

# Octadecanuclear Macrocycles and Nonanuclear Bowl-Shaped Structures Based on Two Analogous Pyridyl-Substituted Imidazole-4,5-dicarboxylate Ligands

Ying-Ying Zhang, Xu-Yu Shen, Lin-Hong Weng, and Guo-Xin Jin\*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

**S** Supporting Information

**ABSTRACT:** Two types of unprecedented Cp<sup>\*</sup>Rh-based (Cp<sup>\*</sup> = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) complexes, two octadecanuclear macrocycles, and a nonanuclear bowl-shaped complex have been synthesized from two analogous pyridyl-functionalized imidazole-4,5-dicarboxylate ligands, 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylate ligand and 2-(pyridin-3-yl)-1*H*-imidazole-4,5-dicarboxylate ligand, respectively.

The self-assembly of metallasupramolecular macrocycles has attracted increasing attention in the past few decades owing to not only their potential applications<sup>1</sup> but also their fascinating structures.<sup>2</sup> In the reported metallacycles, the vast majority of metal–organic coordination macrocycles prepared to date are binuclear, trinuclear, tetranuclear, or hexanuclear.<sup>3</sup> Metal macrocycles of large ring systems with higher nuclearity are currently relatively few,<sup>4</sup> especially for organometallic rings. Higher nuclearity macrocycles are clearly unfavored reactions products, making them challenging to design and assemble selectively. In such an assembly process, it is crucial to select multifunctional organic ligands containing appropriate coordination sites that are linked by a spacer with specific positional orientation if one is to construct a diversity of polynuclear and macrocyclic architectures.<sup>5</sup>

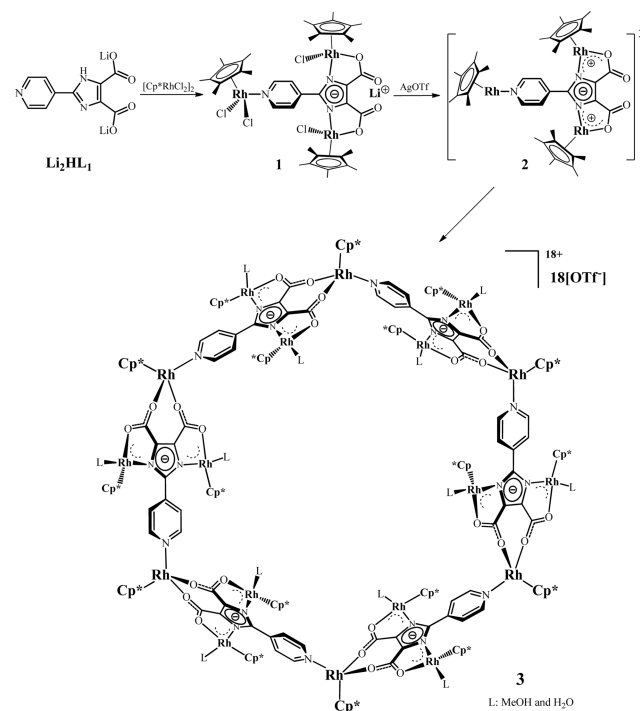
Imidazole-4,5-dicarboxylic acid (H<sub>3</sub>IDC), a multidentate rigid ligand, has been widely investigated in the construction of porous and helical complexes because of its versatile coordination modes and potential hydrogen-bonding donors and acceptors.<sup>6</sup> This system has been functionalized recently by introducing different substituents at the 2-position of the imidazole ring, such as alkyl (Me, Et, and Pr), phenyl, and others.<sup>7</sup> Within this family of ligands, pyridyl-substituted ligands<sup>8</sup> 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid (H<sub>3</sub>L<sub>1</sub>) and 2-(pyridin-3-yl)-1*H*-imidazole-4,5-dicarboxylic acid (H<sub>3</sub>L<sub>2</sub>), which possess seven potential donor atoms, are of great interest because the H<sub>3</sub>IDC groups and pyridine rings can rotate around the C–C bond to meet the different coordination requirements of metal ions in the assembly process. However, there are so many factors governing the final structure in systems with multiligands or multidentate ligands<sup>9</sup> that it is common for the products to be significantly different from those intended.<sup>10</sup>

Supramolecular chemistry based on Cp<sup>\*</sup>Rh units has grown rapidly since the first report of the organometallic Cp<sup>\*</sup>Rh fragment being used as a building block for the construction of

metallasupramolecular frameworks.<sup>11</sup> In this Communication, we report the first examples of 60-membered macrocyclic structures, having 18 half-sandwich Cp<sup>\*</sup>Rh cores based on 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylate ligand, while a nonanuclear bowl-shaped Cp<sup>\*</sup>Rh complex was unexpectedly obtained when 2-(pyridin-3-yl)-1*H*-imidazole-4,5-dicarboxylate was used as the organic linker.

The metallamacrocycle **3** was obtained through a two-step reaction. As shown in Scheme 1, the dilithium salt of H<sub>3</sub>L<sub>1</sub>

**Scheme 1. Synthetic Route to Macrocycle 3**



(Li<sub>2</sub>HL<sub>1</sub>) was added to a solution of [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> in MeOH. The reaction mixture was then stirred with silver salt AgOTf (Tf = O<sub>2</sub>SCF<sub>3</sub>) for 2 h to yield (83%) orange solid **3**, which is soluble in water and most common polar organic solvents.

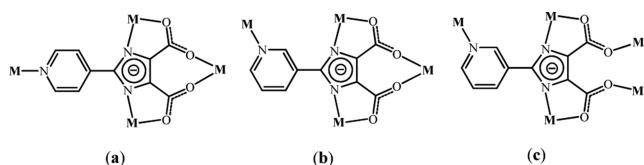
**Received:** September 19, 2014

**Published:** October 20, 2014

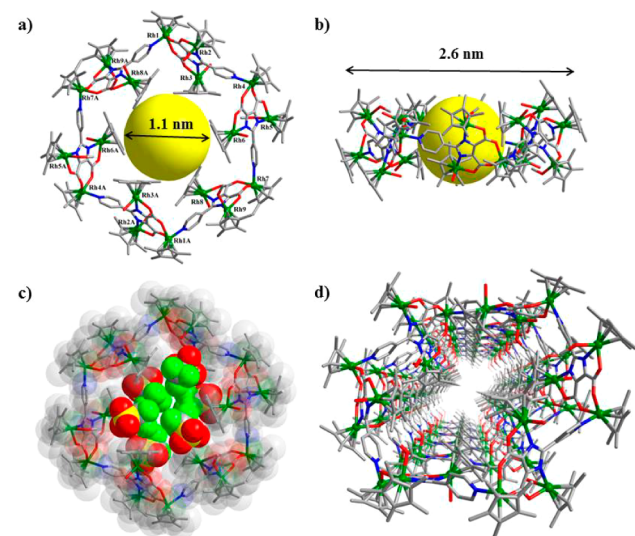
The crystal structure of **1** could not be obtained due to its poor solubility, preventing growth of single crystals suitable for X-ray diffraction analysis; however, the coordination mode can be supported by the structure of the intermediate iridium complex **4**, which formed by the reaction of  $K_2HL_1$  and  $[(Cp^*IrCl_2)_2]$  after the removal of all of the chloride ligands (Scheme S1). As expected, three iridium centers bind to one ligand through the pyridyl N atom and two N<sup>^</sup>O chelating units, except for the coordination of four acetonitrile molecules, respectively (Figure S1). The construction of macrocycle **3** can thus be assumed to proceed through the zwitterionic<sup>12</sup> trinuclear intermediate, similar to the construction of complex **2**.

We speculated that macrocycles may be prepared if the trinuclear building blocks **1** were linked end-to-end after chloride abstraction by AgOTf, and each ligand adopts the coordination mode as shown in Scheme 2a. Gratifyingly, macrocycles **3** indeed

### Scheme 2. Coordination Modes of $L_1^{3-}$ and $L_2^{3-}$



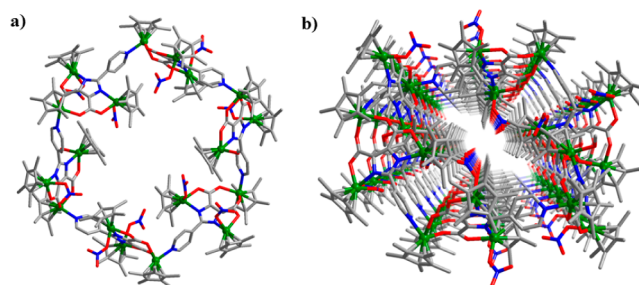
formed, and we obtained single crystals suitable for X-ray diffraction analysis. The cation of complex **3** was confirmed to be a half-sandwich rhodium octadecanuclear metallamacrocycle consisting of 18 Cp<sup>\*</sup>Rh units, six  $L_1^{3-}$  ligands, and 12 coordinated solvent molecules (methanol and water) with an inner diameter of ca. 1.1 nm and an outer diameter of ca. 2.6 nm (Figure 1). There are two distinct Cp<sup>\*</sup>Rh environments in this structure according to the coordination modes of the metal centers. One group is composed of six Cp<sup>\*</sup>Rh units that are ligated by two carboxylate oxygen atoms and one pyridyl



**Figure 1.** (a) Top view and (b) side view of the cationic portion for **3**. The yellow sphere in the center represents the cavity of **3**. (c) Space-filling representation of the framework for **3** encapsulating six triflate anions. (d) Stacking of the molecules in crystals of **3** viewed along the *a* axis. All hydrogen atoms and non-coordinated solvent molecules were omitted for clarity. Color code: N, blue; O, red; C, gray; F, light green; S, yellow; Rh, green.

nitrogen atom from two separated  $L_1^{3-}$  ligands. The other 12 Cp<sup>\*</sup>Rh units are connected by the  $L_1^{3-}$  ligands in a bis-N,O-chelating fashion, with oxygen atoms from methanol or water molecules filling the last coordination site of each of these metal cores. The six Rh atoms in the former group participate in the formation of the 60-membered ring, while the other 12 Rh atoms in the latter group can be seen as accessories of the ring. From the perspective of the ligand, each ligand combines with three rhodium atoms to form  $[(Cp^*Rh)_3L_1]^{3+}$  as the basic building unit, and six of these trinuclear units join together to generate octadecanuclear macrocycle **3**. A remarkable feature of the structure is that the macrocycle encapsulates six triflate anions (Figure 1c) through C–H···O interactions between the S–O units of OTf<sup>−</sup> and the hydrogen atoms of the methyl groups in the Cp<sup>\*</sup> rings or of the pyridyl groups in the ligand  $L_1^{3-}$  (Figure S2). Moreover, a chain of weak hydrogen-bonding interactions between the cation framework, solvent molecules, and triflate anions bridge two adjacent macrocycles to create nanochannel architectures along the crystallographic *a*-axis (Figure 1d). All of these weak interactions further stabilize the host structures.

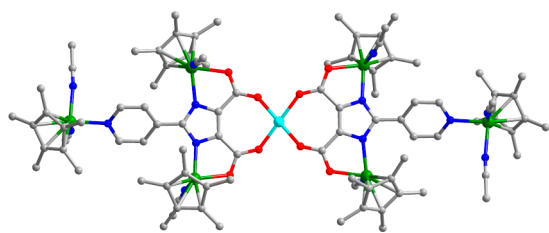
To explore the influence of different anions in this system, we added a range of sodium salts, such as NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>, to the reaction mixture after the reaction was finished and found that Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> have no influence on the formation of the architecture of the final octadecanuclear macrocycle. One small difference was found when NaNO<sub>3</sub> was added to the mixture, in that nitrate was found to be coordinated to the Rh atoms instead of partial solvent molecules in complex **3**, generating the similar macrocycle **3'** (Figure 2).



**Figure 2.** (a) Single-crystal X-ray structure of the cationic portion of **3'**. (b) Stacking of the molecules in crystals of **3'** viewed along the *a* axis. All hydrogen atoms, non-coordinated solvent molecules, and anions were omitted for clarity. Color code: N, blue; O, red; C, gray; Rh, green.

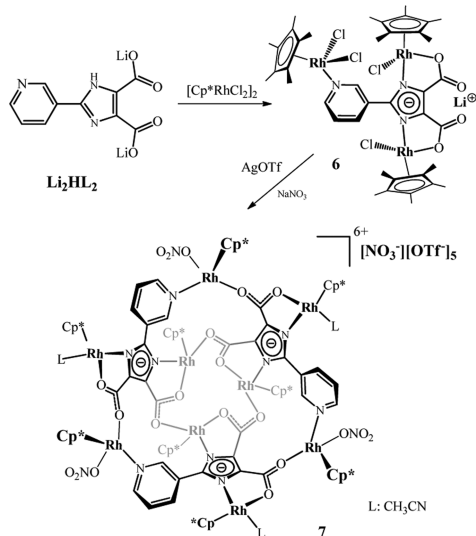
We attempted to introduce another transition metal salt into the system in order to induce similar complexation of the heterometal to the two remaining carboxyl groups. When zinc(II) ions were chosen as the second metal centers, the mixed-metal coordination complex salt **5**, having a Rh<sub>3</sub>ZnRh<sub>3</sub> heptanuclear core, was obtained after halide abstraction (Scheme S2). The coordination mode of the ligand in **5** is the same as that of complex **4**. As shown in Figure 3, zinc ions bridge two trinuclear building blocks together by coordinating to two oxygen atoms of each  $L_1^{3-}$  unit. The two 7-membered rings bridged by the zinc atom are non-coplanar, and the distance between the two planes formed by the imidazole-4,5-dicarboxylate groups is 1.617 Å.

With the intent of exploring the scope of the synthetic approach and changing the cavity size of the macrocycles, the similar multidentate ligand, dilithium salt of  $H_3L_2$  ( $Li_2HL_2$ ) was introduced into the assembled system under the same conditions (Scheme 3). We assumed that similar macrocyclic structures



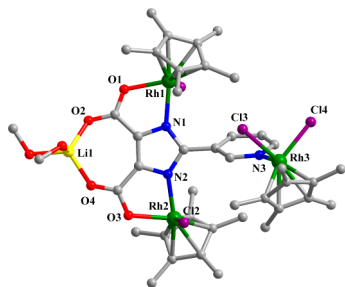
**Figure 3.** Single-crystal X-ray structure of the theme framework of **5**. All hydrogen atoms, solvent molecules, and other ions were omitted for clarity. Color code: N, blue; O, red; C, gray; Zn, turquoise; Rh, green.

### Scheme 3. Synthetic Route to Complex **7**



would be obtained if the deprotonated ligand  $L_2^{3-}$  adopts the same coordination mode as  $L_1^{3-}$  (Scheme 2b). Despite the observation of two  $^1\text{H}$  NMR singlets at 1.30 and 1.54 ppm due to two  $\text{Cp}^*$  environments in a ratio of 2:1 (similar to that of **3**), complex **7** was instead confirmed to be the product (yield: 62%).

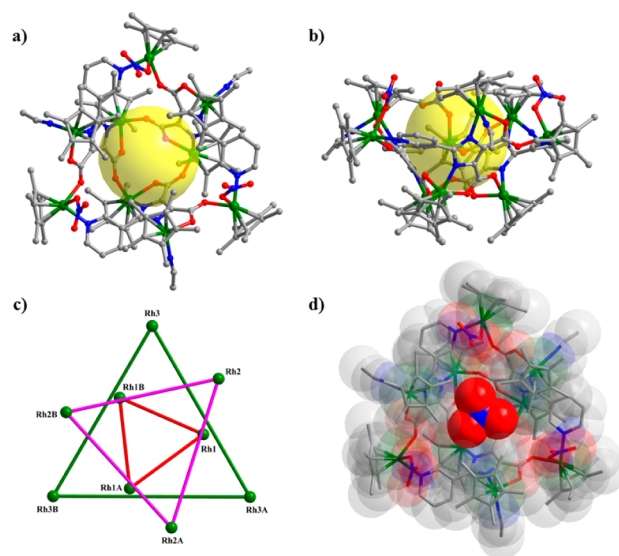
In this process, we initially sought to obtain building blocks with three Rh cores. Single crystals of this building block (**6**) suitable for X-ray diffraction analysis were obtained due to their much better solubility than those of the initial product **1** in the above synthesis of **3**. The molecular structure of **6** thereby allowed us to determine the exact coordination mode of the ligand  $L_2^{3-}$ . Similar to that of **1**, each ligand coordinates to three rhodium atoms through the pyridyl N atom and two N $\backslash$ O chelating units, respectively (Figure 4). The remaining coordination sites of the metal centers are all occupied by chlorine atoms. At this step, the framework is negatively charged;



**Figure 4.** Single-crystal X-ray structure of **6**. All hydrogen atoms were omitted for clarity.

thus, a neutralizing lithium ion is bound to the oxygen atoms of the carboxylate, further confirming **6** to be analogous to **1**.

Similarly, after abstraction of the chlorine atoms from the rhodium centers by  $\text{AgOTf}$ , the “bowl-shaped”  $^{13}$  complex **7** was obtained in the presence of sodium nitrate rather than a metallamacrocycle. Single-crystal X-ray analysis revealed that **7** is a bowl-shaped hexacation with nine half-sandwich rhodium fragments and three 2-(pyridin-3-yl)-1*H*-imidazole-4,5-dicarboxylate ligands, vastly different from **3** and the structure we expected. As shown in Figure 5, the nine Rh atoms can be



**Figure 5.** X-ray crystal structures of the cationic portion of **7**. (a) Top view and (b) side view of the framework of **7**. The yellow sphere represents the cavity of **7**. Triflate anions and non-coordinated solvent molecules, as well as hydrogen atoms are omitted for clarity. (c) The relative size of the three equilateral triangles formed by the Rh atoms of each level. (d) Space-filling representation of the framework of **7** encapsulating one nitrate anion. Color code: N, blue; O, red; C, gray; Rh, green.

obviously divided into three groups according to the coordination modes of the metal centers, each group being composed of three Rh atoms which form equilateral triangles (Figure 5c). Every  $\text{Cp}^*\text{Rh}$  fragment in the bottom triangle (Rh1–Rh1A–Rh1B) is coordinated to one imidazolite nitrogen atom and one carboxylate oxygen atom from the same  $L_2^{3-}$  unit and one carboxylate oxygen atom from the adjacent ligand  $L_2^{3-}$  (symmetry codes: A,  $-x + y, 1 - x, z$ ; B,  $1 - y, 1 + x - y, z$ ). However, the three Rh atoms in the middle layer (Rh3–Rh3A–Rh3B) still adopt three-legged piano-stool geometries, each completed by one nitrate oxygen atom, one pyridyl nitrogen atom and one carboxylate oxygen atom. The coordination environment of each Rh unit of the upper layer (Rh2–Rh2A–Rh2B), in contrast, is completed by one acetonitrile molecule and a chelating N $\backslash$ O site from an imidazole carboxylate. The edge lengths of the bottom triangle are 5.458 Å, while those of the middle layer are 11.780 Å and those of the top layer 9.339 Å (Rh...Rh separation). Notably, the cavity size of **7** is much smaller than that of **3**, such that there is only one nitrate anion hosted in the cavity through C–H...O interactions between the N–O units of  $\text{NO}_3^-$  and the hydrogen atoms of the methyl groups in the  $\text{Cp}^*$  rings (Figure S3).

In summary, two unprecedented octadecanuclear macrocyclic complexes and a Rh–Zn heterometallic complex have been

designed and synthesized from the alkali salt of 2-(pyridin-4-yl)-1H-imidazole-4,5-dicarboxylic acid. Meanwhile, an unexpected bowl-shaped nonanuclear complex was obtained by the use of a similar dilithium salt of 2-(pyridin-3-yl)-1H-imidazole-4,5-dicarboxylic acid. The macrocycles are the highest nuclearity examples known for half-sandwich macrocyclic compounds, and they have nanosized cavities that can encapsulate small molecules and anions such as methanol, triflate anions, and others. The bowl-shaped structure is the first semi-open nonanuclear structure based on Cp\**Rh* building blocks. This work shows again that pyridyl-substituted imidazole-4,5-dicarboxylic acids can be used as versatile organic linkers in the construction of both infinite architectures and surprisingly large discrete structures.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, crystallographic data, and CIF files for complexes 3, 3', 4, 5, 6, and 7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

gxjin@fudan.edu.cn

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (91122017, 21374019), the Shanghai Science and Technology Committee (13JC1400600, 13DZ2275200), and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1117).

## ■ REFERENCES

- (1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (b) Severin, K. *Coord. Chem. Rev.* **2003**, *245*, 3–10. (c) Würthner, F.; You, C.-C.; Saha-Möllner, C. R. *Chem. Soc. Rev.* **2004**, *33*, 133–146. (d) Severin, K. *Chem. Commun.* **2006**, 3859–3867. (e) Lee, S. J.; Lin, W. *Acc. Chem. Res.* **2008**, *41*, 521–537. (f) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810–6918. (g) Cook, T. R.; Vajpayee, V.; Lee, M. H.; Stang, P. J.; Chi, K.-W. *Acc. Chem. Res.* **2013**, *46*, 2464–2474.
- (2) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518. (b) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (c) You, C.-C.; Dobrawa, R.; Saha-Möllner, C. R.; Würthner, F. *Top. Curr. Chem.* **2005**, *258*, 39–82. (d) Li, S. S.; Northrop, B. H.; Yuan, Q. H.; Wan, L. J.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 249–259. (e) Northrop, B. H.; Zheng, Y. R.; Chi, K.-W.; Stang, P. J. *Acc. Chem. Res.* **2009**, *42*, 1554–1563. (f) Conrady, F. M.; Fröhlich, R.; Brinke, C. S.; Pape, T.; Hahn, F. E. *J. Am. Chem. Soc.* **2011**, *133*, 11496–11499. (g) Vajpayee, V.; Song, Y. H.; Cook, T. R.; Kim, H.; Lee, Y.; Stang, P. J.; Chi, K.-W. *J. Am. Chem. Soc.* **2011**, *133*, 19646–19649. (h) Huang, S.-L.; Lin, Y.-J.; Hor, T. S. A.; Jin, G.-X. *J. Am. Chem. Soc.* **2013**, *135*, 8125–8128.
- (3) (a) Fujita, M.; Aoyagi, M.; Ogura, K. *Inorg. Chim. Acta* **1996**, *246*, 53–57. (b) Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *Chem. Commun.* **1996**, 1535–1536. (c) Coronado, E.; Galan-Mascaros, J. R.; Gaviña, P.; Martí-Gastaldo, C.; Romero, F. M.; Tatay, S. *Inorg. Chem.* **2008**, *47*, 5197–5203. (d) Bar, A. K.; Chakrabarty, R.; Chi, K.-W.; Batten, S. R.; Mukherjee, P. S. *Dalton Trans.* **2009**, 3222–3229. (e) Wang, G.-L.; Lin, Y.-J.; Jin, G.-X. *Chem.—Eur. J.* **2011**, *17*, 5578–5587.
- (4) (a) Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Lippard, S. J.; Caneschi, A.; Cornia, A.; Abbati, G. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2774–2776. (b) Müller, A.; Serain, C. *Acc. Chem. Res.* **2000**, *33*, 2. (c) Liu, S. X.; Lin, S.; Lin, B. Z.; Lin, C. C.; Huang, J. Q. *Angew. Chem.,*

*Int. Ed.* **2001**, *40*, 1084–1087. (d) Huang, X. C.; Zhang, J. P.; Chen, X. M. *J. Am. Chem. Soc.* **2004**, *126*, 13218–13219. (e) Jin, J.; Wang, W.; Liu, Y.; Hou, H.; Fan, Y. *Chem. Commun.* **2011**, *47*, 7461–7463.

(5) (a) Wang, R.-H.; Zhou, Y.-F.; Sun, Y.-Q.; Yuan, D.-Q.; Han, L.; Lou, B.-Y.; Wu, B.-L.; Hong, M.-C. *Cryst. Growth Des.* **2005**, *5*, 251–256. (b) Hu, Y.-W.; Li, G.-H.; Liu, X.-M.; Hu, B.; Bi, M.-H.; Gao, L.; Shi, Z.; Feng, S.-H. *CrystEngComm* **2008**, *10*, 888–893.

(6) (a) Majji, T. K.; Mostafa, G.; Chang, H. C.; Kitagawa, S. *Chem. Commun.* **2005**, 2436–2438. (b) Lu, W.-G.; Su, C.-Y.; Lu, T.-B.; Jiang, L.; Chen, J.-M. *J. Am. Chem. Soc.* **2006**, *128*, 34–35. (c) Sun, Y.-Q.; Zhang, J.; Yang, G.-Y. *Chem. Commun.* **2006**, 4700–4702. (d) Liu, Y. L.; Kravtsov, V. C.; Larsena, R.; Eddaoudi, M. *Chem. Commun.* **2006**, 1488–1490. (e) Liu, Y. L.; Kravtsov, V. C.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 8446–8449. (f) Nouar, F.; Eckert, J.; Eubank, J. F.; Forster, P.; Eddaoudi, M. *J. Am. Chem. Soc.* **2009**, *131*, 2864–2870. (g) Gu, Z. G.; Cui, Y. P.; Fang, H. C.; Zhou, Z. Y.; Thallapally, P. K.; Tian, J.; Liu, J.; Exarhos, G. J. *Chem. Commun.* **2010**, 46, 5373–5375.

(7) (a) Wang, S.; Zhang, L.-R.; Li, G.-H.; Huo, Q.-S.; Liu, Y.-L. *CrystEngComm* **2008**, *10*, 1662–1666. (b) Zhang, F.-W.; Li, Z.-F.; Ge, T.-Z.; Yao, H.-C.; Li, G.; Lu, H.-J.; Zhu, Y.-Y. *Inorg. Chem.* **2010**, *49*, 3776–3788. (c) Feng, X.; Zhao, J. S.; Liu, B.; Wang, L. Y.; Ng, S.; Zhang, G.; Wang, J. E.; Shi, X. E.; Liu, Y. Y. *Cryst. Growth Des.* **2010**, *10*, 1399–1408. (d) Wang, W.-Y.; Niu, X.-L.; Gao, Y.-C.; Zhu, Y.-Y.; Li, G.; Lu, H.-J.; Tang, M.-S. *Cryst. Growth Des.* **2010**, *10*, 4050–4059. (e) Feng, X.; Wang, L.-Y.; Zhao, J.-S.; Wang, J.-G.; Weng, N.-S.; Liu, B.; Shi, X.-G. *CrystEngComm* **2010**, *12*, 774–783. (f) Zheng, S.-R.; Cai, S.-L.; Pan, M.; Fan, J.; Xiao, T.-T.; Zhang, W.-G. *CrystEngComm* **2011**, *13*, 883–888.

(8) (a) Li, X.; Wu, B.-L.; Niu, C.-Y.; Niu, Y.-Y.; Zhang, H.-Y. *Cryst. Growth Des.* **2009**, *9*, 3423–3431. (b) Jing, X. M.; Zhang, L. R.; Ma, T. L.; Li, G. H.; Yu, Y.; Huo, Q. S.; Eddaoudi, M.; Liu, Y. L. *Cryst. Growth Des.* **2010**, *10*, 492–494. (c) Jing, X. M.; Meng, H.; Li, G. H.; Yu, Y.; Huo, Q. S.; Eddaoudi, M.; Liu, Y. L. *Cryst. Growth Des.* **2010**, *10*, 3489–3495.

(9) (a) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518. (b) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, No. 1230444. (c) Li, M.; Li, D.; O’Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2014**, *114*, 1343–1370.

(10) (a) Jansen, M.; Schön, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 3406–3412. (b) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400–1417. (c) Férey, G. *Dalton Trans.* **2009**, 4400–4415. (d) Zhao, J.-P.; Zhao, R.; Song, W.-C.; Yang, Q.; Liu, F.-C.; Bu, X.-H. *Cryst. Growth Des.* **2013**, *13*, 437–439.

(11) Klausmeyer, K. K.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1694–1696.

(12) (a) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3603–3606. (b) Boardman, B. M.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1597–1606. (c) Stradiotto, M.; Hesp, K. D.; Lundgren, R. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 494–512. (d) Boone, M. P.; Stephan, D. W. *J. Am. Chem. Soc.* **2013**, *135*, 8508–8511. (e) Kolychev, E. L.; Kronig, S.; Brandhorst, K.; Freytag, M.; Jones, P. G.; Tamm, M. *J. Am. Chem. Soc.* **2013**, *135*, 12448–12459.

(13) (a) Karet, G. B.; Sun, Z.; Heinrich, D. D.; McCusker, J. K.; Folting, K.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1996**, *35*, 6450–6460. (b) Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 5248–5250. (c) Sahoo, D.; Suriyanarayanan, R.; Chandrasekhar, V. *Dalton Trans.* **2014**, 43, 10898–10909.