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Supramolecular Chemistry

Copper β-Diketonate Molecular Squares and Their Host–Guest Reactions**

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In the field of porous supramolecular metal complexes, both molecular[1] and extended-solid[2] materials have been extensively studied in recent years. These materials are attractive due to their applications in gas storage[3] and host–guest chemistry.[4] Among the most often studied of these species are the metal-containing "molecular squares", that is, square-shaped porous tetrameric structures. These have been prepared by several approaches, the most common being the reaction of an organic bridging ligand with a metal complex that has available *cis* coordination sites (Figure 1 a). The bridging ligand is frequently a pyridine derivative (for example, 4,4′-bipyridine (4,4′-bpy)),[5] although bis-chelating ligands have also been used.[6] In these cases, the 90° "corners" in the molecular squares are provided by metal complexes. The resulting metal centers are usually coordinatively saturated, which makes it difficult for guest molecules to interact directly with the metal atoms. Herein we report molecular squares prepared by an alternative approach, in which bifunctional organic moieties serve as the "corners" and join metal atoms in the centers of the "sides" (Figure 1 b).[7] These molecular squares are formed in one step, by reaction of bis(β-diketone) ligands (**1**) with $[Cu(NH_3)_4]^{2+}$ (Scheme 1). The new squares (**2**) are capable of binding guests in both a σ (for example, 4,4′-bpy) and π fashion (for example, C_{60}), and they are also surprisingly effective for hydrogen-gas storage, both at 77 K and at room temperature.

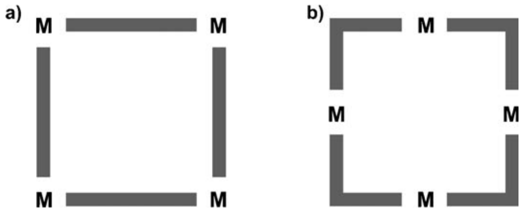

Figure 1. Schematic illustration of metal-organic molecular squares, assembled from: a) linear organic linkers and 90° metal units, or b) linear metal units and organic "corners".

Ligands **1a** and **1b** were synthesized by reaction of isophthalaldehyde with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene and 2,2,2-trimethoxy-4,5-diethyl-1,3,2-dioxaphospholene, respectively, at room temperature and heating the intermediate in methanol under nitrogen.[8] Mixing solutions of **1a** or **1b** in CH_2Cl_2 with aqueous $[Cu(NH_3)_4]^{2+}$ produces **2a** or **2b**, respectively, which can be isolated as dark green solids in approximately 95 % yield.

The angles between the two β-diketone moieties in the new ligands **1** are about 120°. Thus, we anticipated that their reaction with metal ions would yield hexamers, for example, $[M_6(m\text{-pba})_6]$. However, X-ray analysis of the crystalline products **2**, which are formed in nearly quantitative yield, shows that they are actually molecular squares, with diameters of about 14 Å (Figure 2).[9] (We explored a variety of conditions for preparing **2**, but found no evidence of other oligomers.) Thus, **2a** and **2b** are unusual examples of molecular squares in which the corners are organic bridging groups, and the metal atoms are in the centers of the sides.

The angles between the β-diketone moieties in the structures of **2a** and **2b** are still approximately 120°. To accommodate this angle within an overall square shape, there must be some distortion elsewhere in the molecule. The two ligands are coplanar with the metal atoms in an undistorted [Cu(β-diketonate)$_2$] complexes,[10] while, in the present squares, the ligands are all bent away from coplanarity.

The formation of squares, despite the "incorrect" angle between the β-diketonate moieties, may be due to two factors. For example, of the reactions shown in Equations (1) and (2)

$$4\,Cu^{2+} + 4\,m\text{-pba}^{2-} \rightleftharpoons [Cu_4(m\text{-pba})_4] \tag{1}$$

$$6\,Cu^{2+} + 6\,m\text{-pba}^{2-} \rightleftharpoons [Cu_6(m\text{-pba})_6] \tag{2}$$

reaction (1) is expected to be favored on entropy grounds. Although self-assembly of *cis* square-planar or octahedral metal coordination units with linear linkers normally yields molecular squares, several examples have been reported in which significant quantities of trimeric products (that is, molecular triangles) form.[11] Studies of supramolecular self-assembly have measured the entropy change that favors the

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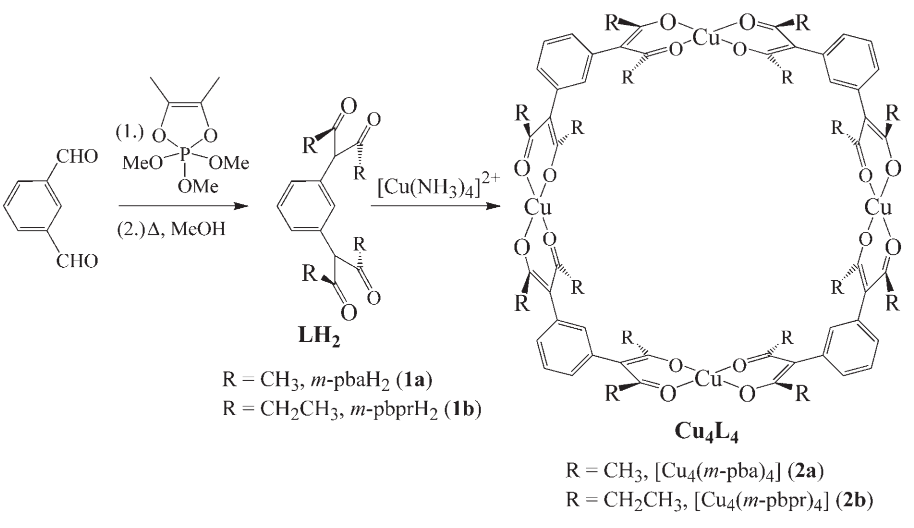

Scheme 1. Synthesis of *m*-phenylenebis(β-diketones) **1** and their copper(II) molecular squares **2**.

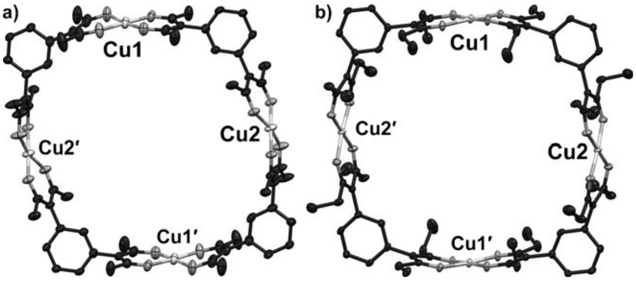

Figure 2. Crystal structure of β-diketonate molecular squares. H atoms and solvent molecules omitted for clarity; ellipsoids shown at 50%. a) [Cu$_4$(*m*-pba)$_4$] (**2a**), Cu1···Cu1′ 14.317(1) Å; Cu2···Cu2′ 14.647(1) Å. b) [Cu$_4$(*m*-pbpr)$_4$] (**2b**), Cu1···Cu1′ 14.012(1) Å; Cu2···Cu2′ 14.661(1) Å.

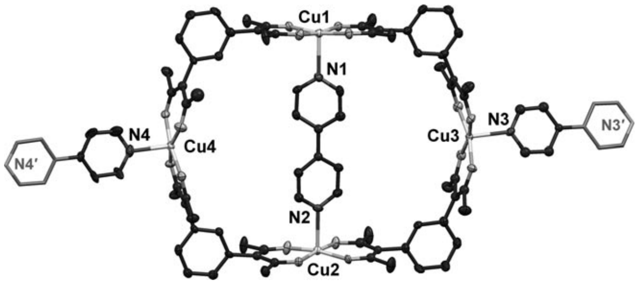

Figure 3. Crystal structure of [Cu$_4$(*m*-pba)$_4$(4,4′-bpy)$_2$]$_n$ (**3a**). H atoms and solvent molecules omitted for clarity; ellipsoids shown at 50%. Cu1···Cu2 11.807(1), Cu3···Cu4 16.226(1), Cu1-N1 2.360(8), Cu2-N2 2.363(8), Cu3-N3 2.251(7), Cu4-N4 2.250(8) Å. (Inversion-related portions of the 4,4′-bpy molecules at N3 and N4 are shown in a lighter shade, without ellipsoids.)

formation of smaller cyclic oligomers over larger ones.[12] Second, the formation of smaller cyclic products can be favored kinetically: Lehn and co-workers reported that the initial reaction of Cu^{I} ions with a polypyridine ligand produced a cyclic mononuclear species, followed by rearrangement to the more stable trinuclear supramolecular product.[13] In their case, this was possible because a coordinating solvent was chosen, which permits ligand dissociation/reassociation. In contrast, the compounds reported here are soluble only in noncoordinating solvents such as CH$_2$Cl$_2$ and CHCl$_3$. Dissociation in these solvents would lead to unstable ionic intermediates, thus making it difficult for [Cu$_4$(*m*-pba)$_4$] to rearrange into higher oligomers that might be more stable.

Squares **2** react with several types of guest molecules. For example, **2a** reacts with 4,4′-bpy to produce the turquoise polymeric complex [Cu$_4$(*m*-pba)$_4$(4,4′-bpy)$_2$]$_n$ (**3a**, Figure 3).[14] In this compound the 4,4′-bpy molecules are intra- and intermolecularly bonded to the molecular square. The Cu···Cu distances in the undistorted squares **2a** are longer than normally observed in 4,4′-bpy-bridged complexes (ca. 10 Å). However, in **3a**, the 4,4′-bpy guest is accommodated by means of smaller distortions at the Cu1 and Cu2 atoms (as compared to those found in **2a** and **2b**) and larger distortions at the Cu3 and Cu4 atoms. The square-pyramidal environment around the Cu atoms favors both changes (bringing the *endo*-coordinated Cu atoms closer together, and the *exo*-coordinated ones farther apart), as do the larger Cu–N bond lengths for the internally bound bpy guest. Reaction of **2** with other pyridine derivatives leads to similar color changes, thus indicating Cu–N coordination.

We studied fullerenes as examples of π-binding guests. Numerous hosts have been reported that bind fullerenes, but only a few of these function by wrapping completely around the guest. One such example is the cofacial diporphyrins reported by Tashiro and Aida.[15] The present molecular squares **2** readily bind fullerenes C$_{60}$ and C$_{70}$ in solvents such as chlorobenzene, as evident from UV/Vis spectral changes on mixing. The C$_{60}$ adduct of **2b**, that is, [Cu$_4$(*m*-pbpr)$_4$·C$_{60}$] (**4b**), formed crystals that were suitable for X-ray analysis. The structure (Figure 4)[16] shows two interesting features: the ethyl

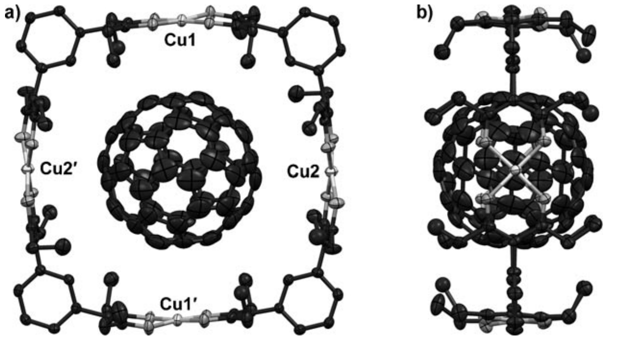

Figure 4. Crystal structure of [Cu$_4$(*m*-pbpr)$_4$·C$_{60}$] (**4b**): a) Front view and b) side view. H atoms and solvent molecules omitted for clarity; ellipsoids shown at 50%. Cu1···Cu1′ 13.955(1) Å; Cu2···Cu2′ 14.060(1) Å.

groups from the *m*-pbpr ligands are all oriented toward the C_{60} guest; and the Cu$\cdots$Cu distances (13.96 and 14.06 Å) are slightly smaller than in the solvated host (**2b**, Figure 2). These structural features suggest that weak attractions between the C_{60} molecule and the C–H bonds and Cu-O-C π systems of the host stabilize the host–guest adduct.

The crystal structures of **2a**, **2b**, and **4b** are all similar, with the Cu_4L_4 squares arranged in parallel so as to create "channels" (see the crystallographic data in the Supporting Information); in **2a** and **2b**, the channels are filled with solvent. This similarity of the structures suggested that it might be possible to remove the solvents from **2** and use the "empty" crystals for gas-storage experiments. However, heating **2** or placing it under vacuum to remove the solvents results in a loss of crystallinity, thus making it impossible to do this experiment directly. Still, even noncrystalline unsolvated **2** cannot pack efficiently and should therefore remain porous; thus, it might serve as a host for gas adsorption. For example, Sudik et al. have recently reported gas-storage properties of "metal-organic polyhedra" as noncrystalline solids.[17] Accordingly, samples of **2a** and **2b** that had been heated to 100 °C under vacuum overnight were used for H_2 adsorption experiments.[18] The results obtained at room temperature and $P_{H_2} = 75$ atm were 0.65% (**2a**) and 0.56% w/w (**2b**), which correspond to approximately 4.3 and 4.4 molecules of H_2 per molecule of **2a** and **2b**, respectively. Greater adsorption was observed at 77 K and $P_{H_2} = 43$ atm: 4.3% (**2a**) and 4.2% w/w (**2b**). These values are among the best recorded for porous metal-organic compounds,[19] and they demonstrate that non-crystalline, molecular hosts can function effectively in H_2 adsorption.

The present study reports the complexation behavior of the new bis(β-diketone) ligands **1** with copper(II) ions to yield molecular squares **2**. The supramolecular product in these reactions is obtained in high yield in a simple room-temperature reaction. The molecular squares **2** function effectively as hosts for guests that bind through σ- (4,4′-bpy), π- (C_{60}), and van der Waals (H_2) interactions. We are now exploring the reactions of **2** and related hosts in more detail, as well as the assembly of supramolecular hosts from other multidentate β-diketone ligands.

Experimental Section

The preparation of the new bis(β-diketones) **1a** and **1b** is described in the Supporting Information.

2a: A solution of $[Cu(NH_3)_4]^{2+}$ was prepared from $CuSO_4{\cdot}5\,H_2O$ (0.35 g, 1.4 mmol) in H_2O (10 mL) by slow addition of conc. aqueous NH_3. A solution of **1a** (0.275 g, 1.00 mmol) in CH_2Cl_2 (20 mL), was then added and the mixture was stirred for 6 h. More CH_2Cl_2 (20 mL) was then added, and the organic layer was collected and dried over $MgSO_4$. The residue was washed with hexane (2 × 10 mL) and dried in air. Yield: 0.325 g (96%). Elemental analysis calcd for $C_{64}H_{64}O_{16}Cu_4$ ($M_r = 1343.40$): C 57.22, H 4.80; found: C 57.43, H 4.69. **2b** was prepared by a similar method; yield: 95%. Elemental analysis calcd for $C_{80}H_{96}O_{16}Cu_4$ ($M_r = 1567.80$): C 61.29, H 6.17; found: C 61.08, H 6.00. Single crystals of these two compounds suitable for X-ray analysis were obtained by layering solutions in CH_2Cl_2 and $CHCl_3$ with hexane and benzene, respectively.

3a: A solution of **2a** (34 mg, 0.025 mmol) and 4,4′-bpy, (16 mg, 0.102 mmol) in $CHCl_3$ (3 mL) was layered with a mixture of CH_2Cl_2 (5 mL) and toluene (10 mL) at −20 °C. After two days, green crystals appeared. The crystals lost solvent rapidly in air to give a light green powder. Yield: 35 mg (84%). Elemental analysis calcd for $C_{84}H_{80}N_4Cu_4O_{16}$ ($M_r = 1655.74$): C 60.93, H 4.87, N 3.38; found: C 60.76, H 4.78, N 3.10. Crystals were attached to glass fibers and quickly cooled to 110 K for X-ray analysis.

4b: A solution of **2b** (25 mg, 0.015 mmol) in $CHCl_3$ (2 mL) was layered with a mixture of $CHCl_3$ and 1,2-dichlorobenzene (1:1, 1 mL) and then with a solution of C_{60} (15 mg, 0.021 mmol) in 1,2-dichlorobenzene (5 mL). Dark brown crystals had formed after several days. These crystals also lost solvent rapidly, but they could be mounted quickly and cooled to 110 K for X-ray analysis. The overall yield after drying was 21 mg of dark brown powder, but analytically pure material could not be obtained by this procedure.

X-ray analyses were performed on a Nonius KappaCCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) equipped with an Oxford Cryosystems Cryostream. CCDC-640918–640923 (compounds **1a**, **1b**, **2a**$\cdot 2\,CH_2Cl_2$, **2b**$\cdot 6\,CHCl_3 \cdot 3\,C_6H_6$, **3a**$\cdot 17.26\,CHCl_3 \cdot 1.74\,CH_2Cl_2 \cdot 0.5\,H_2O$, and **4b**$\cdot 2\,CHCl_3 \cdot 3\,C_6H_4Cl_2$, respectively) contain 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.

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[1] a) M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368; b) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; c) V. Maurizot, M. Yoshizawa, M. Kawano, M. Fujita, *Dalton Trans.* **2006**, 2750.

[2] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; b) C. Janiak, *Dalton Trans.* **2003**, 2781; c) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; ; d) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.* **2004**, *116*, 1490; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466; ; e) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273; f) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217.

[3] a) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem.* **2004**, *116*, 5143; *Angew. Chem. Int. Ed.* **2004**, *43*, 5033; ; b) L. Pan, M. B. Sander, X. Y. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J. K. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 1308; c) X. B. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012; d) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670; e) S. K. Bhatia, A. L. Myers, *Langmuir* **2006**, *22*, 1688; f) H. Frost, T. Duren, R. Q. Snurr, *J. Phys. Chem. B* **2006**, *110*, 9565.

[4] a) J. A. Whiteford, P. J. Stang, S. D. Huang, *Inorg. Chem.* **1998**, *37*, 5595; b) K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81; c) M. Albrecht, I. Janser, S. Burk, P. Weis, *Dalton Trans.* **2006**, 2875; d) Y. Kobayashi, M. Kawano, M. Fujita, *Chem. Commun.* **2006**, 4377.

[5] a) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645; b) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273; c) R. V. Slone, J. T. Hupp, C. L. Stern, T. E. Albrecht-Schmitt, *Inorg. Chem.* **1996**, *35*, 4096.

[6] a) Y. S. Zhang, S. N. Wang, G. D. Enright, S. R. Breeze, *J. Am. Chem. Soc.* **1998**, *120*, 9398; b) F. A. Cotton, C. Lin, C. A. Murillo, *Inorg. Chem.* **2001**, *40*, 478.

[7] Metal-organic supramolecules have been reported previously in which the organic moieties serve as the "corners"; see, for

example, a) J. R. Hall, S. J. Loeb, G. K. H. Shimizu, G. P. A. Yap, *Angew. Chem.* **1998**, *110*, 130; *Angew. Chem. Int. Ed.* **1998**, *37*, 121; b) M. Roitzsch, B. Lippert, *Angew. Chem.* **2006**, *118*, 153; *Angew. Chem. Int. Ed.* **2006**, *45*, 147; c) H. B. Yang, N. Das, F. H. Huang, A. M. Hawkridge, D. D. Diaz, A. M. Arif, M. G. Finn, D. C. Muddiman, P. J. Stang, *J. Org. Chem.* **2006**, *71*, 6644; d) S. B. Zhao, R. Y. Wang, S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 3092. However, these metallacycles typically contain square-planar d^8 metals, which have low affinity for the direct binding of guest molecules.

[8] a) F. Ramirez, A. V. Patwardhan, N. Ramanathan, N. B. Desai, C. V. Greco, S. R. Heller, *J. Am. Chem. Soc.* **1965**, *87*, 543; b) F. Ramirez, S. B. Bhatia, A. V. Patwardhan, C. P. Smith, *J. Org. Chem.* **1967**, *32*, 3547.

[9] Crystal data for **2a**·2 CH_2Cl_2 ($M_r = 1513.24$): Triclinic, space group $P\bar{1}$, $T = 105$ K, $a = 7.577(3)$, $b = 16.419(6)$, $c = 17.423(7)$ Å; $\alpha = 110.17(3)$, $\beta = 92.57(2)$, $\gamma = 92.063(15)°$; $V = 2029.5(14)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.251$ Mg m^{-3}; $R = 0.066$, $wR = 0.193$. Crystal data for **2b**·6 $CHCl_3$·3 C_6H_6 ($M_r = 2518.26$): Triclinic, space group $P\bar{1}$, $T = 110$ K, $a = 9.316(2)$, $b = 16.726(4)$, $c = 18.743(5)$ Å; $\alpha = 78.619(13)$, $\beta = 86.943(13)$, $\gamma = 83.472(9)°$; $V = 2843.1$ (12) Å^3; $Z = 1$; $\rho_{calcd} = 1.471$ Mg m^{-3}; $R = 0.062$, $wR = 0.183$.

[10] a) S. S. Turner, D. Collison, F. E. Mabbs, M. Helliwell, *J. Chem. Soc. Dalton Trans.* **1997**, 1117; b) B. L. Chen, F. R. Fronczek, A. W. Maverick, *Chem. Commun.* **2003**, 2166.

[11] a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535; b) X. Y. Yu, M. Maekawa, M. Kondo, S. Kitagawa, G. X. Jin, *Chem. Lett.* **2001**, 168.

[12] a) T. Yamamoto, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309; b) F. A. Cotton, C. A. Murillo, R. M. Yu, *Dalton Trans.* **2006**, 3900.

[13] N. Fatin-Rouge, S. Blanc, A. Pfeil, A. Rigault, A. M. Albrecht-Gary, J.-M. Lehn, *Helv. Chim. Acta* **2001**, *84*, 1694.

[14] Crystal data for **3a**·17.26 $CHCl_3$·1.74 CH_2Cl_2·0.5 H_2O ($M_r = 3872.89$): Triclinic, space group $P\bar{1}$, $T = 110$ K, $a = 14.824(3)$, $b = 19.384(4)$, $c = 29.616(6)$ Å; $\alpha = 99.043(8)$, $\beta = 97.751(11)$, $\gamma = 101.782(9)°$; $V = 8104(3)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.587$ Mg m^{-3}; $R = 0.088$, $wR = 0.253$.

[15] K. Tashiro, T. Aida, *Chem. Soc. Rev.* **2007**, *36*, 189.

[16] Crystal data for **4b**·2 $CHCl_3$·3 $C_6H_4Cl_2$ ($M_r = 2968.04$): Triclinic, space group $P\bar{1}$, $T = 110$ K, $a = 9.933(3)$, $b = 18.397(7)$, $c = 18.481(6)$ Å; $\alpha = 93.695(15)$, $\beta = 104.441(18)$, $\gamma = 92.017(14)°$, $V = 3259.1(19)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.512$ Mg m^{-3}; $R = 0.065$, $wR = 0.176$.

[17] A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110.

[18] C.-K. Back, G. Sandí, J. Prakash, J. Hranisavljevic, *J. Phys. Chem. B* **2006**, *110*, 16225.

[19] a) G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guegan, *Chem. Commun.* **2003**, 2976; b) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 32; c) B. L. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745; ; d) M. Dinca, J. R. Long, *J. Am. Chem. Soc.* **2005**, *127*, 9376; e) T. Sagara, J. Ortony, E. Ganz, *J. Chem. Phys.* **2005**, *123*, 214707; f) D. F. Sun, S. Q. Ma, Y. X. Ke, D. J. Collins, H. C. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 3896; g) B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas, R. E. Morris, *J. Am. Chem. Soc.* **2007**, *129*, 1203.