DOI: 10.1002/anie.200603270

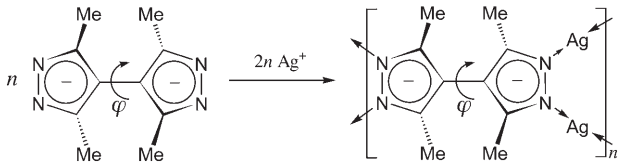
Microporous Materials

A Flexible Porous Coordination Polymer Functionalized by Unsaturated Metal Clusters**

*Jie-Peng Zhang, Satoshi Horike, and Susumu Kitagawa**

Porous coordination polymers (PCPs) have received considerable attention because of their diverse topologies and potential applications in storage, separation, and catalysis.[1–6] Besides porosity, stability, and pore shape and size, framework flexibility and pore-surface modifications are currently considered to be the key factors for the next generation of PCPs.[2,3] The guest-responsive pores of flexible PCPs provide strong confinement effects for specific guest molecules by shrinking or expanding in different guest-inclusion states, which may also be directly visualized by crystallographic analysis if the host framework is strong enough to undergo transformation from single crystal to single crystal (SCSC).[4,5] The incorporation of coordinatively unsaturated metal centers (UMCs)[3d] into a porous host is very attractive as UMCs can strongly interact with guest molecules. Compared to inorganic zeolites, polymeric matrices, and clays, UMCs located inside PCPs have uniform arrangements and well-understood surrounding environments. However, successful immobilization of UMCs onto the PCP pore surface is still rare as only a few PCPs are stable upon thermal liberation of volatile coordinated ligands.[6]

Low-coordinate silver(I) is a potential UMC because silver(I) centers can adopt diverse coordination environments. Silver(I)-exchanged zeolites were used in alkane–alkene separation studies as the silver(I) center has a high affinity for unsaturated hydrocarbon molecules which arises from Ag···π interactions.[7] However, it is very difficult to restrict the coordination number of Ag^{I} by using common pyridine- or carboxylate-like ligands. Conversely, the metal coordination number is always equal to, or lower than, the number of nitrogen atoms in binary metal azolates, such as pyrazolates, imidazolates, and triazolates.[8] A 3D cationic silver-triazolate framework composed of linear coordinate Ag^{I} centers was shown to undergo drastic, temperature/guest-induced SCSC structural transformations.[5j] Nevertheless, simple binary silver-pyrazolate and -imidazolate complexes cannot generate 3D coordination polymers. In this regard, new ligands generated by covalently linking two pyrazolate or imidazolate moieties can solve this problem. 3,3′,5,5′-Tetramethyl-4,4′-bipyrazole (H_2Me_4bpz) is well-studied as a hydrogen-bonding synthon and neutral bidentate ligand, while deprotonated Me_4bpz has received less attention.[9–11] As for simple binary silver azolates, we can readily predict the local coordination environment for $[Ag_2(Me_4bpz)]$. The resulting coordination framework should have a three-connected topology if we consider the N–Ag–N moieties and all the central C–C single bonds as linkers and pyrazolate rings as three-connected nodes. Additionally, framework flexibility may not only arise from the low-connectivity topology but also because two pyrazolate (pz) rings of Me_4bpz can rotate around the central C–C single bond (dihedral angle $\varphi \approx 50$–$90°$; Scheme 1).[9]



Scheme 1. Use of Me_4bpz^{2-} ligands and Ag^{+} ions to construct a flexible framework with two-coordinate Ag centers.

The reaction of a silver–ammonia solution and an ethanol solution of H_2Me_4bpz gives the desired binary compound, $[Ag_2(Me_4bpz)]$·guest (**1·g**), as colorless polyhedral crystals, which are insoluble in common organic solvents or water as are other polymeric binary metal azolates. Compound **1·g** crystallizes in the cubic space group *I*-43*d*, and each asymmetric unit contains two Ag atoms and one Me_4bpz ligand ($\varphi = 63.3°$). As expected, Ag and Me_4bpz are two- and four-coordinated, respectively (Ag–N 2.037(11)–2.047(11) Å, N-Ag-N 168.5(4)°, 176.3(4)°). The interconnection of Ag atoms and Me_4bpz ligands gives a $[Ag_2(Me_4bpz)]$ 3D coordination network that contains $\{Ag_3(pz)_3\}$ trigonal subunits, which is commonly observed in pyrazolates of the coinage metals [12] and similar complexes.[13] Therefore, the $[Ag_2(Me_4bpz)]$ coordination network in **1·g** can be simplified as a highly distorted (10,3)-*a* topology with the $\{Ag_3(pz)_3\}$ subunits behaving as three-connected nodes and the C–C single bonds as linkers (Figure 1).[14] The whole structure of **1·g** consists of two pairs of interweaving (10,3)-*a* $[Ag_2(Me_4bpz)]$ nets with opposite chirality. The closest contact between adjacent $[Ag_2(Me_4bpz)]$ nets is the face-to-face stacking of the

[*] Dr. J.-P. Zhang, S. Horike, Prof. Dr. S. Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering
Kyoto University
Katsura, Nishikyo-ku, Kyoto 615–8510 (Japan)
Fax: (+81) 75-383-2732
E-mail: kitagawa@sbchem.kyoto-u.ac.jp
Homepage: http://www.sbchem.kyoto-u.ac.jp/english/index.html

[**] This work was supported by a Grants-in-Aid for Scientific Research in a Priority Area "Chemistry of Coordination Space" (No. 434) and Core Research for Evolutional Science and Technology (CREST) from the Ministry of Education, Culture, Sports, Science and Technology, Government of Japan. J.-P. Zhang is grateful to JSPS for a postdoctoral fellowship.

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

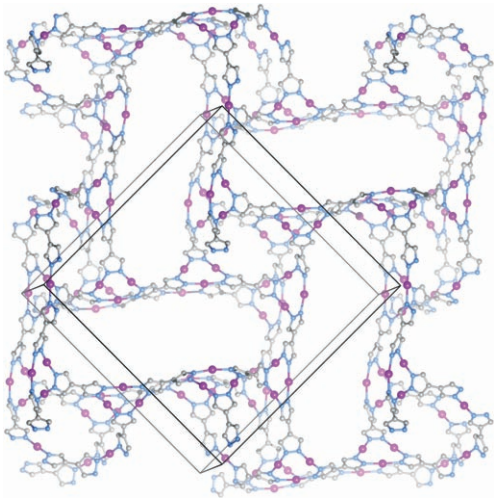


Figure 1. A single $[Ag_2(Me_4bpz)]$ coordination network in **1·g** (methyl groups are omitted for clarity. Ag pink, N blue, C gray.

$\{Ag_3(pz)_3\}$ triangles in an unusual staggered fashion by triple argentophilic interactions (Ag···Ag 3.319 Å; $\{Ag_3\}$···$\{Ag_3\}$ 2.93 Å; see Supporting Information). As only one face of each $\{Ag_3(pz)_3\}$ subunit is occupied, the other face may interact with guest molecules. This UMC trimer is unusual as most of the reported UMCs in PCPs are monomer-based.[6] A cavity is sandwiched between two such UMC trimers (interplanar distance $\{Ag_3\}$···$\{Ag_3\}$ 8.82 Å) and accommodates the highly disordered guest molecules. Furthermore, these threefold symmetric cavities are interconnected through small apertures ($d \approx 3.4$ Å, Figure 2) to generate a 3D bicontinuous channel system (void volume, $V_{void} = 30.4\,\%$).[15] The racemic pair of (10,3)-*a* channel networks is

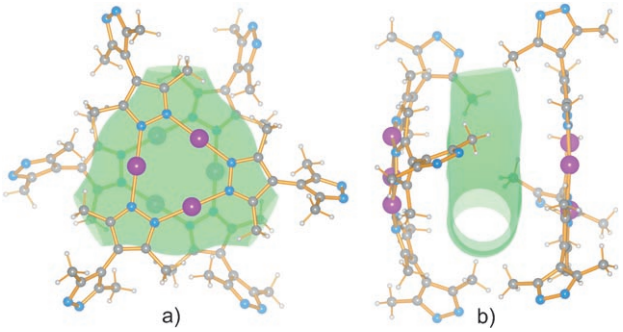


Figure 2. a) Top and b) side views of the local pore environment of **1·g**. Ag pink, N blue, C gray, H light gray; pore surfaces are shown as green structures.

well-separated by the $[Ag_2(Me_4bpz)]$ host. Therefore, the porous structure of **1·g** is composed of four (10,3)-*a* coordination networks, as well as two (10,3)-*a* channel networks (Figure 3), which is unique in coordination polymers. The most relevant structure of **1·g** is the fourfold interpenetrated (10,3)-*a* (slightly distorted) hydrogen-bonded network of $H_2Me_4bpz{\cdot}CHCl_3$. Nevertheless, the N–H···N hydrogen bonds are not strong enough to stabilize the H_2Me_4bpz hydrogen-bonded network upon removal of $CHCl_3$.[9b]

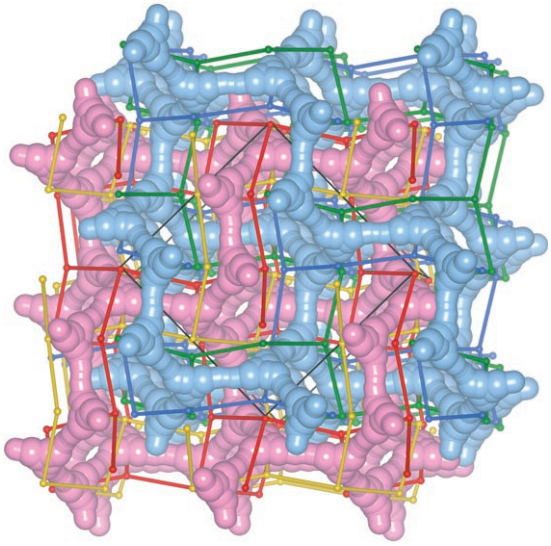


Figure 3. Fourfold interpenetrated (10,3)-*a* $[Ag_2(Me_4bpz)]$ networks (ball-and-stick model, ball: $\{Ag_3\}$ subunit, stick: Me_4bpz ligand) and twofold interpenetrated (10,3)-*a* channels (space-filling model) in **1·g**. Each network is shown in a different color.

Thermogravimetric analysis and temperature-dependent X-ray powder-diffraction measurements revealed that guest molecules in **1·g** can be completely removed below 120 °C and the host framework decomposes above 300 °C (see Supporting Information). The guest-free single-crystal $[Ag_2(Me_4bpz)]$ (**1**) can be obtained by heating the single crystal of **1·g** in a nitrogen flow. Although **1** is isomorphic to **1·g**, the structural parameters ($\varphi = 67.4°$; Ag–N 2.020(8)–2.043(9) Å; N-Ag-N 168.8(4)°, 173.9(4)°; Ag···Ag 3.315 Å; $\{Ag_3\}$···$\{Ag_3\}$ 2.90, 8.89 Å) reveal a distortion from **1·g**. According to the X-ray diffraction data, no residual electron density can be found in the empty cavities of **1**. This SCSC guest removal indicates that the host framework of **1** is thermally stable.

The permanent porosity of **1** was confirmed by measurements of CO_2 and N_2 gas adsorption (Figure 4). Both isotherms exhibit an abrupt sorption at low relative pressure (P/P_0), called a Type I profile, which indicates the presence of uniform micropores in **1**. At a pressure of $0.8\,P_0$, approximately 0.67 CO_2 or 0.75 N_2 molecules were adsorbed per

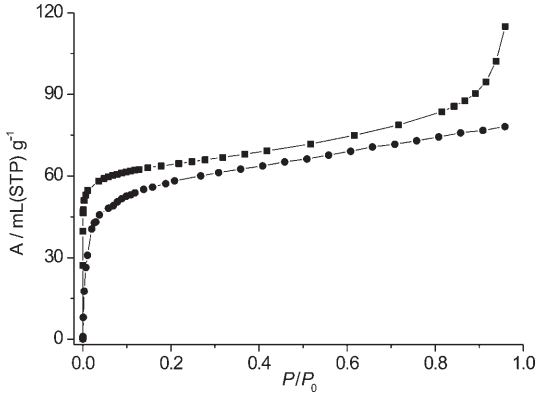


Figure 4. CO_2 (195 K, ●) and N_2 (77 K, ■) adsorption isotherms of **1**.

Ag atom, which corresponds to 4.0 CO_2 or 4.5 N_2 molecules per pore, respectively. Fitting the N_2 adsorption isotherm gives a BET (Brunauer–Emmett–Teller) surface area of 240 $m^2 g^{-1}$ and a Langmuir surface area of 280 $m^2 g^{-1}$.

The adsorption behavior of CO_2 and N_2 indicates that these guest molecules are smaller than the apertures in **1**. From a structural point of view, no apparent flexibility is needed for **1** during the adsorption/desorption of very small guests. Conversely, structural transformation is necessary for **1** to adsorb larger guest molecules. To test the flexibility of **1** and thus obtain direct structural information, we carried out single-crystal adsorption/desorption experiments by using two large guest molecules, benzene (3.3 Å × 6.6 Å) and toluene (4.0 Å × 6.6 Å).[16] Single crystals of **1** were exposed to a saturated vapor of each guest at room temperature. The shape and transparency of the single crystals did not change during the experiments.[16]

X-ray analysis of the single crystals with the arene molecules included revealed a new crystal phase, **2·g** ($I4_1/a$). The formulae of the benzene- and toluene-included compounds are $[Ag_{30}(Me_4bpz)_{15}]\cdot 10(C_6H_6)$ (**2·b**) and $[Ag_{30}(Me_4bpz)_{15}]\cdot 9(C_6H_5CH_3)$ (**2·t**), respectively. After the SCSC transformation, the original metal–ligand connectivity was retained in **2·g**. However, adsorption of the guest molecules severely decreases the symmetry of **2·g**. The structural parameters of **2·g** have a wide distribution as there are 30 Ag atoms and 15 Me_4bpz ligands in its asymmetrical unit (see Supporting Information). The Me_4bpz average dihedral angle ($\varphi = 60.9°$) of **2·g** is remarkably smaller than that of **1** and **1·g**. The threefold symmetric $\{Ag_3(pz)_3\}$ dimers also significantly shift to form different conformations with much shorter intermolecular Ag···Ag contacts (shortest Ag···Ag around 3.0 Å). In consideration of the size difference between the pore aperture and the guest molecules, there should be a more-drastic distortion of the host framework when large guest molecules diffuse through the small apertures of **1**. Most interestingly, in contrast to the uniform cavities in **1**, those in **2·g** have a variety of shapes and sizes, thus accommodating different aggregations of guest molecules, which include monomers, dimers, and trimers. It is clear that the cavities of **1** are too large for one benzene molecule but too small for two. Therefore, the flexible framework expands some cavities and shrinks others simultaneously to accommodate as many guest molecules as possible.[4a] This cooperative movement of the host framework occurs over a long range, so that every five adjacent cavities rearrange their size and shape to form a new periodic unit (Figure 5). This simultaneous shrinking and expanding phenomena is unique for the PCPs.

The main host–guest interactions are Ag···π interactions for monomers and dimers, and C–H···Ag interactions for trimers. The shortest Ag···C contacts (about 3.3–3.5 Å) in **2·g** are longer than the coordination bonds in Ag–arene complexes, but in the range of weak Ag···π interactions. The overall interaction energy for an individual guest molecule should be relatively high, as each guest molecule is confined by three or six silver centers. Although silver has a larger van der Waals radius than carbon, the interplanar distances between $\{Ag_3\}$ and the guest molecules (3.33–3.47 Å, av. 3.38 Å) are shorter than those between the arene dimers (3.53–3.60 Å, av. 3.56 Å). These structural parameters imply that the Ag···π interactions are stronger than π···π interactions of the arene guest molecules in **2·g**. Similar structural motifs have been observed in molecular adducts of $[Hg_3(C_6F_4)_3]$ and arene monomers.[13b]

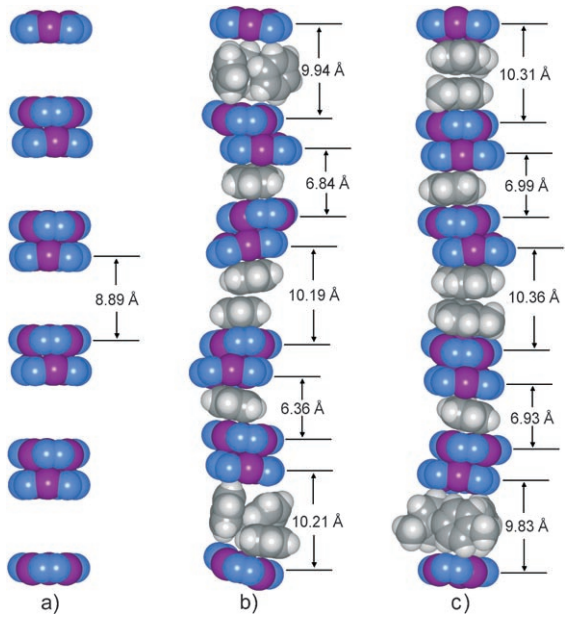


Figure 5. Pore environments of a) **1**, b) **2·b**, and c) **2·t**. Crystallographically independent pore dimensions are given. Only the guest molecules (gray) and the $\{Ag_3N_6\}$ cores (pink, blue) of the host frameworks are shown.

Finally, phase **1** can be recovered by heating the same single crystal of **2·b** and **2·t** at 90–110 °C. These guest-triggered, reversible SCSC transformations further illustrate the stability and flexibility of the $[Ag_2(Me_4bpz)]$ framework.

In summary, using a straightforward strategy, we have combined in a PCP high flexibility and UMC-functionalized pore surfaces. We have shown that the binary silver dipyrazolate has not only high thermal stability and permanent porosity but also exceptional framework flexibility. Further exploration in this area with other coinage metal ions and with modified bipyrazolate ligands will open up a variety of new functions.

Experimental Section

1·g: An ethanol solution of H_2Me_4bpz (0.0190 g, 0.1 mmol in 5 mL) was carefully layered onto an aqueous ammonia solution (26 %) of Ag_2O (0.0232 g, 0.1 mmol in 5 mL). After two weeks, colorless polyhedral crystals were collected and washed with ethanol.

X-ray structure determination of **1·g**, **1**, **2·b**, and **2·t**: Measurements were recorded on a Rigaku mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. All structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL program.[18] All non-hydrogen atoms except disordered solvent molecules were refined anisotropically. Crystal data of **1·g**: cubic, $I\bar{4}3d$ (No. 220), $a = 27.147(2)$ Å, $V = 20006(3)$ Å^3, $Z = 48$, $\rho_{calcd} = 1.701$ g cm^{-3}, $F(000) = 9936$, $T = 213(2)$ K, $\mu = 2.339$ mm^{-1}, total data 33326, unique data 3279, final $R_1 = 0.0773$ ($I > 2\sigma$), $wR_2 = 0.1318$ (all data), $S = 1.035$. **1**: cubic, $I\bar{4}3d$ (No. 220),

$a = 27.2326(15)$ Å, $V = 20196.1(19)$ Å^3, $Z = 48$, $\rho_{calcd} = 1.594$ g cm^{-3}, $F(000) = 9312$, $T = 213(2)$ K, $\mu = 2.310$ mm^{-1}, total data 27313, unique data 3307, final $R_1 = 0.0613$ ($I > 2\sigma$), $wR_2 = 0.1012$ (all data), $S = 1.010$. **2·b**: tetragonal, $I4_1/a$ (No. 88), $a = 61.600(2)$, $c = 26.7475(13)$ Å, $V = 101495(7)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.795$ g cm^{-3}, $F(000) = 53440$, $T = 153(2)$ K, $\mu = 2.311$ mm^{-1}, total data 379509, unique data 49738, final $R_1 = 0.0799$ ($I > 2\sigma$), $wR_2 = 0.1912$ (all data), $S = 1.043$. **2·t**: tetragonal $I4_1/a$ (No. 88), $a = 62.030(2)$, $c = 26.5872(15)$ Å, $V = 102302(8)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.789$ g cm^{-3}, $F(000) = 53760$, $T = 153(2)$ K, $\mu = 2.293$ mm^{-1}, total data 239187, unique data 50157, final $R_1 = 0.0777$ ($I > 2\sigma$), $wR_2 = 0.1924$ (all data), $S = 1.067$. CCDC 617228–617231 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: August 10, 2006
Revised: November 4, 2006
Published online: December 20, 2006

Keywords: coordination modes · inclusion compounds · microporous materials · N ligands · silver

[1] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705 – 714.

[2] G. S. Papaefstathiou, L. R. MacGillivray, *Coord. Chem. Rev.* **2003**, *246*, 169 – 184.

[3] a) S. Kitagawa, R. Kitaura, S. I. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375; b) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109 – 119; c) A. J. Fletcher, K. M. Thomas, M. J. Rosseinsky, *J. Solid State Chem.* **2005**, *178*, 2491 – 2510; d) S. Kitagawa, S. I. Noro, T. Nakamura, *Chem. Commun.* **2006**, 701 – 707.

[4] a) R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike, M. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 14063 – 14070; b) L. Pan, D. L. Olson, L. R. Ciemnolonski, R. Heddy, J. Li, *Angew. Chem.* **2006**, *118*, 632 – 635; *Angew. Chem. Int. Ed.* **2006**, *45*, 616 – 619; c) X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya, M. Schröder, *J. Am. Chem. Soc.* **2006**, *128*, 10745 – 10753.

[5] a) K. Biradha, M. Fujita, *Angew. Chem.* **2002**, *114*, 3542 – 3545; *Angew. Chem. Int. Ed.* **2002**, *41*, 3392 – 3395; b) B. Rather, M. J. Zaworotko, *Chem. Commun.* **2003**, 830 – 831; c) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa , *Angew. Chem.* **2003**, *115*, 444 – 447; *Angew. Chem. Int. Ed.* **2003**, *42*, 428 – 431; d) O. Ohmori, M. Kawano, M. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 16292 – 16293; e) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858 – 2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798 – 2801; f) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373 – 1382; g) G. J. Halder, C. J. Kepert, *J. Am. Chem. Soc.* **2005**, *127*, 7891 – 7900; h) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem.* **2004**, *116*, 5143 – 5146; *Angew. Chem. Int. Ed.* **2004**, *43*, 5033 – 5036; i) C.-D. Wu, W.-B. Lin, *Angew. Chem.* **2005**, *117*, 1994 – 1997; *Angew. Chem. Int. Ed.* **2005**, *44*, 1958 – 1961; j) J.-P. Zhang, Y.-Y. Lin, W.-X. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 14162 – 14163; k) T. K. Maji, G. Mostafa, R. Matsuda, S. Kitagawa, *J. Am. Chem. Soc.* **2005**, *127*, 17152 – 17153.

[6] a) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823 – 4827; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745 – 4749; b) P. D. C. Dietzel, B. Panella, M. Hirscher, R. Bloma, H. Fjellvåg, *Chem. Commun.* **2006**. 959 – 961; c) S. Horike, R. Matsuda, D. Tanaka, M. Mizuno, K. Endo, S. Kitagawa, *J. Am. Chem. Soc.* **2006**, *128*, 4222 – 4223; d) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**. 2563 – 2565.

[7] M. Kargol, J. Zajac, D. J. Jones, Th. Steriotis, J. Rozière, P. Vitse, *Chem. Mater.* **2004**, *16*, 3911 – 3918.

[8] Reviews: a) N. Masciocchi, S. Galli, A. Sironi, *Comments Inorg. Chem.* **2005**, *26*, 1 – 37; b) J.-P. Zhang, X.-M. Chen, *Chem. Commun.* **2006**, 1689 – 1699.

[9] a) I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler, K. V. Domasevitch, *Angew. Chem.* **2001**, *113*, 3543 – 3546; *Angew. Chem. Int. Ed.* **2001**, *40*, 3435 – 3438; b) I. Boldog, E. B. Rusanov, J. Sieler, S. Blaurock, K. V. Domasevitch, *Chem. Commun.* **2003**, 740 – 741.

[10] a) V. V. Ponomarova, V. V. Komarchuk, I. Boldog, A. N. Chernega, J. Sieler, K. V. Domasevitch, *Chem. Commun.* **2002**, 436 – 437; b) E. B. Rusanov, V. V. Ponomarova, V. V. Komarchuk, H. Stoeckli-Evans, E. Fernandez-Ibanez, F. Stoeckli, J. Sieler, K. V. Domasevitch, *Angew. Chem.* **2003**, *115*, 2603 – 2605; *Angew. Chem. Int. Ed.* **2003**, *42*, 2499 – 2501; c) K. V. Domasevitch, I. Boldog, E. B. Rusanov, J. Hunger, S. Blaurock, M. Schröder, J. Sieler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1095 – 1100.

[11] J. He, Y.-G. Yin, T. Wu, D. Li, X.-C. Huang, *Chem. Commun.* **2006**, 2845 – 2847.

[12] a) A. Kishimura, T. Yamashita, T. Aida, *J. Am. Chem. Soc.* **2005**, *127*, 179 – 183; b) G. Yang, R. G. Raptis, *Inorg. Chem.* **2003**, *42*, 261 – 263; c) H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary, M. A. Omary, *J. Am. Chem. Soc.* **2005**, *127*, 7489 – 7501; d) M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonser, O. Elbjeirami, T. Grimes, T. R. Cundari, *Inorg. Chem.* **2005**, *44*, 8200 – 8210.

[13] a) A. Hayashi, M. M. Olmstead, S. Attar, A. L. Balch, *J. Am. Chem. Soc.* **2002**, *124*, 5791 – 5795; b) C. Burress, O. Elbjeirami, M. A. Omary, F. P. Gabbaï, *J. Am. Chem. Soc.* **2005**, *127*, 12166 – 12167.

[14] 3.20^2 topology if C–C single bonds and N–Ag–N coordination bonds are regarded as linkers and the pyrazolate moieties are regarded as 3-connected nodes. A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, **1977**.

[15] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[16] C. E. Webster, R. S. Drago, M. C. Zerner, *J. Am. Chem. Soc.* **1998**, *120*, 5509 – 5516.

[17] Immersing **1**/**1·g** in each guest solvent results in faster guest adsorption or exchange to afford **2·g**.

[18] G. M Sheldrick, SHELXTL 6.10, 2000

