



Porous Solids Arising from Synergistic and Competing Modes of Assembly: Combining Coordination Chemistry and Covalent Bond Formation**

Ananya Dutta, Kyoungmoo Koh, Antek G. Wong-Foy, and Adam J. Matzger*

Abstract: Design and synthesis of porous solids employing both reversible coordination chemistry and reversible covalent bond formation is described. The combination of two different linkage modes in a single material presents a link between two distinct classes of porous materials as exemplified by metal-organic frameworks (MOFs) and covalent organic frameworks (COFs). This strategy, in addition to being a compelling material-discovery method, also offers a platform for developing a fundamental understanding of the factors influencing the competing modes of assembly. We also demonstrate that even temporary formation of reversible connections between components may be leveraged to make new phases thus offering design routes to polymorphic frameworks. Moreover, this approach has the striking potential of providing a rich landscape of structurally complex materials from commercially available or readily accessible feedstocks.

In past two decades the field of porous materials has witnessed rapid advances in the ability to create defined sorbents with exceptional and tunable properties. Two key materials classes contributing to this change are a) coordination polymers possessing micro and/or mesoporosity, often termed metal-organic frameworks (MOFs)^[1] and b) organic polymers wherein directional covalent bonding is exploited to define a porous network as exemplified by covalent organic frameworks (COFs).^[2] Though the details of the assembly processes associated with the production of these two classes of materials are significantly different, reversibility of bond formation is critical for yielding crystalline porous solids. Specifically for coordination polymers, slow decomposition of amide solvent liberating free amine (thus changing the

pH value of the reaction mixture) drives the reversible acid-base reaction between the conjugate base of the linker and metal ions leading to the assembly of the framework.^[3] On the other hand, formation of covalent organic frameworks is generally facilitated by reversible coupling between reactive groups installed on the organic cores, such as boroxine,^[2] borazine,^[4] azodioxy,^[5] imine/enamine,^[6] or hydrazone^[7] linkage formation. Despite the fact that much research has been focused on these two materials classes individually, design and synthesis of extended frameworks employing both reversible coordination processes and reversible covalent bond formation is without precedent.^[8] Herein we investigate a system where both coordination processes and covalent bond formation occur and examine the outcome of the competitive processes to understand the factors influencing each mode of assembly. We also demonstrate that this approach enables access to multiple phases from a set of commercially available or readily accessible reagents.

A derivative of the widely used linker 1,3,5-tris(4-carboxyphenyl)benzene (H₃-BTB)^[9] was chosen for this study where the central benzene ring was modified with a second site of reactivity: a primary amino group (Figure 1). This functionality provides an opportunity for imine formation to take place upon reaction with a carbonyl group. It should be noted that the reaction between a carbonyl moiety and an amino group is one of the reactions successfully employed for the

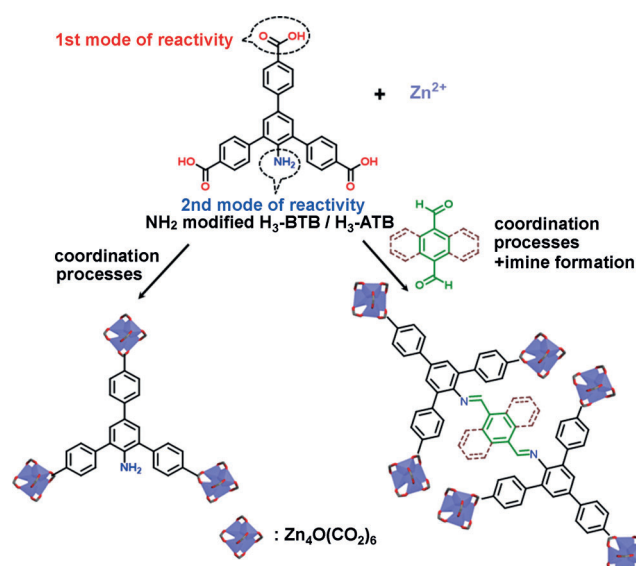


Figure 1. Schematic representation of different materials generated from coordination processes only and from a combination of coordination processes and imine formation.

[*] A. Dutta, Dr. K. Koh, Dr. A. G. Wong-Foy, Prof. A. J. Matzger
Department of Chemistry
University of Michigan
930 N. University Ave, Ann Arbor, MI 48109 (USA)
E-mail: matzger@umich.edu

Dr. K. Koh
Current address: The Dow Chemical Company, Core R&D
Midland, MI 48674 (USA)
Prof. A. J. Matzger
Department of Macromolecular Science and Engineering
University of Michigan, Ann Arbor, MI 48109 (USA)

[**] This work was supported by Department of Energy (Award No. DE-SC0004888). We acknowledge Dr. J. W. Kampf for the X-Ray crystallographic assistance and funding from NSF grant CHE-0840456 for the Rigaku AFC10K Saturn 944 + CCD-based X-ray diffractometer.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201411735>.

synthesis of crystalline COFs.^[6a] The reaction of the modified H₃-BTB (hereafter 2,4,6-tris(4-carboxyphenyl)aniline or H₃-ATB) with Zn^{II} at 85 °C results in the formation of colorless block-shaped crystals after 20 h (Section 1 in Supporting Information). The powder X-ray diffraction pattern of this material (Figure 2) corresponds closely to that of MOF-177^[9] (Section 2 in Supporting Information) and so this material is termed MOF-177-NH₂. This finding is significant in light of the numerous other phases possible for a combination of BTB and Zn^{II}.^[10]

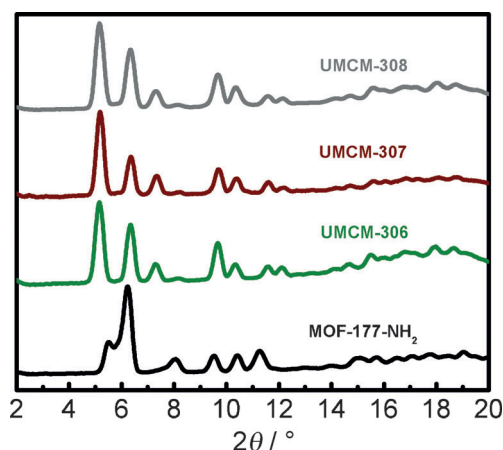


Figure 2. Powder X-ray diffraction patterns of MOF-177-NH₂ (black), UCMC-306 (green), UCMC-307 (red), and UCMC-308 (gray).

The effect of addition of terephthalaldehyde, a dialdehyde with a *para* disposition of functional groups, on the assembly of MOF-177-NH₂ was next examined (Figure 1). Three potential outcomes were expected as a consequence of the dialdehyde addition: a) formation of MOF-177-NH₂ with or without dangling aldehyde residues b) generation of a novel phase resulting from combination of coordination processes and imine formation and/or c) formation of a different phase derived solely from H₃-ATB. The solvothermal reaction of H₃-ATB and terephthalaldehyde in a 1:1.5 molar ratio in the presence of Zn^{II} results in a yellow colored rod-shaped material designated UCMC-306 (Section 1 in Supporting Information). The powder X-ray diffraction pattern of this material exhibits distinct peak positions and intensities as compared to those of MOF-177-NH₂ (Figure 2). ¹H NMR spectroscopy experiments performed on acid digests of evacuated UCMC-306 indicate the presence of terephthalaldehyde and H₃-ATB in the ratio of 1:2.8 (Section 4 in Supporting Information). This finding in combination with the unique PXRD pattern signals the probable occurrence of case (b). Unambiguous confirmation of the structure of UCMC-306, obtained from a single-crystal X-ray diffraction study (Section 3 in Supporting Information), revealed that the structure dramatically differs from the structure of MOF-177-NH₂. The product crystallizes in the space group *P*4₂/*mnm* and the framework consists of octahedral Zn₄O(O₂CR)₆ secondary building units (SBUs) linked together by two ATB linkers condensed with a single terephthalaldehyde residue (Figure 3b). Condensation of two primary amino

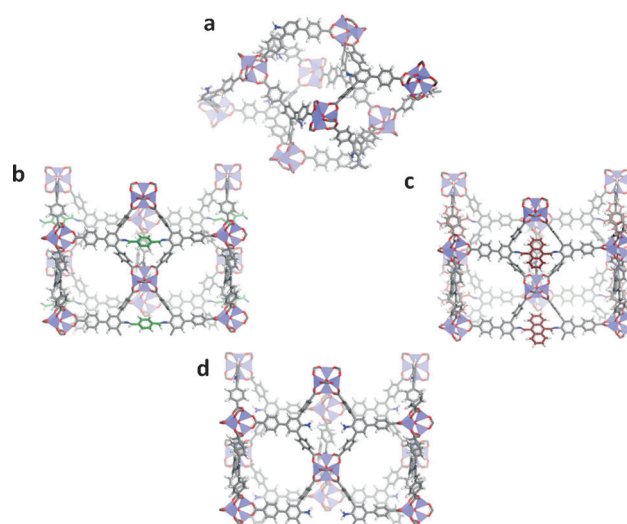


Figure 3. Structure of materials: a) MOF-177-NH₂, b) UCMC-306, c) UCMC-307, and d) UCMC-308. (a) is modelled based on MOF-177 whereas (c) and (d) are modelled based on (b); (b) is obtained from single X-ray diffraction data.

groups from ATB linkers with one terephthalaldehyde molecule gives rise to two covalent imine linkages, which effectively provides a hexatopic linker coordinated to tetrahedral Zn₄O metal clusters. However, it should be noted that the occurrence of the di-imine linkage in the structure is approximately 70 % complete as indicated by the ¹H NMR spectroscopy results and supported by the single-crystal X-ray diffraction data suggesting that the imine formation is not complete in this case. For additional structural confirmation, especially to further confirm the presence of imine linkages, Raman spectroscopy was also employed. Comparison of the Raman spectrum of UCMC-306 with that of MOF-177-NH₂ (Section 5 in Supporting Information) reveals differences especially in two primary wavenumber regions: 3300–3500 cm⁻¹ and 1500–1800 cm⁻¹. UCMC-306 shows no detectable peak at the 3300–3500 cm⁻¹ region whereas MOF-177-NH₂ exhibits a peak at 3398 cm⁻¹ attributable to NH₂ stretching. Moreover, the emergence of a peak at 1634 cm⁻¹ in UCMC-306 can be ascribed to the formation of a new imine linkage in UCMC-306 which is absent in MOF-177-NH₂.

Given the fact that both coordination processes between the carboxylates and metal ions as well as covalent imine bond formation occur in the assembly of UCMC-306, the system was selected as a platform for investigating the competition between coordination processes and imine formation. We hypothesized that a major contributor influencing this competition would be the relative rate of imine formation versus coordination processes which can be affected by different variables including the incubation time of amino functionalized linker and the dialdehyde as well as the extent of solvent decomposition/base formation within the reaction mixture. To determine if the incubation time of the two organic components plays a role in phase selection, a series of experiments were conducted with timed addition of terephthalaldehyde. The dialdehyde was added after various delay

times (delay time $t = 1, 6, 9, 12, 15, 16, 18, 19, 20, 24$ h) into the homogenous reaction mixture (in cases of $t = 1, 6, 9, 12, 15, 16, 18$ h) or heterogeneous reaction mixture (in cases of $t = 19, 20, 24$ h) containing H_3 -ATB and $Zn(NO_3)_2 \cdot 6H_2O$ at $85^\circ C$ and all the reactions mixtures were analyzed after 30 h. Two morphologically different phases were observed: rod-shaped UCM-306 at early delay times and primarily block-shaped MOF-177-NH₂ at late stages of addition (Figure 4) indicating

processes and imine formation presumably by tuning the extent of solvent decomposition/base formation. For the solutions preheated for relatively short times, imine formation outperforms coordination processes resulting in formation of UCM-306, whereas coordination processes compete with the imine formation in cases of solutions preheated for longer times leading to MOF-177-NH₂.^[11]

To explore the generality of the approach of combining coordination polymerization with covalent imine bond formation and its potential to accommodate a diversity of aldehyde partners, a bulkier dialdehyde, anthracene-9,10-dialdehyde was chosen. The solvothermal reaction of H_3 -ATB and anthracene-9,10-dialdehyde with Zn^{II} yields orange rod-shaped crystals designated UCM-307. Comparison of powder X-ray diffraction patterns of this material with UCM-306 reveals nearly identical peak positions and intensities of the two materials confirming their isostructural nature (Figures 2 and 3). ¹H NMR spectroscopy experiments performed on acid digests of evacuated UCM-307 show the presence of anthracene-9,10-dialdehyde and H_3 -ATB in a 1:3.8 ratio. This result is consistent with the generation of the desired motif arising from both coordination processes and imine formation with the di-imine formation efficiency of about 50 % (Section 4 in Supporting Information).

To further extend the above strategy to another class of carbonyl compounds, a diketone, 1,4-diacetylbenzene, was employed to react with H_3 -ATB and Zn^{II} under solvothermal conditions.^[12] The reaction affords colorless rod-shaped crystals designated UCM-308. This material exhibits a powder X-ray diffraction pattern closely matching those of UCM-306 and UCM-307 suggesting the isostructural nature of all these materials (Figure 2). However, the ¹H NMR spectrum obtained after acid digestion of evacuated UCM-308 shows the presence of only H_3 -ATB indicating that the organic part of

the framework exclusively consists of the ATB linker without incorporation of the diketone residue (Section 4 in Supporting Information); this observation demonstrates the formation of a different phase derived solely from H_3 -ATB (case (c) described above). Moreover, the Raman spectrum has a peak at 3390 cm^{-1} assigned to NH₂ stretching and also features in the $1500\text{--}1800\text{ cm}^{-1}$ wavenumber region similar to those of MOF-177-NH₂ (Section 5 in Supporting Information). These results confirm that UCM-308 is a polymorphic framework^[10,13] of MOF-177-NH₂ (Figure 3). In other words, MOF-177-NH₂ and UCM-308 are composed of an identical SBU and linker but differ in net topology and pore structure. This finding highlights that a combination of a SBU and a linker can assemble in more than one arrangement in principle, yet in practice only a few phases can be obtained depending on reaction parameters. For example, $Zn_4O(O_2CR)_6$ with the BTB linker has been reported to yield three MOFs with different net topologies: MOF-177 (**qom**), Zn/BTB (**ant**), and

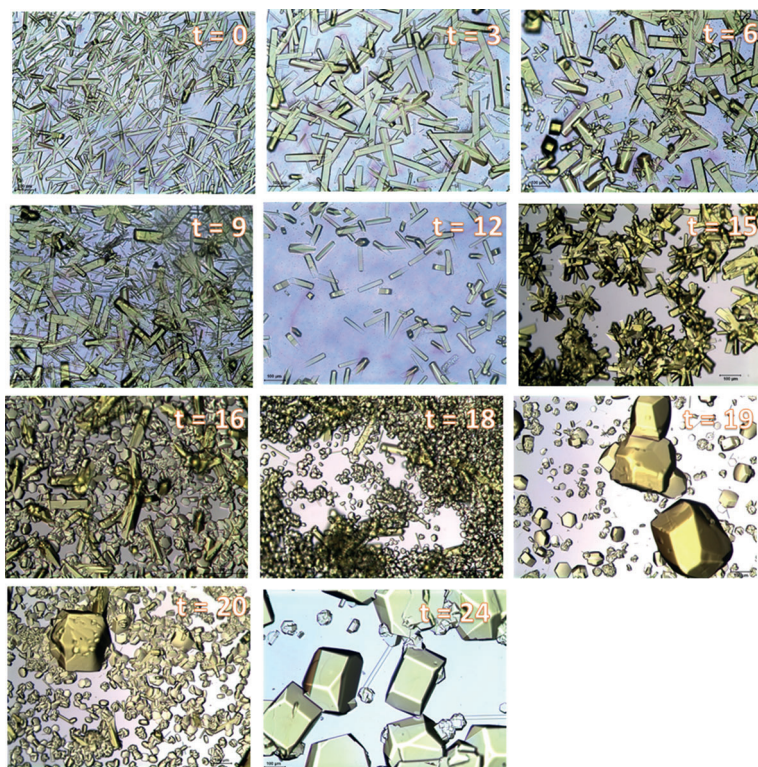


Figure 4. Optical micrographs showing the population of rod-shaped UCM-306 and block-shaped MOF-177-NH₂ resulting from different delay times (t in h) of terephthalaldehyde addition into the reaction mixtures. UCM-306 is observed at early delay times whereas MOF-177-NH₂ appears at late stages of dialdehyde addition. Total reaction time is 30 h.

that the incubation time of the two organic components is critical in dictating the outcome of the competition. However, the appearance of MOF-177-NH₂ upon delayed addition of dialdehyde in homogenous reaction mixtures ($18 \geq t \geq 16$) may be a consequence of the extent of solvent decomposition/base formation upon extended reaction rather than only a result of short incubation time of the two organic components. To investigate the role of solvent decomposition/base formation on the competition of the two processes, a series of solutions containing $Zn(NO_3)_2 \cdot 6H_2O$ in *N,N*-dimethylformamide (DMF) were prepared and pre-heated at $85^\circ C$ for 1, 2, 4, 8, 16, and 17 h prior to addition of the organic components. The preheated solutions for 1, 2, 4, and 8 h lead to formation of UCM-306 whereas the ones heated for 16 and 17 h afford primarily MOF-177-NH₂ crystals (Section 6 in Supporting Information). These observations demonstrate that the duration of the aging of $Zn(NO_3)_2 \cdot 6H_2O$ and DMF also controls the competition between the coordination

Zn/BTB (**tsx**).^[10] Surprisingly, UMCM-308, derived from $\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6$ with an amino-modified BTB linker, adopts an **rtl**^[14] net distinct from these three MOFs (Figure 5). The difference between these nets originates from the linker

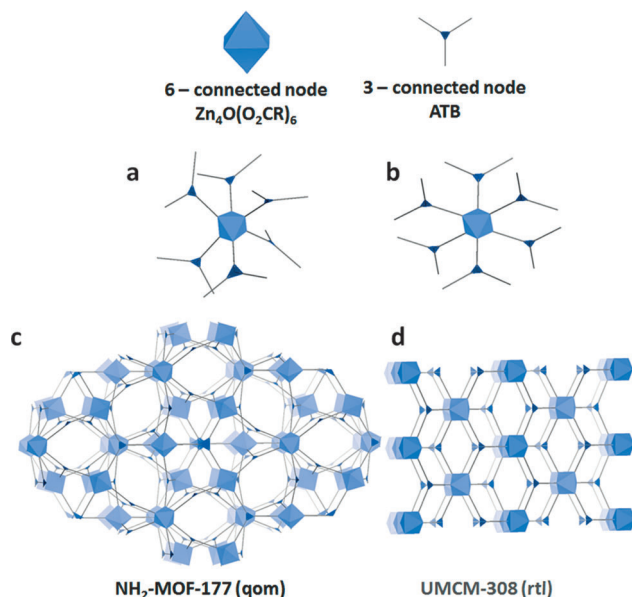


Figure 5. Linker orientations in the first coordination sphere (a and b) and underlying network topologies (c and d) of two polymorphic frameworks MOF-177-NH₂ and UMCM-308 constructed from same 6-connected and 3-connected nodes.

orientations in the 2nd or 3rd coordination sphere connecting the trigonal and octahedral nodes. Despite the same first coordination sphere in these nets, wherein each tritopic linker is connected to 3 octahedral SBUs and each octahedron is attached to 6 tritopic linkers, the second and/or third coordination sphere are different; this outcome stems from the various orientations of linkers about the octahedral SBU in the first coordination sphere (Figure 5). The diketone acts as a phase-directing agent^[15] favoring the **rtl** net. This finding prompted us to examine if the interaction of the amino group on H₃-ATB with an aromatic monoaldehyde/monoketone is adequate to direct a phase like UMCM-306 or UMCM-308, perhaps through a torsion-angle change induced in the ATB linker. Solvothermal reaction of H₃-ATB with Zn^{II} was carried out in presence of benzaldehyde or acetophenone to yield materials exhibiting nearly identical PXRD patterns to MOF-177-NH₂. This fact verifies that the presence of two carbonyl moieties in *para* positions of the carbonyl partner is critical for the production of UMCM-306 or related phases, suggesting a role, no matter how transient, of linking two amino-modified BTB linkers covalently.

The N₂-sorption studies of activated materials show high N₂ uptakes (Figure 6). N₂-sorption isotherms of all these porous solids can be classified as Type I with a sharp uptake below $P/P_0 = 0.05$. Applying the BET model over the proper ranges^[16] of the isotherms yields BET surface areas as follows: 4631 m² g⁻¹ for MOF-177-NH₂, 2820 m² g⁻¹ for UMCM-306, 2520 m² g⁻¹ for UMCM-307, and 1190 m² g⁻¹ for UMCM-308.

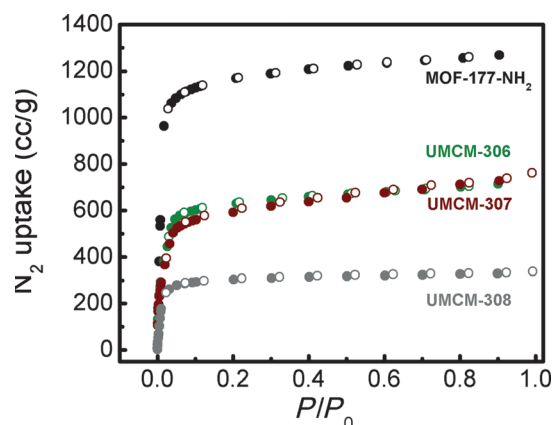


Figure 6. Nitrogen sorption isotherms for MOF-177-NH (black), UMCM-306 (green), UMCM-307 (red), and UMCM-308 (gray).

The surface area of UMCM-308 is significantly lower than the predicted one which is indicative of structural change of the material upon activation as judged by PXRD (Section 1 in Supporting Information). Notably, the surface areas of the materials resulting from both coordination processes and imine formation are higher than those of COF-42, COF-43,^[6a] or COF-300^[7] in which imine formation alone is exploited for materials synthesis.

To conclude, employing coordination processes in tandem with imine formation presents a link between two orthogonal classes of porous materials as exemplified by metal–organic frameworks (MOFs) and covalent organic frameworks (COFs). This approach of combining two different linkage modes in a single material, in addition to being a compelling materials discovery method, offers a platform for developing a fundamental understanding of factors influencing competing modes of assembly. The incubation time of the organic components as well as the extent of solvent decomposition/base formation have been identified as key parameters in governing the competition between coordination processes and imine formation. Moreover, even temporary formation of reversible connections between components may be leveraged to make new phases. It was found that using a diketone in place of a dialdehyde unit leads to formation of a polymorphic framework of MOF-177-NH₂ wherein the assembly of octahedral $\text{Zn}_4\text{O}(\text{O}_2\text{CR})_6$ with triangular ATB nodes gives rise to a **rtl** net without incorporation of a dicarbonyl compound. This network topology is otherwise unavailable from a functionalized/non-functionalized BTB linker and Zn^{II}. We are extending this work to investigate an array of commercially available or readily accessible multifunctional aldehydes and amine-functionalized carboxylate linkers that can be combined using the described approach with the potential of providing a wide range of structurally complex materials derived from simple feedstocks.

Experimental Section

Synthesis, characterization of materials, and other additional details are provided in the Supporting Information. CCDC 1037542 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.

Keywords: coordination modes · covalent organic frameworks · crystal engineering · metal–organic frameworks · microporous materials

Zitierweise: *Angew. Chem. Int. Ed.* **2015**, *54*, 3983–3987
Angew. Chem. **2015**, *127*, 4055–4059

- [1] H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279.
- [2] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166–1170.
- [3] a) S. Hausdorf, J. Wagler, R. Mößig, F. O. R. L. Mertens, *J. Phys. Chem. A* **2008**, *112*, 7567–7576; b) S. Hausdorf, F. Baitalow, J. Seidel, F. O. R. L. Mertens, *J. Phys. Chem. A* **2007**, *111*, 4259–4266.
- [4] T. E. Reich, K. T. Jackson, S. Li, P. Jena, H. M. El-Kaderi, *J. Mater. Chem.* **2011**, *21*, 10629–10632.
- [5] D. Beaudoin, T. Maris, J. D. Wuest, *Nat. Chem.* **2013**, *5*, 830–834.
- [6] a) F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O’Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571; b) C. R. DeBlase, K. E. Silberstein, T.-T. Truong, H. D. Abruña, W. R. Dichtel, *J. Am. Chem. Soc.* **2013**, *135*, 16821–16824.
- [7] F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, *J. Am. Chem. Soc.* **2011**, *133*, 11478–11481.
- [8] In this context it should be noted that in situ ligand formation from irreversible covalent coupling in tandem with coordination chemistry has been demonstrated. See for example: D. Zhao, D. Yuan, A. Yakovenko, H.-C. Zhou, *Chem. Commun.* **2010**, *46*, 4196–4199.
- [9] H. K. Chae, D. Y. Siberio-Pérez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O’Keeffe, O. M. Yaghi, *Nature* **2004**, *427*, 523–527.
- [10] S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *Inorg. Chem.* **2008**, *47*, 7751–7756.
- [11] A role for diethylamine as a competitive species for imine formation cannot be ruled out as an additional contributing factor.
- [12] To our knowledge, ketimine COFs are absent from the literature.
- [13] As we have noted elsewhere, and in contrast to its misuse in the field, such framework materials must not be termed “polymorphs”. Polymorphs have a strict isomeric relationship that is not easily satisfied in porous material containing varying degrees of solvation. This fact motivates the use of the present term “polymorphic frameworks”. The distinction is critical because, for example, stability ordering of polymorphic framework materials is expected to be solvent dependent whereas this is forbidden for true polymorphs. In fact, the closest molecular analogy is in solvate stability where solvate inclusion engenders relative stability relationships that can depend strongly on solvent and temperature. In molecular compounds such relationships are sometimes termed “pseudopolymorphic”. Thus by this logic the different topologies of coordination polymers could be considered to be pseudopolymorphs. However, such a term is esoteric and subject to debate even within the small-molecule community and so “polymorphic framework” is preferred.
- [14] V. A. Blatov, L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm* **2004**, *6*, 378–395.
- [15] Z. Zhang, M. J. Zaworotko, *Chem. Soc. Rev.* **2014**, *43*, 5444–5455.
- [16] J. Rouquerol, P. Llewellyn, F. Rouquerol in *Studies in Surface Science and Catalysis, Vol. 160* (Eds.: F. R.-R. J. R. P. L. Llewellyn, N. Seaton), Elsevier, Amsterdam, **2007**, pp. 49–56.

Received: December 8, 2014

Published online: February 9, 2015