

Two Elongated Octahedral Coordination Cages Constructed by M_4 -TC4A Secondary Building Units ($M = Co^{II}$ and Fe^{II}) and 2,2'-Bipyridine-4,4'-dicarboxylic Acids

Huaqiao Tan,^{†,‡} Shangchao Du,[†] Yanfeng Bi,[†] and Wuping Liao^{*,†}

[†]State Key Laboratory of Rare Earth Resource Utilization, ERC for the Separation and Purification of REs and Thorium, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

[‡]State Key Laboratory of Luminescence and Application, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

S Supporting Information

ABSTRACT: Two nanoscale coordination cages based on M_4 -TC4A ($M = Co^{II}$ and Fe^{II} ; $H_4TC4A = p$ -tert-butylthiacalix[4]arene) and 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2bpdC) have been synthesized and characterized. In these isostructural structures, there are two kinds of shuttlecock-like M_4 -TC4A secondary building units, $\{M_4(TC4A)(Cl)\}$ and $\{M_4(TC4A)(SO_4)\}$, which have different coordination environments and are bridged by $bpdC$ molecules into an elongated octahedron through a [6 + 8] condensation. The gas sorption and magnetic properties were studied.

Coordination cages¹ as a class of nanosized molecular containers have achieved increasing prominence because of their appeal in two distinct areas.^{1,2} First, their formation by the self-assembly of relatively simple components provides an opportunity to understand the process of self-assembly and a probability to control it.³ Over the past few years, a variety of compounds have been prepared using different strategies, including symmetry interaction, molecular library, directional bonding, supramolecular blueprint, molecular paneling, and weak-link and reticular chemistry approaches.^{4,5} In these strategies, the steric, geometric, and electronic characteristics embedded within individual components have collectively allowed “controllable” construction, which makes the reasonable design and synthesis of new polyhedral cages and its derivatives one of the most challenging issues in synthetic and coordination chemistry.³ Second, the cages act as hosts for a range of small molecules or ions, which provide some constrained containers that can be used for storage,⁶ recognition,⁷ catalysis,⁸ and so on.⁹

Calixarenes (including resorcinarenes and pyrogallolarenes), macrocyclic ligands with methylene/heteroatom-bridging phenolic groups, have been documented as versatile candidates for the construction of coordination cages,^{10,11} most of which are constructed by bonding the metals with the upper rims of calixarenes. In contrast, coordination cages concerning the lower rim of calixarene are relatively less. A shuttlecock-like M_4 -calix[4]arene ($M = Co^{II}$, Mn^{II} , and Fe^{II}) subunit¹² was reported to be an excellent secondary building unit (SBU) for coordination cage construction. We successfully obtained a series of octahedral nanocages using some planar ternary

aromatic carboxylic acids with D_{3h} symmetry to interconnect these SBUs.¹³ Hong and Wang also reported similar cages using di- or ternary carboxylic acids.¹⁴ Also, very recently, we obtained two extended 2D assemblies containing predesigned nanocages with linear monocarboxylic ligand isonicotinic acid as the bridge^{15a} and a tetragonal prismatic $\{Co_{32}\}$ nanocage with an in situ generated tetrazole ligand.^{15b} Another tetrahedral nanocage was obtained in the presence of 5-sulfoisophthalic acid.¹⁶ All of these indicated that the shuttlecock-like M_4 -calixarene SBU holds the desired curvature necessary for the construction of coordination cages, and the structure and coordination mode of the bridge ligand play a crucial role in the formation of the coordination cages and affect their geometries. It can be asserted that some novel coordination cages would be obtained with the ligands having different geometries and coordination modes.

Herein, we present two nanoscale coordination cages, $[Et_3NH]_2\{[M_4(TC4A)(Cl)]_2[M_4(TC4A)(SO_4)]_4bpdC_8\}$ [$H_2bpdC = 2,2'$ -bipyridine-4,4'-dicarboxylic acid; $M = Co^{2+}$ (CIAC-112) and Fe^{2+} (CIAC-113)], by the assembly of M_4 -TC4A SBUs and H_2bpdC (Figure 1). In these structures, two $\{M_4(TC4A)(Cl)\}$ moieties and four $\{M_4(TC4A)(SO_4)\}$ subunits are connected by eight $bpdC$ molecules to a elongated octahedral $\{M_{24}\}$ cage, which exhibits good gas sorption.

Typically, fusiform crystals of CIAC-112 and CIAC-113 were obtained by the solvothermal reaction of MCl_2 , MSO_4 ($M = Co^{II}$ and Fe^{II}), H_4TC4A , and H_2bpdC in a 1:1 (v/v) CH_3OH -DMF mixed solvent (total 6 mL) with a small amount of triethylamine at 130 °C. Comparative experiments indicated that the SO_4^{2-} anion plays a crucial role in the formation of such compounds. If there was no SO_4^{2-} in the reaction system, no crystalline phase was found but some unknown mixed powders.

CIAC-112 and CIAC-113 are isostructural, and both crystallize in the monoclinic system with the space group $P2_1/c$. So, compound CIAC-112 is described in detail as an example hereafter. In CIAC-112, there are two kinds of shuttlecock-like Co_4 -TC4A SBUs, $\{Co_4(TC4A)(Cl)\}$ and $\{Co_4(TC4A)(SO_4)\}$. The $\{Co_4(TC4A)(Cl)\}$ entity is similar to those reported.^{13,15} Each Co center of the Co_4 square adopts a distorted octahedral geometry coordinated by two phenoxy O atoms, one S atom

Received: May 5, 2014

Published: July 2, 2014

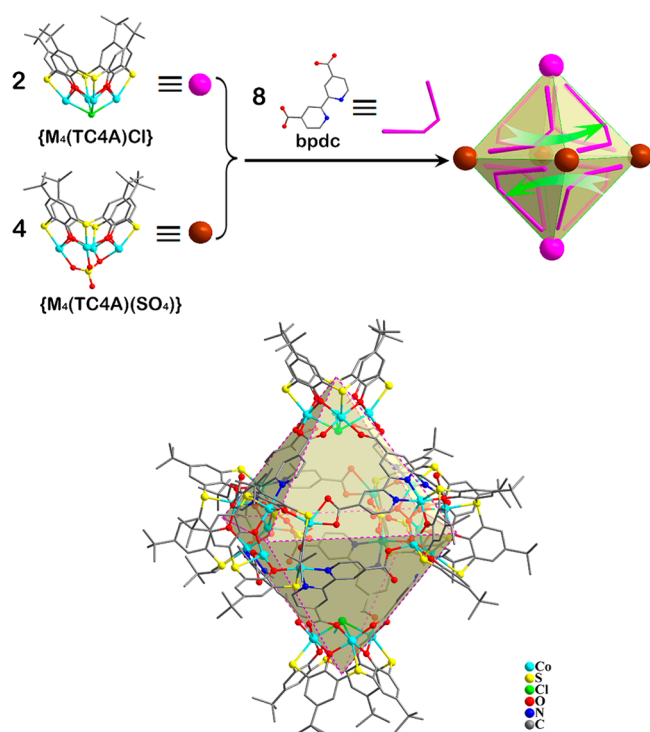


Figure 1. Two kinds of shuttlecock-like M_4 -TC4A SBUs, $\{Co_4(TC4A)(Cl)\}$ and $\{Co_4(TC4A)(SO_4)\}$, acting as the vertices bridged by eight bpdc molecules into an elongated octahedral cage through a $[6 + 8]$ condensation.

from one fully deprotonated TC4A ligand, one μ_4 -chloride anion, and two carboxylate O atoms from different bpdc molecules. Four edge-sharing $Co(O_4SCl)$ octahedra form a quadrilateral Co_4 cluster, with the $Co \cdots Co$ edges being in the range 3.23–3.27 Å and $Co-Co-Co$ angles being 88.8–91.2°. A TC4A ligand adopting a cone conformation caps on the tetranuclear Co_4 square through four phenoxy O atoms and four S bridges to form the shuttlecock-like SBU (Figure S1 in the Supporting Information, SI). In the $\{Co_4(TC4A)(SO_4)\}$ entity, there are two kinds of Co atoms, one being six-coordinated by two phenoxy O atoms, one S atom, one O atom from the SO_4^{2-} anion, and two N atoms from one bpdc molecule and the other adopting a trigonal-bipyramidal geometry coordinated by two phenoxy O atoms, one S atom, one O atom from SO_4^{2-} , and one carboxylate O atom from a bpdc molecule. Two $Co(O_3N_2S)$ octahedra and two $Co(O_4S)$ trigonal bipyramids are alternately interconnected by sharing the vertex and edge to form a distorted quadrilateral Co_4 cluster, with the $Co \cdots Co$ edges being in the range 3.28–3.61 Å and $Co-Co-Co$ angles being 84.0–97.9°. One SO_4^{2-} anion and one TC4A molecule were capped on both sides of the Co_4 cluster to form a new shuttlecock-like SBU. Two $\{Co_4(TC4A)(Cl)\}$ SBUs occupied the polar positions, while four $\{Co_4(TC4A)(SO_4)\}$ SBUs are located on the equator, all of which are bridged by eight bpdc molecules into an elongated octahedral $\{Co_{24}\}$ nanocage (Figure 1). The distances between two adjacent vertices on the equator are shorter than the others (Figure S3 in the SI). Although the bpdc ligand also acts as a tripodal linker and bonds one $\{Co_4(TC4A)(Cl)\}$ and two $\{Co_4(TC4A)(SO_4)\}$ SBUs, these nanocages are different from those involving aromatic tricarboxylic acids with D_{3h} symmetry¹³ and show some similarity to that obtained with dicarboxylic acid (Figure S3 in the SI).^{14a} A bpdc ligand interconnects three Co_4 -TC4A SBUs through two octahedral edges, and two adjacent

$\{Co_4(TC4A)(SO_4)\}$ SBUs on the equator are bridged by double bpdc linkers. All four U-shaped bpdc ligands at the upper part of the coordination octahedron are located in a counterclockwise direction, with those at the lower part being clockwise (Figure 1). The size of the nanocage is $30.3 \times 30.5 \times 31.5 \text{ \AA}^3$ (the $C_{\text{butyl}} \cdots C_{\text{butyl}}$ distance), and that of the inner cavity is $8.7 \times 8.9 \times 14.4 \text{ \AA}^3$ (the distances between the SO_4^{2-} anions and between the μ_4 -Cl anions; actually, it would be a little larger), which is comparable with that of the octahedral $\{Co_{24}\}$ nanocage linked by dicarboxylic acids (with the spheric diameter being about 3.2 nm).^{14a} There are 12 apertures, 8 triangular ones on the octahedral facets and 4 quadrilateral ones at the equatorial edges (Figure S4 in the SI), which would be helpful for the uptake or release of small gas molecules (e.g., N_2). The discrete nanocages are stacked through molecular interactions into a 3D supramolecular extended structure (Figure S5 in the SI). The total potential solvent-accessible volume estimated using PLATON¹⁷ reaches ca. 41.2%. The cavities are presumably occupied by some Et_3NH^+ counterions and solvent molecules whose contribution was subtracted from the diffraction data by the SQUEEZE command.

To confirm the porosity of these compounds, the gas-sorption properties of compound CIAC-112 were measured. As shown in Figure 2, the N_2 adsorption isotherm at 77 K exhibits a type I

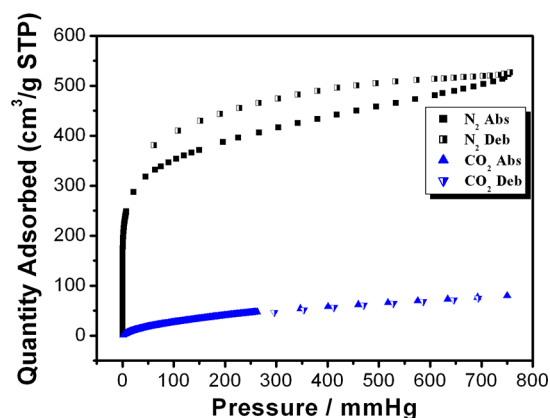


Figure 2. Gas-sorption isotherms on CIAC-112 (“ads” and “des” represent adsorption and desorption, respectively).

behavior in the range $P/P_0 = 0-1.0$, indicative of the presence of permanent microporosity. From the N_2 adsorption branch of the isotherm, the Brunauer–Emmett–Teller (BET) surface area was calculated to be $1211 \text{ m}^2 \text{ g}^{-1}$, which is larger than that of the reported largest octahedral cage CIAC-107 ($770 \text{ m}^2 \text{ g}^{-1}$) treated by supercritical carbon dioxide methods.^{13b} That might be due to the introduction of uncoordinated cobalt sites in the $\{Co_4(TC4A)(SO_4)\}$ SBUs and the N-containing bpdc ligands.¹⁸ Similar improvement of CO_2 sorption was also observed. The CO_2 adsorption isotherm shows a CO_2 uptake capacity of $80 \text{ cm}^3 \text{ g}^{-1}$ at 273 K and 1 bar, which is about twice that of the previous polyhedral coordination cage based on M_4 -TC4A subunits.^{14a}

The magnetic susceptibility of CIAC-112, measured in an applied field of 1 kOe for fresh samples over the temperature range of 2–300 K, is shown in Figure 3. The $\chi_M T$ value decreases gradually from $69.45 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $4.04 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. The magnetic property of this compound can be attributed to 24 isolated Co^{II} cations. For each Co^{II} center, the experimental $\chi_M T$ value at room temperature is $2.89 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is consistent with the typical value of the Co^{II} ion (for

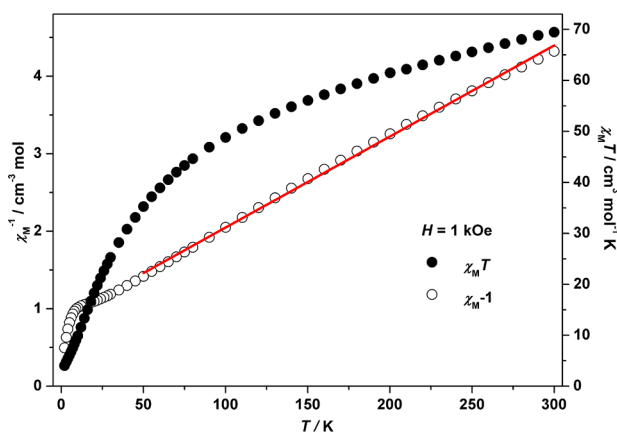


Figure 3. Plots of $\chi_M T$ vs T and $1/\chi_M$ vs T for CIAC-112 in a 1 kOe field.

Co^{II} , the $\chi_M T$ value normally ranges from 2.7 to 3.4 $\text{cm}^3 \text{mol}^{-1} \text{K}$. The reciprocal molar susceptibility in 50–300 K follows the Curie–Weiss law of $1/\chi_M = (T - \theta)/C$ with $C = 63.01 \text{ cm}^3 \text{mol}^{-1} \text{K}$ and $\theta = -55.03 \text{ K}$. The negative Weiss constant (θ) value suggests an antiferromagnetic interaction between the metal centers and/or the spin–orbit coupling effect of Co^{II} . This is consistent with other compounds built from $\text{Co}_4\text{-TC4A}$ SBUs.

In summary, two new nanoscale coordination cages were assembled by two kinds of shuttlecock-like $\text{M}_4\text{-TC4A}$ SBUs, $\{\text{M}_4(\text{TC4A})(\text{Cl})\}$ and $\{\text{M}_4(\text{TC4A})(\text{SO}_4)\}$ ($\text{M} = \text{Co}^{\text{II}}$ and Fe^{II}), and H_2bpdc , in which two $\{\text{M}_4(\text{TC4A})(\text{Cl})\}$ SBUs occupy the polar positions while four $\{\text{M}_4(\text{TC4A})(\text{SO}_4)\}$ SBUs are located on the equator, and the bpdc ligand acts as a U-shaped bridge to bond three $\text{M}_4\text{-TC4A}$ SBUs. Although these elongated octahedral cages are also constructed by $[6 + 8]$ condensation, there are eight triangular apertures on the octahedral facets and four quadrilateral ones on the equatorial edges. The uncoordinated metal sites and the N-containing bridge ligands in the cage improve the gas-adsorption properties of the compounds. N_2 sorption of CIAC-112 reveals that the compounds possess permanent microporosity, with the BET surface area being approximately $1211 \text{ m}^2 \text{g}^{-1}$, which is the highest among those of coordination cages based on $\text{M}_4\text{-TC4A}$ SBUs.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section and crystallographic data (CCDC 998115 and 998116), additional figures, thermogravimetric–differential scanning calorimetric analyses, and powder X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Author

*E-mail: wpliao@ciac.ac.cn. Tel: +86-431-8526-2726. Fax: +86-431-8569-8041.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Grants 21221061, 21301170, and 51222404).

■ REFERENCES

- (a) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (c) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2009**, *42*, 1650. (d) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (e) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810.
- (a) Clever, G. H.; Kawamura, W.; Tashiro, S.; Shiro, M.; Shionoya, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2606. (b) Zhou, X. P.; Liu, J.; Zhan, S. Z.; Yang, J. R.; Li, D.; Ng, K. M.; Sun, R. W. Y.; Che, C. M. *J. Am. Chem. Soc.* **2012**, *134*, 8042.
- (a) Stephenson, A.; Argent, S. P.; Riis-Johannessen, T.; Tidmarsh, I. S.; Ward, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 858.
- (a) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
- (a) Gianneschi, N. C.; Maser, M. S.; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825. (b) Tranchemontagne, D. J.; Ni, Z.; O’Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5136. (c) Hamilton, T. D.; Papaefstathiou, G. S.; Frišćić, T.; Bučar, D.-K.; MacGillivray, L. R. *J. Am. Chem. Soc.* **2008**, *130*, 14366.
- (a) Lu, Z.; Knobler, C. B.; Furukawa, H.; Wang, B.; Liu, G.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 12532. (b) Li, J.-R.; Zhou, H.-C. *Nat. Chem.* **2010**, *2*, 893.
- (a) Wang, Z. J.; Brown, C. J.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 7358.
- (a) Hastings, C. J.; Backlund, M. P.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2011**, *50*, 10570.
- (a) Takao, K.; Suzuki, K.; Ichijo, T.; Sato, S.; Asakura, H.; Teramura, K.; Kato, K.; Ohba, T.; Morita, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5893. (b) Sun, Q. F.; Iwasa, J.; Ogawa, D.; Ishido, Y.; Sato, S.; Ozeki, T.; Sei, Y.; Yamaguchi, K.; Fujita, M. *Science* **2010**, *328*, 1144.
- (a) Dalgarno, S. J.; Thallapally, P. K.; Barbour, L. J.; Atwood, J. L. *Chem. Soc. Rev.* **2007**, *36*, 236. (b) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. *Coord. Chem. Rev.* **2010**, *252*, 825. (c) Jin, P.; Dalgarno, S. J.; Atwood, J. L. *Coord. Chem. Rev.* **2008**, *254*, 1760. (d) Bi, Y. F.; Du, S. C.; Liao, W. P. *Coord. Chem. Rev.* DOI: 10.1016/j.ccr.2014.06.011.
- (a) Iyer, K. S.; Norret, M.; Dalgarno, S. J.; Atwood, J. L.; Raston, C. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6362. (b) Kumari, H.; Mossine, A. V.; Kline, S. R.; Dennis, C. L.; Fowler, D. A.; Teat, S. J.; Barnes, C. L.; Deakynne, C. A.; Atwood, J. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 1452. (c) Ugono, O.; Moran, J. P.; Holman, K. T. *Chem. Commun.* **2008**, 1404. (d) Shivanyuk, A. *J. Am. Chem. Soc.* **2007**, *129*, 14196. (e) Pasquale, S.; Sattin, S.; Escudero-Adán, E. C.; Martínez-Belmonte, M.; de Mendoza, J. *Nat. Commun.* **2012**, *3*, 785.
- (a) Xiong, K. C.; Jiang, F. L.; Gai, Y. L.; Yuan, D. Q.; Han, D.; Ma, J.; Zhang, S. Q.; Hong, M. C. *Chem.—Eur. J.* **2012**, *18*, 5536. (b) Xiong, K. C.; Jiang, F. L.; Gai, Y. L.; Zhou, Y. F.; Yuan, D. Q.; Su, K. Z.; Wang, X. Y.; Hong, M. C. *Inorg. Chem.* **2012**, *51*, 3283. (c) Bi, Y. F.; Wang, X. T.; Liao, W. P.; Wang, X. F.; Wang, X. W.; Zhang, H. J. *J. Am. Chem. Soc.* **2009**, *131*, 11650. (d) Kajiwara, T.; Kobashi, T.; Shinagawa, R.; Ito, T.; Takaishi, S.; Yamashita, M.; Iki, N. *Eur. J. Inorg. Chem.* **2006**, 1765.
- (a) Liu, M.; Liao, W. P.; Hu, C. H.; Du, S. C.; Zhang, H. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 1585. (b) Du, S. C.; Hu, C. H.; Xiao, J. C.; Tan, H. Q.; Liao, W. P. *Chem. Commun.* **2012**, *48*, 9177.
- (a) Xiong, K. C.; Jiang, F. L.; Gai, Y. L.; Yuan, D. Q.; Chen, L.; Wu, M. Y.; Su, K. Z.; Hong, M. C. *Chem. Sci.* **2012**, *3*, 2321. (b) Dai, F. R.; Wang, Z. Q. *J. Am. Chem. Soc.* **2012**, *134*, 8002.
- (a) Tan, H. Q.; Du, S. C.; Bi, Y. F.; Liao, W. P. *Chem. Commun.* **2013**, *49*, 8211. (b) Bi, Y. F.; Wang, S. T.; Liu, M.; Du, S. C.; Liao, W. P. *Chem. Commun.* **2013**, *49*, 6785.
- (a) Liu, M.; Du, S. C.; Bi, Y. F.; Liao, W. P. *Inorg. Chem. Commun.* **2014**, *41*, 96.
- (a) van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.
- (a) Poloni, R.; Smit, B.; Neaton, J. B. *J. Am. Chem. Soc.* **2012**, *134*, 6714. (b) Cui, P.; Ma, Y. G.; Li, H. H.; Zhao, B.; Li, J. R.; Cheng, P.; Balbuena, P. B.; Zhou, H. C. *J. Am. Chem. Soc.* **2012**, *134*, 18892.