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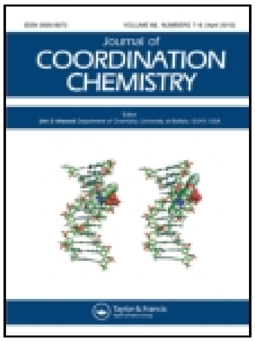

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2-D metalloporphyrin coordination network of cobalt-meso-tetra(4-carboxyphenyl)porphyrin

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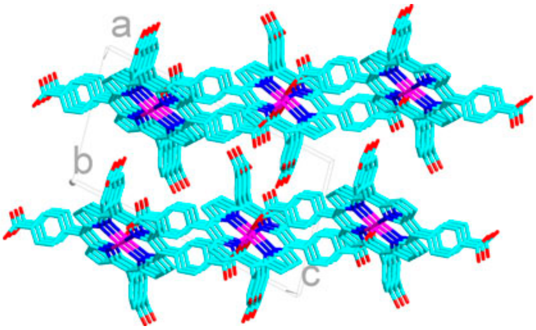

A new metalloporphyrin coordination framework [Co(H_3TCPP)] (H_6TCPP = meso-tetra(4-carboxyphenyl)porphyrin) has been synthesized hydrothermally. Single-crystal X-ray analysis revealed it exhibits a 2-D layered coordination network structure. Hydrogen bonds are observed between carboxyl groups within the 2-D layer as well as from adjacent layers. The UV–Vis diffuse reflectance spectrum indicates the presence of the expected *B* (410 nm) and *Q* (540 and 690 nm) absorption bands. The fluorescence spectrum shows four emission bands centered at 648 nm.

Keywords: Metalloporphyrin; 2-D; Cobalt; Metal-organic framework; Crystal structure; Fluorescence; Hydrogen bond

1. Introduction

In the last decade, a number of metalloporphyrin-based metal-organic frameworks (MOFs) have been synthesized [1–5] because of their potential applications in areas such as gas adsorption [6], artificial light-harvesting [7], biomimetic catalysis [8], and photocatalysis [9]. One advantage of porphyrin derivatives as building units of MOFs is that there are a variety of organic functional groups such as pyridyl, carboxylates which may be attached to porphyrins at the meso-positions. For example, meso-tetra(4-carboxyphenyl)porphyrin

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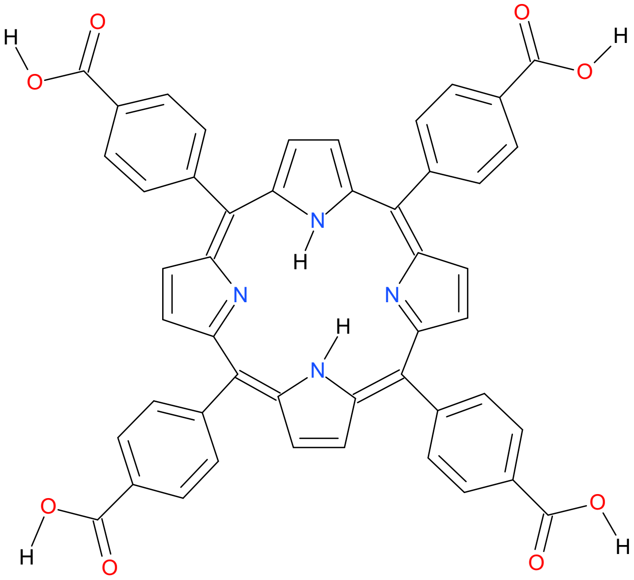

Figure 1. Meso-tetra(4-carboxyphenyl)porphyrin.

(H_6TCPP, as shown in figure 1) has four carboxyphenyl groups and is a versatile building block for MOFs because of its rigid structure and polydentate features. It offers two distinct coordinating sites: a structural metal-binding site at the carboxylate ligands and a reactive metal-binding site at the porphyrin center. The coordination of metal ions to H_4TCPP^{2-} not only strengthens the structural rigidity, but also provides additional binding sites to other ligands. There are a handful of MOFs that were made using merely H_6TCPP ligands as linkers, including 2-D [10] or 3-D [3, 11–14] metalloporphyrin-based MOFs. Further, using a second type of ligand in combination with H_6TCPP in the synthesis can provide interesting structures such as layered structures pillared by organic ligands [15–19] or inorganic clusters [20]. Our effort is to explore the synthesis of hybrid materials using polyoxometallates (POMs) as inorganic ligands or counter ions to metalloporphyrins [21]. In this process, we found POMs can promote the assembly of metalloporphyrin-based MOFs without incorporating into the resulting structures. Here, we report the synthesis and structure of a new metalloporphyrin-cobalt MOF [Co(H_3TCPP)].

2. Experimental

2.1. *Materials and equipment*

All chemicals purchased were of reagent grade and used without purification. Water used in the reactions was deionized. IR spectra were recorded from 400 to 4000 cm^{-1} on a Perkin–Elmer spectrum one FTIR spectrometer using KBr pellets. Fluorescence spectra were obtained by a Perkin–Elmer LS55 fluorescence spectrophotometer. UV–Vis diffusion reflectance spectra were recorded on a Varian Cary 100 UV–Vis spectrophotometer equipped with the DRA-CA-30 Diffuse reflectance accessory.

2.2. *Preparation of [Co(H_3TCPP)] (1)*

The title compound was synthesized through hydrothermal reaction from a mixture of cobalt (II) nitrate hexahydrate (0.012 g, 0.041 mmol), tetra(4-carboxyphenyl)porphyrin (0.025 g, 0.032 mmol), $3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$ (0.046 g, 0.015 mmol), and deionized water (0.50 mL). A typical reaction is as follows: 0.025 g of tetra(4-carboxyphenyl)porphyrin was dissolved in 1 mL 0.25 M KOH forming a dark brown solution. To this solution, 0.012 g of cobalt(II) nitrate hexahydrate and 2 drops of 1.0 M H_2SO_4 were added. To this resulting dark green solution (pH 5.0), 0.046 g $3Na_2WO_4 \cdot 9WO_3 \cdot H_2O$ was added. The mixture was heated in a Teflon-lined steel autoclave at 180 °C for 4 days and cooled to room temperature naturally. The purple crystals were filtered and dried in air (yield: 0.012 g, 45%). IR data (KBr, cm^{-1}): 3074(m, broad), 1688(s), 1603(s), 1373(s), 1200(s), 1000(s), 797(s), 709(s).

2.3. *X-ray crystallographic study*

Single-crystal X-ray diffraction data of the title compound were collected on an Apex II CCD diffractometer. Data were integrated with a Bruker SAINT package and corrected for absorption effect using SADABS. The structure was solved by direct methods and was refined against F^2 by weighted full-matrix least-squares calculations. Hydrogens bound to carbon were placed at calculated positions and refined using a riding mode. Hydrogens on oxygen were found by successive Fourier syntheses and refined using a riding mode. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International tables for crystallography [22]. Crystal data and relevant details of the structure determinations are summarized in table 1 and selected geometrical parameters are given in table 2.

3. Results and discussion

Although numerous metalloporphyrin-based coordination polymers have been synthesized [23], the rational design or prediction of coordination network topologies/structures has

Table 1. Crystal data of [Co(H_3TCPP)].

Empirical formula	$C_{48}H_{26}CoN_4O_8$
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.0564(2)
b (Å)	8.8909(1)
c (Å)	20.0440(2)
α (°)	100.270(1)
β	90.00
γ	102.975(1)
V (Å^3), Z	1920.05(5), 2
θ range for data collection (°)	52.70
Reflections collected	37,650
Independent reflections	7813 [R(int) = 0.00351]
Completeness (%)	99.8
Goodness of fit on F^2	1.040
Final R_1, $wR_2[I > 2\sigma(I)]$	$R_1 = 0.0515$, $wR_2 = 0.1521$
R indices (all data)	$R_1 = 0.0582$, $wR_2 = 0.1588$

Notes: $w = \frac{1}{[s^2(F_o^2)+(0.107P)^2+1.143P]}$, where $P = \frac{(F_o^2+2F_c^2)}{3}$.

Table 2. Selected interatomic distances (Å) of [Co(H_3TCPP)].

Co(1)–O(4)#1	1.987(3)	O(2)–C(27)	1.225(7)
Co(1)–N(4)	2.021(3)	O(3)–C(34)	1.254(5)
Co(1)–N(2)	2.027(3)	O(4)–C(34)	1.260(5)
Co(1)–N(3)	2.056(3)	O(5)–C(41)	1.311(7)
Co(1)–N(1)	2.062(3)	O(6)–C(41)	1.226(7)
Co(1)–O(7)	2.264(3)	O(7)–C(48)	1.240(5)
O(1)–C(27)	1.293(6)	O(8)–C(48)	1.301(5)

Notes: #1 $-x + 1$, $y + 1/2$, $-z$.

been a challenge. Nevertheless, synthetic strategies such as using pillars and constructing metal-organic polyhedra are extremely useful for seeking new functional coordination polymers. We have reported the self-assembly of the nano-sized Keggin ion $[SiW_{12}O_{40}]^{4-}$ with metalloporphyrin complexes ([M(TypP)], M = Zn, Cu; H_2TypP = meso-tetra(4-pyridyl)porphine) [21]. While we were trying to make hybrid compounds using H_6TCPP and POMs, the title compound was obtained with the presence of sodium metatungstate. Even though $H_2W_{12}O_{40}^{6-}$ is not present in the structure, the compound could not be made without it. Sodium metatungstate is a strong acid in aqueous solution. Its acidity may play an important role in the synthesis. However, the title compound could not be made using strong acids such as nitric acid or sulfuric acid. It is unclear the actual role of metatungstate in the synthesis mixture. One possible explanation is that metatungstate may act as a buffer in the reaction mixture. Before adding metatungstate, the pH of the reaction mixture was 5. The pH of metatungstate solution was around 3–4. The addition of metatungstate solution may generate other POMs such as paratungstates A and/or B [24]. These POM species can form a buffer solution, which may provide an appropriate reaction condition. However, replacing POM solutions with buffer (potassium hydrogen phthalate) solutions of pH 2, 3, or 4 in the preparation did not yield **1**. We also changed the amount of the POM in the preparation. Compound **1** can be made with a very low POM : H_6TCPP mole ratio (1 : 12).

X-ray single-crystal analysis reveals that the structure of the title compound is a layered coordination framework with a square-net topology. In the asymmetric unit, there is one unique cobalt site, which exhibits octahedral coordination geometry. Co(III) is six-coordinate to four nitrogens of one $[H_3TCPP]^{3-}$ and two carboxylate oxygens from two other $[H_3TCPP]^{3-}$ ligands. The Co–N bond lengths (2.022, 2.028, 2.057, and 2.061 Å) are slightly longer than those in other six-coordinate cobalt(III)-TCPP complexes (1.968 Å) [16] or four-coordinate Co(II)-TCPP complexes (average 1.98(1) Å) [25]. Co in the title compound is located slightly above the plane of the four nitrogens (0.130(1) Å).

It is interesting to compare the structure of the title compound to those of related systems. The structure of the layer in the title compound is the same as that of Mn-tetra(carboxyphenyl)porphyrin [10]. As shown in figure 2a, each Co(H_3TCPP) unit connects to two other Co(H_3TCPP) units through two of its four carboxylates as ligands, and two Co (H_3TCPP) units through its center metal ion to form a 2-D coordination polymer (figure 2b) with (4,4) net topology. The core of the metalloporphyrin is a 4-connected node. The phenyl rings of the four carboxyphenyl groups are not coplanar with the core ring of $[H_3TCPP]^{3-}$ molecular ion. Unlike the crystal structure of Mn-tetra(carboxyphenyl)porphyrin, the title compound does not have interlayer solvents.

The use of pyridine as a solvent led to the synthesis of a porous 3-D coordination framework ($[Co_5(TCPP)_2]$) [3]. Different from the 2-D structure of the title compound which contains uniformly [Co(H_3TCPP)] units, the porous 3-D structure of $[Co_5(TCPP)_2]$ contains

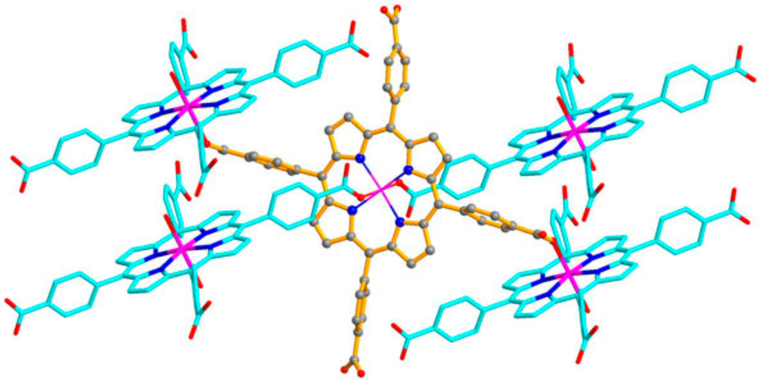

Figure 2a. The ball-and-stick and wire representation of the linkage of the [Co(H_3TCPP)] unit. The unit highlighted with yellow connected to four other units (see http://dx.doi.org/10.1080/00958972.2015.1061657 for color version).

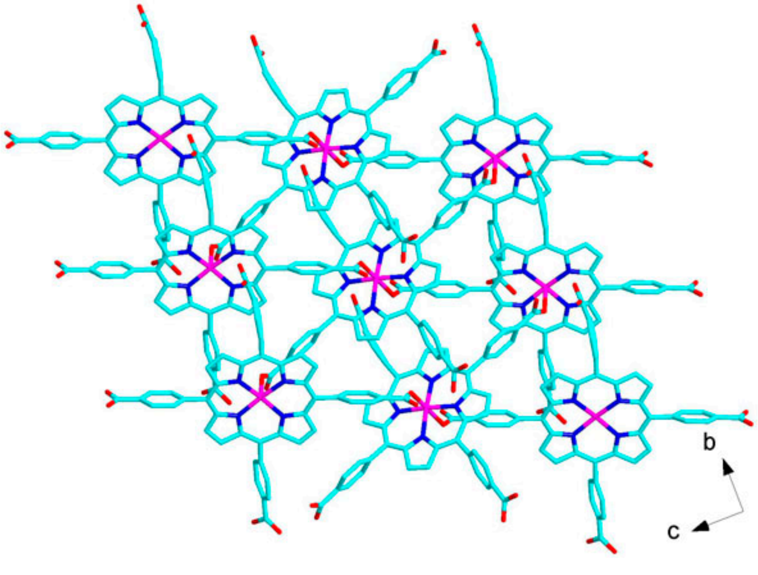

Figure 2b. A wire representation of the 2-D coordination network of [Co(H_3TCPP)].

trinuclear Co(II)-carboxylate clusters which are bridges between [Co(TCPP)] units. Also, H_6TCPP is fully deprotonated to $TCPP^{6-}$. This indicated solvent and pH can affect the structures formed, and it is difficult to predict the structures of the crystals in the self-assembly of MOFs.

Another related MOF synthesized using H_6TCPP as building blocks is [Zn_2(H_2TCPP)]·x (etg) (etg = ethylene glycol) [11]. In this structure, H_6TCPP is deprotonated to H_2TCPP^{4-}, whose porphyrin core is coordinated by a Zn(II) to form $[Zn(H_2TCPP)]^{2-}$. A four-coordinated external zinc ion connects the $[Zn(H_2TCPP)]^{2-}$ units to form a 3-D coordinated framework. A common structural feature of [Zn_2(H_2TCPP)]·x(etg) and [$Co_5(TCPP)_2$] is that their porphyrin ligands are highly deprotonated and thus allow for a second type of ion, while in the title compound, there is only one type of metal ion. This feature of these structures indicates that changing pH of the reaction mixture may alternate the charge of the TCPP ligand and therefore help to control the structures of the crystals formed.

Bond valence sum calculation shows that Co is in the 3+ oxidation state [26]. Based on the charge balance of the compound, three of the four carboxylate groups of TCPP ligand should be protonated. The C–O distances of the COO groups agree with the existence of three carboxyl groups (−COOH) in [Co(H_3TCPP)]. The two C–O bond lengths on C34 are almost equal (1.247 and 1.252 Å), indicating a carboxylate COO^- on C34. The C–O bond lengths on C27, C41, and C48 show clearly a single bond (1.225(7)–1.240(5) Å) and a double bond (1.293(6)–1.311(7) Å) in [Co(H_3TCPP)]. These bond length values are comparable to those of acetic acid (C–O 1.21 Å, C=O 1.36 Å). Further, the C=O double bond on C48 is longer (1.237 Å) than those of C27 (1.229 Å) and C21 (1.220 Å) which could be attributed to the coordination of −COOH of C48 to the cobalt(III) center.

The layers of [Co(H_3TCPP)] stack along the *a* direction with the AAA…mode by shifting one cell unit (11.0564 Å). The interlayer van der Waals interactions and hydrogen bonding connect adjacent layers into a 3-D hydrogen-bonded framework (figure 3). Interlayer hydrogen bonds are found between carboxyl groups with the O(1)–H···O(3) D···A distance of 2.640(6) Å and ∠D-H···A of 165 °. Intralayer hydrogen bonds between carboxyl groups are also formed (O(5)–H···O(3) and O(8)–H···O(2)). 1-D channels are formed along the *b* direction through hydrogen interlayer bonds. The dimensions of the 1-D rectangular channels are *ca.* 6.27 × 3.25 Å. However, no solvent accessible space was found when the structure was examined using Platon. Clearly, the hydrogen-bond interactions between layers offer stronger forces than the van der Waals interactions to hold the layered network together. Numerous hydrogen-bonded porphyrinic solids have been reported in the last few decades, especially those with nanoporous structures [27].

IR spectra (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1061657) of the compound also show C=O vibration of the carboxyl group (COOH) at 1724 cm^{-1} and broad band at 3300–2600 cm^{-1} for O–H in COOH. The carboxylate COO stretching mode from the carboxylate ion (COO−) appears at 1373 cm^{-1}.

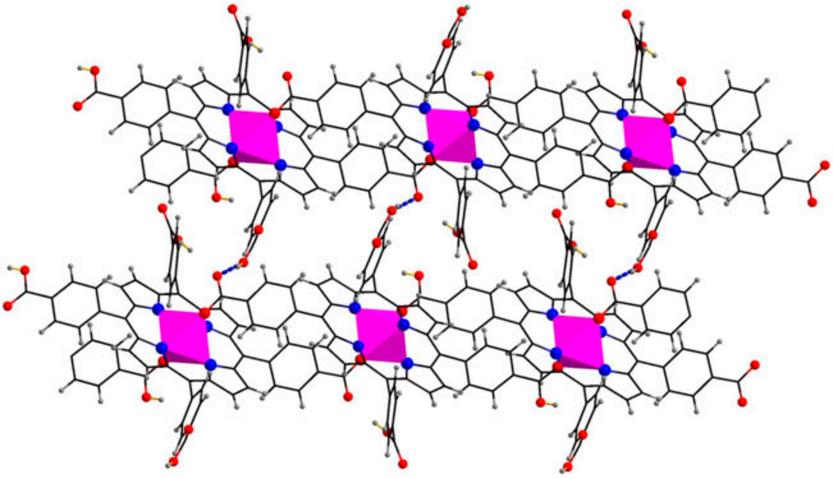

Figure 3. Hydrogen bonds connect adjacent 2-D coordination layers in [Co(H_3TCPP)].

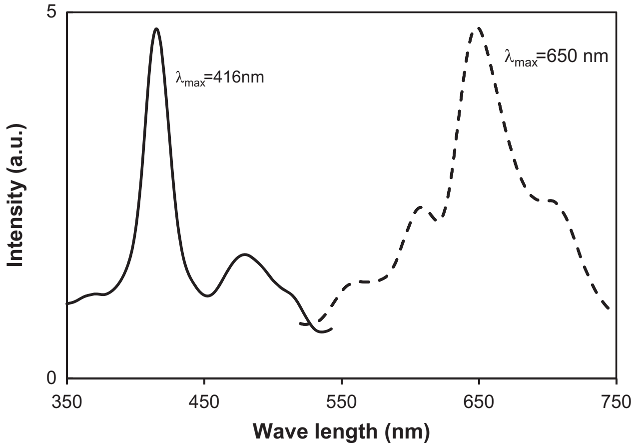

Figure 4. The fluorescence excitation (solid line, λ_{em} = 648 nm) and emission (dashed line, λ_{ex} = 410 nm) spectra of [Co(H_3TCPP)].

Porphyrins usually exhibit an intense *B* band (Soret band) at about 400 nm and four less intense *Q* bands between 500 and 650 nm. The *B* band and four *Q* bands for free-base TCPP are located at 416, 512, 546, 590, and 645 nm [28]. Figure S2 displays the diffuse reflectance spectrum. The *B* band is observed at 410 nm. Similar observation was reported for [Co(TCPP-Me_4)] (TCPP-Me_4 = meso-tetra(4-carboxyphenyl)porphine tetramethyl ester) [28]. The *B* band is red shifted relative to that of the free base. The *Q* bands peaks are at 540 and 690 nm. This can be attributed to the formation of metalloporphyrins; the four *Q* bands of the free base in the visible region collapse into essentially two bands due to their higher D_{4h} symmetry.

The fluorescence emission spectra measured at room temperature are shown in figure 4. The fluorescence spectrum shows four emission bands at 560, 609, 648, and 704 nm by excitation at 410 nm. The main emission band of 648 nm is same as the free base of TCPP [28]. The main excitation bands are located at 416 and 479 nm.

4. Conclusion

Although there are many MOFs in which TCPP was used as ligand [3, 6, 10–20], the title compound is the only example of a metalloporphyrin-based MOF built only from cobalt ions and TCPP. The presence of metatungstate in the reaction mixture may play an important role in the synthesis of this compound. The structure of the compound is a 2-D coordination network in which the [Co(H_3TCPP)] building units are linked through the core cobalt ions and carboxylate groups of the TCPP ligands. Inter-/intralayer interactions such as hydrogen bonds are observed and play an important role in the assembly of the network.

Supplementary material

Further details on the crystal structure investigations can be obtained from the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

[Telephone: 44-(0)1223-762-910; Fax: 44-(0)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk/deposit], on quoting the depository number CCDC: 1031269.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] I. Beletskaya, V.S. Tyurin, A.Y. Tsivadze, R. Guilard, C. Stern. *Chem. Rev.*, **109**, 1659 (2009).
[2] R.K. Kumar, I. Goldberg. *Angew. Chem. Int. Ed.*, **37**, 3027 (1998).
[3] M.E. Kosal, J.-H. Chou, S.R. Wilson, K.S. Suslick. *Nat. Mater.*, **1**, 118 (2002).
[4] L. Pan, X. Wang, B.C. Noll. *Chem. Commun.*, 157 (1999).
[5] K. Wang, D. Feng, T.-F. Liu, J. Su, S. Yuan, Y.-P. Chen, M. Bosch, X. Zou, H.-C. Zhou. *J. Am. Chem. Soc.*, **136**, 13983 (2014).
[6] W.-Y. Gao, Z. Zhang, L. Cash, L. Wojtas, Y.-S. Chen, S. Ma. *Cryst. Eng. Commun.*, **15**, 9320 (2013).
[7] H.-J. Son, S. Jin, S. Patwardhan, S.J. Wezenberg, N.C. Jeong, M. So, C.E. Wilmer, A.A. Sarjeant, G.C. Schatz, R.Q. Snurr, O.K. Farha, G.P. Wiederrecht, J.T. Hupp. *J. Am. Chem. Soc.*, **135**, 862 (2012).
[8] D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei, H.-C. Zhou. *Angew. Chem. Int. Ed.*, **51**, 10307 (2012).
[9] A. Fateeva, P.A. Chater, C.P. Ireland, A.A. Tahir, Y.Z. Khimyak, P.V. Wiper, J.R. Darwent, M.J. Rosseinsky. *Angew. Chem. Int. Ed.*, **51**, 7440 (2012).
[10] M. Shmilovits, M. Vinodu, I. Goldberg. *New J. Chem.*, **28**, 223 (2004).
[11] Y. Diskin-Posner, S. Dahal, I. Goldberg. *Chem. Commun.*, 585 (2000).
[12] M. Shmilovits, Y. Diskin-Posner, M. Vinodu, I. Goldberg. *Cryst. Growth Des.*, **3**, 855 (2003).
[13] H. Chung, P.M. Barron, R.W. Novotny, H.-T. Son, C. Hu, W. Choe. *Cryst. Growth Des.*, **9**, 3327 (2009).
[14] E.-Y. Choi, P.M. Barron, R.W. Novotny, H.-T. Son, C. Hu, W. Choe. *Inorg. Chem.*, **48**, 426 (2008).
[15] P.M. Barron, H.-T. Son, C. Hu, W. Choe. *Cryst. Growth Des.*, **9**, 1960 (2009).
[16] P.M. Barron, C.A. Wray, C. Hu, Z. Guo, W. Choe. *Inorg. Chem.*, **49**, 10217 (2010).
[17] O.K. Farha, A.M. Shultz, A.A. Sarjeant, S.T. Nguyen, J.T. Hupp. *J. Am. Chem. Soc.*, **133**, 5652 (2011).
[18] S. George, S. Lipstman, I. Goldberg. *Cryst. Growth Des.*, **6**, 2651 (2006).
[19] A.M. Smelser, Y.-F. Li, C.N. Carmichael, H.-Y. Zhao, W.-P. Pan, S. Parkin, B. Yan. *Inorg. Chim. Acta*, **375**, 122 (2011).
[20] A.J.C. Wilson (Ed.). *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht (1992).
[21] W.-Y. Gao, M. Chrzanowski, S. Ma. *Chem. Soc. Rev.*, **43**, 5841 (2014).
[22] J.J. Cruywagen. *Adv. Inorg. Chem.*, **49**, 127 (2000).
[23] C. Zou, M.-H. Xie, G.-Q. Kong, C.-D. Wu. *Cryst. Eng. Commun.*, **14**, 4850 (2012).
[24] N.E. Brese, M. O'Keeffe. *Acta Crystallogr., Sect. B: Struct. Sci*, **47**, 192 (1991).
[25] J.-H. Chou, M.E. Kosal, H.S. Nalwa, N.A. Rakow, K.S. Suslick. In *Porphyrin Handbook*, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), p. 41, Academic Press, New York (2000).
[26] W. Chen, S. Fukuzumi. *Eur. J. Inorg. Chem.*, **2009**, 5494 (2009).
[27] R. Kempe. *Z. Anorg. Allg. Chem.*, **631**, 1038 (2005).
[28] A. Fateeva, S. Devautour-Vinot, N. Heymans, T. Devic, J.-M. Grenèche, S. Wuttke, S. Miller, A. Lago, C. Serre, G. De Weireld, G. Maurin, A. Vimont, G. Férey. *Chem. Mater.*, **23**, 4641 (2011).