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Self-Assembly of a Polyrotaxane Containing a Cyclic “Bead” in Every Structural Unit in the Solid State: Cucurbituril Molecules Threaded on a One-Dimensional Coordination Polymer

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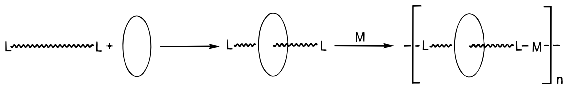
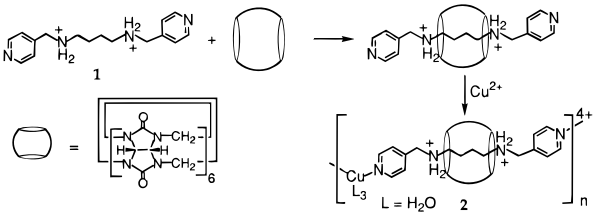
Polyrotaxanes[1−5] in which many cyclic molecular “beads” are threaded by a long “string” have received much attention in recent years because of their structures and properties as well as the potential use as a material for molecular devices.[6−9] Most of the polyrotaxanes reported thus far contain macrocycles threaded onto organic polymers. However, no polyrotaxane polymer proven to contain *a cyclic “bead” in every structural unit* of the polymer chain has been reported. Polyrotaxanes with such high structural regularity may have interesting physical properties not observed in those without such structural regularity. Our strategy to synthesize polyrotaxanes with high structural regularity is to form a pseudorotaxane by threading a molecular “bead” with a “string” having suitable functional groups at both ends and then to allow the end functional groups of the pseudorotaxane to coordinate to metal centers forming a coordination polymer[10] (Scheme 1). Neither this approach nor any other synthesis of a polyrotaxane based on a coordination polymer has been previously reported. We have recently developed[11] a simple way to construct a rotaxane containing cucurbituril[12] as a “bead” and spermine as a thread by taking advantage of the strong tendency of cucurbituril to form inclusion complexes with aliphatic diammonium ions.[13] Herein we report the self-assembly and X-ray crystal structure of a polyrotaxane containing curcurbituril molecules threaded on an 1D coordination polymer in the solid state. This polyrotaxane is unique in several aspects, being (1) the first formed on a coordination polymer, (2) the first containing a cyclic component in every repeating unit, and (3) the first to be structurally characterized by single-crystal X-ray crystallography.[14]

Scheme 1



Scheme 2



The construction of the polyrotaxane **2** was achieved in one step by threading cucurbituril molecules with *N*,*N*′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydrochloride (**1**)[15] and then allowing the resulting pseudorotaxane to react with $Cu(NO_3)_2$ to form a coordination polymer (Scheme 2).[16] The X-ray crystal structure[17] of **2** reveals, as expected, cucurbituril “beads” threaded on the coordination polymer, the chain of which is composed of alternating copper ions and **1**. The asymmetric unit of **2** consists of a copper ion, two independent

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(14) Stoddart and co-workers recently published syntheses and X-ray crystal structures of *pseudopolyrotaxanes* in which pseudorotaxane repeating units are linked by hydrogen bonding in the solid states: Asakawa, M.; Ashton, P. R.; Brown, G. R.; Hayes, W.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Adv. Mater.* **1996**, *8*, 37. We also have observed a similar pseudopolyrotaxane formation by hydrogen bonding in the solid state.[11] The major difference between these reports and the present work is that the present work uses coordinative bonds whereas the referred works used much weaker hydrogen bonds to link pseudorotaxane repeating units.

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(16) Cucurbituril (1.00 g, 0.86 mmol) and *N*,*N*′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydrochloride (**1**·2HCl) (0.207 g, 0.60 mmol) were added to water (20 mL). After overnight stirring, undissolved cucurbituril was filtered off. The ^{1}H NMR spectrum of the filtrate (using D_2O) indicates the formation of a 1:1 complex of cucurbituril and **1**. ^{1}H NMR (300 MHz, D_2O): δ 0.55 (4H, b, s), 2.45 (4H, b, s), 4.29 (12H, d, $J = 15.6$ Hz), 4.47 (4H, s), 5.56 (12H, s), 5.61 (12H, d, $J = 15.6$ Hz), 7.99 (4H, d, $J = 5.0$ Hz), 8.65 (4H, d, $J = 5.0$ Hz). Neither free cucurbituril nor free **1** in the filtrate was detected by ^{1}H NMR spectroscopy. A 0.2 M solution of $Cu(NO_3)_2$ in methanol was layered over the filtrate in a diffusion tube to produce blue, needle-shape, X-ray quality crystals of **2** in 1 week (44%). Anal. Calcd for $CuC_{52}H_{66}N_{32}O_{27}\cdot 5H_2O$: C, 36.21; H, 4.44; N, 25.98%. Found: C, 36.08; H, 4.05; N, 25.94% (the sample was dried under vacuum for 2 days before the analysis).

(17) Crystal data of **2**: $[Cu(C_{16}H_{24}N_4)(H_2O)_3\cdot C_{36}H_{36}N_{24}O_{12}](NO_3)_4\cdot 14(H_2O)$, fw = 1887.13, triclinic, $P\bar{1}$, $a = 14.690(2)$ Å, $b = 14.923(2)$ Å, $c = 19.665(3)$ Å, $\alpha = 84.96(1)°$, $\beta = 74.98(1)°$, $\gamma = 68.90(1)°$, $V = 3884.4(9)$ Å^3, $Z = 2$, μ (Mo Kα) = 4.01 cm^{-1}, $T = 295$ K, Enraf-Nonius CAD4 diffractometer, Mo Kα ($\lambda = 0.710\,73$ Å), anisotropic refinement for all nonhydrogen atoms except disordered water molecules, final cycle of full-matrix least-squares refinement on F^2 with 8965 independent reflections and 1114 variables (SHELXL-93), $R1$ ($I > 2\sigma(I)$) = 0.100, $wR2$ (all data) = 0.269, GOF = 1.127.[18]

S0002-7863(96)01551-X CCC: $12.00

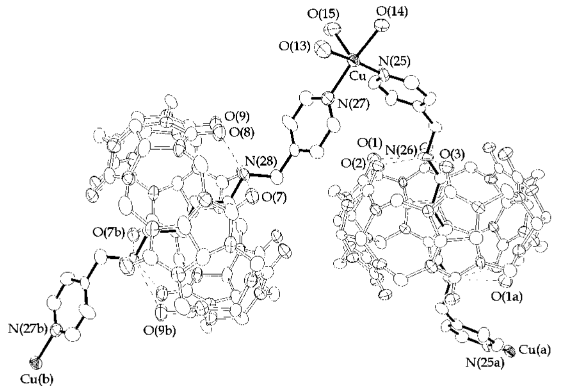

Figure 1. Asymmetric unit of **2**. Nitrate ions and water molecules in the lattice are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−N(25), 2.002(8); Cu−N(27), 2.002(9); Cu−O(13), 1.968(7); Cu−O(14), 1.979(7); Cu−O(15), 2.270(8); N(25)−Cu−N(27), 89.7(3); N(25)−Cu−O(13), 173.8(4); N(25)−Cu−O(14), 91.7(3); N(25)−Cu−O(15), 90.8(4); N(27)−Cu−O(13), 87.7(3); N(27)−Cu−O(14), 171.0(4); N(27)−Cu−O(15), 98.9(4); O(13)−Cu−O(14), 89.9(3); O(13)−Cu−O(15), 95.2(4); O(14)−Cu−O(15), 89.9(3). Hydrogen bonding interactions: N(26)···O(1), 2.960(12); N(26)···O(2), 2.786(10); N(26)···O(3), 2.825(12); N(28)···O(7), 2.954(12); N(28)···O(8), 2.847(11); N(28)···O(9), 2.933(12).

halves of a cucurbituril molecule, two independent halves of the "string" **1** (the pyridine nitrogen atoms of which are coordinated to the copper ion), and three water molecules bound to the copper ion (Figure 1). Four nitrate ions balance the charge on each repeating unit of the polymer backbone. No unusual bond parameters are observed. The cucurbituril "beads" are held tightly on the polymer backbone by strong hydrogen bonds between the protonated amine nitrogen atoms of the "string" and the oxygen atoms at the cucurbituril portals: N(26)···O(1), 2.960(12) Å; N(26)···O(2), 2.786(10) Å; N(26)···O(3), 2.825(12) Å; N(28)···O(7), 2.954(12) Å; N(28)···O(8), 2.847(11) Å; N(28)···O(9), 2.933(12) Å. The coordination geometry of the copper ion is square pyramidal. The two pyridine nitrogen atoms occupy two adjacent basal positions: Cu−N(25), 2.002(8) Å; Cu−N(27), 2.002(9) Å; N(25)−Cu−N(27), 89.7(3)°. The remaining basal and apical positions of the square pyramid are taken by three water molecules: Cu−O(13), 1.968(7) Å; Cu−O(14), 1.979(7) Å; Cu−O(15), 2.270(8) Å. The *cis* coordination of the two pyridine units to the metal center makes the polymer chain change its direction abruptly at the metal center; consequently, the polymer chain adopts a zigzag shape (Figure 2). In the crystal, the coordination polymer chain runs along the $[\bar{1}11]$ direction. Hydrogen bonding interactions exist between the water molecules bound to the copper ions of one chain and the oxygen atoms of cucurbituril "beads" on the adjacent polymer chains: O(5)···O(14), 2.783(10) Å; O5···O(15), 2.853(10) Å (Figure S2).[18] Attempts to measure solution properties of the polyrotaxane have been hampered by its extremely poor solubility in any solvents.

When other divalent first-row transition metal salts were used instead of $Cu(NO_3)_2$ in our synthetic procedure, no polyrotaxane coordination polymer was obtained. For example, when $MnCl_2$ was employed, a simple rotaxane **3**[19] was produced in which both ends of the "string" **1** threading a cucurbituril molecule are attached to $MnCl_3(H_2O)$ groups existing in a trigonal bipyramidal coordination geometry with three Cl^- ions at the equatorial positions (Figure S3).[18] This result demonstrates that proper choice of metal ions is also important for constructing a polyrotaxane coordination polymer.

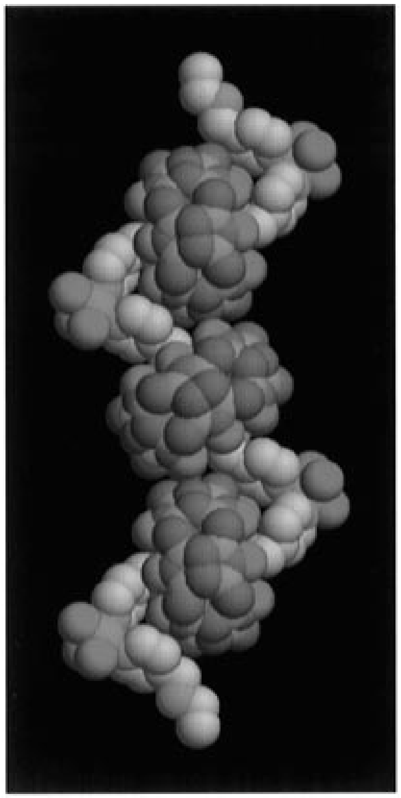

Figure 2. Space filling representation of **2**. Hydrogen atoms are omitted for clarity. Cucurbituril "beads" are highlighted. Color codes: carbon, grey; nitrogen, purple; oxygen, red; copper, green.

In conclusion, we present here a novel one-step approach to synthesizing polyrotaxanes with high structural regularities in the solid states by utilizing the principles of self-assembly and coordination chemistry. A key to the success of this synthesis is the high affinity of cucurbituril toward alkyl diammonium ions[13,20] which allows formation of a stable pseudorotaxane with **1** before polymerization occurs. Unlike cyclodextrins, which have been used widely as "beads" in the synthesis of rotaxanes and polyrotaxanes, cucurbituril has a highly symmetrical structure with two identical portals that helps to form polyrotaxane polymers with high structural regularity. Our approach should be easily extended to constructing 2D and 3D polyrotaxane network polymers, which remain unexplored, by judicious choice of metal ions and "strings". We are currently working along this line.

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Supporting Information Available: X-ray crystallographic tables and listing of atomic coordinates, thermal parameters, and bond distances and angles for **2** and **3** (19 pages). See any current masthead page for ordering and Internet access instructions.

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[18] See Supporting Information for details.

[19] Crystal data of **3**: $\{[MnCl_3(H_2O)]_2(C_{16}H_{24}N_4)\cdot C_{36}H_{36}N_{24}O_{12}\}\cdot 8.5(H_2O)$, fw = 1781.03, triclinic, $P1$, $a = 11.6967(2)$ Å, $b = 12.9124(2)$ Å, $c = 13.3946(1)$ Å, $\alpha = 112.3895(7)°$, $\beta = 100.7180(4)°$, $\gamma = 96.2288(4)°$, $V = 1801.71(4)$ Å^3, $Z = 1$, μ (Mo Kα) = 6.68 cm^{-1}, $T = 297$ K, Siemens SMART diffractometer, Mo Kα ($\lambda = 0.710\ 73$ Å), anisotropic refinement for all nonhydrogen atoms, final cycle of full-matrix least-squares refinement on F^2 with 4592 independent reflections and 535 variables (SHELXL-93), $R1$ ($I > 2\sigma(I)$) = 0.078, $wR2$ (all data) = 0.221, GOF = 0.968.[18]

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