

distance is 2.26(3) Å, which is qualitatively the same as an ab initio theoretical Sc–C bond length (2.135 Å) of a ScC<sub>2</sub> cluster.<sup>[13]</sup> The number of electrons belonging to the Sc<sub>2</sub>C<sub>2</sub> cluster is estimated to be 51.9(2) e from the MEM charge density; hence, the Sc<sub>2</sub>C<sub>2</sub> species is in the divalent charge state in the C<sub>84</sub> fullerene cage. The formal electronic structure of (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> can thus be described as (Sc<sub>2</sub>C<sub>2</sub>)<sup>2+</sup>@C<sub>84</sub><sup>2-</sup>. The nature of the bonding between Sc and C<sub>2</sub> might be highly ionic as in the case of the ScC<sub>2</sub> cluster.<sup>[13a]</sup> As one of the two major isomers of C<sub>84</sub> (namely, D<sub>2</sub> and D<sub>2d</sub>), D<sub>2d</sub>-C<sub>84</sub> not only has much higher abundance than the other C<sub>84</sub> isomers,<sup>[7]</sup> but also has an unique ability to encage both metal atoms to form Sc<sub>2</sub>@C<sub>84</sub>,<sup>[10c]</sup> and metal carbide clusters to form (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub>.

### Experimental Section

The details of the production, separation, and isolation of endohedral scandium fullerenes has been described elsewhere.<sup>[2, 14, 15]</sup> Briefly, soot containing (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> and other scandium metallofullerenes such as Sc<sub>2</sub>@C<sub>84</sub><sup>[15]</sup> and Sc<sub>2</sub>@C<sub>82</sub><sup>[14]</sup> was generated in a direct-current (350 A, 21 V) arc discharge of Sc<sub>2</sub>O<sub>3</sub>/graphite composite rods (12 × 12 × 300 mm, 0.8 atom %, heat treated at 1600 °C, Toyo Tanso Co.) under a 17 L min<sup>-1</sup> flow of helium at 50–100 Torr. The soot was Soxhlet-extracted with carbon disulfide for 12 h. (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> was isolated by multistage high performance liquid chromatography (HPLC)<sup>[2, 14, 15]</sup> with two complementary 5PYE (21 × 250 mm) and Buckyclutcher (21 × 500 mm) columns. Stage 1 was HPLC on a 5PYE column, which was used primarily to remove C<sub>60</sub> and C<sub>70</sub>. In stage 2, the (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub>-containing fraction (yellow) collected in stage 1 was re-injected into the 5PYE column, and recycling HPLC was performed. After a few cycles, the (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> sub-fraction containing some Sc<sub>2</sub>@C<sub>82</sub> and C<sub>90</sub> was collected. In stage 3, recycling HPLC on a Buckyclutcher column was employed to completely separate (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> from the other fullerenes. Stages 2 and 3 were repeated several times to increase the sample purity to 99 %, as confirmed by laser-desorption time-of-flight (LD-TOF) mass spectrometry.

Solvent-free (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>84</sub> powder sample was sealed in a silica-glass capillary (0.3 mm inside diameter). To collect an X-ray powder pattern with good counting statistics, a synchrotron radiation (SR) X-ray powder experiment with an imaging plate (IP) as a detector was carried out at SPring-8 BL02B2. The exposure time on the IP was 80 min. The wavelength of incident X-rays was 0.75 Å. The X-ray powder pattern of (Sc<sub>2</sub>C<sub>2</sub>)@C<sub>82</sub> was obtained in 0.02° steps in the range 3.0 ≤ 2θ ≤ 30.5°, which corresponds to 1.45 Å resolution in the *d* spacing.

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## A Two-Dimensional Polyrotaxane with Large Cavities and Channels: A Novel Approach to Metal–Organic Open-Frameworks by Using Supramolecular Building Blocks\*\*

Eunsung Lee, Jaheon Kim, Jungseok Heo, Dongmok Whang, and Kimoon Kim\*

*Dedicated to Professor James A. Ibers on the occasion of his 70th birthday*

Mechanically interlocked supermolecules such as rotaxanes and catenanes have received much attention because of their intriguing structures as well as their potential applications.<sup>[1, 2]</sup> We have been interested in the self-assembly of such

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[\*] Prof. K. Kim, E. Lee, Dr. J. Kim, J. Heo, Dr. D. Whang  
National Creative Research Initiative Center  
for Smart Supramolecules and Department of Chemistry  
Division of Molecular and Life Sciences  
Pohang University of Science and Technology  
San 31 Hyojadong, Pohang 790-784 (Republic of Korea)  
Fax: (+82) 54-279-8129  
E-mail: kkim@postech.ac.kr

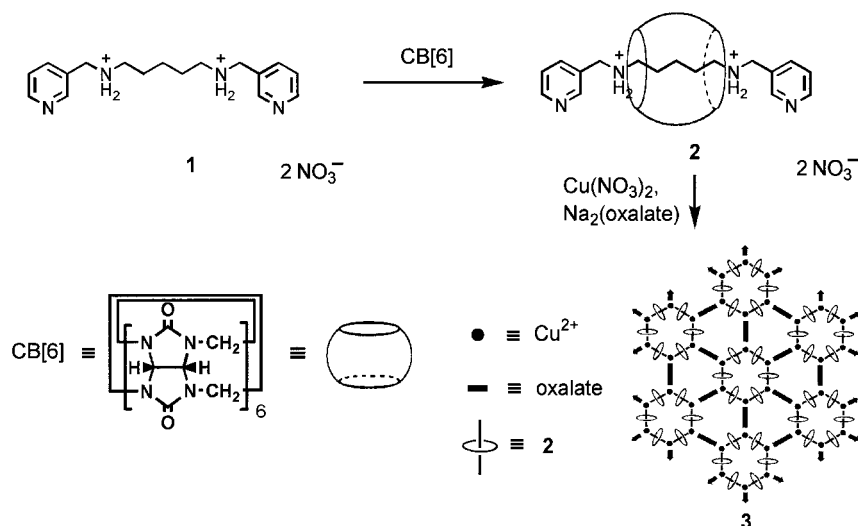
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Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

interlocked supramolecular species, particularly polyrotaxanes and molecular necklaces, through the use of coordination bonds.<sup>[3]</sup> Our approach to the interlocked structures involves reaction of a pseudorotaxane, composed of a cucurbituril (CB[6])<sup>[4,5]</sup> “bead” threaded on a short “string”, with a transition metal ion or metal complex to form an infinite chain coordination polymer or a discrete supramolecular species. The large two- and three-dimensional networks<sup>[3c,h]</sup> found in some of the polyrotaxanes suggest that this building principle can also be applied to the construction of metal–organic open-framework materials, which is another subject of intense current investigation.<sup>[6]</sup> For example, we have reported a 2D polyrotaxane net consisting of large edge-sharing chair-shaped hexagons with an Ag<sup>I</sup> ion at each corner and a pseudorotaxane unit at each edge.<sup>[3c]</sup> Although interpenetration of two independent nets prevents formation of large voids in this structure, the large 2D net suggests that such pseudorotaxanes can be used as large, rigid supramolecular building blocks for the construction of metal–organic open-frameworks. We now report a novel 2D polyrotaxane network with large cavities and channels which demonstrates that this is indeed a viable approach to modular porous solids.

The pseudorotaxane **2** is prepared by threading CB[6] with *N,N'*-bis(3-pyridylmethyl)-1,5-diaminopentane dihydronitrate (**1**).<sup>[3d]</sup> The 2D polyrotaxane **3** is then obtained by reaction of pseudorotaxane **2** with Cu(NO<sub>3</sub>)<sub>2</sub> in the presence of oxalate ions (Scheme 1). The X-ray crystal structure of **3** reveals a 2D polyrotaxane in which CB[6] beads are threaded on a 2D coordination polymer network (Figure 1). A close inspection of the structure reveals that hexagonal, seven-membered molecular necklaces [7]MN<sup>[3e,f]</sup> composed of six copper ions and six pseudorotaxanes behave as a secondary building block of the 2D polyrotaxane (Figure 1). Each corner of the supramolecular hexagon is occupied by a copper ion that is coordinated by two pyridyl units of **2**, a bidentate oxalate anion, and two water molecules in a distorted octahedral geometry. The Cu...Cu distances are approximately 13.9 Å for the side and approximately 27.8 Å for the diagonal. The molecular necklaces are connected to each other through coordination of the oxalate anion to the copper corners to form a large 2D hexagonal array of the hexagon. There are two different types of cavities (A and B) as shown in Figure 1. Cavity A is surrounded by six CB[6]s whereas cavity B is surrounded by three CB[6]s; therefore, the latter cavity is much larger than the former (see below).

The 2D layers stack along the *c* axis in the crystal, with a mean interlayer separation of 12.88 Å, in such a way that the cavities are aligned vertically to form 1D channels along the *c* axis (Figure 2). Each channel has an identical repeating unit consisting of a type A cavity and two type B cavities (Figure 3). Cavity A provides the 1D channel with a small aperture having an effective diameter of about 5 Å. The



Scheme 1. Synthesis of the 2D polyrotaxane **3**.

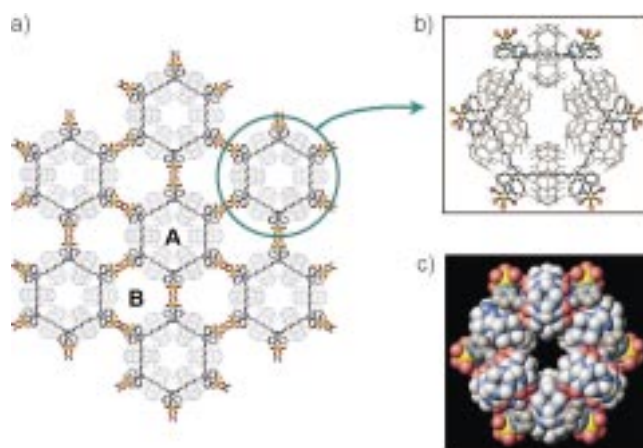


Figure 1. The 2D polyrotaxane layer in **3** built with a molecular necklace [7]MN as a secondary building block (a), which is highlighted in a ball and stick representation (b), and in a space-filling representation (c). Two different types of cavities A and B exist in the 2D network as noted. Color: copper: yellow; oxygen: red; nitrogen: blue; carbon: gray.

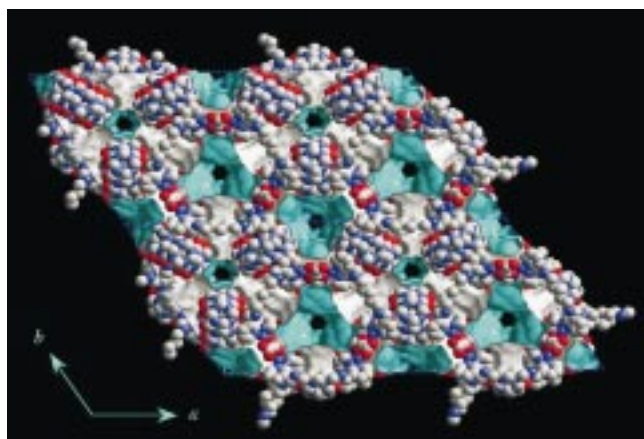


Figure 2. Structure of **3** showing the 1D channels along the *c* axis. The red, blue, and gray spheres represent oxygen, nitrogen, and carbon atoms, respectively. The accessible surface in the channels is shown in light blue. Each channel has a small aperture (shown in black) with an effective diameter of approximately 5 Å.

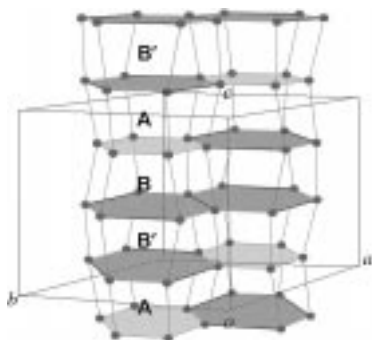


Figure 3. Schematic representation of how the cavities A and B are aligned to form 1D channels along the *c* axis.

fusion of two B cavities generates a long cylindrical void in the channel with a diameter of approximately 14 Å and a length of about 20 Å (Figure 4a). The 1D channels are interconnected to form a 3D channel network as seen in the cross-sectional view on the *ab* plane (Figure 4b): two neighboring A cavities are interconnected through another cavity (type C) with dimensions of approximately  $14 \times 14 \times 7$  Å<sup>3</sup>. The channels are filled with nitrate counterions and water molecules.

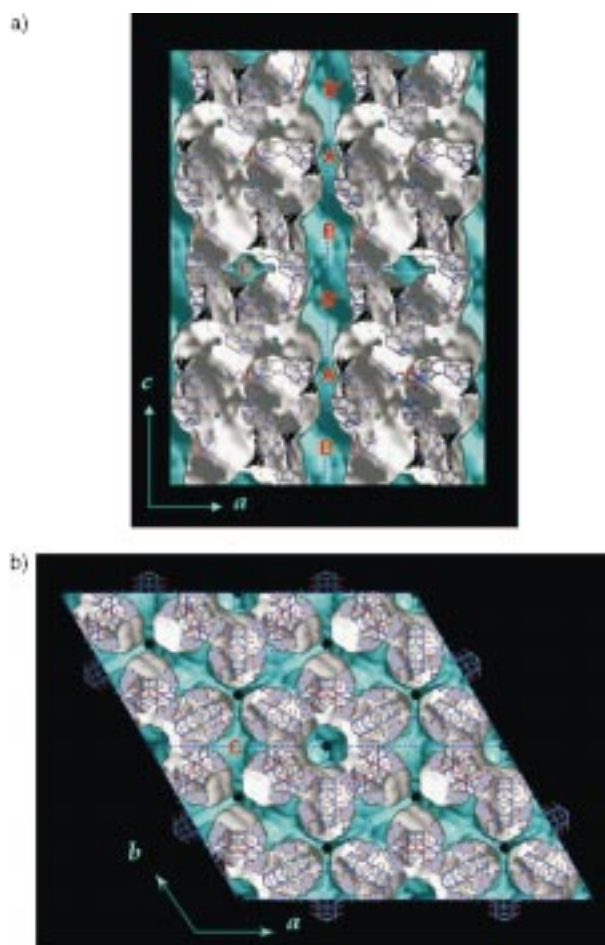


Figure 4. Cross-sectional views of **3** in the *ac* plane (a) and in the *ab* plane (b) showing the channels (in blue) formed with three different types of cavities A, B, and C: a) shows the 1D channels along the *c* axis and b) shows how they are interconnected to form 3D channels.

The total and accessible<sup>[7]</sup> void volumes are estimated to be 48 and 22 %, respectively, of the total volume.

The layer structure appears to be stabilized by efficient van der Waals interactions arising from the self-complementarity between the 2D layers. The framework of **3** is stable indefinitely in air and in nonpolar organic solvents, and only slightly soluble in water. Upon removal of the guest water molecules by evacuation, however, **3** loses its crystallinity,<sup>[8]</sup> but restores it upon exposure of the evacuated sample to water vapor, as judged by powder X-ray diffraction patterns. A similar behavior has been observed before,<sup>[6]</sup> but is not fully understood yet.

The ion-exchange properties of **3**, which has a cationic framework, have been studied. Stirring a suspension of **3** in an aqueous solution containing a slight excess of NaPF<sub>6</sub> at room temperature results in the exchange of NO<sub>3</sub><sup>−</sup> with PF<sub>6</sub><sup>−</sup> ions. The IR and elemental analysis data indicate that nearly 80 % of the anions are exchanged after 6 h (see the Supporting Information). The larger tosylate anion is also exchanged with NO<sub>3</sub><sup>−</sup> ions, but the exchange rate is slower than that of PF<sub>6</sub><sup>−</sup> ions: only approximately 20 % of the anion is exchanged after 6 h. Larger anions such as tetraphenylborate are not exchanged with NO<sub>3</sub><sup>−</sup>. These results demonstrate the size selectivity in anion exchange in **3**. X-ray powder diffraction studies (see the Supporting Information) show that the crystallinity of **3** is maintained during the anion exchanges.

The aqua ligands coordinated to the copper centers in **3** can be replaced by other ligands. For example, treatment of a suspension of blue crystalline **3** in dichloromethane with NH<sub>3</sub> gas for five minutes results in a color change to deep blue. The X-ray powder diffraction pattern of the crystalline solid remains essentially the same. The elemental analysis of the new solid (**3'**) is consistent with the idea that the coordinated aqua ligands are replaced by NH<sub>3</sub> during this process (see the Supporting Information). However, no evidence was found for replacement of the aqua ligands with pyridine, which may be too large to be coordinated to the metal center. The exchangeable aqua ligands suggest the metal centers in **3** may be used for recognition, binding, and activation of specific substrates. Further studies along this line are in progress.

In summary, we have synthesized a novel 2D polyrotaxane with large cavities and channels. The metal–organic framework is built with a seven-membered molecular necklace which behaves as a secondary building block. This cationic framework allows size-selective anion exchange as well as coordinated ligand exchanges. Most importantly, this work demonstrates a new synthetic strategy to modular porous solids that utilizes large, rigid, interlocked supermolecules as primary or secondary building blocks.

### Experimental Section

**3**: Sodium oxalate (24 mg, 0.18 mmol) and **2** (500 mg, 0.36 mmol) were added to a solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (86 mg, 0.36 mmol) in water (15 mL). The solution was then heated in air until its volume had reduced to about 5 mL. Cooling the solution to room temperature produced blue, hexagonal, X-ray-quality crystals which were collected, washed with water, and dried in air (340 mg, 51 %). Elemental analysis (%) calcd for C<sub>108</sub>H<sub>132</sub>N<sub>60</sub>O<sub>46</sub>Cu<sub>12</sub>·28H<sub>2</sub>O: C 35.38, H 5.17, N 23.69; found: C 35.53, H 5.13, N 23.62. Crystal data of **3**: [Cu(C<sub>17</sub>H<sub>26</sub>N<sub>4</sub>)·(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)·(C<sub>2</sub>O<sub>4</sub>)<sub>0.5</sub>·2H<sub>2</sub>O]·(NO<sub>3</sub>)<sub>3</sub>·

20H<sub>2</sub>O,  $M_r = 1973.24$ , trigonal,  $R\bar{3}m$ ,  $a = b = 33.2194(3)$ ,  $c = 38.9594(4)$  Å,  $V = 37232.8(6)$  Å<sup>3</sup>,  $Z = 18$ ,  $\rho_{\text{calc}} = 1.584$  g cm<sup>-3</sup>,  $T = 188$  K, Siemens SMART CCD diffractometer, MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å),  $\mu = 3.84$  cm<sup>-1</sup>. The structure was solved by Patterson methods (SHELXS-86). Of the three nitrate ions, only 1.5 were found because of disorder. Solvent molecules were also badly disordered. All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final block-diagonal matrix least-squares refinement on  $F^2$  with all 6888 reflections and 653 variables converged to  $R1$  ( $I > 2\sigma(I)$ ) = 0.129,  $wR2$  (all data) = 0.418, and GOF = 1.77. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147742. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Design of a Molecular Beacon DNA Probe with Two Fluorophores\*\*

Peng Zhang, Terry Beck, and Weihong Tan\*

DNA/RNA analysis is of great importance in molecular biology, genetics, and molecular medicine. DNA hybridization is a major tool for the diagnosis of genetic disease, of which the clinical symptoms are linked to alterations in DNA. Identifying the mutations in the human genome has become the focus of many research efforts. One recent development is that of a novel class of oligonucleotide probe: molecular beacons (MBs).<sup>[1]</sup> Molecular beacons are single-stranded oligonucleotide probes with a hairpin structure. A fluorophore and a quencher are linked to the two ends of the strand. The five to seven bases at both ends of the beacon are complementary to each other, forming the stem, which keeps the fluorophore and the quencher in proximity to each other. The fluorescence of the fluorophore is thus quenched by the quencher through energy transfer. The loop portion of the molecule beacon is so designed that it is complementary to a target oligonucleotide of interest.<sup>[1–8]</sup> When the probe encounters the target DNA molecule it forms a hybrid and forces the stem apart. Such a conformational change moves the fluorophore and the quencher away from each other, which leads to the restoration of fluorescence. Therefore, molecular beacons emit an intense fluorescent signal at room temperature only when hybridized to their target molecules. Molecular beacons have been shown to have very high selectivity in regards to the identification of a single base-pair mismatch.<sup>[1,2]</sup> Also, since the signal transduction mechanism is built within the MB molecules, no DNA intercalation reagent or labeling of the target molecule is needed. There have been a number of different applications of molecular beacons, such as real-time monitoring of polymerase chain reactions,<sup>[1,2]</sup> detection of DNA/RNA hybridization in living cells,<sup>[3]</sup> DNA/RNA biosensors,<sup>[4]</sup> bacterial detection,<sup>[5]</sup> monitoring of enzymatic cleavage,<sup>[6]</sup> investigation of the progression of HIV-1 disease,<sup>[7,8]</sup> and the study of DNA–protein interactions.<sup>[9]</sup> Molecular beacons hold great promise in studying genetics and disease mechanisms, in disease diagnostics, and in new drug development.

While MBs have been used successfully in DNA assays, their utility for quantification is limited. Currently, MBs use a

[\*] Dr. W. Tan, P. Zhang  
Department of Chemistry and UF Brain Institute  
University of Florida  
Gainesville, FL 32601 (USA)  
Fax: (+1) 352-846-2410  
E-mail: tan@chem.ufl.edu  
T. Beck  
TriLink BioTechnologies, Inc.  
6310 Nancy Ridge Drive, Suite 101  
San Diego, CA 92121 (USA)

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