CO$_2$ Capture

Deutsche Ausgabe: DOI: 10.1002/ange.201607745
Internationale Ausgabe: DOI: 10.1002/anie.201607745

Mediating Order and Modulating Porosity by Controlled Hydrolysis in a Phosphonate Monoester Metal–Organic Framework

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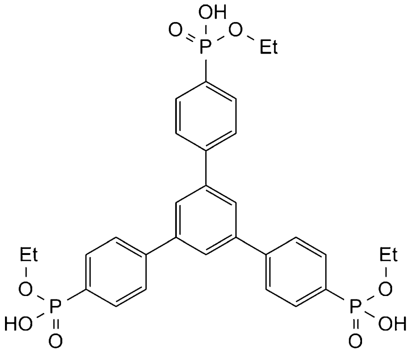
Abstract: *A crystalline and permanently porous copper phosphonate monoester framework has been synthesized from a tetraaryl trigonal phosphonate monoester linker. This material has a surface area over 1000* $m^2 g^{-1}$*, as measured by* N_2 *sorption, the highest reported for a phosphonate-based metal–organic framework (MOF). The monoesters result in hydrophobic pore surfaces that give a low heat of adsorption for* CO_2 *and low calculated selectivity for* CO_2 *over* N_2 *and* CH_4 *in binary mixtures. By careful manipulation of synthetic conditions, it is possible to selectively remove some of the monoesters lining the pore to form a hydrogen phosphonate while giving an isomorphous structure. This increases the affinity of the framework for* CO_2 *giving higher ambient uptake, higher heat of adsorption, and much higher calculated selectivity for* CO_2 *over both* N_2 *and* CH_4*. Formation of the acid groups is noteworthy as complexation with the parent acid gives a different structure.*

Increasing greenhouse gas concentration have been linked to climate change with the energy sector responsible for 80 % of carbon dioxide emissions.[1] Post-combustion capture, one of the possible ways of reducing CO_2 emissions, involves removing CO_2 from a gas stream containing primarily nitrogen.[2] Biogas or natural gas upgrading are other important processes where carbon dioxide must be removed from methane in order to more efficiently compress, transport, and use methane.[3] There are many opportunities for improving sorbent materials and capture technologies for removing CO_2 from nitrogen as well as from methane. Metal–organic frameworks (MOFs) are a promising candidate for gas separations owing to their versatile structures and systematically tunable components.[4] MOFs are a class of material in which metal atoms or clusters are connected by organic ligands to generate potential pores. Phosphonates, and more recently phosphonate monoesters (PMEs), are potentially advantageous ligands for MOFs owing to their ability to enhance hydrolytic stability.[5] Unfortunately in the absence of strong structure directing features, phosphonate ligands can easily form dense structures due to their three protonation states and eighteen coordination modes that allow many options for self-assembly.[5a,6] In contrast to carboxylate MOFs, there are no regular and robust cluster (0-D) secondary building units for phosphonate coordination polymers that would favor more open structures. PMEs reduce the degrees of freedom, relative to phosphonates, and provide an opportunity to more easily form open frameworks. Additionally, the use of the phosphonate monoesters facilitates ordering of the structure and formation of crystalline solids compared to the phosphonates. Previously, we have reported that the coordination of benzene polyphosphonate monoesters with copper(II) resulted in the formation of Cu-PME chains as the building units in ultramicroporous solids.[5b,7]

Here, we report the use of the design principles developed for the simple benzene PME derivatives to make a more porous structure based on a triphenylbenzene core, $H_3L1\text{-}Et_3$ (Figure 1). The copper(II) complex of this ligand forms a porous MOF, $[Cu_3(L1\text{-}Et_3)_2]_n$, CALF-33-Et$_3$ (CALF = Calgary Framework), with a surface area over 1000 $m^2 gm^{-1}$, to our knowledge, the highest reported for phosphonate related MOF materials. Furthermore, by subtle modification of the synthesis, it is possible to selectively hydrolyze one PME group in an isomorphous structure to tune the pore surface and enhance the gas sorption behavior.



$H_3L1\text{-}Et_3$

Figure 1. Chemical structure of $H_3L1\text{-}Et_3$.

The ligand, $H_3L1\text{-}Et_3$ was synthesized in three steps per literature (see the Supporting Information (SI) for details).[5a,b,6a] Blue needle-like crystals of $[Cu_3(L1\text{-}Et_2H)_2]_n$ (CALF-33-Et$_2$H) were grown by combining $Cu(NO_3)_2$, $H_3L1\text{-}Et_3$, ethanol, water, and 1,3-diisopropylbenzene in a hydrothermal vessel and heating to 120 °C. CALF-33-Et$_2$H crystallizes as a three-dimensional coordination material (Figure 2 a).[8] It is composed of stacked $L1\text{-}Et_2H^{3-}$ units connected by two types of copper-phosphonate pillars: square planar copper-phosphonate chains (Figure 2 b) and square pyramidal copper-phosphonate mono ethyl ester double chains (Figure 2 c). This results in one-dimensional pores measuring approximately

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201607745.

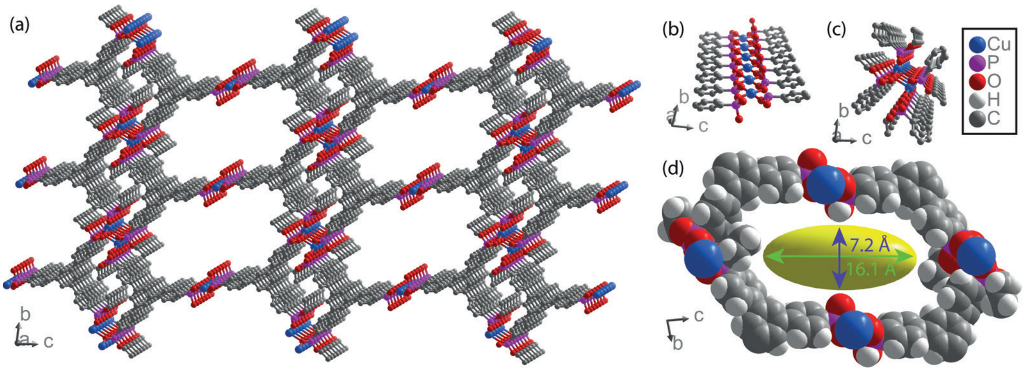

Figure 2. a) Overall structure of CALF-33-Et$_2$H highlighting b) the square planar copper-phosphonate chains, c) the square pyramidal copper-PME double chain, and d) the overall pore dimensions. Hydrogen atoms are omitted in parts (a)–(c) for clarity.

7.2 Å × 16.1 Å, including van der Waals radii (Figure 2 d). This structure crystallizes in the $P\bar{1}$ space group with one ligand and one and a half Cu^{II} per asymmetric unit (Figure S1 in SI). The in situ hydrolysis of a single PME to a hydrogen phosphonate was confirmed by ^{31}P{^{1}H} NMR (see SI for details). The presence of phosphonate and PME groups in the same structure suggested that careful manipulation of the synthesis could result in variable degrees of hydrolysis.

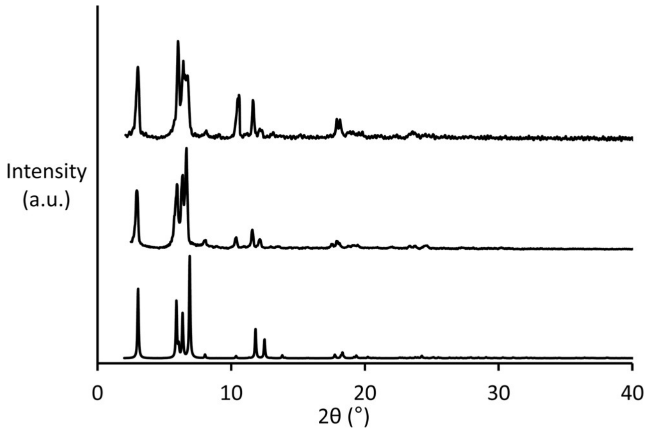

Figure 3. Simulated powder X-ray diffraction pattern (PXRD) for CALF-33-Et$_2$H (bottom) and experimental PXRD patterns for CALF-33-Et$_3$ (middle) and CALF-33-Et$_2$H (top) after activation.

By slight variation of the amount of water in the preparation of CALF-33-Et$_2$H, the unhydrolyzed analogue, CALF-33-Et$_3$, was synthesized (see SI). As synthetic conditions necessary to form single crystals resulted in partial hydrolysis of the ligand, ethyl ester groups were added to the CALF-33-Et$_2$H model in silico.[9] The powder X-ray diffraction (PXRD) pattern of prepared and evacuated CALF-33-Et$_3$ corresponds well to the simulated pattern for CALF-33-Et$_3$ (Figure 3). CALF-33-Et$_3$ gives a modeled surface area between 916 m^{2}g^{-1} and 1021 m^{2}g^{-1} (1.8 Å probe radius), depending on the orientation of the ester groups, a dependence which has previously been shown to significantly impact a material's gas uptake.[7] To confirm this virtual porosity, an N$_2$ sorption isotherm was collected (Figure 4), that gave a calculated Langmuir surface area of 1030 m^{2}g^{-1} (BET = 842 m^{2}g^{-1}). To test the separation capabilities and binding affinity for CO$_2$, gas sorption isotherms for CO$_2$, N$_2$, and CH$_4$ were collected at ambient temperatures (Figure 4).

As mentioned, the ratio of ester hydrolysis can be controlled based on the synthetic conditions (Table S2), to either retain all of the esters, hydrolyze selectively one third of the esters, or any stage between these two points. By this method, CALF-33-Et$_2$H, was synthesized in bulk with a PXRD pattern that matched the single crystal (Figure 3). CALF-33-Et$_2$H has a modeled surface area of 969 m^{2}g^{-1} (1.8 Å probe radius) and N$_2$ sorption at 77 K (Figure 4) result in a calculated Langmuir surface area of 950 m^{2}g^{-1} (BET = 810 m^{2}g^{-1}), confirming retention of the porosity after hydrolysis. Again, ambient gas sorption isotherms were collected for CO$_2$, N$_2$, and CH$_4$ (Figure 4) in order to calculate the binding affinity for CO$_2$ and the selectivity.

Phosphonate monoesters are fundamentally different from phosphonate groups with respect to their ligating ability. The bonding is weaker, which critically promotes crystallinity, but is still sufficiently strong to be able to sustain open

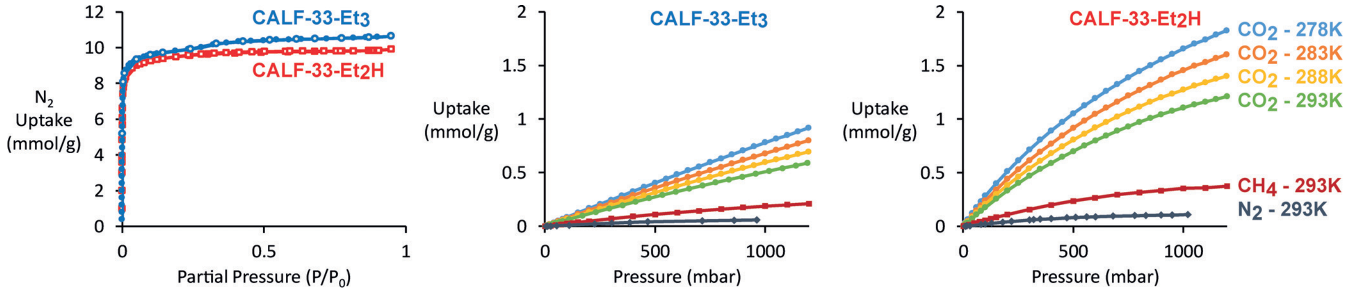

Figure 4. Left: N$_2$ uptake at 77 K for CALF-33-Et$_3$ and CALF-33-Et$_2$H. Center and Right: Ambient CO$_2$, CH$_4$ and N$_2$ uptake of CALF-33-Et$_3$ (center) and CALF-33-Et$_2$H (right).

structures. In this specific case, the triphosphonic acid analogue of L1 with Cu^{2+} yields a poorly crystalline material (Figure S5), but with a clearly different structure. L1 in combination with Ni^{2+} or Co^{2+} does result in crystalline materials, though these materials contain heavily hydrated metal atoms and porosity has not been observed.[6a] Thus, beyond enabling a more crystalline solid, the PME group actually directs a new structure but one that can ultimately contain phosphonate groups. The concept of using phosphonate monoesters to create a framework, followed by removal of the ester has been previously attempted. In these cases, however, the hydrolyzed frameworks were vastly different from the unhydrolyzed parent structure, suggesting that dissolution and precipitation likely occurred.[10] Conversely, the materials reported here are isostructural, differing only in the absence of a single ethyl ester per triphosphonate ligand.

The mechanism of PME hydrolysis was probed. It was found that the post-synthetic conversion of CALF-33-Et_3 to CALF-33-Et_2H was not possible in analogous hydrothermal conditions. Similarly, ^{31}P NMR of the mother liquor of CALF-33-Et_2H showed a statistical distribution of the hydrolyzed and unhydrolyzed ligand (Figure S4). These results suggest that the ligand is hydrolyzed prior to being incorporated in the framework, rather than being a solid–solid transformation via a post-synthetic modification. Thus, generating and controlling the formation of the monoacid, L1-Et_2H^{3-} in situ is key to the formation of the selectively hydrolyzed framework. While there is an elegance to a post-synthetic modification of a MOF structure, this in situ result still generates an isostructural material. Moreover, the enhanced stability of the ester group in the MOF versus the free ligand is a key enabler for functional PME MOFs.

To the best of our knowledge, CALF-33-Et_3 gives the highest reported surface area of any phosphonate- or PME-based coordination framework. This surface area is much lower than those reported for many carboxylate- or azolate-based MOFs, which often contain three-dimensional pores and thus a higher surface area. However, the surface area is comparable to other MOFs with one-dimensional pores, though higher surface areas have been reported.[11]

Despite CALF-33-Et_3 and CALF-33-Et_2H being formed from the same starting materials and having the same topology, they have very different properties owing to the hydrophobic ester being converted to a hydrophilic hydrogen phosphonate group. The most immediately evident result is an approximate doubling of ambient CO_2 uptake when comparing CALF-33-Et_3 to the hydrolyzed CALF-33-Et_2H, such as a maximum of uptake of approximately 0.9 $mmol\,g^{-1}$ at 278 K and 1200 mbar in CALF-33-Et_3 to over 1.8 $mmol\,g^{-1}$ at the same conditions in CALF-33-Et_2H.

The calculated CO_2 heat of adsorption for CALF-33-Et_3 (Figure S15) shows a very weak interaction of 16.8 $kJ\,mol^{-1}$ CO_2 at low loadings, which increases as the loading increases to 21.2 $kJ\,mol^{-1}$ CO_2. For CALF-33-Et_2H, the heat of adsorption is 20.8 $kJ\,mol^{-1}$ CO_2 at low loadings. As the loading is increased, the heat of adsorption increases to nearly 29.6 $kJ\,mol^{-1}$ CO_2 (Figure S15). Low heat of adsorption values, similar to the CALF-33-Et_3, have previously been reported in MOFs that contain primarily alkyl- or aryl-lined pores.[12] The increasing heat of adsorption with increasing CO_2 loading has been previously reported and has been attributed to CO_2–CO_2 interactions. Vaidhyanathan et al. reported an increase of 4.6 $kJ\,mol^{-1}$ with increased loading and attributed 3.9 $kJ\,mol^{-1}$ of this to CO_2–CO_2 interactions, primarily because of dispersion.[13] Higher heat of adsorption values, similar to CALF-33-Et_2H, have previously been reported in MOFs that contain CO_2–hydroxy or CO_2–amine interactions. Modeling of CO_2 in the pores of various MOFs have shown that hydroxy or amines on the framework can either act as a Lewis acid[14] or Lewis base,[15] depending on the accessibility of the functional groups' lone pairs or hydrogen atoms. As the loading in CALF-33-Et_2H increases, the heat of adsorption increases and cooperative CO_2–CO_2 interactions become significant similar to the results found for CALF-33-Et_3. The heat of adsorption increases similarly for these two materials, indicating that the hydrogen phosphonate is likely unable to induce long range changes in the dipole moment of CO_2.

Based on the increase in both uptake and enthalpy of adsorption when using the hydrolyzed CALF-33-Et_2H, ideal adsorbed solution theory (IAST) calculations were used to calculate the selectivity of both CALF-33-Et_3 and CALF-33-Et_2H for CO_2 over CH_4 and N_2.[16] The selectivity for CO_2 over CH_4, in an equimolar mixture, was 3.0 in CALF-33-Et_3 and 5.4 in CALF-33-Et_2H. Similarly, in a 1:4 mixture of CO_2 and N_2, the selectivity for CO_2 was 11.5 for CALF-33-Et_3 and increased to 29.8 in CALF-33-Et_2H. The separation ability of CALF-33-Et_2H is similar to many common MOFs, including some containing unsaturated metal sites.[17] Interestingly, the higher surface area MOF, CALF-33-Et_3, has lower performance for uptake at ambient temperatures, enthalpy of adsorption, and selectivity for CO_2. This supports the notion that the highest surface area materials, which are so commonly investigated, may not be the best materials for gas separation or storage as noted by Snurr.[18]

Here a new phosphonate monoester-based framework has been hydrothermally synthesized from a new trigonal planar phosphonate monoester and copper(II). CALF-33-Et_3 possesses over 1000 $m^2\,g^{-1}$ surface area but makes only weak binding interactions with carbon dioxide. An analogous framework, CALF-33-Et_2H, has been synthesized featuring two phosphonate monoesters and one hydrogen phosphonate lining the pores, giving an increased affinity for CO_2 and subsequently higher selectivity for carbon dioxide over both methane and nitrogen. To the best of our knowledge, this is the first example of isostructural MOFs with phosphonate versus PME groups. The methods developed here provide an intriguing opportunity to form hydrolyzed analogues of existing PME-based MOFs, most of which have esters lining the pores, in order to improve their selectivity for CO_2 over other gases. Although not the first example of a mixed phosphonate-PME material coordination material[19] nor the first example of in situ hydrolysis of a PME,[5c,10,20] the CALF-33 system is the first to exhibit permanent porosity and an isostructural relationship. This structure retention with hydrolyzed PMEs could be used to access new topologies and properties that would be unavailable beginning with the phosphonic acids directly. Moreover, these structures formed from PMEs are more likely to be open frameworks and more likely to be ordered owing to the fundamental coordination chemistry of the PME group.

Acknowledgements

We thank Carbon Management Canada for support of this research and the Natural Sciences and Engineering Research Council (NSERC) of Canada for a CGS-D Award to B.S.G.

Keywords: gas capture · metal–organic frameworks · phosphonate monoester · phosphonates · porous solids

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 14614–14617
Angew. Chem. **2016**, *128*, 14834–14837

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[1] R. Quadrelli, S. Peterson, *Energy Policy* **2007**, *35*, 5938.

[2] E. J. Granite, H. W. Pennline, *Ind. Eng. Chem. Res.* **2002**, *41*, 5470.

[3] L. Deng, M. B. Hägg, *Int. J. Greenhouse Gas Control* **2010**, *4*, 638.

[4] a) T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena, J. Gascon, *Nat. Mater.* **2014**, *14*, 48; b) S. S. Nagarkar, A. K. Chaudhari, S. K. Ghosh, *Inorg. Chem.* **2012**, *51*, 572; c) P. S. Bárcia, L. Bastin, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues, B. Chen, *Sep. Sci. Technol.* **2008**, *43*, 3494; d) J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **2011**, *255*, 1791.

[5] a) R. K. Mah, B. S. Gelfand, J. M. Taylor, G. K. H. Shimizu, *Inorg. Chem. Front.* **2015**, *2*, 273; b) B. S. Gelfand, J. Lin, G. K. H. Shimizu, *Inorg. Chem.* **2015**, *54*, 1185; c) J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, *J. Am. Chem. Soc.* **2012**, *134*, 14338; d) J.-W. Zhang, C.-C. Zhao, Y.-P. Zhao, H.-Q. Xu, Z.-Y. Du, H.-L. Jiang, *CrystEngComm* **2014**, *16*, 6635.

[6] a) S. Pili, S. P. Argent, C. G. Morris, P. Rought, V. Garc, I. P. Silverwood, T. L. Easun, M. Li, M. R. Warren, C. A. Murray, C. C. Tang, S. Yang, M. Schröder, *J. Am. Chem. Soc.* **2016**, *138*, 6352; b) K. J. Gagnon, H. P. Perry, A. Clearfield, *Chem. Rev.* **2012**, *112*, 1034; c) M. Taddei, F. Costantino, R. Vivani, *Eur. J. Inorg. Chem.* **2016**, 1; d) J. Goura, V. Chandrasekhar, *Chem. Rev.* **2015**, *115*, 6854; e) R. Vaidhyanathan, A. H. Mahmoudkhani, G. K. H. Shimizu, *Can. J. Chem.* **2009**, *87*, 247; f) A. U. Ortiz, A. Boutin, K. J. Gagnon, A. Clearfield, F.-X. Coudert, *J. Am. Chem. Soc.* **2014**, *136*, 11540; g) N. Hermer, N. Stock, *Dalton Trans.* **2015**, *44*, 3720; h) P. L. Llewellyn, M. Garcia-Rates, L. Gaberová, S. R. Miller, T. Devic, J.-C. Lavalley, S. Bourrelly, E. Bloch, Y. Filinchuk, P. A. Wright, et al., *J. Phys. Chem. C* **2015**, *119*, 4208; i) K. Maeda, F. Mizukami, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2335; *Angew. Chem.* **1994**, *106*, 2427; j) R. Howlader, M. G. Walawalkar, R. Murugavel, *Inorg. Chim. Acta* **2013**, *405*, 147; k) M. Taddei, F. Costantino, F. Marmottini, A. Comotti, P. Sozzani, R. Vivani, *Chem. Commun.* **2014**, *50*, 14831; l) A. Kondo, T. Satomi, K. Azuma, R. Takeda, K. Maeda, *Dalton Trans.* **2015**, *44*, 12717; m) S. Hossain, S. K. Gupta, R. Murugavel, *CrystEngComm* **2015**, *17*, 4355.

[7] S. S. Iremonger, J. Liang, R. Vaidhyanathan, I. Martens, G. K. H. Shimizu, T. D. Daff, M. Z. Aghaji, S. Yeganegi, T. K. Woo, *J. Am. Chem. Soc.* **2011**, *133*, 20048.

[8] Structure data for CALF-33-Et$_2$H (see SI for details): $C_{56}H_{52}Cu_3O_{18}P_6$ (Mw = 1389.45), $T = 173(2)$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 5.08130(10)$, $b = 15.1585(3)$, $c = 29.3246(7)$ Å, $\alpha = 83.8820(10)$, $\beta = 85.7280(10)$, $\gamma = 82.705(2)°$, $V = 2223.42(8)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.036\ g\,cm^{-3}$, $\mu = 0.866\ mm^{-1}$, measured reflections, 7376 unique reflections ($R_{int} = 0.0939$), $R1 = 0.0700$ for 3758 observed reflections ($I > 2\sigma(I)$) and 379 parameters (after accounting for disordered solvent with the SQUEEZE function in Platon[21]). CCDC 1496410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[9] Accelrys Software Inc., **2011**.

[10] T. Yamada, H. Kitagawa, *CrystEngComm* **2012**, *14*, 4148.

[11] a) 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.* **2014**, *136*, 13983; b) P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom, H. Fjellvåg, *Chem. Commun.* **2006**, 959.

[12] a) B. Mu, P. M. Schoenecker, K. S. Walton, *J. Phys. Chem. C* **2010**, *114*, 6464; b) P. S. Bárcia, L. Bastin, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues, B. Chen, *Sep. Sci. Technol.* **2008**, *43*, 3494; c) L. Bastin, P. S. Bárcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues, B. Chen, *J. Phys. Chem. C* **2008**, *112*, 1575.

[13] R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, T. K. Woo, *Science* **2010**, *330*, 650.

[14] a) Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao, B. Chen, *Inorg. Chem.* **2011**, *50*, 3442; b) M. Du, C.-P. Li, M. Chen, Z.-W. Ge, X. Wang, L. Wang, C.-S. Liu, *J. Am. Chem. Soc.* **2014**, *136*, 10906.

[15] a) I. A. Ibarra, A. Mace, S. Yang, J. Sun, S. Lee, J.-S. Chang, A. Laaksonen, M. Schröder, X. Zou, *Inorg. Chem.* **2016**, *55*, 7219; b) K. Jayaramulu, S. K. Reddy, A. Hazra, S. Balasubramanian, T. K. Maji, *Inorg. Chem.* **2012**, *51*, 7103.

[16] a) C. M. Simon, B. Smit, M. Haranczyk, *Comput. Phys. Commun.* **2015**, 1; b) A. L. Myers, J. M. Prausnitz, *AIChE J.* **1965**, *11*, 121.

[17] a) M. T. Wharmby, G. M. Pearce, J. P. S. Mowat, J. M. Griffin, S. E. Ashbrook, P. A. Wright, L.-H. Schilling, A. Lieb, N. Stock, S. Chavan, et al., *Microporous Mesoporous Mater.* **2012**, *157*, 3; b) J. M. Simmons, H. Wu, W. Zhou, T. Yildirim, *Energy Environ. Sci.* **2011**, *4*, 2177.

[18] A. Ö. Yazaydın, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. Levan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, et al., *J. Am. Chem. Soc.* **2009**, *131*, 18198.

[19] a) M. Kontturi, E. Laurila, R. Mattsson, S. Peräniemi, J. J. Vepsäläinen, M. Ahlgrén, *Inorg. Chem.* **2005**, *44*, 2400; b) J. Jokiniemi, J. J. Vepsäläinen, H. Nätkinniemi, S. Peräniemi, M. Ahlgrén, *CrystEngComm* **2009**, *11*, 2431.

[20] P. Ayyappan, O. R. Evans, Y. Cui, K. A. Wheeler, W. Lin, *Inorg. Chem.* **2002**, *41*, 4978.

[21] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2007**.

Received: August 9, 2016
Revised: September 13, 2016