

# Metal–organic polyhedra constructed from dinuclear ruthenium paddlewheels<sup>☆</sup>

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## ABSTRACT

Reactions of  $\text{Ru}_2^{n+}$  [ $n = 4$  for  $\text{Ru}_2(\text{OAc})_4$  and  $n = 5$  for  $\text{Ru}_2(\text{OAc})_4\text{Cl}$ ] with  $\text{H}_2\text{CDC}$  (9H-3,6-carbazoledicarboxylic acid),  $\text{H}_2\text{BBDC}$  (5-tert-butyl-1,3-benzenedicarboxylic acid) and  $\text{H}_2\text{BDC}$  (1,3-benzenedicarboxylic acid) were conducted in inert atmospheres under solvothermal conditions in a sealed tube. Two octahedral cages,  $[\text{Ru}_2(\text{CDC})_2\text{Cl}]_6$ , **1** and  $[\text{Ru}_2(\text{CDC})_2]_6$ , **2** were obtained when starting from  $\text{Ru}_2^{n+}$  with CDC, and two cuboctahedral cages,  $[\text{Ru}_2(\text{BBDC})_2\text{Cl}]_{12}$ , **3** and  $[\text{Ru}_2(\text{BDC})_2]_{12}$ , **4** were yielded when starting from  $\text{Ru}_2^{n+}$  with BDC based linkers. Structures of these MOPs were characterized by single crystal X-ray analyses. The resulted MOPs have shown redox activity and magnetic properties similar to their parent metal complexes.

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## 1. Introduction

Metal–organic frameworks (MOFs) have garnered significant interest and growth over the past decade [1]. Owing to their high ratio of surface area to mass, frameworks that possess permanent porosity have been prepared and characterized for use as storage media for fuels such as hydrogen and methane [2], as well as small molecule separations [3] and sequestration of carbon dioxide [4]. Additional applications have been suggested or investigated for these porous frameworks, including drug delivery [5], use as sensors [6], or as heterogeneous catalysts [7]. However, these fields remain far behind gas storage in terms of effort and development. For most of these potential applications, open metal sites have been proved to be beneficial for the process, particularly for hydrogen storage and chemical reactions that happen on Secondary Building Units (SBUs) [8]. These sites can most easily be achieved by choosing suitable linkers and SBUs, such as isophthalate-based linkers and dinuclear paddlewheel SBUs, which will direct the open metal sites toward voids in the framework. Secondly, the metal must be capable of participating in the desired reaction. In other words, the metal serves as the catalytic active center for the transformation of small molecules, such as in the recent report

of ethanol generation from ethane by the iron(II) atoms in Fe-MOF-74 [9]. The redox active metal centers could act as a Lewis acid or base, or undergo a spin transition in response to certain stimuli to induce the catalytic transformation.

Toward these goals, our laboratory has been working on the process of design and construction of metal–organic polyhedra (MOPs) [10] and sequentially converting them to MOFs [11]. This allows the pre-selection of structural nodes that fulfill the above mentioned requirements. The first generation of MOPs was based on the  $\text{M}_2\text{L}_4$  paddlewheel structure, with  $\text{M} = \text{Mo}$  and  $\text{Cu}$  [12]. The ligands used were isophthalate (BDC), 5-(tert-butyl)isophthalate (BBDC), and 9H-carbazole-3,6-dicarboxylate (CDC). In the case of molybdenum, quadruply bonded Mo–Mo paddlewheel nodes were used to construct a series of cages through Ligand-Angle-Driven Assembly [10b]. Cotton and Chisholm have pioneered the synthesis of metal–metal bonded dimers, including multiple bonded ones, and introduction of metal–metal bonded clusters into molecular assemblies [13]. Others have prepared MOPs using  $\text{Cu}_2$ ,  $\text{Zn}_2$ ,  $\text{Pt}$  and  $\text{Pd}$  as the metal building block [14]. In these cases, potential reactivity at the metal sites is limited due to the inertness of these metal centers.

Dinuclear ruthenium compounds  $\text{Ru}_2^{n+}$  with oxidation states ranging from +4 to +6 have been extensively studied, with different bridging ligands such as carboxylates, formamidates, and guanidates [15]. The redox active Ru–Ru cores have been well explored as catalysts for small molecule activations. In particular,  $\text{Ru}_2^{4+}$  carboxylates have shown catalytic activity for the hydrogenation of alkenes and alkynes, as well as the cyclopropanation of alkenes

<sup>☆</sup> Dedicated to the 50th anniversary of the publication in Science of the paper by F.A. Cotton describing the quadruple bond.

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[16]. As such, MOPs based on  $\text{Ru}_2^{n+}$  paddlewheels represent a great family of candidate for the formation of MOFs with catalytically active sites.

Herein, we have investigated the reaction of  $\text{Ru}_2^{n+}$  paddlewheel clusters with ditopic BDC/CDC based linkers. Two octahedral cages were obtained when starting from  $\text{Ru}_2^{n+}$  with CDC, and two cuboctahedral cages were constructed by reacting  $\text{Ru}_2^{n+}$  with BDC based linkers. The resulting MOPs show interesting redox activity and magnetic properties. Moreover, the oxidation states of  $\text{Ru}_2^{n+}$  show insignificant impact on the overall structure of MOPs, which have created a new horizon for constructing electro-active and magnetic MOFs as the framework will not suffer from dramatic changes when the redox reactions take place on open metal centers.

## 2. Results and discussion

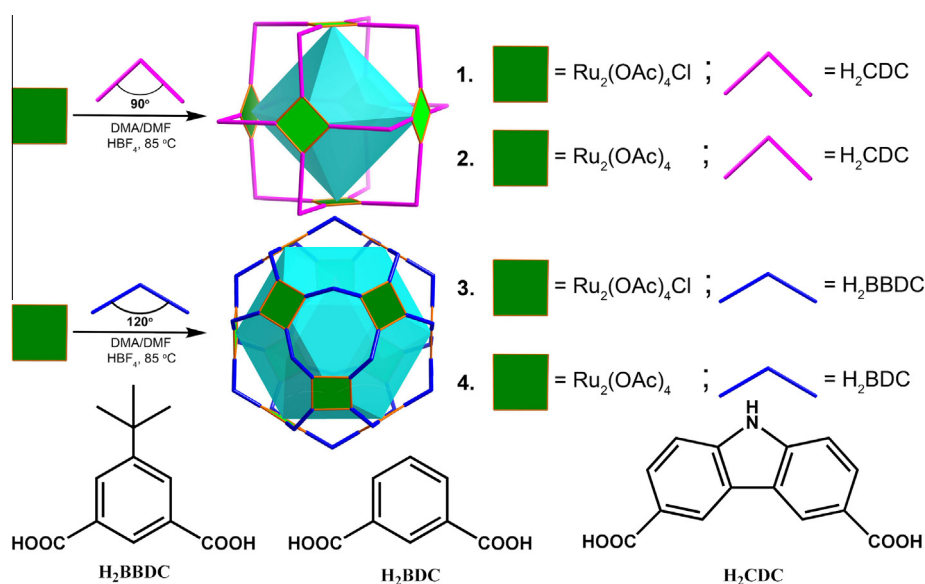
The general synthesis of Ru-MOPs follows a typical solvothermal process. The dinuclear metal paddlewheel precursor ( $\text{Ru}_2(\text{OAc})_4\text{Cl}$  for **1** and **3**,  $\text{Ru}_2(\text{OAc})_4$  for **2** and **4**) and the neutral carboxylic acid were placed in a glass tube along with approximately 1.5 mL of solvent, as illustrated in Scheme 1. In the case of **1** and **3**, one drop of  $\text{HBF}_4$  was added to accelerate the displacement of the otherwise kinetically inert acetate ligands from the dinuclear metal precursor [17].

The  $90^\circ$  angle of the CDC ligand causes the structures of compounds **1** and **2** to form an idealized octahedron, with the six paddlewheel centers as the vertices and the twelve linkers forming the edges, as shown in Fig. 1. The average Ru–Ru bond length in **1** is 2.2694 Å, shorter than that of 2.3259 Å in **2**, which is mainly due to the addition of an electron to the  $\delta^*$  orbital of the  $\text{Ru}_2^{4+}$  centers in **2** [18]. Compound **1** is refined as a 6+ cation, as the counter-ions ( $\text{Cl}^-$  or  $\text{BF}_4^-$ ), which are highly disordered, could not be located by residual electron density analysis. The anions are assumed to be disordered at positions both inside and outside the polyhedral cage. For each paddlewheel, the coordinating atom at the inner axial position is refined as oxygen, which is assumed to be from a coordinating DMF molecule. The exterior coordination sites are occupied by oxygen atoms from DMF molecules. For compound **2**, both the inner and exterior sites for each paddlewheel are refined as oxygen atoms, due to the disorder of the solvent molecules (see ESI for details).

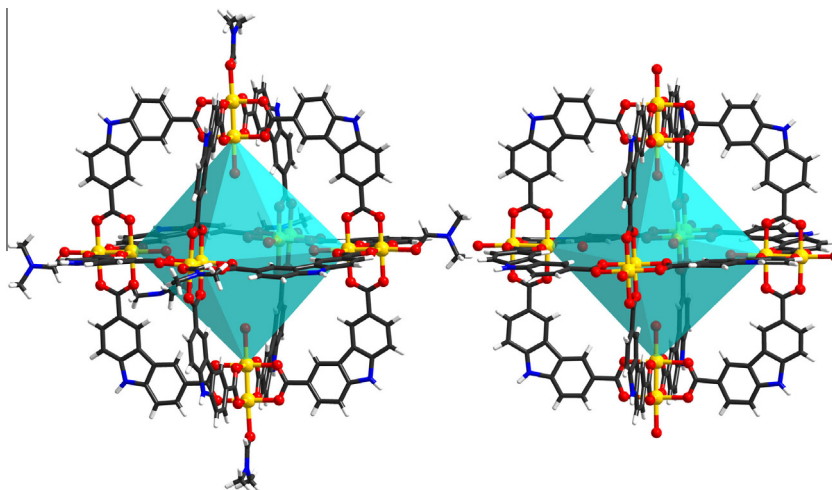
The structures of **3** and **4**, shown in Fig. 2, were found to form cuboctahedra structures which are isostructural with earlier  $\text{M}_2$ -based MOPs such as  $[\text{Cu}_2(\text{BBDC})_2]_{12}$  and  $[\text{Mo}_2(\text{BBDC})_2]_{12}$ . This is different than the previous reported  $[\text{M}_2(\text{BDC})_2]_{12}$ , where  $[\text{Mo}_2(\text{BDC})_2]_{12}$  was found to be an anticuboctahedron. Subsequent work has shown that  $[\text{Mo}_2(\text{BDC})_2]_{12}$  will transform to a cuboctahedron when heated to higher temperature for longer duration, which leads to an empirical rule that the cuboctahedron is thermodynamically preferred to the anticuboctahedron. Compounds **3** and **4** likely forms a cuboctahedron due to the increased solubility of the  $\text{Ru}_2^{4+}$  species; whereas the  $\text{Mo}_2$  compounds will form crystals at the elevated oven temperatures, the  $\text{Ru}_2^{4+}$  compounds are soluble until the reaction tube is cooled. Thus, shorter reaction times are needed to form the more thermodynamically favored compound because the intermediate species stay in solution. As was the case for the octahedral compounds, the average Ru–Ru bond distance in **3** (2.2780 Å) is shorter than that in **4** (2.2957 Å), again owing to the addition of an electron to a  $\delta^*$  orbital of the  $\text{Ru}_2^{4+}$  center in compound **4**.

Taking into account the van der Waal radii, the average distance between the inner Ru atoms on opposite vertices of the polyhedron for **1** and **3** are 14.6050 Å and 16.7037 Å respectively. For compounds **2** and **4**, these distances are 14.5030 Å and 16.7378 Å. Putting aside the necessary counter ions for **1** and **2** or **3** and **4**, these small differences indicate that there is no significant structural effect on the polyhedra when the oxidation states of the dinuclear metal sites are changed. This has important implications for any MOFs built from these MOPs, as it suggests that redox chemistry at the  $\text{Ru}_2^{n+}$  centers would have little impact on the overall framework structure.

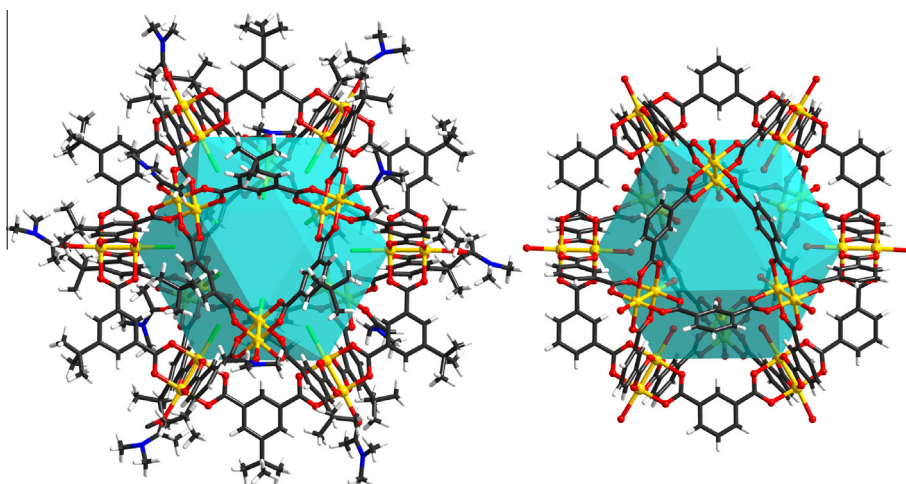
The cyclic voltammograms of compounds **2** and **4** were measured versus  $\text{Ag}/\text{AgCl}$  in DMF with 0.1 M  $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$  as the supporting electrolyte. As seen in Fig. 3, a shift to higher potential is observed in **4** relative to **2** (217 mV) and  $\text{Ru}_2(\text{OAc})_4$  (measured at 254 mV under identical conditions, see Supporting information). This can be explained by the presence of electronic communication between the  $\text{Ru}_2$  centers in **4**, indicated by the appearance of multiple peaks in the CV of **4**. The first shoulder in the oxidative direction appears at approximately 400 mV, relatively close to the 300 mV seen in the other two compounds. The main oxidative peak is then shifted to 594 mV, with the return sweep showing corresponding reduction peaks for multiple redox events. This



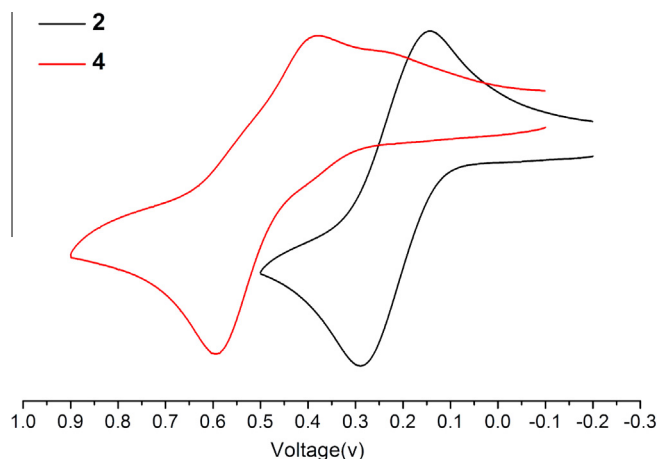
**Scheme 1.** The reaction pathways for MOP preparation and carboxylate linkers used, DMA stands for Dimethylacetamide, DMF stands for Dimethylformamide.



**Fig. 1.** Molecular structures of **1** (left) and **2** (right). The turquoise polyhedron within each molecular cage represents the polyhedral presentation of the molecular cage when considering Ru–Ru clusters as vertices and ligands as edges. Ru, gold; O, red; C, dark gray; N, blue; H, white.



**Fig. 2.** Molecular structures of **3** (left) and **4** (right). The turquoise polyhedron within each molecular cage represents the polyhedral presentation of the molecular cage when considering Ru–Ru clusters as vertices and ligands as edges. Ru, gold; O, red; C, dark gray; N, blue; H, white.



**Fig. 3.** Cyclic voltammograms of **2** and **4**. Voltage is vs. Ag/AgCl in DMF with 0.1 M [(*n*-Bu)<sub>4</sub>N][PF<sub>6</sub>].

observation of communication through the isophthalate ligand is similar to previous measurements made for a molecular square of Ru<sub>2</sub><sup>5+</sup> centers connected by terephthalate ligands [19]. In the case

of compound **2**, no electronic communication is observed, and each Ru<sub>2</sub> site behaves as if it were isolated. This is to be expected, as there is no conjugated  $\pi$  system that extends over the length of the ligand. Through-space interactions in **2** are limited, with the Ru<sub>2</sub>–Ru<sub>2</sub> sites being approximately 12 Å apart (~16 Å through the ligand).

Due to the apparent electronic communication present in the cuboctahedral compound **4**, the idea to measure its magnetic susceptibility was naturally followed. Owing to the air sensitivity of **4** [20], however, compound **3** was chosen as a more suitable candidate for magnetic studies. Compound **3** also benefits from each Ru<sub>2</sub><sup>5+</sup> core having up to three unpaired electrons, allowing the communication to be observed through spin-center coupling at low temperatures. A significant correction was made to the data by correcting the mass of the sample used, estimated from a TGA measurement taken on the sample immediately following the magnetic measurements (see [Supporting information](#)). This was done to allow for better modeling of the data to isolate contributions from the MOP and from the solvent molecules. Shown in [Fig. 4](#), the temperature dependent magnetic susceptibility data indicated that an  $S = 3/2$  state exists at room temperature, with the fitting done for a simplified Ru<sub>2</sub>(BBDC)<sub>2</sub>Cl unit. As the

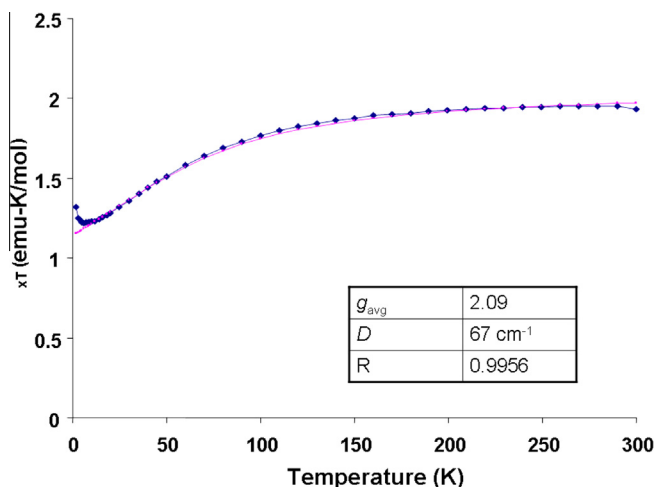


Fig. 4. The experimental and calculated magnetic susceptibility data for compound **3**. Experimental data is denoted by (♦).

temperature is decreased, zero-field splitting common in  $Ru_2^{5+}$  compounds begin to depopulate the  $S = 3/2$  state in favor of  $S = 1/2$ . This continues until  $T < 20$  K, when ferromagnetic coupling between  $Ru_2^{5+}$  sites is observed.

The data were fit to the equations

$$\chi_{||} = \frac{Ng_{||}^2\beta^2}{kT} \cdot \frac{1 + 9e^{-2D/kT}}{4(1 + e^{-2D/kT})} \quad (1)$$

$$\chi_{\perp} = \frac{Ng_{\perp}^2\beta^2}{kT} \cdot \frac{4 + (3kT/D)(1 - e^{-2D/kT})}{4(1 + e^{-2D/kT})} \quad (2)$$

with  $g_{avg}$  being calculated as

$$g_{avg} = 1/3(g_{||} + 2g_{\perp}) \quad (3)$$

The calculated values for  $g_{avg} = 2.09$  and  $D$  of  $67 \text{ cm}^{-1}$  are consistent with previous  $Ru_2^{5+}$  carboxylate compounds exhibiting strong zero-field splitting [21]. Given the complexity of the system, no attempt was made to model the magnetic coupling constant  $J$ .

### 3. Conclusions

Four metal–organic polyhedra based on  $Ru_2^{n+}$  cores have been prepared and structurally characterized. Cyclic voltammetry measurements indicate that reversible oxidation and reduction between  $Ru_2^{4+}$  and  $Ru_2^{5+}$  oxidation states should be possible under mild conditions. Weak electron communication has been found between  $Ru_2$  nodes in compound **4**. The different oxidation states show only minor changes in structure, suggesting that these polyhedra could be incorporated into a larger framework that would allow redox reactions to take place at a Ru atom site. The moderate solubility of these compounds in DMF and DMA should allow the extension to a MOF by layering with a solution of a secondary linker. Work in this direction is currently under investigation.

### 4. Experimental details

All the reagents and solvents (AR grade) were commercially available and used as received. Solvents for CV were further dried in glass contour solvent systems (SG Water USA, LLC) before use. The dicarboxylate ligands were all obtained from their parent diacids during the assembly of the metal–organic architectures. The parent diacids, i.e., 1,3-benzenedicarboxylic acid [ $H_2(1,3-BDC)$ ], 5-tert-butyl-1,3-benzenedicarboxylic acid [ $H_2(5-t-Bu-1,3-BDC)$ ], were purchased from VWR. 9H-3,6-carbazoledicarboxylic

acid [ $H_2(9H-3,6-CDC)$ ], was synthesized according to our published procedures.  $Ru_2(OAc)_4Cl$  and  $Ru_2(OAc)_4$  were prepared by following literature methods [1]. TGA data were recorded on a TGA-50 (SHIMADZU) Thermogravimetric analyzer. About 10 mg of sample was heated from room temperature to  $700^\circ\text{C}$  at a ramp rate of  $2^\circ\text{C}/\text{min}$  under a  $N_2$  flow. Electrochemical measurements were made with a model 610A electrochemical analyzer (CH Instrument Inc., USA) using a Pt working electrode,  $0.1 \text{ M } [Bu_4N][PF_6]$  supporting electrolyte, and a Ag/AgCl reference electrode.

#### $[Ru_2(CDC)_2Cl]_6$ , **1**

15.0 mg  $Ru_2(OAc)_4Cl$  (0.032 mmol) was placed inside a glass reaction tube together with 20.0 mg  $H_2CDC$  (0.087 mmol). Approximately 1.5 mL of DMA was added, after which the tube was frozen in liquid nitrogen, evacuated, and sealed with a torch. The tube was then placed inside an oven set at  $85^\circ\text{C}$  for 5 days. Some crystals were observed in the tube upon removal from the oven, with additional growth seen as the tube was cooled and rested at room temperature for several days.

#### $[Ru_2(CDC)_2]_6$ , **2**

Initial manipulation was performed inside an Argonne glove box. Freshly prepared 15.0 mg  $Ru_2(OAc)_4$  (0.034 mmol) and 20.0 mg  $H_2CDC$  (0.087 mmol) were placed in a glass reaction tube with one end sealed. Approximately 1.5 mL of dry DMF was added, after which the open side of tube was temporarily sealed by an attached hose with stopcock. The apparatus was then removed from the glove box and attached to a Schlenk line, where the tube was purged and backfilled with  $N_2$ . The tube was then frozen in liquid nitrogen, evacuated, and sealed with a torch. The tube was then placed inside an oven set at  $85^\circ\text{C}$  for 2 days. Crystals were obtained after removing the tube from the oven and allowing it to rest at room temperature for 1 week. Additional solid material could be obtained by placing the tube in a freezer at  $-20^\circ\text{C}$ .

#### $[Ru_2(BBDC)_2Cl]_{12}$ , **3**

The synthesis of **3** is similar to that of **1**, except 20 mg  $H_2BBDC$  (0.090 mmol) was used instead of  $H_2CDC$ .

#### $[Ru_2(BDC)_2]_{12}$ , **4**

The synthesis of **4** is similar to that of **2**, except 20.0 mg  $H_2BDC$  (0.120 mmol) was used instead of  $H_2CDC$ .

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### Appendix A. Supplementary material

CCDC 1007919–1007922 contain the supplementary crystallographic data for compounds **1–4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2014.09.010>.

## References

- [1] (a) J.R. Long, O.M. Yaghi, *Chem. Soc. Rev.* 38 (5) (2009) 1213;  
(b) H.-C. Zhou, J.R. Long, O.M. Yaghi, *Chem. Rev.* 112 (2) (2012) 673.
- [2] (a) S.S. Han, J.L. Mendoza-Cortes, W.A. Goddard III, *Chem. Soc. Rev.* 38 (5) (2009) 1460;  
(b) L.J. Murray, M. Dinca, J.R. Long, *Chem. Soc. Rev.* 38 (5) (2009) 1294;  
(c) M.P. Suh, H.J. Park, T.K. Prasad, D.-W. Lim, *Chem. Rev.* 112 (2) (2012) 782;  
(d) R.B. Getman, Y.-S. Bae, C.E. Wilmer, R.Q. Snurr, *Chem. Rev.* 112 (2) (2012) 703;  
(e) H. Wu, Q. Gong, D.H. Olson, J. Li, *Chem. Rev.* 112 (2) (2012) 836.
- [3] (a) J.-R. Li, R.J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* 38 (5) (2009) 1477;  
(b) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* 112 (2) (2012) 869.
- [4] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long, *Chem. Rev.* 112 (2) (2012) 724.
- [5] P. Horcajada, R. Gref, T. Baati, P.K. Allan, G. Maurin, P. Couvreur, G. Férey, R.E. Morris, C. Serre, *Chem. Rev.* 112 (2) (2012) 1232.
- [6] (a) M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, *Chem. Soc. Rev.* 38 (5) (2009) 1330;  
(b) L.E. Kreno, K. Leong, O.K. Farha, M. Allendorf, R.P. Van Duyne, J.T. Hupp, *Chem. Rev.* 112 (2) (2012) 1105.
- [7] (a) J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, *Chem. Soc. Rev.* 38 (5) (2009) 1450;  
(b) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* 38 (5) (2009) 1248;  
(c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* 112 (2) (2012) 1196.
- [8] D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe, O.M. Yaghi, *Chem. Soc. Rev.* 38 (5) (2009) 1257.
- [9] D.J. Xiao, E.D. Bloch, J.A. Mason, W.L. Queen, M.R. Hudson, N. Planas, J. Borycz, A.L. Dzuba, P. Verma, K. Lee, F. Bonino, V. Crocell, J. Yano, S. Bordiga, D.G. Truhlar, L. Gagliardi, C.M. Brown, J.R. Long, *Nat. Chem.* (2014), <http://dx.doi.org/10.1038/nchem.1956>.
- [10] (a) W. Lu, D. Yuan, A. Yakovenko, H.-C. Zhou, *Chem. Commun.* 47 (17) (2011) 4968;  
(b) J.-R. Li, A.A. Yakovenko, W. Lu, D.J. Timmons, W. Zhuang, D. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* 132 (49) (2010) 17599;  
(c) J.-R. Li, H.-C. Zhou, *Nat. Chem.* 2 (10) (2010) 893.
- [11] J.-R. Li, D.J. Timmons, H.-C. Zhou, *J. Am. Chem. Soc.* 131 (18) (2009) 6368.
- [12] Y. Ke, D.J. Collins, H.-C. Zhou, *Inorg. Chem.* 44 (12) (2005) 4154.
- [13] (a) F.A. Cotton, N.F. Curtis, C.B. Harris, B.F.G. Johnson, S.J. Lippard, J.T. Mague, W.R. Robinson, J.S. Wood, *Science* 145 (3638) (1964) 1305;  
(b) R.H. Cayton, M.H. Chisholm, J.C. Huffman, E.B. Lobkovsky, *J. Am. Chem. Soc.* 113 (23) (1991) 8709;  
(c) F.A. Cotton, L.M. Daniels, C. Lin, C.A. Murillo, *J. Am. Chem. Soc.* 121 (18) (1999) 4538;  
(d) F. Albert Cotton, C. Lin, C.A. Murillo, *J. Chem. Soc., Dalton Trans.* 19 (1998) 3151;  
(e) M.J. Byrnes, M.H. Chisholm, N.J. Patmore, *Inorg. Chem.* 44 (25) (2005) 9347;  
(f) F. Albert Cotton, L.M. Daniels, C. Lin, C.A. Murillo, *Chem. Commun.* 9 (1999) 841;  
(g) F.A. Cotton, C. Lin, C.A. Murillo, *Inorg. Chem.* 40 (3) (2001) 575;  
(h) F.A. Cotton, C. Lin, C.A. Murillo, *Inorg. Chem.* 40 (3) (2001) 472;  
(i) F.A. Cotton, C. Lin, C.A. Murillo, *Inorg. Chem.* 40 (3) (2001) 478;  
(j) F.A. Cotton, C. Lin, C.A. Murillo, *J. Am. Chem. Soc.* 123 (11) (2001) 2670;  
(k) F.A. Cotton, C. Lin, C.A. Murillo, *Proc. Natl. Acad. Sci. U.S.A.* 99 (8) (2002) 4810;  
(l) F.A. Cotton, C. Lin, C.A. Murillo, *Acc. Chem. Res.* 34 (10) (2001) 759.
- [14] (a) Z. Ni, A. Yassar, T. Antoun, O.M. Yaghi, *J. Am. Chem. Soc.* 127 (37) (2005) 12752;  
(b) M.J. Prakash, Y. Zou, S. Hong, M. Park, M.-P.N. Bui, G.H. Seong, M.S. Lah, *Inorg. Chem.* 48 (4) (2009) 1281;  
(c) D.J. Tranchemontagne, Z. Ni, M. O'Keeffe, O.M. Yaghi, *Angew. Chem., Int. Ed.* 47 (28) (2008) 5136;  
(d) Q.-F. Sun, S. Sato, M. Fujita, *Nat. Chem.* 4 (4) (2012) 330;  
(e) M. Tominaga, K. Suzuki, M. Kawano, T. Kusakawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem., Int. Ed.* 43 (42) (2004) 5621.
- [15] (a) T.A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* 28 (10) (1966) 2285;  
(b) P. Angaridis, F.A. Cotton, C.A. Murillo, D. Villagrán, X. Wang, *J. Am. Chem. Soc.* 127 (14) (2005) 5008;  
(c) J.L. Bear, Y. Li, B. Han, K.M. Kadish, *Inorg. Chem.* 35 (5) (1996) 1395;  
(d) R. Lee, Y. Yang, G.K. Tan, C.-H. Tan, K.-W. Huang, *Dalton Trans.* 39 (3) (2010) 723.
- [16] (a) P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick, G. Wilkinson, *J. Chem. Soc. A* (1970) 3322;  
(b) A.J. Lindsay, G. McDermott, G. Wilkinson, *Polyhedron* 7 (14) (1988) 1239;  
(c) A.F. Noels, A. Demonceau, E. Carlier, A.J. Hubert, R.-L. Marquez-Silva, R.A. Sanchez-Delgado, *J. Chem. Soc., Chem. Commun.* 12 (1988) 783.
- [17] G.M. Chiarella, F.A. Cotton, C.A. Murillo, M.D. Young, Q. Zhao, *Inorg. Chem.* 49 (6) (2010) 3051.
- [18] (a) F.A. Cotton, L.M. Daniels, E.A. Hillard, C.A. Murillo, *Inorg. Chem.* 41 (6) (2002) 1639;  
(b) F.A. Cotton, J.P. Donahue, P. Huang, C.A. Murillo, D. Villagrán, *Z. Anorg. Allg. Chem.* 631 (13–14) (2005) 2606;  
(c) F.A. Cotton, N.S. Dalal, C.Y. Liu, C.A. Murillo, J.M. North, X. Wang, *J. Am. Chem. Soc.* 125 (42) (2003) 12945.
- [19] P. Angaridis, J.F. Berry, F.A. Cotton, C.A. Murillo, X. Wang, *J. Am. Chem. Soc.* 125 (34) (2003) 10327.
- [20] H. Miyasaka, N. Motokawa, R. Atsuumi, H. Kamo, Y. Asai, M. Yamashita, *Dalton Trans.* 40 (3) (2011) 673.
- [21] (a) J. Telser, R.S. Drago, *Inorg. Chem.* 23 (20) (1984) 3114–3120;  
(b) F.D. Cukiernik, D. Luneau, J.-C. Marchon, P. Maldivi, *Inorg. Chem.* 37 (15) (1998) 3698–3704.