Porous Materials

DOI: 10.1002/ange.200601668

A Multifunctional Metal–Organic Open Framework with a bcu Topology Constructed from Undecanuclear Clusters[**]

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The synthesis and characterization of metal–organic frameworks (MOFs) have attracted much attention, owing to their enormous variety of interesting structural topologies and wide potential applications as functional materials.[1] Recently, the design of MOFs with excellent properties that combine porosity with magnetism, luminescence, or opto-

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[**] This work was supported by the National Natural Science Foundation of China (grant nos. 20371020 and 20531030) and the Graduate Innovation Lab of Jilin University. We are very grateful for the help provided by Ankersmid Company, Netherlands. bcu = body-centered cubic.

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

electronic effects has become one of the major challenges in the pursuit of multifunctional materials.[2–4] Yaghi and co-workers, for example, have reported the synthesis of $[Tb_2(bdc)_3]\cdot 4H_2O$, which has an extended structure (pore volume: 0.099 $cm^3 g^{-1}$), from terbium nitrate and 1,4-benzenedicarboxylic acid (H_2bdc) in the presence of triethylamine, and have investigated its luminescence lifetime.[2a] As for the study of multifunctional materials that are both porous and magnetic, Riou, Férey, and co-workers have synthesized the hybrid organic–inorganic solid $[V(OH)(bdc)]\cdot xH_2bdc$ ($x \approx 0.75$), which has very large pores (BET surface area: 930(30) $m^2 g^{-1}$) and good magnetic characteristics (antiferromagnetic below 95 K), by using rigid organic linkers containing delocalized π electrons to connect chains of corner-sharing vanadium-centered octahedra.[3a] Our group has successfully prepared the novel 3D noninterpenetrating MOF $[Zn_7O_2(bda)_5(H_2O)_2]\cdot 5DMF\cdot 4EtOH\cdot 6H_2O$ (H_2bda = 1,4-benzenediacrylic acid; DMF = dimethylformamide), which is constructed from heptanuclear zinc carboxylate secondary building units (SBUs) and contains an intersecting channel system with a spacing of approximately 17.3 Å. This compound exhibits excellent adsorption, H_2 storage, and photoelectronic properties.[4]

Our strategy for preparing novel multifunctional structures is to construct metal carboxylate SBUs. The construction of metal carboxylate cluster SBUs has been demonstrated to be an effective and powerful synthetic method to produce a new generation of highly porous MOFs.[5,6] Interestingly, Powell and co-workers have pioneered studies on aluminum–ligand units with Al_{15} cluster aggregates containing the flexible ligand hpdta ($H_5hpdta = HOCH_2[CH_2N(CH_2COOH)_2]_2$), such as $[Al_{15}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{14}(hpdta)_4]^{3-}$.[7] However, although many MOFs built from different transition-metal carboxylate cluster SBUs have been synthesized, they usually consist of di-, tri-, or tetranuclear metal carboxylate clusters, in which a water molecule plays an important role as a bridging ligand.[8] The number of metal centers held together by the bridging water molecule is limited by its weak coordination ability. To overcome this difficulty, our strategy is to substitute the bridging water molecule with formic acid (HCOOH), which has a strong coordination ability, to construct stable metal carboxylate cluster SBUs. As an example of our design principle, we describe herein the synthesis and structure, as well as the sorption and optoelectronic properties of the large-pore open-framework complex $[Cd_{11}(\mu_4\text{-}HCOO^-)_6(bpdc)_9]\cdot 9DMF\cdot 6H_2O$ (**1**; H_2bpdc = 4,4′-biphenyldicarboxylic acid), which is constructed from undecanuclear clusters. To our knowledge, this MOF has the largest transition-metal carboxylate cluster SBUs reported to date.

Polymer **1** was synthesized under mild conditions by carefully adjusting the relative quantities of the rigid (bpdc) and flexible (HCOOH) ligands. X-ray crystallography revealed that **1** crystallizes in the trigonal system (space group *R*3*c* (no. 161)).[9] All of the cadmium atoms in the structure of **1** have octahedral coordination environments. As shown in Figure 1 a, the Cd^{II}-centered octahedra are linked together by 18 carboxylate groups from bpdc anions, which bind in a didentate or a chelating/bridging didentate fashion, and six $\mu_4\text{-}HCOO^-$ moieties to build up a nanosized undecanuclear $\{Cd_{11}(\mu_4\text{-}HCOO^-)_6(CO_2)_{18}\}$ cluster with C_3 symmetry and dimensions of approximately $10.5\times11.5\times12.8$ Å^3 (measured between opposite atoms along the three directions). These undecametallic clusters, which behave as SBUs, are interconnected through the biphenyl groups of bpdc molecules to generate an extended 3D framework (Figure 1 b). Figure 1 c shows the rectangular channels of 9.7×12.2 Å^2 (measured between opposite atoms) in **1**, which run along the [$\bar{1}$11] and [211] directions, and are filled with guest H_2O and DMF molecules, as established by elemental,

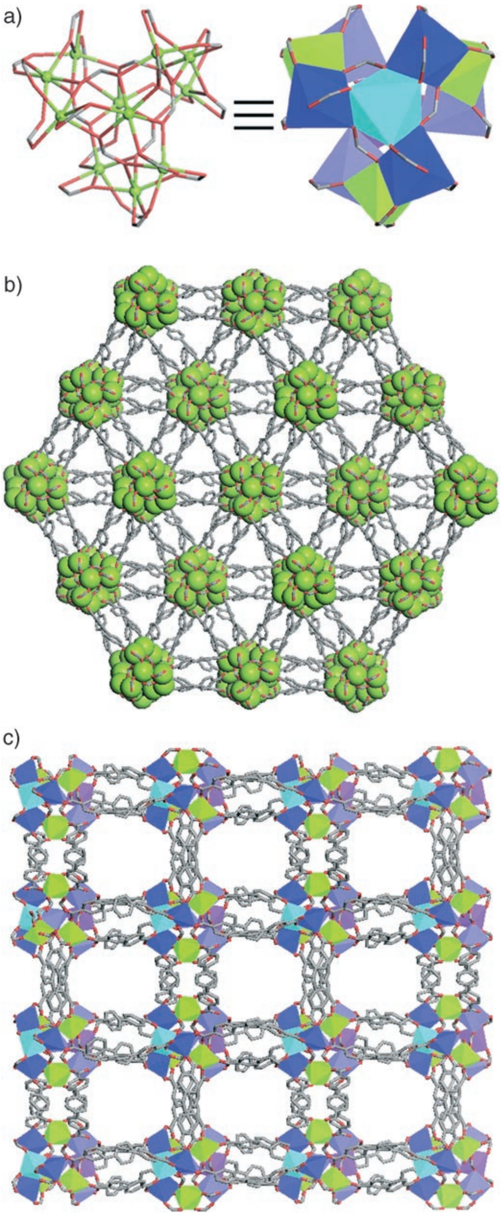

Figure 1. a) Ball-and-stick (left) and polyhedral (right) representations of the $\{Cd_{11}(\mu_4\text{-}HCOO^-)_6(CO_2)_{18}\}$ SBU of **1**, which has dimensions of approximately $10.5\times11.5\times12.8$ Å^3. b) View of the 3D framework of **1** along the [001] direction. c) View of the 3D framework of **1** along the [$\bar{1}$11] direction, showing large channels with dimensions of approximately 9.7×12.2 Å^2. Cd green, O red, C gray; CdO_6 octahedra; H atoms omitted for clarity

inductively coupled plasma (ICP), and thermogravimetric (TG) analysis (see Supporting Information).

A better insight into the structure of **1** can be obtained by the standard procedure of reducing multidimensional structures to simple node-and-linker reference nets known as the topological approach.[11] As shown in Figure 2a, each undecanuclear SBU in **1** is connected to adjacent SBUs through three biphenyl groups of bpdc molecules along the [001] direction and through two biphenyl groups along three other directions. Therefore, each SBU of **1** can be defined as an eight-connected node. As bpdc only acts as a bridging ligand, there is no need to consider it in the topological analysis. On the basis of this simplification, the structure of **1** can be described as an eight-connected 3D network with the Schläfli symbol ($4^{24}\cdot6^4$), which corresponds to a body-centered cubic (bcu) topology that is rare for MOFs (Figure 2b).[12]

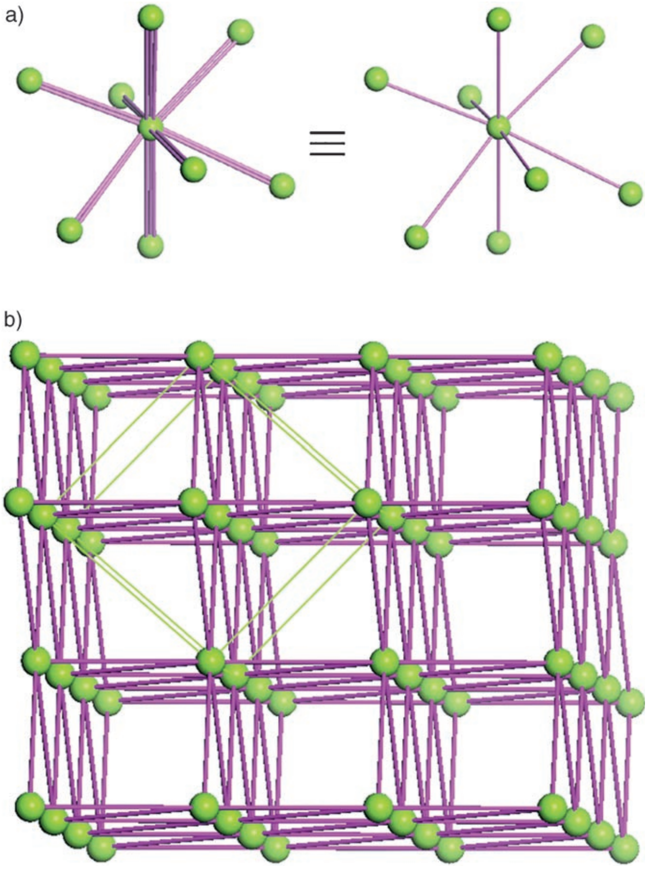

Figure 2. a) Left: each SBU (green circle) of **1** is connected to eight adjacent SBUs through eighteen biphenyl groups (pink lines) of bpdc molecules; right: the SBU represented as an eight-connected node. b) Schematic representation of the bcu topology of the eight-connected framework of **1**; the bcu unit cell is indicated by green lines.

Adsorption isotherms for **1** were measured at room temperature (293 K). As shown in Figure 3, type I behavior, which is characteristic of solids with micropores, is observed for the H_2O, CH_3OH, and C_2H_5OH adsorption isotherms in the range $P/P_0 = 0$–0.7. These results indicate that the incoming guests can move freely into the channels and that the framework maintains its rigidity and porosity throughout the analyses. The second increase in the adsorption isotherms above $P/P_0 = 0.7$ can be attributed to adsorption on the external crystallite surface.[13] At the first saturation, the amounts of H_2O, CH_3OH, and C_2H_5OH adsorbed by **1** are 314, 277, and 269 mg g^{-1}, respectively, equivalent to the adsorption of approximately 468 molecules of H_2O, 234 molecules of CH_3OH, and 162 molecules of C_2H_5OH per unit cell. The pore volume for **1** is, therefore, approximately 0.35 cm^3 g^{-1}. Detailed sorption data for **1** are presented in Table 1.

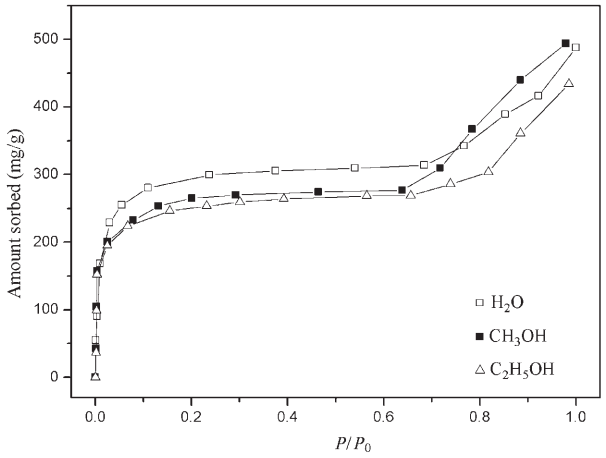

Figure 3. H_2O, CH_3OH, and C_2H_5OH adsorption isotherms for **1** at 293 K.

Table 1: Sorption data for **1**.

Guest	Adsorption amount [mg g^{-1}]	Guests per asymmetric unit	Guests per unit cell	Pore volume [cm^3 g^{-1}]
H_2O	314	26	468	0.31
CH_3OH	277	13	234	0.35
C_2H_5OH	269	9	162	0.34

Encouraged by the single-crystal X-ray diffraction results, which reveal the presence of undecanuclear cadmium clusters in the framework, photovoltage (PV) transients were recorded for **1** at atmospheric pressure and room temperature (293 K).[14] As is well known, PV transients can be used to characterize semiconductor materials, and a PV signal will arise whenever light-induced excess charge carriers are separated in space.[15] Figure 4 shows the PV transients for **1** at different intensities of the exciting laser pulse (355 nm). The transient PV signals of **1** clearly exhibit a time lag caused by the slow and independent diffusion of excess electrons and holes. Although the intensities of the exciting laser pulses are different (0.05, 0.10, 0.20, and 0.30 mJ), the times of their PV maxima are similar ($t \approx 0.013$ s). These maxima are related to the separation of charge at the **1**/indium tin oxide (ITO) interface, and the gradient of excess electron and hole concentrations is caused by the nonhomogeneous absorption of light with photons with $h\nu$ larger than the optical bandgap

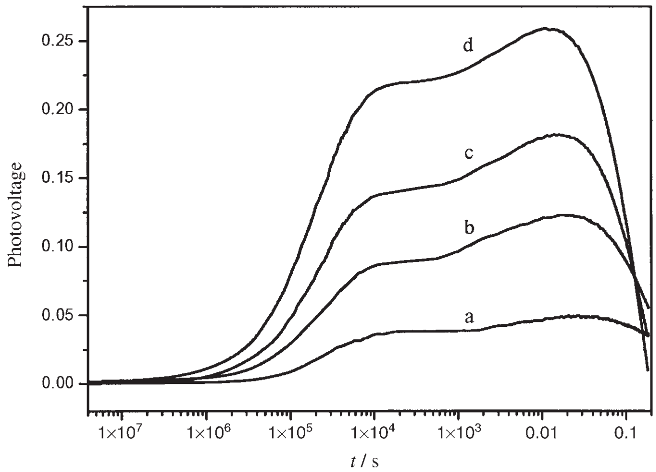

Figure 4. PV transients for **1** upon illumination by a 355-nm pulse laser at intensities of a) 0.05, b) 0.10, c) 0.20, and d) 0.30 mJ.

(E_g). Additionally, the PV transient signals are positive, which means that the photoexcited electrons move faster than holes towards the **1**/ITO interface. The maxima of the transients are linearly enhanced when the intensity of the pulse is increased from 0.05 to 0.30 mJ. This observation implies that **1** possesses the characteristics of a diffusion PV transient, but not of a Dember PV transient, which is similar to the case for nanosized metal oxide semiconductors.[16]

In summary, we have successfully synthesized the large-pore, open-framework complex $[Cd_{11}(\mu_4\text{-}HCOO^-)_6(bpdc)_9]\cdot 9DMF\cdot 6H_2O$ (**1**), which contains the largest known Cd^{II}–carboxylate cluster SBU and has a rare bcu topology, by rationally utilizing a flexible organic acid (HCOOH) as a strong bridging ligand. Polymer **1** shows good sorption and optoelectronic properties. Other novel architectures with unusual topologies and metal carboxylate cluster SBUs should be obtainable by following a similar synthetic strategy. We believe that such MOFs with large clusters and channels will further facilitate the exploration of new types of multifunctional materials with interesting properties, including the combination of porosity and magnetic, luminescence, or optoelectronic properties.

Experimental Section

1: A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.03 g, 0.1 mmol), H_2bpdc (0.01 g, 0.05 mmol), HCOOH (0.02 mL), and DMF (15.0 mL) was stirred in air for 4 h, and then a DMF solution (0.5 mL) of 2-propanolamine (0.05 mL) was slowly diffused into the mixture over 7 d at 60 °C. The resulting colorless, block-shaped single crystals of **1** were collected in 32 % yield based on cadmium. The complex is insoluble in common organic solvents such as acetone, methanol, ethanol, dichloromethane, acetonitrile, chloroform, and DMF. Elemental and ICP analysis (%) calcd for $C_{159}H_{153}Cd_{11}N_9O_{63}$ (4434.5): C 43.07, H 3.48, Cd 27.88, N 2.84; found: C 43.11, H 3.52, Cd 27.94, N 2.78. FT-IR (KBr): $\tilde{\nu}$ = 3433 (m), 3067 (w), 2928 (w), 1931 (w), 1659 (s), 1593 (s), 1504 (s), 1394 (s), 1267 (w), 1180 (m), 1105 (m), 1063 (w), 1007 (m), 860 (m), 771 (s), 677 (m), 526 cm^{-1} (w).

Received: April 27, 2006

Keywords: cadmium · carboxylate ligands · clusters · materials science · supramolecular chemistry

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[1] a) N. W. Ockwig, O. Delgado-Friederichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176; b) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460; d) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217; e) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012; f) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; g) A. Erxleben, *Coord. Chem. Rev.* **2003**, *246*, 203; h) C. Janiak, *Dalton Trans.* **2003**, 2781; i) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, Y. Wei, S. L. Qiu, R. R. Xu, *Angew. Chem.* **2005**, *117*, 3913; *Angew. Chem. Int. Ed.* **2005**, *44*, 3845.

[2] a) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1999**, *121*, 1651; b) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, F. X. Sun, S. L. Qiu, *Inorg. Chem.* **2006**, *45*, 3582.

[3] a) K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.* **2002**, *114*, 291; *Angew. Chem. Int. Ed.* **2002**, *41*, 281; b) K. Barthelet, K. Adil, F. Millange, C. Serre, D. Riou, G. Férey, *J. Mater. Chem.* **2003**, *12*, 2208; c) K. Barthelet, D. Riou, G. Férey, *Chem. Commu.* **2002**, 1492; d) K. Barthelet, D. Riou, M. Nogues, G. Férey, *Inorg. Chem.* **2003**, *42*, 1739.

[4] Q. R. Fang, G. S. Zhu, M. Xue, Q. L. Zhang, J. Y. Sun, X. D. Guo, S. L. Qiu, S. T. Xu, P. Wang, D. J. Wang, Y. Wei, *Chem. Eur. J.* **2006**, *12*, 3754.

[5] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319; b) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148; c) L. Pan, H. M. Liu, X. G. Lei, X. Y. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560; *Angew. Chem. Int. Ed.* **2003**, *42*, 542.

[6] a) Q. R. Fang, G. S. Zhu, M. Xue, J. Y. Sun, G. Tian, G. Wu, S. L. Qiu, *Dalton Trans.* **2004**, 2202; b) Q. R. Fang, G. S. Zhu, X. Shi, G. Wu, G. Tian, R. W. Wang, S. L. Qiu, *J. Solid State Chem.* **2004**, *177*, 1060; c) Q. R. Fang, X. Shi, G. Wu, G. Tian, G. S. Zhu, R. W. Wang, S. L. Qiu, *J. Solid State Chem.* **2003**, *176*, 1.

[7] W. Schmitt, E. Baissa, A. Mandel, C. E. Anson, A. K. Powell, *Angew. Chem.* **2001**, *113*, 3689; *Angew. Chem. Int. Ed.* **2001**, *40*, 3578.

[8] a) H. L. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; b) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239; c) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982; d) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; e) B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, W. B. Lin, *Angew. Chem.* **2005**, *117*, 74; *Angew. Chem. Int. Ed.* **2005**, *44*, 72.

[9] A colorless block-shaped crystal of **1** was selected for X-ray structural analysis, and intensity data were collected on a Bruker SMART CCD diffractometer at 298 K. Crystal data: 0.40 × 0.40 × 0.38 mm^3, trigonal, space group *R*3*c*, $a = 31.936(5)$, $c = 42.607(9)$ Å, $V = 37634(11)$ $Å^3$, $Z = 6$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 0.971$ $g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 0.958$ mm^{-1}, $F(000) = 10692$. 65660 reflections were collected in the range $0.88 < \theta < 25.00$, of which 12567 were unique. The structure was solved and refined by full-matrix least-squares on F^2 (SHELXL-97).[10] Non-hydro-

gen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined by using a riding model. The final $R1$ and $wR2$ values for 11332 independent reflections with $[I > 2\sigma(I)]$ were 0.0642 and 0.1770, respectively. CCDC-603457 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.

[10] G. M. Sheldrick, SHELX-97, Program for Structure Refinement, University of Göttingen, Germany, **1997**.

[11] a) A. F. Wells, *Further Studies of Three-Dimensional Nets*, American Crystallographic Association, New York (distributed by Polycrystal Book Service, Pittsburgh, PA), **1979**; b) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York, **1977**; c) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; d) O. D. Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, *59*, 22; e) C. Qin, X. L. Wang, E. B. Wang, Z. M. Su, *Inorg. Chem.* **2005**, *44*, 7122.

[12] a) D. L. Long, A. J. Blake, N. R. Champness, C. Wilson, M. Schröder, *Angew. Chem.* **2001**, *113*, 2509; *Angew. Chem. Int. Ed.* **2001**, *40*, 2443; b) D. L. Long, R. J. Hill, A. J. Blake, N. R. Champness, P. Hubberstey, D. M. Proserpio, C. Wilson, M. Schröder, *Angew. Chem.* **2004**, *116*, 1887; *Angew. Chem. Int. Ed.* **2004**, *43*, 1851; c) R. J. Hill, D. L. Long, P. Hubberstey, M. Schröder, N. R. Champness, *J. Solid State Chem.* **2005**, *178*, 2414; d) T. T. Luo, H. L. Tsai, S. L. Yang, Y. H. Liu, R. D. Yadav, C. C. Su, C. H. Ueng, L. G. Lin, K. L. Lu, *Angew. Chem.* **2005**, *117*, 6217; *Angew. Chem. Int. Ed.* **2005**, *44*, 6063; e) J. Lu, W. T. A. Harrison, A. J. Jacobson, *Angew. Chem.* **1995**, *107*, 2759; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2557; f) J. U. Schutze, R. Eckhardt, R. D. Fischer, D. C. Apperley, N. A. Davies, R. K. Harris, *J. Organomet. Chem.* **1997**, *534*, 187.

[13] M. Eddaoudi, H. L. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391.

[14] Q. L. Zhang, D. J. Wang, X. Wei, T. F. Xie, Z. H. Li, Y. H. Lin, M. Yang, *Thin Solid Films* **2005**, *491*, 242.

[15] V. Duzhko, V. Yu. Timoshenko, F. Koch, T. Dittrich, *Phys. Rev. B* **2001**, *64*, 075204.

[16] T. Dittrich, V. Duzhko, F. Koch, V. Kytin, J. Rappich, *Phys. Rev. B* **2001**, *65*, 155319.