DOI: 10.1002/anie.201106732

Nanocages

Calixarene-Based Nanoscale Coordination Cages[**]

Mei Liu, Wuping Liao, Chunhua Hu, Shangchao Du, and Hongjie Zhang**

Coordination cages with large internal voids have attracted considerable attention because of their intriguing structures and well-defined cavities, high symmetry and stability, and rich chemical and physical properties.[1] They have also found a variety of applications such as gas separation and storage.[2] During the past few decades, many elaborate coordination cages with various sizes and shapes have been synthesized by bridging geometrically pre-fixed metal-containing nodes with highly directional organic ligands.[3] Those with multimetal entities or metal clusters acting as the nodes were mostly constructed by the paddle-wheel secondary building units (SBUs) and the binary acid linkers.[4] Coordination cages having other metal clusters as the nodes have not been described except for a recently reported cubic cage with polyoxometalates as the vertexes.[5] In contrast, although the planar ternary acids such as 1,3,5-benzenetricarboxylic acid (H_3BTC) and 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid (H_3BTB) have been used as the tritopic linker to build the octahedral cagelike substructures in metal–organic frameworks (MOFs),[6] discrete cages with these planar ternary acids as the tritopic linkers have not been described.

Calixarenes (including resorcinarenes and pyrogallolarenes) have been used as an important class of macrocyclic host molecules in supramolecular chemistry.[7] Various calixarene- and resorcinarene-based nanoscale coordination cages have been prepared through metal-mediated self-assembly.[8] However, most cages, especially capsules, are constructed by two metal-bridged calixarenes. Larger cages have been built from six calixarenes linked with 12 or 24 metal ions as Atwood and co-workers reported. In these cages, pyrogallol[4]arenes bonded with Ga, Cu, Ga + Cu, or Ga + Zn to form either open- or closed-shell hexameric metal–organic nanoscale cages.[9] To the best of our knowledge, there is no example of coordination cages having metal–calixarene subunits as vertexes that are linked by other small organic molecules. The introduction of an ancillary ligand would lead to the formation of some larger metal–calixarene-based cages and might generate some extra-large multicomponent cages with unique properties—an attractive but challenging topic.

p-tert-Butylthiacalix[4]arene (H_4TC4A), a cyclic polyphenol compound bridged by sulfur atoms, has demonstrated the ability in constructing polynuclear complexes especially with transition metals (M).[10] The M_4/TC4A shuttlecock-like entity is a common building unit in these structures, and can be joined together to form bigger entities or extended structures by using other ligands such as azides and triazoles.[11–12] Importantly, the quadrangle arrangement of four metal atoms ensures that the shuttlecock-like unit can act as an independent four-connected SBU. Six Co_4/TC4A SBUs having an octahedral arrangement can be bridged by eight $\{MO_6\}$ octahedra into a nanosized $\{Co_{24}M_6\}$ sphere.[13] It would be feasible to build some hollow nanospheres or cages by replacing $\{MO_6\}$ octahedra with proper bridging ligands. Herein, we present four large analogous calixarene-based cages, $\{[Co_4(calix)Cl]_6(TC)_8\}^{6-}$ (CIAC-101: calix = TC4A, TC = BTC; CIAC-102: calix = PTC4A, TC = BTC; CIAC-103: calix = TC4A, TC = BTB; CIAC-104: calix = PTC4A, TC = BTB), which were prepared by using this strategy (Scheme 1). Our calixarene-based cages have large periphery diameters (up to 4.7 nm) and internal voids (up to 1.7 nm).

All four nanocages were synthesized by introducing ternary acids, H_3BTC or H_3BTB, into the solvothermal reaction of cobalt chloride and H_4TC4A or H_4PTC4A (*p*-phenyl-thiacalix[4]arene, a derivative of H_4TC4A) systems. It is found that the D_{3h} symmetry of ternary acids is important for the formation of the cages, and is supported by the fact that the introduction of biphenyl-3,4′,5-tricarboxylate with C_{2v} symmetry does not lead to the formation of a similar cage but rather some wavelike chains (which will be reported elsewhere). The characteristic feature of these cages is given by the Co_4/calixarene shuttlecock-like nodes in an octahedral arrangement and tritopic BTC or BTB linkers on the triangular facets (e.g., CIAC-103; Figure 1). It should be noted that although a variety of molecular cages have been reported,[1–5] these four structures represent the first examples of discrete calixarene-based coordination cages involving a ternary carboxylate ligand. Thermogravimetric analyses revealed that the structures of all the four cages can be maintained at more than 350 °C.

X-ray analyses reveal that CIAC-101 crystallizes in the tetragonal system with the space group $I4m$, CIAC-102 in the trigonal system with the space group $R\bar{3}$, and CIAC-103 and CIAC-104 in the triclinic system with the space group $P\bar{1}$. The extended structures are stacked by the discrete nanosized calixarene-based coordination cages, which are constructed from six Co_4/TC4A or Co_4/PTC4A SBUs and eight BTC or

---

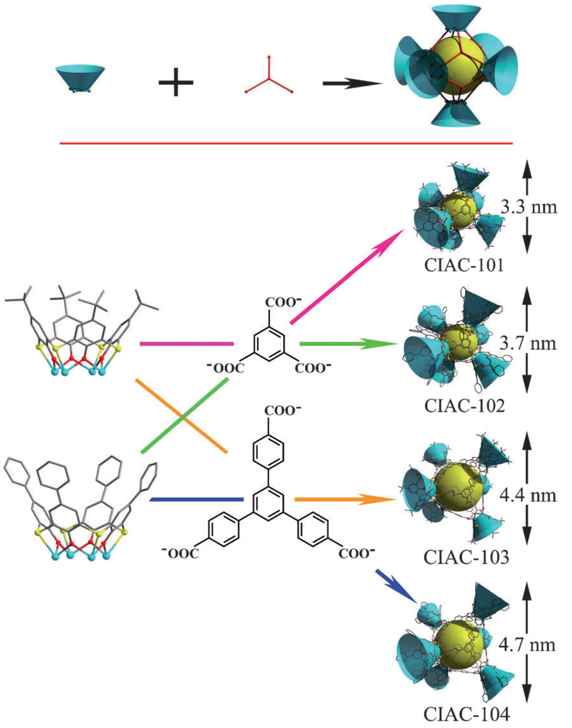
[*] M. Liu, Prof. Dr. W. P. Liao, S. C. Du, Prof. Dr. H. J. Zhang
State Key Laboratory of Rare Earth Resource Utilization
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, No. 5625, Renmin Str., Changchun 130022 (China)
E-mail: wpliao@ciac.jl.cn
hongjie@ciac.jl.cn

Dr. C. H. Hu
Department of Chemistry, New York University
New York, NY 10003 (USA)

M. Liu, S. C. Du
Graduate University of the Chinese Academy of Sciences
Beijing 100049 (China)

[**] This work was supported by the National Natural Science Foundation of China (No. 20971119 and 91026024). We thank Prof. Song Gao for magnetic measurements and Mr. Kuiyue Yang for gas sorption analyses.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201106732.



Scheme 1. Co_4/TC4A or Co_4/PTC4A shuttlecock-like SBUs (left) are connected with tripodal ternary acids (middle) to form the nanocages (right).

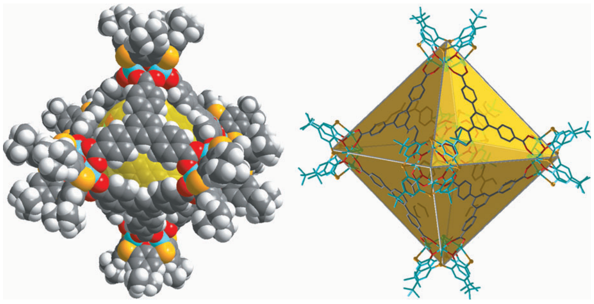


Figure 1. A discrete coordination cage (left) and the arrangement of Co_4/TC4A shuttlecock SBUs and BTB ligands (right) in CIAC-103.

BTB linkers, and the countercations and disordered solvent molecules whose contribution was subtracted from the diffraction data by the *SQUEEZE* command in *PLATON* (see the Supporting Information). There are four (CIAC-101, CIAC-102) or twelve (CIAC-103, CIAC-104) crystallographically independent cobalt sites. All the cobalt sites are six-coordinate with two phenoxy oxygen, one sulfur, and two carboxyl oxygen atoms as well as one chloride anion. Bond-valence calculations suggested that all the cobalt ions in the nanocages are divalent, which is confirmed by the magnetic measurement.

Similar to those in the $\{Co_{24}M_8\}$ nanosphere,[13] four cobalt atoms in the quadrangle arrangement are connected to the lower rim of a calixarene by bonding all the phenolic oxygen and bridging sulfur atoms to form a shuttlecock-like SBU with a bonded chloride anion. Six Co_4/TC4A or Co_4/PTC4A SBUs reside on the vertices of an octahedron and eight tritopic BTC or BTB ligands bridging these SBUs are located on all the triangular facets. The connection modes of a Co_4/PTC4A SBU and a BTB molecule in CIAC-103 are illustrated in Figure S2 in the Supporting Information. One SBU is bonded by four BTBs through four quadrangle borders while each BTB ligand is bonded to three Co_4/PTC4A SBUs with its three carboxyl groups. Thus each Co_4/PTC4A unit acts as a four-connected cross-SBU and each BTB ligand acts as a three-connected triangular linker. And then every six such four-connected cross-SBUs are jointed together by eight BTB linkers into a discrete molecular cage. In other words, the coordination cage is constructed by the [6+8] condensation of Co_4/PTC4A SBUs and tritopic BTB linkers.

The [6+8] condensation of two different kinds of components was also observed in the formation of other cages. Warmuth et al. synthesized a giant organic rhombicubocatahedral cage by a [6+8] condensation of a D_{3h}-symmetric triamine and the tetraformycavitand.[14] Atwood and coworkers also assembled six pyrogallol[4]arenes and eight $[Cu_3O_3]$/$[Ga_xCu_{3-x}O_3]$/$[Ga_xZn_{3-x}O_3]$ planar arrays into some large cages through the [6+8] condensation.[9b,e] In addition, different from those bridged head-to-head in the reported cages,[9b,e] the calixarenes herein are bonded through their lower rims, that is, they are bridged tail-to-tail.

The diameters of the internal spherical cavity and the whole hollow sphere are approximately 1.1 and 3.3 nm (CIAC-101), 1.1 and 3.7 nm (CIAC-102), 1.7 and 4.4 nm (CIAC-103), and 1.7 and 4.7 nm (CIAC-104), respectively. It is obvious that these four hollow spheres are larger than $\{Co_{24}M_8\}$ nanospheres (ca. 2.3 nm).[12] The internal cavity communicates with the outside through twelve shuttle-like apertures located on the edges of the coordination octahedron (Figure 1, right). However, the communication between the internal void and the well-known calixarene cavity is blocked by the chloride anion bonded at the lower rim of the shuttlecock SBU. The presence of chloride anions might be determined by the six-coordination of cobalt. It is potentially promising that the gate between the internal void and the calixarene cavity can be opened by substituting some five-coordinate metal cations for the six-coordinate cobalt atoms.

To evaluate the porosity of the calixarene-capped nanocages, N_2 and H_2 adsorption measurements of CIAC-103 and CIAC-104 activated with supercritical carbon dioxide (SCD) were carried out at 77 K. N_2 sorption of both activated cages gave a type I adsorption isotherm, thus suggesting that these materials possess permanent porosity. H_2 sorption isotherms also show the adsorption/desorption hysteresis. From the adsorption branch of the nitrogen sorption isotherm, the Langmuir surface area, BET surface area, and pore volume were estimated to be 605 $m^2 g^{-1}$, 504 $m^2 g^{-1}$, and 0.49 $cm^3 g^{-1}$, respectively, for activated CIAC-103, and 568 $m^2 g^{-1}$, 477 $m^2 g^{-1}$, and 0.97 $cm^3 g^{-1}$, respectively, for activated CIAC-104. A whole hysteresis of desorption was observed in the isotherm, which might be attributed to the adsorption of the interstices between the nanocages packing in the solid state and the partially blocked apertures by the adjacent cages.[4a]

In fact, as a result of the relative motion of the nanocages with respect to one another and their inefficient packing, the samples of both CIAC-103 and CIAC-104 became amorphous upon activation. However, the N_2 sorption measurement suggested that the individual nanocage and its porosity for both structures were maintained, and I_2 adsorption experiments also demonstrated this. After immersion in the cyclohexane solution of I_2 for 12 hours, the very light purple (nearly white) powders of activated CIAC-103 and CIAC-104 became brown (see Figure S16 in the Supporting Information) and did not return to the original light purple when washed with cyclohexane. At the same time, the color of the cyclohexane solution of I_2 became lighter. That is, iodine in the solution was adsorbed by the activated samples. Because both calixarenes (H_4TC4A and H_4PTC4A) cannot adsorb iodine from the cyclohexane solution, it would suggest that the nanocages were not damaged upon activation by supercritical CO_2 and that iodine diffused into the internal cavities of the nanocages such that they could not be washed away by cyclohexane. The iodine uptake by sublimation[15] was also examined, and about 32 iodine atoms were adsorbed per nanocage molecule of CIAC-104 after 345 hours (Figure S17). It is uncommon for the samples of CIAC-103 and CIAC-104 to lose their crystalline order and still retain permanent microporosity. As far as we are aware, there is only one report on the amorphous cagelike materials. Cooper et al.[16] reported a series of organic molecular solids prepared by dynamic covalent scrambling. In contrast to CIAC-103 or CIAC-104 composed of homogeneous nanocages, their amorphous materials are mixtures comprising a distribution of cagelike species. Notably, their porous properties can be fine-tuned by controlling the syntheses of the mixtures.

In summary, we have successfully synthesized four novel discrete calixarene-based nanoscale coordination cages through a [6+8] condensation by introducing a tritopic ternary acid. The cages can be thought of as an octahedral arrangement of six Co_4/TC4A or Co_4/PTC4A SBUs bridged by eight BTC or BTB linkers, and exhibit high thermal stability. It would be possible to replace the BTC or BTB ligands with larger linkers to construct giant cages. If six-coordinate cobalt is substituted by other metals, it is also possible to remove the chloride anions in these cages and obtain the cages wherein the internal void communicates with the calixarene cavities. The construction of some cages having interesting magnetic properties for the beam transmission of the ions or small organic molecules by inclusion/complexation would also be possible. This work sheds light on the design and preparation of functional super-large molecular cages with calixarenes and some ancillary ligands. Our efforts to prepare giant molecular cages with other bigger ancillary ligands are ongoing.

Experimental Section

Purple single crystals of CIAC-101 were obtained from reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.07 g, 0.1 mmol), $CoCl_2{\cdot}6H_2O$ (0.1 g, 0.4 mmol), 1,3,5-benzenetricarboxylic acid (0.03 g, 0.15 mmol), and tetramethylammonium hydroxide solution (25%, 0.5 mL) in $CHCl_3$ (5 mL) and CH_3OH (5 mL) in a 20 mL Teflon-lined autoclave. The autoclave was kept at 130°C for 3 days and then slowly cooled to 20°C at about 4°Ch^{-1}. The crystals were isolated by filtration and then washed with a 1:1 methanol/chloroform solution. Yield: ca. 70% with respect to the calixarene. Purple single crystals of CIAC-102, CIAC-103, and CIAC-104 were prepared by the analogous methods using the corresponding calixarene and ternary carboxylic acid (as shown in Scheme 1) with the same feed ratio for CIAC-101 but with different solvents. The yields for CIAC-102, CIAC-103, and CIAC-104 were ca. 70%, 30%, and 30%, respectively (for full synthesis details see the Supporting Information).

Received: September 22, 2011
Revised: November 7, 2011

Keywords: cage compounds · calixarenes · cobalt · crystal engineering · tripodal ligands

---

[1] a) W. J. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg, J. R. Nitschke, *Angew. Chem.* **2011**, *123*, 3541–3545; *Angew. Chem. Int. Ed.* **2011**, *50*, 3479–3483; b) S. T. Zheng, F. Zuo, T. Wu, B. Irfanoglu, C. Chou, R. A. Nieto, P. Y. Feng, X. H. Bu, *Angew. Chem.* **2011**, *123*, 1889–1892; *Angew. Chem. Int. Ed.* **2011**, *50*, 1849–1852; c) Q. F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144–1147; d) S. Mirtschin, A. Slabon-Turski, R. Scopelliti, A. H. Velders, K. Severin, *J. Am. Chem. Soc.* **2010**, *132*, 14004–14005; e) A. Granzhan, T. Riis-Johannessen, R. Scopelliti, K. Severin, *Angew. Chem.* **2010**, *122*, 5647–5650; *Angew. Chem. Int. Ed.* **2010**, *49*, 5515–5518; f) M. Mastalerz, *Angew. Chem.* **2010**, *122*, 5164–5175; *Angew. Chem. Int. Ed.* **2010**, *49*, 5042–5053; g) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973–978; h) K. Ono, J. K. Klosterman, M. Yoshizawa, K. Sekiguchi, T. Tahara, M. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 12526–12527.

[2] a) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 1650–1659; b) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247–262; c) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 349–358.

[3] a) M. L. Ma, X. Y. Li, K. Wen, *J. Am. Chem. Soc.* **2009**, *131*, 8338–8339; b) H. B. Wu, Q. M. Wang, *Angew. Chem.* **2009**, *121*, 7479–7481; *Angew. Chem. Int. Ed.* **2009**, *48*, 7343–7345; c) T. Ahnfeldt, N. Guillou, D. Gunzelmann, I. Margiolaki, T. Loiseau, G. Férey, J. Senker, N. Stock, *Angew. Chem.* **2009**, *121*, 5265–5268; *Angew. Chem. Int. Ed.* **2009**, *48*, 5163–5166; d) Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang, X. M. Chen, *Angew. Chem.* **2009**, *121*, 5391–5394; *Angew. Chem. Int. Ed.* **2009**, *48*, 5287–5290; e) Z. Ni, A. Yassar, T. Antoun, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 12752–12753; f) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; g) B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435.

[4] a) J. R. Li, A. A. Yakovenko, W. Lu, D. J. Timmons, W. Zhuang, D. Yuan, H. C. Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 17599–17610; b) J. R. Li, H. C. Zhou, *Nat. Chem.* **2010**, *2*, 893–898; c) M. Jaya Prakash, M. Oh, X. Liu, K. N. Han, G. H. Seong, M. S. Lah, *Chem. Commun.* **2010**, *46*, 2049–2051; d) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 11650–11661; e) F. A. Cotton, P. Lei, C. Lin, C. A. Murillo, X. Wang, S. Y. Yu, Z. X. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 1518–1525; f) M. Eddaoudi, J. Kim, J. B. Wachter,

H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368 – 4369.

[5] S. T. Zheng, J. Zhang, X. X. Li, W. H. Fang, G. Y. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 15102 – 15103.

[6] a) Y. X. Tan, Y. P. He, J. Zhang, *Chem. Commun.* **2011**, *47*, 10647 – 10649; b) F. J. Ma, S. X. Liu, C. Y. Sun, D. D. Liang, G. J. Ren, F. Wei, Y. G. Chen, Z. M. Su, *J. Am. Chem. Soc.* **2011**, *133*, 4178 – 4181; c) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim, O. M. Yaghi, *Science* **2010**, *329*, 424 – 428; d) L. J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C. M. Brown, J. R. Long, *J. Am. Chem. Soc.* **2010**, *132*, 7856 – 7857; e) L. J. Murray, M. Dincă, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294 – 1314; f) J. Y. Lee, J. Li, J. Jagiello, *J. Solid State Chem.* **2005**, *178*, 2527 – 2532.

[7] a) N. Nishimura, K. Kobayashi, *Angew. Chem.* **2008**, *120*, 6351 – 6354; *Angew. Chem. Int. Ed.* **2008**, *47*, 6255 – 6258; b) R. Warmuth, J. Yoon, *Acc. Chem. Res.* **2001**, *34*, 95 – 105; c) P. Molenveld, J. F. J. Engbersen, D. N. Reinhoudt, *Chem. Soc. Rev.* **2000**, *29*, 75 – 86.

[8] a) T. Schröder, R. Brodbeck, M. C. Letzel, A. Mix, B. Schnatwinkel, M. Tonigold, D. Volkmer, J. Mattay, *Tetrahedron Lett.* **2008**, *49*, 5939 – 5942; b) K. Kobayashi, Y. Yamada, M. Yamanaka, Y. Sei, K. Yamaguchi, *J. Am. Chem. Soc.* **2004**, *126*, 13896 – 13897.

[9] a) P. Jin, S. J. Dalgarno, J. L. Atwood, *Coord. Chem. Rev.* **2010**, *254*, 1760 – 1768; b) P. Jin, S. J. Dalgarno, J. E. S. Warren, J. Teat, J. L. Atwood, *Chem. Commun.* **2009**, 3348 – 3350; c) S. J. Dalgarno, N. P. Power, J. E. Warren, J. L. Atwood, *Chem. Commun.* **2008**, 1539 – 1541; d) P. Jin, S. J. Dalgarno, C. Barnes, S. J. Teat, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 17262 – 17263; e) R. M. McKinlay, P. K. Thallapally, G. W. V. Cave, J. L. Atwood, *Angew. Chem.* **2005**, *117*, 5879 – 5882; *Angew. Chem. Int. Ed.* **2005**, *44*, 5733 – 5736; f) R. M. McKinlay, G. W. V. Cave, J. L. Atwood, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 5944 – 5948.

[10] a) A. Bilyk, J. W. Dunlop, R. O. Fuller, A. K. Hall, J. M. Harrowfield, M. Wais Hosseini, G. A. Koutsantonis, I. W. Murray, B. W. Skelton, R. L. Stamps, A. H. White, *Eur. J. Inorg. Chem.* **2010**, *132*, 2106 – 2107; b) T. Kajiwara, N. Iki, M. Yamashita, *Coord. Chem. Rev.* **2007**, *251*, 1734 – 1746.

[11] Y. F. Bi, W. P. Liao, G. C. Xu, R. P. Deng, M. Y. Wang, Z. J. Wu, S. Gao, H. J. Zhang, *Inorg. Chem.* **2010**, *49*, 7735 – 7740.

[12] Y. F. Bi, G. C. Xu, W. P. Liao, S. C. Du, X. W. Wang, R. P. Deng, H. J. Zhang, S. Gao, *Chem. Commun.* **2010**, *46*, 6362 – 6364.

[13] a) Y. F. Bi, S. C. Du, W. P. Liao, *Chem. Commun.* **2011**, *47*, 4724 – 4726; b) Y. F. Bi, X. T. Wang, W. P. Liao, X. F. Wang, X. W. Wang, H. J. Zhang, S. Gao, *J. Am. Chem. Soc.* **2009**, *131*, 11650 – 11651.

[14] Y. Liu, X. Liu, R. Warmuth, *Chem. Eur. J.* **2007**, *13*, 8953 – 8959.

[15] T. Hasell, M. Schmidtmann, A. I. Cooper, *J. Am. Chem. Soc.* **2011**, *133*, 14920 – 14923.

[16] S. Jiang, J. T. A. Jones, T. Hasell, C. E. Blythe, D. J. Adams, A. Trewin, A. I. Cooper, *Nat. Commun.* **2011**, *2*, 207.