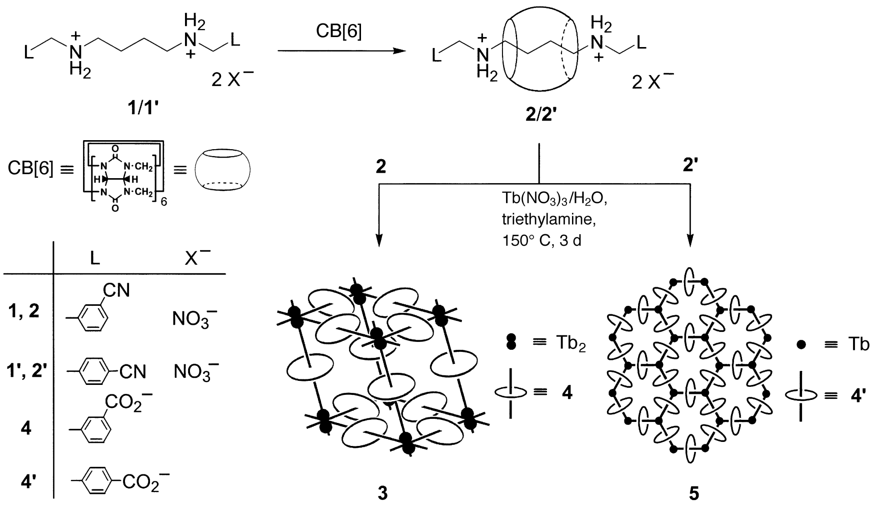
A Three-Dimensional Polyrotaxane Network**

Eunsung Lee, Jungseok Heo, and Kimoon Kim*

In memory of Chung Hoe Koo

The design and synthesis of supramolecular architectures with desired structures, properties, and functions have been the subjects of intense research in recent years.[1] Polyrotaxanes[2–9]—in which many molecular "beads" are threaded on a long molecular "string"—have received much attention because of their intriguing structures as well as their potential applications.[8, 9] Our interest in interlocked structures[10] led us to develop a simple approach to one-dimensional polyrotaxanes with high structural regularity.[10b] This approach involves formation of a pseudorotaxane by threading a bead with a short string having a pyridyl group at both ends, followed by reaction of the pseudorotaxane with a transition metal ion to produce a coordination polymer. The key to the success of this approach is the use of cucurbituril (CB[6])[11, 12] as a molecular bead: It has a highly symmetric structure and is able to form exceptionally stable pseudorotaxanes with strings derived from diaminoalkanes. The versatility of this approach has been demonstrated by the fact that a variety of one-dimensional (1D) polyrotaxanes with different structures are obtained simply by changing metal ions, counterions, and the string.[10b–d] Furthermore, the same approach allowed us to construct the first 2D polyrotaxane.[10c] Immediately following our work, Robson and co-workers also reported different types of 2D polyrotaxanes.[13]



Scheme 1. Synthesis of 3D polyrotaxane **3** and 2D polyrotaxane **5**.

The successful construction of a 2D polyrotaxane encouraged us to pursue unprecedented 3D polyrotaxanes. At first, construction of 3D polyrotaxanes appeared to be a simple extension of the work on 2D polyrotaxanes, but it turned out to be a challenging goal. For example, all attempts to produce 3D polyrotaxanes using transition metal ions and pseudorotaxanes with pyridyl terminal groups have failed. We therefore decided to modify our approach by using the reaction between lanthanide metal ions—which in general have larger ionic radii and higher coordination numbers than transition metal ions—and pseudorotaxanes with other terminal groups such as carboxylate and cyano groups under hydrothermal conditions. This effort has successfully produced the first 3D polyrotaxane network. Here we report the self-assembly and X-ray crystal structure of the novel supramolecular 3D net.

The pseudorotaxane **2**, prepared by threading CB[6] with *N,N'*-bis(3-cyanobenzyl)-1,4-diammoniobutane dinitrate (**1**), was treated with Tb(NO$_3$)$_3$ under hydrothermal conditions to produce **3** (Scheme 1). The X-ray crystal structure of **3** reveals an unprecedented 3D polyrotaxane in which CB beads are threaded on a 3D coordination polymer network. The basic building unit of the framework consists of a binulcear Tb^{3+} center and six pseudorotaxane units (**4**), each of which contains 3-phenylcarboxylate groups at the terminals. Apparently, under the hydrothermal conditions **1** with cyano groups was first converted into **4** with carboxylate terminals,[14] which then reacted with Tb^{3+} to form **3**.

Two different types of pseudorotaxane **4** exist in the 3D framework: One (type I) has η^1,η'^1-bridging caroxylate terminal groups, whereas the other (type II) has η^2-chelating carboxylate moieties. The two Tb^{3+} ions, which are related to each other by an inversion center located at the midpoint between the two metal centers, are linked by four η^1,η'^1-bridging carboxylate groups of type I pseudorotaxane **4** (Tb ··· Tb 3.9774(8) Å, Figure 1). Each Tb ion is further coordinated by an η^2-carboxylate group of a type II pseudorotaxane **4** and two water molecules. The coordination geometry around the metal center is best described as a distorted square antiprism with four oxygen atoms O3, O5, O4A, and O6A forming a square base. Similar binuclear lanthanide metal centers linked by four bridging carboxylate ligands are known.[15]

The binuclear terbium centers and type I pseudorotaxanes **4** form a 2D polyrotaxane network in the *bc* plane. The 2D networks, which are stacked along the normal to the *bc* plane with a mean distance of 19.8 Å, are interconnected by η^2 coordination of the carboxylate terminals of type II pseudo-

---

[*] Prof. K. Kim, E. Lee, J. Heo
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) 562-279-8129
E-mail: kkim@postech.ac.kr

[**] This paper is dedicated to the memory of Professor Chung Hoe Koo, who first introduced X-ray crystallography to Korea. We gratefully acknowledge the Korean Ministry of Science and Technology (Creative Research Initiative Program) for support of this work and the Korean Ministry of Education (Brain Korea 21 program) for graduate studentships to E.L. and J.H.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

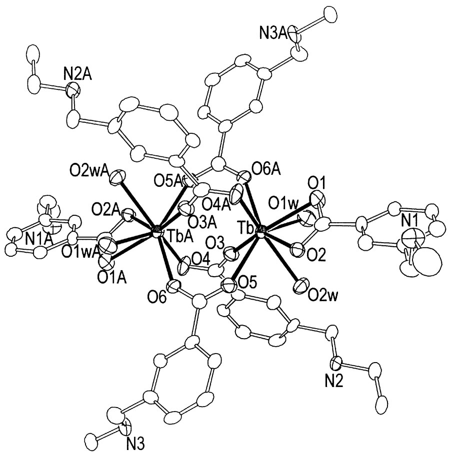


Figure 1. Coordination geometry around the binuclear terbium centers in **3**. An inversion center is located at the midpoint between the two terbium ions. The CB[6] beads are omitted for clarity. Selected bond lengths [Å]: Tb⋯TbA 3.9774(8), Tb–O1 2.409(6), Tb–O2 2.473(6), Tb–O3 2.349(6), Tb–O4A 2.417(6), Tb–O5 2.345(6), Tb–O6A 2.296(6), Tb–O1w 2.451(7), Tb–O2w 2.442(6).

rotaxane **4** to the terbium ions in the 2D nets to form a 3D polyrotaxane network (Figures 2 and 3). The 3D polyrotaxane has an inclined α-polonium topology with the binuclear terbium centers behaving as six-connected nodes.[16] The unit cell of the α-polonium-like net is depicted in Figure 4. The void space in the unit cell of **3** is filled with a free pseurorotaxane **4**, counteranions (nitrate and hydroxide ions), and water molecules.

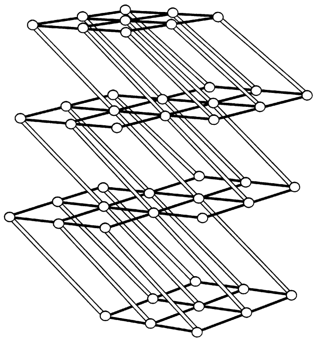


Figure 2. Schematic representation of the 3D framework in **3**. The circles represent binuclear Tb centers, and the solid and open connections represent type I and type II pseudorotaxanes, respectively.

A small change in the building block results in a totally different solid-state structure. For example, under the same conditions the reaction of $Tb(NO_3)_3$ with the isomeric pseudorotaxane **2′**, which has 4-cyanophenyl terminal groups, produces **5** (Scheme 1). The X-ray crystal structure of **5** reveals a polycatenated 2D polyrotaxane (see the Supporting Information) similar to that formed by the reaction of $Ag(NO_3)$ with a pseudorotaxane with pyridyl terminal groups.[10c] Here again pseudorotaxane **2′** is first converted into **4′** with carboxylate terminals under hydrothermal conditions before being coordinated to Tb metal ions to form **5**. Each Tb metal center in **5**, which is coordinated by three pseudorotaxanes **4′**, behaves as a three-connected node. The details of this structure will be reported elsewhere.

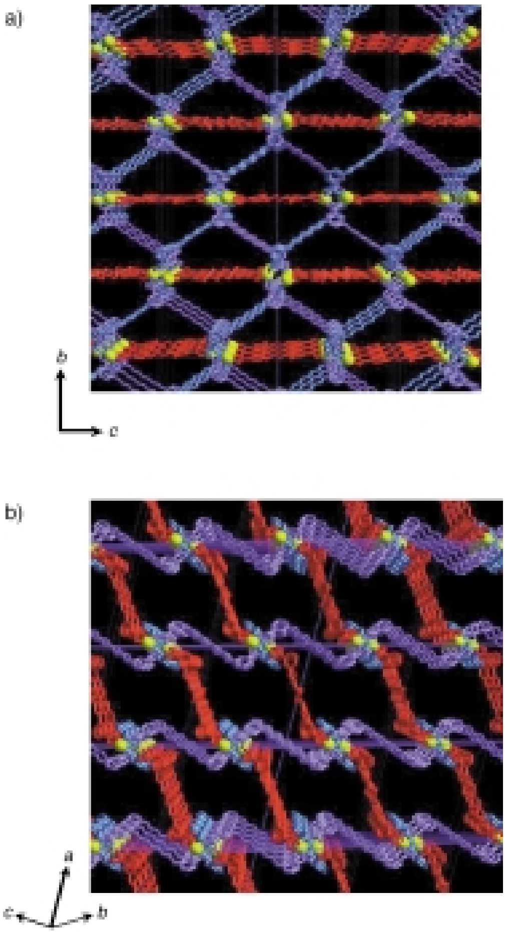


Figure 3. The 3D coordination polymer network in **3**: a) view down the *a* axis; b) view down the [011] direction. The CB[6] beads are omitted for clarity. Tb ion: yellow; type I pseudorotaxane **4**: dark and light blue; type II pseudorotaxane **4**: red.

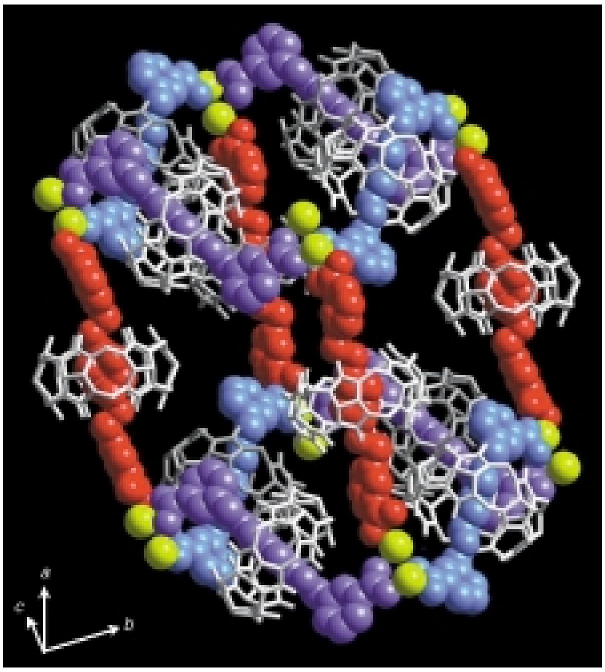


Figure 4. View of the unit cell of the α-polonium-like net in **3**. Tb ion: yellow; type I pseudorotaxane **4**: dark and light blue; type II pseudorotaxane **4**: red; CB: gray.

In conclusion, we have presented the first 3D polyrotaxane net in which beads are threaded onto 3D coordination polymer networks containing binuclear lanthanide metal centers. This novel supramolecular 3D network provides not only an intriguing example of chemical topology[17] but also new insights into the construction of solid-state materials, in particular modular open-framework or porous materials,[18] which is a subject of current intense investigation.

Experimental Section

3: Pseudorotaxane **2** (0.100 g, 0.065 mmol; see the Supporting Information), $Tb(NO_3)_3 \cdot 5H_2O$ (120 mg, 0.28 mmol), and triethylamine (0.001 mL, 0.007 mmol) were suspended in water (5 mL) in a stainless-steel bomb, which was then sealed, heated at 150 °C for 3 d, and cooled gradually to room temperature. Large, colorless crystals of **3** were collected, washed with water, and dried in air (73 mg, 68 %). Elemental analysis calcd for $C_{112}H_{123}N_{54}O_{40}Tb \cdot 20H_2O$: C 39.74, H 4.85, N 22.35; found: C 39.64, H 4.76, N 22.53.

5: Under the same conditions as for the synthesis of **3**, the reaction of **2′** and $Tb(NO_3)_3 \cdot 5H_2O$ yielded pale-yellow crystalline **5** (80 mg, 74 %). Elemental analysis calcd for $C_{168}H_{180}N_{84}O_{66}Tb_2 \cdot 24H_2O$: C 38.94, H 4.43, N 22.70; found: C 39.00, H 4.58, N 22.69.

Crystal data for **3**: $[Tb(C_{20}H_{24}N_2O_4)_{1.5}(C_{36}H_{36}N_{24}O_{12})_{1.5} \cdot 2H_2O][(C_{20}H_{26}N_2O_4)_{0.5}(C_{36}H_{36}N_{24}O_{12})_{0.5}] \cdot (NO_3)_2 \cdot (OH)_2 \cdot 20H_2O$, $M_r = 3429.92$, monoclinic, space group $P2_1/c$, $a = 19.8530(4)$, $b = 30.5734(5)$, $c = 24.1512(2)$ Å, $\beta = 109.411(1)°$, $V = 13825.9(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.643$ g cm^{-3}, $T = 243$ K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$), $\mu = 6.33$ cm^{-1}. The structure was solved by the Patterson method (SHELXS-86). Because only two nitrate ions were found, two hydroxide ions were assumed to be present in the lattice for charge neutrality. All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final block-diagonal matrix least-squares refinement on F^2 with all 21 230 reflections and 2136 variables converged to $R1$ ($I > 2\sigma(I)$) = 0.0805, $wR2$ (all data) = 0.2042, and GOF = 1.108.

Crystal data for **5**: $[Tb_2(C_{20}H_{24}N_2O_4)_3(C_{36}H_{36}N_{24}O_{12})_3 \cdot 6H_2O] \cdot (NO_3)_6 \cdot 28H_2O$, $M_r = 5362.34$, rhombohedral, space group Rm, $a = b = 32.8554(2)$, $c = 17.2678(2)$ Å, $V = 16142.9(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.655$ g cm^{-3}, $T = 243$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$), $\mu = 7.77$ cm^{-1}. Final block-diagonal matrix least-squares refinement on F^2 with all 3030 reflections and 274 variables converged to $R1$ ($I > 2\sigma(I)$) = 0.1058, $wR2$ (all data) = 0.3122, and GOF = 1.129.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142050 (**5**) and CCDC-142051 (**3**). 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).

Received: March 31, 2000 [Z 14929]

---

[1] a) J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinhein, **1995**; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154; c) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853.

[2] Recent reviews: a) S. A. Nepogodiev, J. F. Stoddart, *Chem. Rev.* **1998**, *98*, 1959; b) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; c) H. W. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843; e) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930; f) F. Vögtle, T. Dünnwald, T. Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451.

[3] a) A. Harada, M. Kamachi, *Macromolecules* **1990**, *23*, 2821; b) A. Harada, J. Li, M. Kamachi, *J. Am. Chem. Soc.* **1990**, *23*, 2821; c) A. Harada, J. Li, M. Kamachi, *Nature* **1992**, *356*, 325; d) A. Harada, J. Li, M. Kamachi, *Nature* **1993**, *364*, 516; e) A. Harada, J. Li, M. Kamachi, *Nature* **1994**, *370*, 126; f) A. Harada, J. Li, M. Kamachi, *Macromolecules* **1994**, *27*, 4538.

[4] a) Y. X. Shen, H. W. Gibson, *Macromolecules* **1992**, *25*, 2058; b) Y. X. Shen, D. Xie, H. W. Gibson, *J. Am. Chem. Soc.* **1994**, *116*, 537; c) H. W. Gibson, S. Liu, P. Lecavalier, C. Wu, Y. X. Shen, *J. Am. Chem. Soc.* **1995**, *117*, 852; d) E. Marand, Q. Hu, H. W. Gibson, B. Veytsman, *Macromolecules* **1996**, *29*, 2555; e) C. Gong, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 323; *Angew. Chem. Int. Ed.* **1998**, *37*, 310.

[5] a) G. Wenz, B. Keller, *Angew. Chem.* **1992**, *104*, 201; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 197; b) G. Wenz, F. Wolf, M. Wagner, S. Kubik, *New J. Chem.* **1993**, *17*, 729.

[6] a) I. Yamaguchi, K. Osakada, T. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 1811; b) M. Born, H. Ritter, *Angew. Chem.* **1995**, *107*, 342; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 309.

[7] a) C. Meschke, H.-J. Buschmann, E. Schollmeyer, *Macromol. Rapid Commun.* **1998**, *19*, 59; b) C. Meschke, H.-J. Buschmann, E. Schollmeyer, *Polymer* **1999**, *40*, 945; c) D. Tuncel, J. H. G. Steinke, *Chem. Commun.* **1999**, 1509.

[8] a) M. J. Marsella, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 9347; b) S. S. Zhu, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **1996**, *118*, 8713; c) S. S. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 12 568; d) J. Buey, T. M. Swager, *Angew. Chem.* **2000**, *112*, 608; *Angew. Chem. Int. Ed.* **2000**, *39*, 608.

[9] H. Fujita, T. Ooya, N. Yui, *Polym. J.* **1999**, *31*, 1099; T. Ooya, N. Yui, *J. Controlled Release* **1999**, *58*, 251; H. Fujita, T. Ooya, N. Yui, *Macromolecules* **1999**, *32*, 2534.

[10] a) Y.-M. Jeon, D. Whang, J. Kim, K. Kim, *Chem. Lett.* **1996**, 503; b) D. Whang, Y.-M. Jeon, J. Heo, K. Kim, *J. Am. Chem. Soc.* **1996**, *118*, 11 333; c) D. Whang, K. Kim, *J. Am. Chem. Soc.* **1997**, *119*, 451; d) D. Whang, J. Heo, C.-A. Kim, K. Kim, *Chem. Commun.* **1997**, 2361; e) D. Whang, K.-M. Park, J. Heo, P. Ashton, K. Kim, *J. Am. Chem. Soc.* **1998**, *120*, 4899; f) S.-G. Roh, K.-M. Park, G.-J. Park, S. Sakamoto, K. Yamaguchi, K. Kim, *Angew. Chem.* **1999**, *111*, 672; *Angew. Chem. Int. Ed.* **1999**, *38*, 638; g) S. I. Jun, J. W. Lee, S. Sakamoto, K. Yamaguchi, K. Kim, *Tetrahedron Lett.* **2000**, *41*, 471.

[11] Reviews: a) W. L. Mock in *Comprehensive Supramolecular Chemistry, Vol. 2* (Ed.: F. Vögtle), Pergamon, Oxford, **1996**, p. 477; b) W. L. Mock, *Top. Curr. Chem.* **1995**, *175*, 1; c) P. Cintas, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *17*, 205.

[12] The new cucurbituril homologues CB[5], CB[7], and CB[8]—which are pentameric, heptameric, and octameric species, respectively—have been recently reported: J. Kim, I. S, Jung, S. Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, *J. Am. Chem. Soc.* **2000**, *122*, 540.

[13] a) B. F. Hoskins, R. Robson, D. A. Slizys, *J. Am. Chem. Soc.* **1997**, *119*, 2952; b) B. F. Hoskins, R. Robson, D. A. Slizys, *Angew. Chem.* **1997**, *109*, 2402; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2336.

[14] The conversion of the cyanophenyl group into phenylcarboxylate under hydrothermal conditions is known: O. R. Evans, Z. Wang, W. Lin, *Chem. Commun.* **1999**, 1903. Attempts to synthesize **3** by allowing **4** and $Tb(NO_3)_3$ to react under hydrothermal conditions have been unsuccessful, presumably due to the extremely poor solubility of **4**.

[15] a) Z.-B. Daun, Z.-S. Jin, N.-H. Hu, J.-Z. Ni, *J. Struct. Chem.* **1989**, *8*, 168; b) J.-F. Ma, Z.-S. Jin, J.-Z. Ni, *Acta Crystallogr. Sect. C* **1994**, *50*, 1010.

[16] A. F. Wells, *Three-dimensional Nets and Polyhedra*, Wiley-Interscience, New York, **1977**.

[17] a) J.-P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319; b) G. A. Breault, C. A. Hunter, P. C. Mayers, *Tetrahedron* **1999**, *55*, 5265.

[18] Representative examples: a) B. F. Abrahams, B. F. Hoskins, D. M. Michail, R. Robson, *Nature* **1994**, *369*, 727; b) R. Robson in *Comprehensive Supramolecular Chemistry, Vol. 6* (Eds.: D. D. MacNicol, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, 733; c) S. Subramanian, M. J. Zawarotko, *Angew. Chem.* **1995**, *107*, 2295; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127; d) O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **1998**, *31*, 474; e) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; f) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; g) S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739; h) J. Heo, S. Y. Kim, D. Whang, K. Kim, *Angew. Chem.* **1999**, *111*, 675; *Angew. Chem. Int. Ed.* **1999**, *38*, 641; i) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148; j) J.-S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982.

1433-7851/00/3915-2701 $ 17.50+.50/0