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

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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.
The effect of addition of terephthaldehyde, a dialdehyde with a para disposition of functional groups, on the assembly of MOF-177-NH$_2$ was next examined (Figure 1). Three potential outcomes were expected as a consequence of the dialdehyde addition: a) formation of MOF-177-NH$_2$ 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 H$_2$-ATB. The solvothermal reaction of H$_2$-ATB and terephthaldehyde in a 1:1.5 molar ratio in the presence of Zn$^{II}$ results in a yellow colored rod-shaped material designated UMCM-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-NH$_2$ (Figure 2). A Raman spectroscopy experiment performed on a single X-ray powder 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 UMCM-306 with that of MOF-177-NH$_2$ (Section 5 in Supporting Information) reveals differences especially in two primary wavenumber regions: 300–3500 cm$^{-1}$ and 1500–1800 cm$^{-1}$. UMCM-306 shows no detectable peak at the 3300–3500 cm$^{-1}$ region whereas MOF-177-NH$_2$ exhibits a peak at 3398 cm$^{-1}$ attributable to NH$_2$ stretching. Moreover, the emergence of a peak at 1634 cm$^{-1}$ in UMCM-306 can be ascribed to the formation of a new imine linkage in UMCM-306 which is absent in MOF-177-NH$_2$.

Given the fact that both coordination processes between the carboxylate and metal ions as well as covalent imine bond formation occur in the assembly of UMCM-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 terephthaldehyde. The dialdehyde was added after various delay periods from 0 to 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-NH$_2$ (Section 2 in Supporting Information) and so this material is termed MOF-177-NH$_2$. This finding is significant in light of the numerous other phases possible for a combination of BTB and Zn$^{II}$.

Figure 2. Powder X-ray diffraction patterns of MOF-177-NH$_2$ (black), UMCM-306 (green), UMCM-307 (red), and UMCM-308 (gray).

Figure 3. Structure of materials: a) MOF-177-NH$_2$, b) UMCM-306, c) UMCM-307, and d) UMCM-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.
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 \( \text{H}_2\text{-ATB} \) and \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) at 85 \( ^\circ \)C and all the reactions mixtures were analyzed after 30 h. Two morphologically different phases were observed: rod-shaped UMCM-306 at early delay times and primarily block-shaped MOF-177-NH\(_3\) at late stages of addition (Figure 4) indicating that the incubation time of the two organic components is critical in dictating the outcome of the competition. However, the appearance of MOF-177-NH\(_3\) upon delayed addition of dialdehyde in homogenous reaction mixtures (18 \( \geq t \geq 16 \) h) 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 \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) in \( N_2\text{N-dimethylformamide} \) (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 UMCM-306 whereas the ones heated for 16 and 17 h afford primarily MOF-177-NH\(_3\) crystals (Section 6 in Supporting Information). These observations demonstrate that the duration of the aging of \( \text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) and DMF also controls the competition between the coordination 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 UMCM-306, whereas coordination processes compete with the imine formation in cases of solutions preheated for longer times leading to MOF-177-NH\(_3\).

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 \( \text{H}_2\text{-ATB} \) and anthracene-9,10-dialdehyde with \( \text{Zn}^{11} \) yields orange rod-shaped crystals designated UMCM-307. Comparison of powder X-ray diffraction patterns of this material with UMCM-306 reveals nearly identical peak positions and intensities of the two materials confirming their isostructural nature (Figures 2 and 3). \(^1\text{H}\) NMR spectroscopy experiments performed on acid digests of evacuated UMCM-307 show the presence of anthracene-9,10-dialdehyde and \( \text{H}_2\text{-ATB} \) 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 \( \text{H}_2\text{-ATB} \) and \( \text{Zn}^{11} \) under solvothermal conditions.\(^{12}\) The reaction affords colorless rod-shaped crystals designated UMCM-308. This material exhibits a powder X-ray diffraction pattern closely matching those of UMCM-306 and UMCM-307 suggesting the isostructural nature of all these materials (Figure 2). However, the \(^1\text{H}\) NMR spectrum obtained after acid digestion of evacuated UMCM-308 shows the presence of only \( \text{H}_2\text{-ATB} \) 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 \( \text{H}_2\text{-ATB} \) (case (e) described above). Moreover, the Raman spectrum has a peak at 3390 cm\(^{-1}\) assigned to NH\(_2\) stretching and also features in the 1500–1800 cm\(^{-1}\) wavenumber region similar to those of MOF-177-NH\(_3\) (Section 5 in Supporting Information). These results confirm that UMCM-308 is a polymorphic framework\(^{10,15}\) of MOF-177-NH\(_3\) (Figure 3). In other words, MOF-177-NH\(_3\) and UMCM-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, \( \text{ZnO}_3\text{(O,Cr)} \), with the BTB linker has been reported to yield three MOFs with different net topologies: MOF-177 (qom), Zn/BTB (ant), and
Su-ray, UMCM-308, derived from 
ZnII (SSS) [10] Surprisingly, UMCM-308, derived from 
ZnII(OOCR)3, with an amino-modified BTB linker, adopts an 
rtl net distinct from these three MOFs (Figure 5). The 
difference between these nets originates from the linker 
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 coordi-
nation 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 H2-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 H2-ATB with ZnII 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/P0 = 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. 
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 [17] 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 
methods in a single material, in addition to being a compelling 
materials discovery method, offers a platform for developing 
a fundamental understanding of factors influencing compet-
ing 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 lever-
aged to make new phases. It was found that using a diketone 
in place of a dialdehyde unit leads to formation of a poly-
omorphic framework of MOF-177-NH2 wherein the assembly 
of octahedral ZnII(OOCR)3, 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 
ZnII. We are extending this work to investigate an array of 
commercially available or readily accessible multifunctional 
alddehydes 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
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[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.
[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.

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