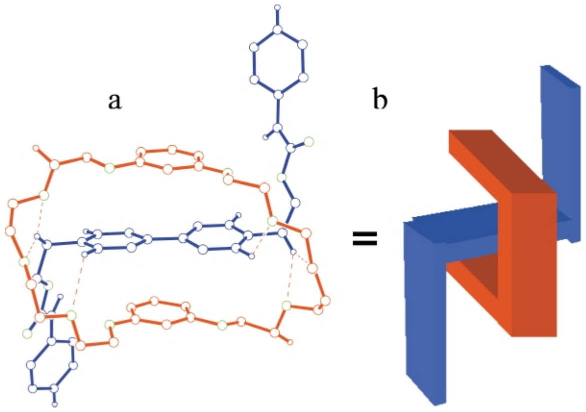

Fig. 3 Ball–stick (a) and cartoon (b) representations of **3·4**. (a) Oxygens are green, **3** is blue, and **4** is red. Two acetone molecules, two PF_6^- ions, and hydrogens, except the ones involved in hydrogen bonding, have been omitted for clarity. Hydrogen-bonding parameters: C–O distances (Å) 3.114, 3.252, 3.254; H···O distances (Å) 2.281, 2.489, 2.584; C–H···O angles (°) 140.8, 133.5, 124.0. Face-to-face π-stacking parameters: centroid–centroid distances (Å) and dihedral angles (°) 3.936 and 5.2, 4.196 and 7.7. The dihedral angle and the centroid–centroid distance between two crown aromatic rings (° and Å): 3.2 and 6.898. (b) **3** is blue and **4** is red.

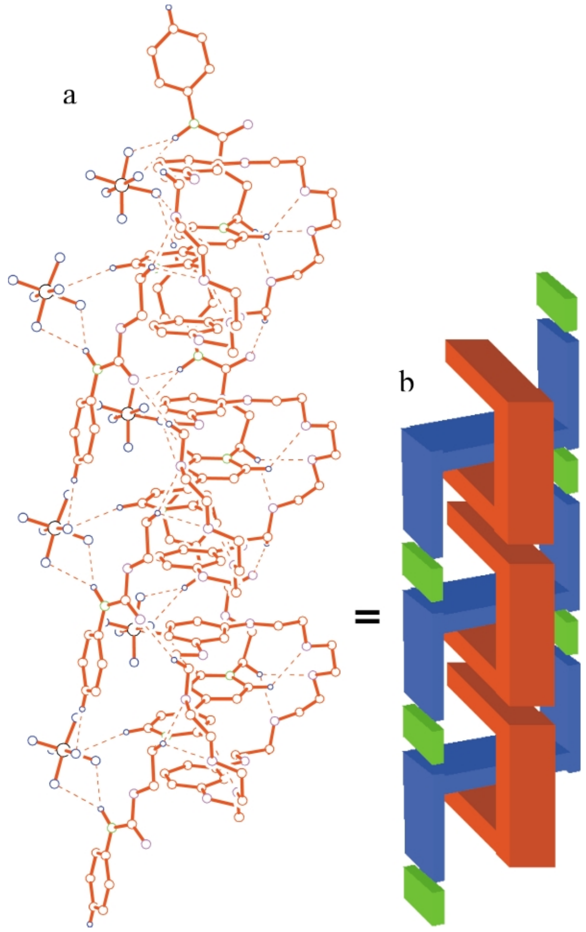

Fig. 4 Ball–stick (a) and cartoon (b) representations of **3·4** packing structure. (a) Fluorines and hydrogens are blue, nitrogens are green, phosphoruses are black, and oxygens are magenta. Six acetone molecules and hydrogens, except the ones involved in hydrogen bonding, have been omitted for clarity. Hydrogen-bonding parameters: N(C)–F(O) distances (Å) 3.460, 3.368, 3.337, 3.465, 3.281; H···F(O) distances (Å) 2.514, 2.416, 2.384, 2.539, 2.374; N(C)–H···F(O) angles (°) 157.0, 157.0, 167.1, 169.5, 149.2. Face-to-face π-stacking interaction between complex monomers: centroid–centroid distances (Å) and dihedral angles (°) 3.765 and 3.2. (b) **3** molecules are blue, **4** molecules are red, and PF_6^- counterions are green.

In summary, we prepared the first supramolecular poly(taco complex) as shown by its crystal structure. In the structure, hydrogen bonding of the PF_6 counterions with the urethane linkages of guest **3** play a key role. We plan to prepare the poly(taco complex) from the corresponding covalent polyurethane.

This work was supported by the National Science Foundation (DMR0097126, HWG).

Notes and references

‡ ^1H NMR characterizations were done on solutions with constant [**4**] and varied [**3**]. Based on these NMR data, Δ_0, the difference in δ values for protons of **4** in the uncomplexed and fully complexed species, was calculated by using the Benesi–Hildebrand method.[6] Then K_a was calculated from $K_a = (\Delta/\Delta_0)[\mathbf{4}]_0/\{\{[\mathbf{4}]_0 - (\Delta/\Delta_0)[\mathbf{4}]_0\}\{[\mathbf{3}]_0 - (\Delta/\Delta_0)[\mathbf{4}]_0\}\}$. Errors are based on a 5% variation in Δ/Δ_0 values. We found that apparent association constants K_a for these systems are concentration dependent so it is necessary to specify initial concentrations.

§ *Crystal data*: blade, orange, 0.05 × 0.18 × 0.45 mm^3, $C_{62}H_{80}F_{12}N_4O_{16}P_2$, FW 1427.26, monoclinic, space group $C2/c$, a = 10.594(1), b = 22.508(3), c = 28.391(5) Å, β = 99.557(7)°, V = 6675.9(16) $Å^3$, Z = 4, D_c = 1.420 g cm^{-3}, T = 100 K, μ = 1.68 cm^{-1}, 11912 measured reflections, 6103 independent reflections, 436 parameters, $F(000)$ = 2984, $R1$ = 0.1859, $wR2$ = 0.2262 (all data), $R1$ = 0.1275, $wR2$ = 0.2019 [$I > 3\sigma(I)$], max. residual density 1.02 e $Å^{-3}$, max./min. transmission 0.992/0.890, and goodness-of-fit (F^2) = 0.9604. Non-hydrogen atoms were treated anisotropically and hydrogen atoms were placed in calculated positions. 3366 reflections were used in refinements by full-matrix least-squares on F^2. The structure was solved by direct methods using SIR[8] and refined by full-matrix least squares, using CRYSTALS.[9] CCDC 205087. See http://www.rsc.org/suppdata/cc/b3/b302682e/ for crystallographic files in .cif or other electronic format.

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