A Designed Three-Dimensional Porous Hydrogen-Bonding Network Based on a Metal−Organic Polyhedron

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S *Supporting Information*

ABSTRACT: By employment of sulfonate-decorated metal−organic cuboctahedra (MOCs) as tectons, we report an interesting example of molecular tectonics strategy for the rational construction of three-dimensional (3D) porous network **1** through complementary and metrically matched N−H$^+$···$^-$O−S hydrogen bonds between guanidinium and sulfonate (GS) moieties. Built from the MOCs as 24-connected nodes and the GS H-bonding motifs as 3-connected nodes, **1** was expected to have a (3,24)-connected network topology, which has been verified by the single crystal X-ray analysis. In addition, the porous H-bonding network **1** displays good stability under ambient conditions and modest absorption of cationic dye molecules.
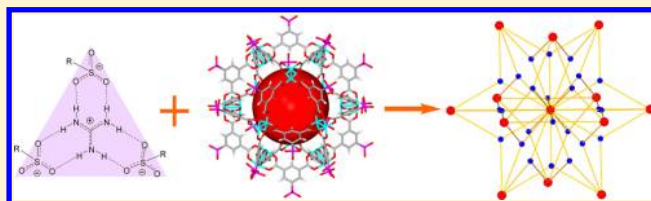
Designing molecules to form crystalline materials with particular structures and properties has become a rapidly developing research area.[1] Molecular tectonics, exploited by Wuest[2] and Hosseini[3] et al., has recently been a powerful strategy for the design and construction of highly ordered materials. This strategy is based on tectons, which are building units bearing potential binding sites and thus capable of linking each other for the purposeful construction of new materials.[4] Hydrogen bonds have been widely exploited in this strategy because of their favorable strength and directionality.[5] The monohapto mode of H bonding, although synthetically simpler to achieve, does not allow forming steady geometrical patterns between tectons. By the use of the multihapto mode of H bonding, however, one may control the spatial arrangements to a certain extent and thus predict the connectivity pattern between tectons and even the overall topology of the resulting network. For example, Ward and co-workers have reported a series of crystalline guanidinium−sulfonate (GS) compounds based on complementary and metrically matched N−H$^+$···$^-$O−S hydrogen bonds or GS tiles with 3-fold symmetry.[6] The given pattern greatly prompts the formation of a two-dimensional (2D) quasihexagonal network. To obtain new GS compounds with alternative architectures, the same group recently used the rigid polysulfonate as a tecton that tends to frustrate the formation of layered structures and constructed a supramolecular cage with large interior volume through 72 hydrogen bonds also generated from 3-fold symmetric GS motifs.[7]

Inspired by the rational design of specific structure through the GS H-bonding motif, we attempt to construct more sophisticated GS compounds with nanoscopic pores, which may encapsulate various guest species. To achieve this aim, selection of a structure-directing tecton of polysulfonate moiety with high symmetry and connectivity is critical during the assembly process. Because of the well-defined cavities, high symmetry and stability, and rich properties and functions, the hollow metal−organic polyhedra (MOPs) are excellent candidates as building units.[8] The unique sulfonate-decorated hollow MOP reported by Li and co-workers was a metal−organic cuboctahedron (MOC), which consists of 12 dicopper paddlewheel clusters and 24 5-sulfoisophthalate moieties.[9] Structural analysis demonstrates that by connecting the 24 edges of a MOC with linkers having C_3 symmetry, the packing arrangement of the MOCs will be restricted to a cubic close packing (CCP) arrangement and produce a three-dimensional (3D) framework with the (3,24)-connected network topology. In fact, an isoreticular series of metal−organic frameworks have been obtained on the basis of this connection mode.[10] We reasoned that a novel 3D H-bonding network with the identical topology will come into being by use of the sulfonate-decorated MOC as a tecton and the 3-fold symmetric H-bonding motif from sulfonate groups and guanidinium cations. Here, we report an interesting example of molecular tectonics strategy involving GS compounds by use of the predesigned hollow MOP as a tecton instead of conventional organic tectonic subunits. Due to the large interior cavities, the dye absorption property of this network has also been investigated.

A CH$_3$OH solution containing guanidinium (G) chloride was slowly diffused into a mixed CH$_3$OH/DMA (DMA = N,N-dimethylacetamide) solution of sodium 5-sulfoisophthalate (NaL) and Cu$_2$(OAc)$_4$, and large amounts of bulk blue crystals were obtained in a high yield after several days. The formula {Na$_{12}$G$_4$[Cu$_{24}$L$_{24}$G$_8$(H$_2$O)$_{24}$]·74DMF} (**1**) was determined through thermal gravimetric analysis and inductively coupled plasma-atomic emission spectrometry (ICP-AES) after **1** was immersed in DMF for 48 h (see the Supporting Information).
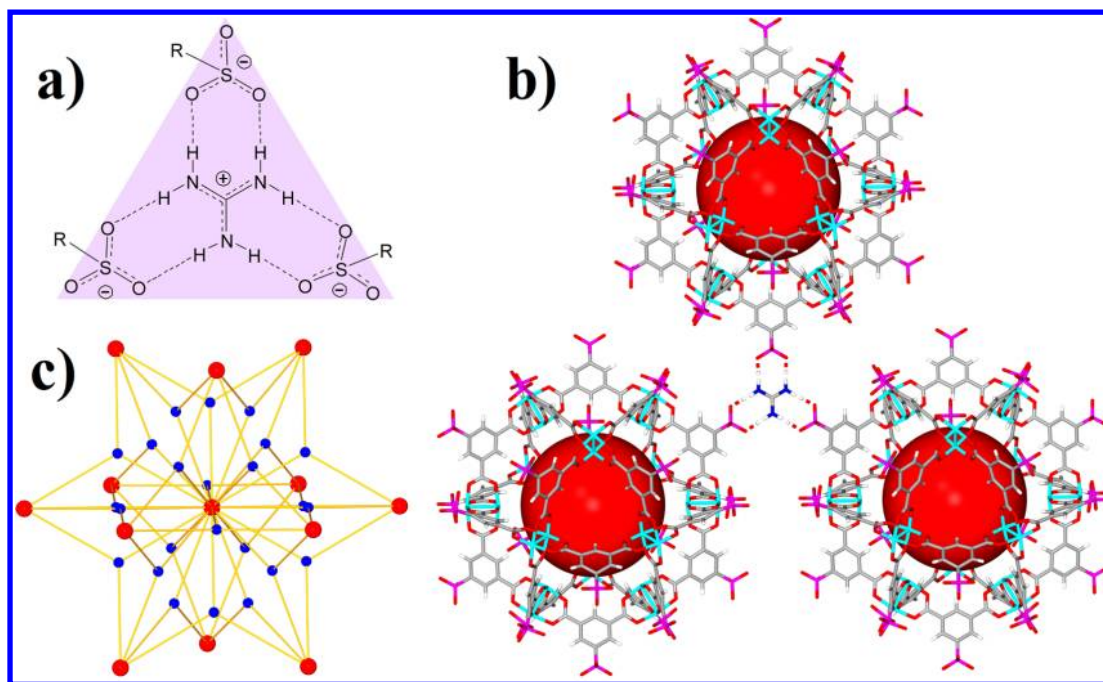
Figure 1. (a) $[GS_3]^{2-}$ tile consists of one guanidinium cation and three sulfonate groups through the complementary charge-assisted $N-H^+\cdots^-O-S$ hydrogen bonds. (b) Cuboctahedra of $Cu_{24}L_{24}$ as structural tectons connected by the $[GS_3]^{2-}$ tile. (c) Highly connected (3,24) network, in which the MOCs are cubic close-packed. The red spheres refer to 24-connected nodes and the blue spheres refer to three-connected nodes.

In accordance with the literature reported by Li et al.,[9] the MOCs of $Cu_{24}L_{24}$ have formed in the CH_3OH/DMA solution, and crystals were grown through cocrystallization of the MOCs and the introduced guanidinium cations.

Single-crystal X-ray diffraction reveals that **1** crystallizes in the space group $Fm\bar{3}m$ and $a = 43.0$ Å.[11] As shown by Figure 1b, 24 isophthalate moieties are linked by 12 ubiquitous dicopper paddle-wheel building blocks to form the MOC structural unit with eight triangular and six square windows. The substituted sulfonate groups of isophthalate at the 5 position do not interact with copper centers, probably owing to their relatively weak coordination affinity. Instead, the sulfonate groups that contain multiple lone pairs act as acceptors of hydrogen bonds from the guanidinium cations. As expected, one guanidinium cation can interact with three sulfonate groups through the complementary charge-assisted $N-H^+\cdots^-O-S$ hydrogen bonds, and the formed $[GS_3]^{2-}$ tile indeed has a 3-fold symmetry (Figure 1a). Consequently, the MOC, which acts as a 24-connected node, is linked by the $[GS_3]^{2-}$ tiles as three-connected nodes to link 12 surrounding MOCs as a CCP arrangement and construct a 3D framework with the predictable (3,24)-connected net (Figure 1c). This network also can be viewed as the stacking of three types of polyhedron, namely a MOC, a truncated tetrahedron (T-Td), and a truncated octahedron (T-Oh) (Figure 2a). Despite the original MOC as a coordination molecule, the T-Td and T-Oh both use the $[GS_3]^{2-}$ tiles as faces, and they belong to a type of rarely observed supramolecular polyhedron that are constructed via mixed hydrogen bonds and coordination interactions. The cavities inside the three types of polyhedra are represented by the colored spheres, and their diameters are about 13 Å for the MOC (red), 14 Å for the T-Td (green) and 22 Å for the T-Oh (blue). Each MOC shares its eight triangular and six square faces with eight T-Td and six T-Oh motifs, respectively (Figure 2b). The void volume of network **1** is 57377 Å^3 per unit cell, which is ~71% of the total crystal volume as calculated by
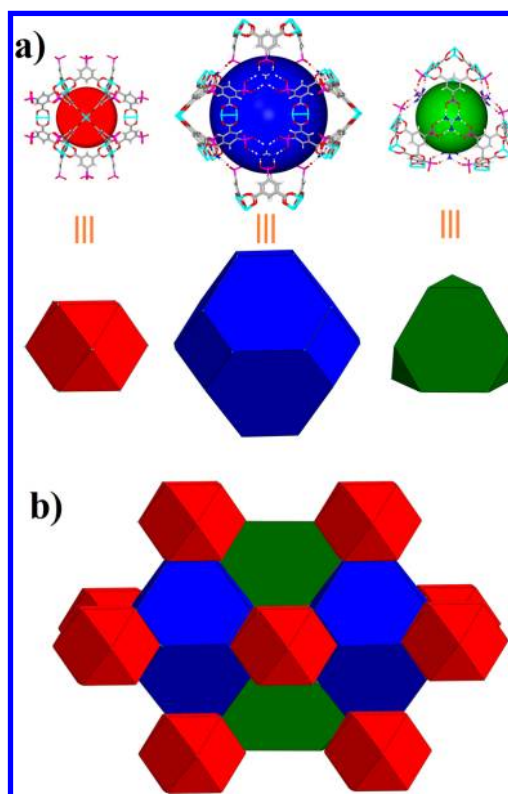

Figure 2. (a) Three types of polyhedra in the network: a MOC (red), a truncated octahedron (blue), and a truncated tetrahedron (green). (b) Their 3D packing in **1**.

PLATON. Although there have been many reported coordination polymers involving hydrogen bonds,[12] it is rarely observed that the network topology of a porous framework is rationally designed simultaneously relying on the steady H

bonding and coordination motifs. As far as we know, it also represents the first example of 3D H-bonding network based on hollow MOPs.

Phase purity of the bulky crystals was confirmed by the similarity between the experimental and simulated powder X-ray diffraction (PXRD) patterns (Figure S1 of the Supporting Information). In order to check the stability of the title compound, we placed **1** in air at room temperature for 2 days, and the experimental PXRD patterns of the dealt samples are also in good agreement with the simulated patterns generated from single-crystal diffraction data, thus indicating that **1** is rather stable under ambient conditions. Indeed, the crystals of **1** even retain transparency in air at ambient temperature after one week. Such stability is rarely observed in the crystals of discrete molecular polyhedron,[13] which is probably ascribed to relatively strong H bonding of GS moieties. Unfortunately, substitution of the DMF by volatile solvents, such as chloroform, dichloromethane, and acetone, and the subsequent removal of them lead to the loss of its crystallinity. A typical type II isotherm for N_2 sorption indicates that the desolvated framework is a nonporous material (Figure S9 of the Supporting Information).

Dye absorption experiments were performed to verify the accessibility of the large porosity of **1**. We had tried different kinds of dye molecules, including methyl orange, phenolphthalein, methyl red, crystal violet (CV), rhodamine 6G (R6), and tris(2,2′-bipyridyl)ruthenium [$Ru(bpy)_3^{2+}$]. The results demonstrated that only cation dye molecules such as CV, R6, and $Ru(bpy)_3^{2+}$ can enter the pores of **1** with the indication of changing colors (Figure 3, panels a−d), while there was no detectable adsorption toward other dyes. Because the framework of **1** is negatively charged and the free sodium and guanidinium cations occupy the cavities, it is reasonable to assume that the absorption process is accompanied with the
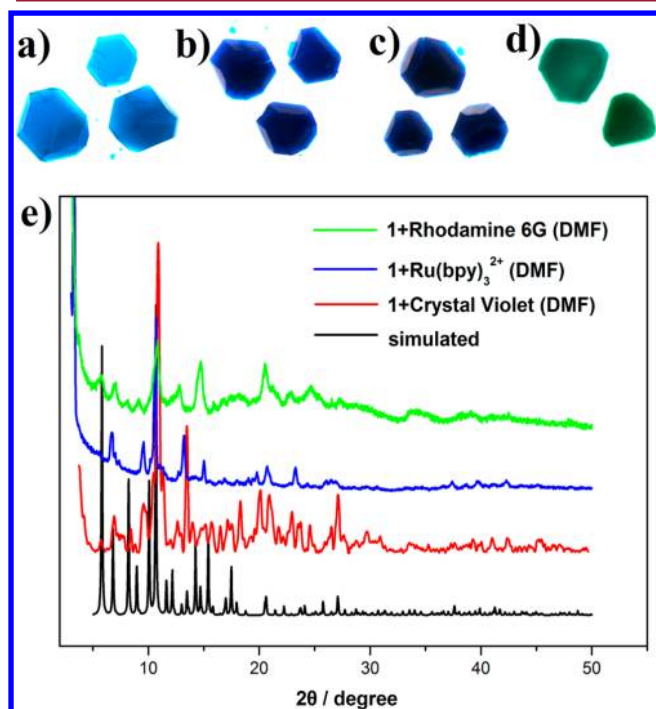
cation exchange. The data exhibit that a unit cell of **1** can absorb about one CV, 0.44 R6, and 4.57 $Ru(bpy)_3^{2+}$, which were estimated from the UV−visible, luminescence spectra or ICP-AES (Figure S3−S8 of the Supporting Information). PXRD analyses showed that the resulting solids possess the broadly similar patterns as the pristine **1** (Figure 3e), which indicates that the structural integrity and the architectures of these microporous materials are retained after absorption of the dye molecules.

In conclusion, we have demonstrated an interesting example of molecular tectonics strategy for design and construction of a sophisticated guanidinium−sulfonate network with nanoscopic pores, by use of the sulfonate-decorated MOCs with high symmetry and connectivity as tectons and metrically matched hydrogen bonds. The (3,24)-connected network topology can be predicted on the basis of MOCs as 24-connected nodes and H-bonding motifs as 3-connected nodes, which may be viewed as a successful topological mimic of the known metal−organic frameworks. In addition, the 3D H-bonding network displays good stability under ambient conditions and modest absorption of cationic dye. Currently, we are investigating the extension of this strategy to the design and formation of more porous H-bonding architectures using other hollow MOP tectons.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional figures, X-ray crystallographic information file (CIF), TGA and PXRD data, gases sorption data, and details of the UV−vis absorption and fluorescence emission spectra analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714. (b) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375. (c) Kole, G. K.; Vittal, J. J. *Chem. Soc. Rev.* **2013**, *42*, 1755−1775. (d) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 1650−1659. (e) Li, J. R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477−1504.
(2) (a) Wuest, J. D. *Chem. Commun. (Cambridge, U.K.)* **2005**, 5830−5837. (b) Fournier, J.-H.; Maris, T.; Wuest, J. D.; Guo, W.; Galoppini, E. *J. Am. Chem. Soc.* **2003**, *125*, 1002−1006. (c) Malek, N.; Maris, T.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 5910−5916. (d) Lie, S.; Maris, T.; Malveau, C.; Beaudoin, D.; Helzy, F.; Wuest, J. D. *Cryst. Growth Des.* **2013**, *13*, 1872−1877. (e) Duong, A.; Dubois,

Figure 3. Photographic images of crystals for (a) **1** and that after absorbing (b) crystal violet, (c) rhodamine 6G, and (d) $Ru(bpy)_3^{2+}$. (e) The PXRD patterns of **1** after absorption.

M.-A.; Maris, T.; Métivaud, V.; Yi, J.-H.; Nanci, A.; Rochefort, A.; Wuest, J. D. *J. Phys. Chem. C* **2011**, *115*, 12908−12919. (f) Duong, A.; Maris, T.; Wuest, J. D. *CrystEngComm* **2011**, *13*, 5571−5577.

(3) (a) Lin, M.-J.; Jouaiti, A.; Kyritsakas, N.; Hosseini, M. W. *CrystEngComm* **2011**, *13*, 776−778. (b) Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313−323. (c) Hosseini, M. W. *Coord. Chem. Rev.* **2003**, *240*, 157−166. (d) Larpent, P.; Jouaiti, A.; Kyritsakas, N.; Hosseini, M. W. *Chem. Commun. (Cambridge, U.K.)* **2013**, *49*, 4468−4470. (e) Lin, M.-J.; Jouaiti, A.; Kyritsakas, N.; Hosseini, M. W. *CrystEngComm* **2010**, *12*, 67−69. (f) Lin, M. J.; Jouaiti, A.; Grosshans, P.; Kyritsakas, N.; Hosseini, M. W. *Chem. Commun. (Cambridge, U.K.)* **2011**, *47*, 7635−7637. (g) Lin, M.-J.; Jouaiti, A.; Pocic, D.; Kyritsakas, N.; Planeix, J.-M.; Hosseini, M. W. *Chem. Commun. (Cambridge, U.K.)* **2010**, *46*, 112−114.

(4) (a) Zou, Y.; Park, M.; Hong, S.; Lah, M. S. *Chem. Commun. (Cambridge, U.K.)* **2008**, 2340−2342. (b) Shao, K.-Z.; Zhao, Y.-H.; Lan, Y.-Q.; Wang, X.-L.; Su, Z.-M.; Wang, R.-S. *CrystEngComm* **2011**, *13*, 889−896.

(5) (a) Helzy, F.; Maris, T.; Wuest, J. D. *Cryst. Growth Des.* **2008**, *8*, 1547−1553. (b) Maly, K. E.; Gagnon, E.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 4306−4322. (c) Zhou, H.; Dang, H.; Yi, J.-H.; Nanci, A.; Rochefort, A.; Wuest, J. D. *J. Am. Chem. Soc.* **2007**, *129*, 13774−13775.

(6) (a) Swift, J. A.; Pivovar, A. M.; Reynolds, A. M.; Ward, M. D. *J. Am. Chem. Soc.* **1998**, *120*, 5887−5894. (b) Horner, M. J.; Holman, K. T.; Ward, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 14640−14660. (c) Soegiarto, A. C.; Comotti, A.; Ward, M. D. *J. Am. Chem. Soc.* **2010**, *132*, 14603−14616.

(7) Liu, Y.; Hu, C.; Comotti, A.; Ward, M. D. *Science* **2011**, *333*, 436−440.

(8) (a) Perry, J. J.; Kravtsov, V. C.; Zaworotko, M. J.; Larsen, R. W. *Cryst. Growth Des.* **2011**, *11*, 3183−3189. (b) Furukawa, H.; Kim, J.; Plass, K. E.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 8398−8399. (c) Hamilton, T. D.; Papaefstathiou, G. S.; Friščić, T.; Bučar, D.-K.; MacGillivray, L. R. *J. Am. Chem. Soc.* **2008**, *130*, 14366−14367. (d) Zhao, D.; Tan, S.; Yuan, D.; Lu, W.; Rezenom, Y. H.; Jiang, H.; Wang, L.-Q.; Zhou, H.-C. *Adv. Mater.* **2011**, *23*, 90−93. (e) Chepelin, O.; Ujma, J.; Wu, X.; Slawin, A. M. Z.; Pitak, M. B.; Coles, S. J.; Michel, J.; Jones, A. C.; Barran, P. E.; Lusby, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 19334−19337.

(9) Li, J.-R.; Zhou, H.-C. *Nat. Chem.* **2010**, *2*, 893−898.

(10) (a) Zhao, D.; Yuan, D.; Sun, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 9186−9188. (b) Yan, Y.; Telepeni, I.; Yang, S.; Lin, X.; Kockelmann, W.; Dailly, A.; Blake, A. J.; Lewis, W.; Walker, G. S.; Allan, D. R.; Barnett, S. A.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2010**, *132*, 4092−4094. (c) Yan, Y.; Yang, S.; Blake, A. J.; Lewis, W.; Poirier, E.; Barnett, S. A.; Champness, N. R.; Schröder, M. *Chem. Commun. (Cambridge, U.K.)* **2011**, *47*, 9995−9997. (d) Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 748−751. (e) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5357−5361. (f) Zheng, B.; Yang, Z.; Bai, J.; Li, Y.; Li, S. *Chem. Commun. (Cambridge, U.K.)* **2012**, *48*, 7025−7027. (g) Yuan, D.; Zhao, D.; Zhou, H.-C. *Inorg. Chem.* **2011**, *50*, 10528−10530. (h) Yan, Y.; Blake, A. J.; Lewis, W.; Barnett, S. A.; Dailly, A.; Champness, N. R.; Schröder, M. *Chem.—Eur. J.* **2011**, *17*, 11162−11170. (i) Farha, O. K.; Eryazici, I.; Jeong, N. C.; Hauser, B. G.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Nguyen, S. T.; Yazaydın, A. Ö.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 15016−15021. (j) Wang, H.-N.; Meng, X.; Yang, G.-S.; Wang, X.-L.; Shao, K.-Z.; Su, Z.-M.; Wang, C.-G. *Chem. Commun. (Cambridge, U.K.)* **2011**, *47*, 7128−7130.

(11) Crystal data for **1**: $C_{426}H_{710}Cu_{24}N_{110}Na_{12}O_{266}S_{24}$, M_r = 14199.32, cubic, space group $Fm\bar{3}m$, a = 43.0209 (2) Å, V = 79623.0 (6) Å^3, Z = 4, D_c = 1.185 g cm^{-3}, F_{000} = 29504, Siemens SMART APEX II CCD, Cu Kα radiation, λ = 1.5418 Å, T = 110 (2) K, $2\theta_{max}$ = 115.2°, 45898 reflections collected, 2705 unique (R_{int} = 0.0489). Final GooF = 1.119, $R1$ = 0.0800, $wR2$ = 0.2518. CCDC: 945013, which contains 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.

(12) (a) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109−119. (b) Uemura, K.; Kitagawa, S.; Kondo, M.; Fukui, K.; Kitaura, R.; Chang, H.-C.; Mizutani, T. *Chem.—Eur. J.* **2002**, *8*, 3586−3600. (c) Uemura, K.; Kitagawa, S.; Fukui, K.; Saito, K. *J. Am. Chem. Soc.* **2004**, *126*, 3817−3828. (d) Uemura, K.; Saito, K.; Kitagawa, S.; Kita, H. *J. Am. Chem. Soc.* **2006**, *128*, 16122−16130.

(13) (a) Prakash, M. J.; Zou, Y.; Hong, S.; Park, M.; Bui, M.-P. N.; Seong, G. H.; Lah, M. S. *Inorg. Chem.* **2009**, *48*, 1281−1283.