Polycatenated Two-Dimensional Polyrotaxane Net

Dongmok Whang and Kimoon Kim*

Department of Chemistry and
Center for Biofunctional Molecules
Pohang University of Science and Technology (POSTECH)
San 31 Hyojadong, Pohang 790-784, South Korea

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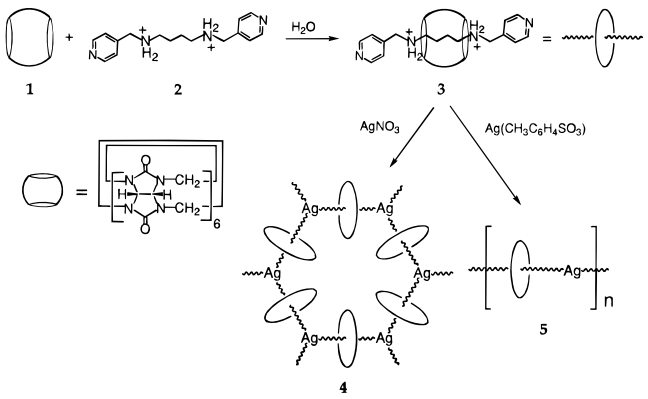
One of the fascinating developments in supramolecular chemistry during the last decade is the construction of interlocked molecular structures such as catenanes, rotaxanes, and knots.[1] Pioneering work by Sauvage and Stoddart demonstrated that such elegant structures can be achieved relatively easily by use of metal templating and/or employment of noncovalent interactions. Concurrent with this has been development of 2D or 3D networks composed of linking metal centers and rigid organic bridging components.[2−9] These metal−organic framework materials often exhibit interesting electronic[8] and magnetic properties[9] as well as zeolite-like properties.[4b,5c]

We have recently reported[10] a simple one-step approach to construct 1D polyrotaxane coordination polymers containing a cyclic "bead" in every structural unit of the polymer chain. It involves the formation of a pseudorotaxane by threading a molecular "bead" with a "string" having suitable functional groups at both ends followed by the formation of a 1D polyrotaxane coordination polymer by allowing the end functional groups of the pseudorotaxane to coordinate to the metal centers. Extending this approach, we now constructed an unprecedented polyrotaxane containing cyclic beads threaded on 2D coordination polymer networks. Moreover, the 2D polyrotaxane networks are fully interlocked; therefore, it represents the first example of polycatenated polyrotaxane nets. Herein, we report the self-assembly and X-ray crystal structure of the novel supramolecular species.

Scheme 1



The formation of the pseudorotaxane **3**, by threading cucurbituril (**1**)[11] with *N*,*N*′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**2**),[12] followed by the reaction of **3** with $AgNO_3$ yielded **4** (Scheme 1).[13] The X-ray crystal structure[14] of **4** reveals an unprecedented polyrotaxane in which cucurbituril beads are threaded on a 2D coordination polymer network (Figure 1). The 2D network consists of large edge-sharing chair-shaped hexagons with a Ag(I) ion at each corner and a molecule of **2** at each edge connecting two Ag(I) ions. The mean length of the edge is 20.9 Å, and the mean separation of the opposite corners is 38.0 Å. Each silver ion, sitting on a mirror plane, is coordinated by three "supermolecules" (**3**) and a nitrate ion in a distorted tetrahedral geometry.[15] A cucurbituril bead is held tightly at the middle of each edge of the hexagon by strong hydrogen bonds between the protonated amine nitrogen atoms of the string (**2**) and the oxygen atoms of cucurbituril. The 2D polyrotaxane network forms layers stacked on each other along the [011] direction with a mean interplane separation of 9.87 Å (Figure 2). There is another 2D polyrotaxane network (denoted **B**) almost perpendicular to the first one (denoted **A**). The dihedral angle between the mean planes of the two networks **A** and **B** is 69.34°. These networks interpenetrate with full interlocking of the hexagons, as il-

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(13) Cucurbituril (**1**) decahydrate (1.00 g; 0.86 mmol) and *N*,*N*′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate **2** (0.207 g; 0.60 mmol) were added to water (20 mL). After overnight stirring, undissolved cucurbituril was filtered. The ^{1}H NMR spectrum of the filtrate (using D_2O) indicates the formation of a 1:1 complex (pseudorotaxane **3**) of **1** and **2**. Neither free **1** nor free **2** was detected in the filtrate by ^{1}H NMR spectroscopy. A 0.2 M solution of $AgNO_3$ in methanol was layered over the filtrate in a diffusion tube to produce colorless, plate-like, X-ray quality crystals of **4** in a week (37%). Anal. Calcd for $AgC_{78}H_{90}N_{46}O_{30}\cdot 10H_2O$: C, 38.39; H, 4.54; N, 26.40. Found: C, 38.62; H, 4.51; N, 26.12. The elemental analysis sample was dried under vacuum overnight. When a solution of $Ag(C_7H_7SO_3)$ in methanol was used instead of $AgNO_3$ in the above procedure crystals of **5** were produced (29%). Anal. Calcd for $AgC_{73}H_{81}N_{28}O_{21}S_3\cdot 9H_2O$: C, 42.73; H, 4.86; N, 19.11; S, 4.69. Found: C, 43.10; H, 5.32; N, 18.73; S, 5.10.

(14) Crystal data of **4**: $[Ag_2(C_{16}H_{24}N_4)_3\cdot(C_{36}H_{36}N_{24}O_{12})_3](NO_3)_8\cdot 40H_2O$, fw = 5240.30, orthorhombic, *Cmca*, a = 31.408(3) Å, b = 32.508(4) Å, c = 22.479(3) Å, V = 22951(5) Å^3, Z = 4, d_{calcd} = 1.517 g cm^{-3}, T = 293 K, Enraf−Nonius CAD4 diffractometer, Mo Kα (λ = 0.710 73), μ = 2.88 cm^{-1}. The structure was solved by direct methods (SHELXS-86). All nonhydrogen atoms were refined anisotropically (SHELXL-93). Final full-matrix least-squares refinement on F^2 with all 6266 reflections and 637 variables converged to R_1 ($I > 2\sigma(I)$) = 0.118, wR$_2$ (all data) = 0.383 and GOF = 1.08. Crystal data of **5**: $[Ag(C_{16}H_{24}N_4)\cdot(C_{36}H_{36}N_{24}O_{12})](C_7H_7O_3S)_3\cdot 11H_2O$, fw = 2100.89, triclinic, *P*1̄, a = 15.001(2) Å, b = 15.491(2) Å, c = 23.580(2) Å, α = 91.896(10)°, β = 105.538(9)°, γ = 116.707(13)°, V = 4641(1) Å^3, Z = 2, d_{calcd} = 1.504 g cm^{-3}, T = 293 K, Mo Kα (λ = 0.71073), μ = 3.82 cm^{-1}. Final full-matrix least-squares refinement on F^2 with all 9913 reflections and 987 variables converged to R_1 ($I > 2\sigma(I)$) = 0.111, wR$_2$ (all data) = 0.330 and GOF = 1.06.

(15) A PLUTO diagram of the asymmetric unit of **4** along with atom-labeling scheme is given in Supporting Information.

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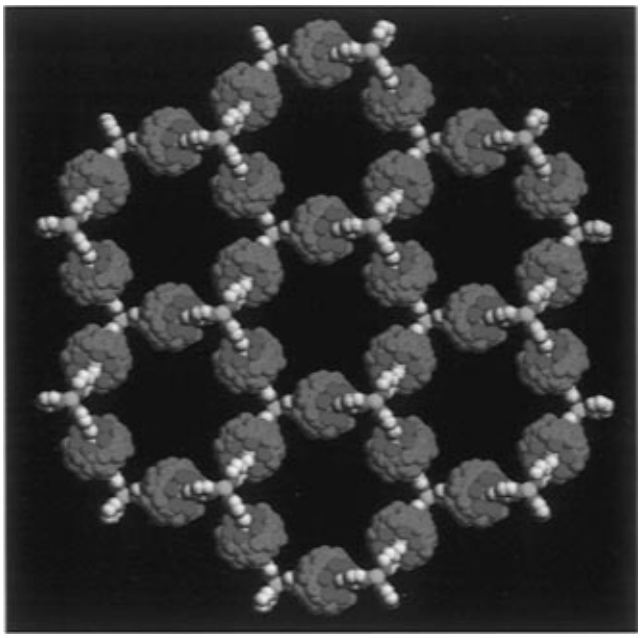

Figure 1. Cucurbituril "beads" threaded onto the 2D coordination polymer network in **4**. The nitrate ion coordinated to each silver ion is omitted for clarity. The mean length of the edge of the hexagon is 20.9 Å, and the mean separation of the opposite corners is 38.0 Å. Color codes: carbon (2D network), gray; carbon (cucurbituril bead), green; nitrogen, blue; oxygen, red; silver, brown.

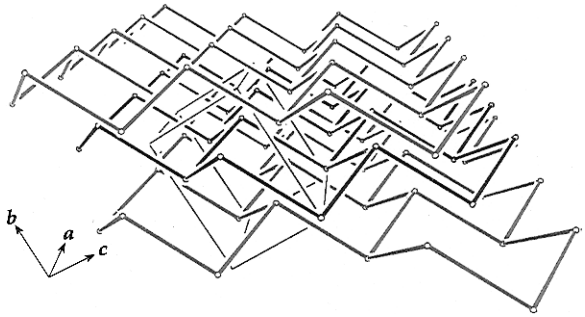

Figure 2. Schematic representation of stacking of the 2D polyrotaxane layers in **4**. Small circles represent silver ions and lines represent pseudorotaxane **3** linking two silver ions. The mean separation between the layers is 9.8 Å.

lustrated in Figure 3: a hexagon belonging to the network **A** (blue) interlocked with four hexagons belonging to **B** (red) and *vice versa*. Although interlocking of simple 2D networks has been known (polycatenated 2D nets),[2−9] the present structure is the first example of *polycatenated 2D polyrotaxane nets*.

Counteranions seem to play an important role in determining the solid state structure, since when silver tosylate is used instead of silver nitrate to react with the pseudorotaxane **3** the 1D polyrotaxane coordination polymer **5** is formed (Scheme 1). In the structure of **5** (Figure S3, Supporting Information)[16] a two-coordinate Ag^+ ion links two molecules of pseudorotaxane **3**

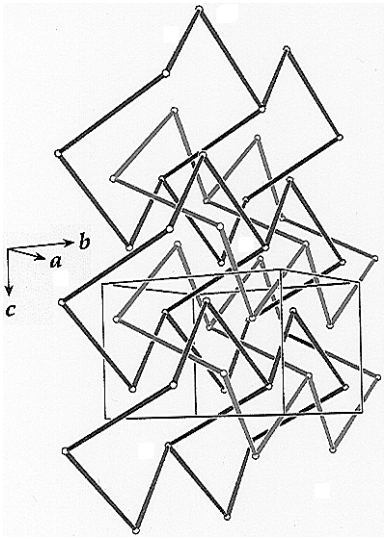

Figure 3. Schematic illustration representing interlocking of the hexagons in **4**: a hexagon belonging to the network **A** (blue) interlocked with four hexagons belonging to **B** (red) and *vice versa*. As in Figure 2, small circles represent silver ions and lines represent pseudorotaxane **3** linking two silver ions.

to form an 1D polyrotaxane coordination polymer similar to the one formed with Cu^{2+} ion.[10] The major structural difference between the two 1D polyrotaxane coordination polymers is that the two pyridyl units are coordinated to the silver ion in a *trans* geometry whereas they are bound to the copper ion in a *cis* geometry.[10] As a result, the former has an almost straight polymer chain whereas the latter exhibits a zigzag shaped polymer chain.[10]

In conclusion, we present here an unprecedented polycatenated 2D polyrotaxane net in which cyclic beads are threaded onto 2D coordination polymer networks that are in turn fully interlocked with themselves. This interlocked supramolecular network provides not only an intriguing example of chemical topology but also a new possibility for designing "smart" solid state materials.[17] We continue to explore unusual supramolecular species by utilizing the principles of self-assembly and coordination chemistry.

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Supporting Information Available: X-ray crystallographic tables of atomic coordinates, thermal parameters, bond distances and angles for **4** and **5** (25 pages). See any current masthead page for ordering and Internet access instructions.

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(16) See Supporting Information.

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