

Molecular Necklace: Quantitative Self-Assembly of a Cyclic Oligorotaxane from Nine Molecules

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Interlocked structures¹ such as catenanes and rotaxanes have attracted considerable attention due not only to their unusual structures but also to their potential applications as nanoscale molecular devices and new materials. Here, we define a molecular necklace (MN) as a cyclic oligorotaxane in which a number of small rings are threaded onto a large ring. It differs from $[n]$ catenanes where rings are mechanically interlocked with each other one-by-one in a linear fashion. A minimal molecular necklace ([4]MN) consists of three small rings threaded onto a large ring.² In an elegant synthesis of [3]catenanes, Sauvage observed unexpected formation of a mixture of $[n]$ MN ($n = 4-7$), some of which were isolated and characterized by electrospray mass spectrometry.^{3,4} We recently reported⁵ a simple one-step approach to construct 1D and 2D polyrotaxane coordination polymers. It involves threading a molecular "bead" with a "string" to form a pseudorotaxane followed by linking the pseudorotaxanes with metal ions. Combining this strategy with that for molecular squares developed by Fujita,⁶ Stang,⁷ and others,⁸ we have now constructed molecular necklaces. Here, we report the one-pot, quantitative self-assembly of the minimal molecular necklace [4]MN from nine species including three molecular "beads", three "strings", and three "angle connectors".

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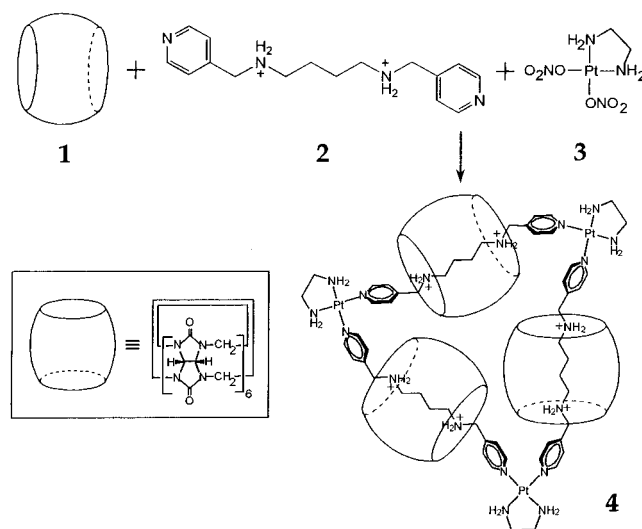
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Scheme 1



Stirring a 1:1:1 mixture of cucurbituril (**1**),⁹ *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**2**) and Pt(en)-(NO₃)₂ (en = ethylenediamine) (**3**) in refluxing water for 24 h followed by addition of ethanol into the concentrated solution produces **4** (Scheme 1) in 90% yield.¹⁰ Figure 1 shows evolution of ¹H NMR spectra of the reaction mixture during the formation of **4**. As the reaction proceeds the initial singlet peak (marked with ♦) for ethylenediamine attached to Pt decreases while two new singlet peaks (marked with ● and *) grow downfield (Figure 1c). The further-downfield-shifted single peak (*) slowly replaces the two other peaks (Figure 1d). A similar evolution of the peaks corresponding to the pyridyl protons are observed. Upon completion of the reaction, the spectrum of the reaction mixture becomes very simple (Figure 1e), which suggests the quantitative self-assembly of a single supermolecule with a highly symmetric structure. The electrospray mass spectrum and elemental analysis of **4** are consistent with the formula [1·2·3]₃·18H₂O.

The structure of **4** was confirmed by X-ray crystallography.¹¹ In the crystal, the molecular necklace **4** is sitting on a mirror plane. A 3-fold symmetry axis perpendicular to the mirror plane passes through the center of the supermolecule. The asymmetric unit,

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(10) Cucurbituril (**1**) decahydrate (53 mg; 53 mmol), *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate (**2**) (21 mg; 53 mmol), and Pt(en)-(NO₃)₂ (**3**) (20 mg; 53 mmol) were added to water (20 mL). The mixture was heated at reflux for 24 h. After the volume of the solution was reduced to ~3 mL under a reduced pressure, ethanol was added to the solution to precipitate the product **4**, which was filtered, washed with ethanol, and dried (89.6 mg, 90%). Slow recrystallization of the crude product from water/ethanol gave crystalline product (65.5 mg; 66%). ¹H NMR (300 MHz, D₂O): δ 0.47 (br s, 4H), 2.43 (br s, 4H), 2.82 (s, 4H), 4.31 (s, 4H), 4.34 (d, 12H), 5.54 (d, 12H), 5.68 (s, 12H), 7.93 (br s, 4H), 8.99 (d, 4H). ESI-MS: *m/z* 1959 (4 - 3PF₆⁻)³⁺, 1687 (4 - PR - 2Pt(en) - 8PF₆⁻)²⁺, 1413 (4 - 2PR - 3Pt(en) - 1PF₆⁻)⁺, 1297 (4 - Pt(en) - 6PF₆⁻)⁴⁺, 1118 (4 - 5PF₆⁻)⁵⁺, 1076 (4 - PR - 2Pt(en) - 9PF₆⁻)³⁺, 1009 (4 - Pt(en) - 7PF₆⁻)⁵⁺, where PR is the pseudorotaxane dication⁵ [(C₂H₆N₂O₁₂)₂]²⁺ formed from cucurbituril (**1**) and *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane. The electrospray mass spectrometry data were obtained with the sample whose counterions had been exchanged with PF₆⁻ ions. Anal. Calcd for (PtC₂₄H₆₈N₃₄O₂₄)₃·18H₂O: C, 34.49; H, 4.29; N, 25.32%. Found: C, 34.31; H, 4.03; N, 25.03%.

(11) Crystal data of **4**: [(Pt(C₂H₈N₂)(C₁₆H₂₄N₄)₃·(C₃₀H₃₆N₂₄O₁₂)₃](NO₃)₁₂·87H₂O, fw = 6884.93, hexagonal, *P*6₃/*m*, *a* = 26.7074(1) Å, *c* = 23.3649(2) Å, *V* = 14433.0(2) Å³, *Z* = 2, *d*_{calc} = 1.584 g cm⁻³, *T* = 188 K, Siemens SMART CCD diffractometer, Mo Kα (λ = 0.710 73), μ = 15.8 cm⁻¹. Structure was solved by Patterson method. All nonhydrogen atoms were refined anisotropically except for solvent water molecules. Final full-matrix least-squares refinement on *F*² with all 7075 reflections and 629 variables converged to *R*₁ (*I* > 2σ(*I*)) = 0.096, *wR*₂ (all data) = 0.252, and *GOF* = 1.07.

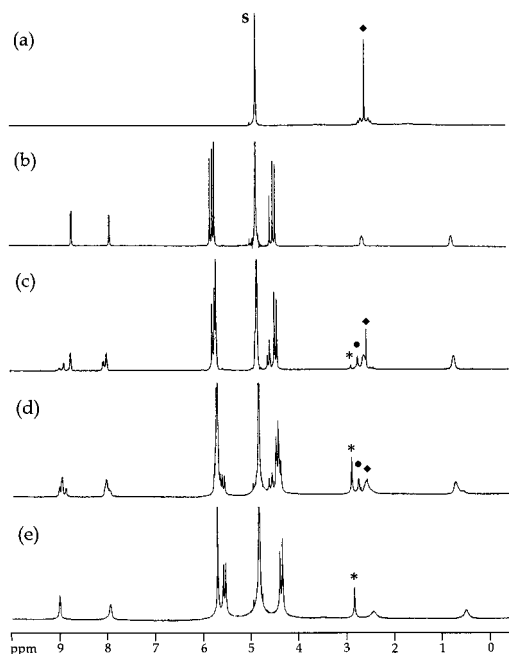


Figure 1. Evolution of ^1H NMR (300 MHz, D_2O) spectra during the formation of **4**: (a) $\text{Pt}(\text{en})(\text{NO}_3)$ (**3**), (b) pseudorotaxane formed from **1** and **2**, (c) a few minutes after the reaction of **1**, **2**, and **3** in refluxing H_2O , (d) after 6 h, and (e) after 24 h.

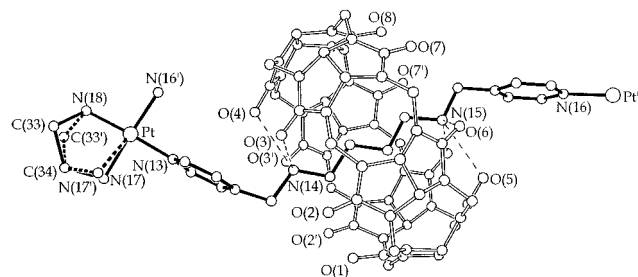


Figure 2. Asymmetric unit of **4**. Nitrate ions and water molecules are omitted for clarity. N(17) and C(33) are disordered over two sites. Selected bond distances (\AA) and angles (deg): Pt–N(13) 2.029(12), Pt–N(16) 2.025(10), Pt–N(17) 2.142(15), Pt–N(18) 2.060(13), N(13)–Pt–N(16) 89.3(4), N(17)–Pt–N(18) 84.3(6). Hydrogen bonding interactions (\AA): N(14)···O(3) = N(14)···O(3'), 2.853(8); N(14)···O(4), 2.856(13); N(15)···O(5), 2.869(12); N(15)···O(6) = N(15)···O(6'), 2.795(7).

therefore, consists of a half of $\text{Pt}(\text{en})$ moiety, a half of cucurbituril, and a half of "string" **3** (Figure 2). No unusual bond parameters are observed including the Pt–N distances and the N–Pt–N angles: Pt–N(13) = 2.029(12) \AA , Pt–N(16) = 2.025(10) \AA , Pt–N(17) = 2.142(15) \AA , Pt–N(18) = 2.060(13) \AA ; N(13)–Pt–N(16) = 89.3(4) $^\circ$, N(17)–Pt–N(18) = 84.3(6) $^\circ$. The molecular "bead" **1** is tightly held on the "string" **2** by hydrogen bonding between their carbonyl oxygen atoms and the protonated amine groups of **2**. Figure 3 shows a space-filling representation of the structure of **4** in which three cucurbituril molecular "beads" are threaded on a molecular triangle.¹² Each corner of the triangle

(12) A molecular triangle containing three $\text{Pt}(\text{en})$ units has recently been reported: Schnebeck, R.-D.; Randaccio, L.; Zangrando, E.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 119.

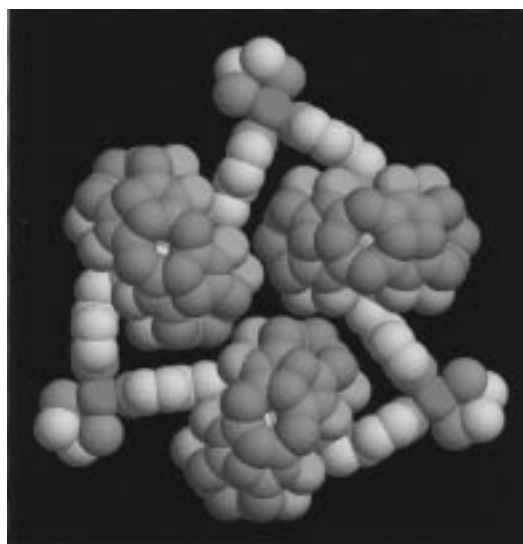


Figure 3. Space-filling representation of the molecular necklace **4**. Nitrate ions and water molecules are omitted for clarity. The Pt···Pt separation is 19.476(1) \AA . Color codes: carbon (molecular triangle), gray; carbon (cucurbituril "bead"), dark gray; nitrogen, blue; oxygen, red; platinum, green.

is occupied by a $\text{Pt}(\text{en})$ moiety and each side by a sigmoidal-shaped molecule **2**, which links the two Pt moieties by coordination at its terminal pyridyl groups. The Pt···Pt separation is 19.476(1) \AA . The three cucurbituril molecules in **4** are arranged in such a way that no vacant space exists inside the molecular triangle. The pyridyl unit is parallel to a glycoluril unit of cucurbituril with a mean distance of 3.48 \AA . A close contact between a cucurbituril oxygen and an equator carbon of the neighboring cucurbituril is observed: O(8)···C(13') = 2.975(10) \AA .¹³

In conclusion, we have shown a one-step, quantitative self-assembly of the molecular necklace [4]MN from nine molecular species. Such a highly efficient synthesis of a topologically intriguing supermolecule may provide insights into construction of nanoscale particles with well-defined structures and functions. It appears from the crystal structure that the hydrophobic interactions between the three cucurbituril rings may assist in the efficient formation of the necklace. By varying the length and shape of the molecular "string" and the "angle connectors", we should be able to construct a variety of molecular necklaces with different sizes, shapes, and numbers of molecular "beads".

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Supporting Information Available: X-ray crystallographic table and listing of atomic coordinates, thermal parameters, bond distances and angles for **4** (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(13) See the Supporting Information.