

Mesostructured Imidazolate Frameworks

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Metal-organic frameworks (MOFs) are crystalline hybrid framework materials composed of inorganic metal “nodes” bridged by rigid organic linkers, thereby featuring exceptionally high surface areas and porosities. Despite the successful synthesis of a plethora of intricate framework topologies, a major objective in current MOF chemistry is the extension of pore sizes from the micropore (> 2 nm) to the mesopore regime (2 – 50 nm). In contrast, siliceous materials constitute a large class of inorganic materials spanning different pore size regimes with pore topologies on the micro-, meso- and macroscale. Here, microporous zeolites and mesoporous silica represent the most famous of such ordered siliceous materials.[1] While zeolites have already found MOF analogues named zeolitic imidazolate frameworks (ZIFs), featuring zeolite-like framework topologies, materials that combine metal-organic building blocks with supramolecular templates such as those found in mesostructured silica materials are still elusive.

Therefore, the combination of mesophase synthesis, which employs surfactants as supramolecular templates, with the solvothermal synthesis of MOFs and especially ZIFs is one promising avenue that may ultimately afford mesostructured materials with hierarchical, i.e. micro and meso, porosity. Here we describe the first representative of a mesostructured zinc coordination polymer with imidazolate linkers, which has been obtained by an inverse microemulsion-based synthesis.[2]

Different zinc imidazolate-based hybrid materials were obtained by combining aqueous zinc acetate and imidazole (IM) or methylimidazole (MeIM) solutions with a solution containing 1-hexanol, *n*-heptane and cetyltrimethylammonium bromide / chloride (CTAB/CTAC) or other trimethylalkylammonium bromide surfactants with different chain lengths (C10 to C18) as emulsifying agents. The products were obtained as white precipitates after refluxing the reaction mixture at 100 °C for 2 h and are denoted *mesostructured imidazolate frameworks*, MIFs, (MIF-1: Zn/MeIM/CTAB, MIF-2: Zn/IM/CTAB) in the following in order to stress their relationship to ZIFs. Chemical analysis and spectroscopic evidence infer that the materials are hybrid structures composed of zinc imidazolate coordination polymers interleaved with organic surfactant slabs inducing a high level of order and a pronounced layered character [2].

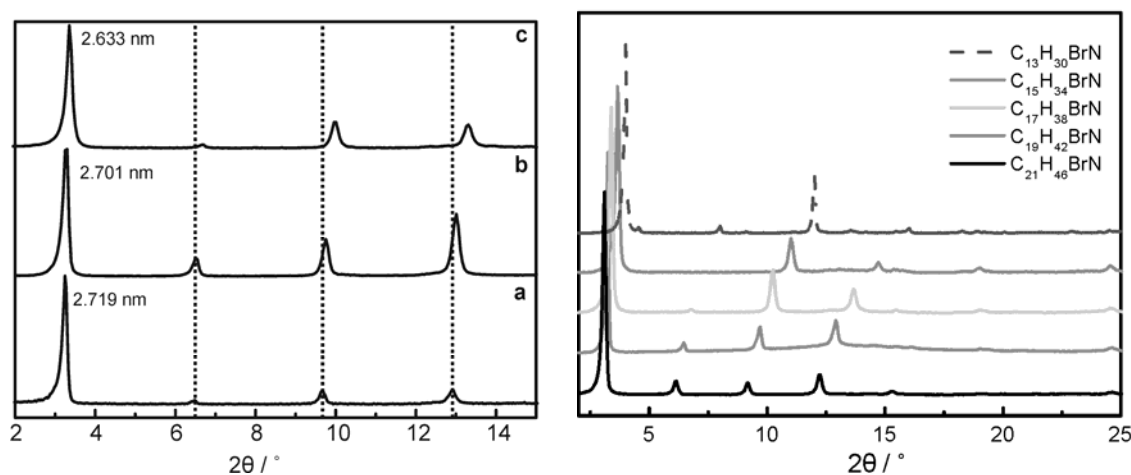


Figure 1: Left: XRD powder patterns of lamellar MIFs with different surfactants/ligands: a) CTAB/MeIM (MIF-1), b) CTAC/MeIM, and c) CTAB/IM (MIF-2). The first peaks correspond to the basal spacing of the mesostructures, demonstrating their lamellar morphology. Right: XRD powder patterns of MeIM-based MIFs obtained using different surfactants with varying chain lengths (C₁₃H₃₀NBr - C₂₁H₄₆NBr). The systematic shift in the basal spacings suggests the incorporation of the surfactants and corroborates their role as templates. Copyright ©2012 by John Wiley & Sons, Inc.

Figure 1 shows the X-ray powder patterns of different MIFs, highlighting their layered structure. The 00 l reflections are systematically shifted to lower angles as the ligand or halogenide size (Fig. 1, left)

and the surfactant chain length increases (Fig. 1, right), thereby suggesting the role of the surfactants as templates. The peaks indexed as 001 ($2\theta = 3.2^\circ$ for MIF-1 and $2\theta = 3.4^\circ$ for MIF-2) infer lamellar structures with a basal spacing of $d_{001} = 27.19 \text{ \AA}$ for MIF-1 and $d_{001} = 26.33 \text{ \AA}$ for MIF-2. The incorporation of the surfactants is also clearly evidenced by infrared and solid-state NMR spectroscopy. While both spectroscopies show that the imidazole ligands are deprotonated as in ZIFs, the ^{13}C NMR chemical shifts of the methylene carbons around 33 ppm suggest that the surfactants adopt an all-*trans* conformation, which points to an ordered, close packed surfactant arrangement as likewise found in other lamellar mesostructures.

Elemental analysis (EA) turned out to be a helpful tool in obtaining more detailed information on the type and dimensionality of the “inorganic” substructure based on zinc-imidazolate coordination polymers. As the composition of the MIFs was determined as $[\text{Zn}^{2+}] : [\text{IM}^-] : [\text{Br}^-/\text{Cl}^-] : [\text{CTA}^+] = 1 : 1 : 2 : 1$ ($\text{CTA}^+ = \text{C}_{19}\text{H}_{42}\text{N}^+$) by EA and energy dispersive X-ray spectroscopy (EDX), the tentative molecular formula of MIF-1/2 can be given as $[\text{Zn}(\text{MeIM})_{2/2}\text{Br}_2]\text{CTA} / [\text{Zn}(\text{IM})_{2/2}\text{Br}_2]\text{CTA}$, respectively. Therefore, the incorporation of excess halogenide ions, together with the assumption of a tetrahedral Zn coordination environment and electroneutrality suggest the formation of zinc imidazolate chains with composition $\text{Zn}(\text{IM})_{2/2}$ rather than zinc imidazolate networks with composition $\text{Zn}(\text{IM})_{4/2}$ as observed in ZIFs. As a working model, we assume anionic corner-sharing $\text{Zn}(\text{IM})_{2/2}\text{Br}_2^-$ chains that are electrostatically bonded to positively charged CTA^+ ions, a motive that has earlier congeners in the literature.[3]

Transmission electron microscopy (TEM) imaging of the MIFs is hampered by the strong beam sensitivity of the samples. Nevertheless, selected area electron diffraction (SAED) images could be recorded by using very short acquisition times. D values d_{1a} , d_{1b} for MIF-1 and d_{2a} , d_{2b} for MIF-2 were determined to be $11.43 \pm 0.45 \text{ \AA}$, $9.55 \pm 0.35 \text{ \AA}$ and $10.98 \pm 0.90 \text{ \AA}$, $8.95 \pm 0.95 \text{ \AA}$, respectively (Fig. 2, left), assuming orthorhombic metrics in both cases. The value 10.98 \AA has been reported in the literature as the translational parameter of a zigzag zinc imidazolate chain,[3] suggesting that the found values represent the in-plane (i.e. a and b) lattice parameters of the respective unit cells.

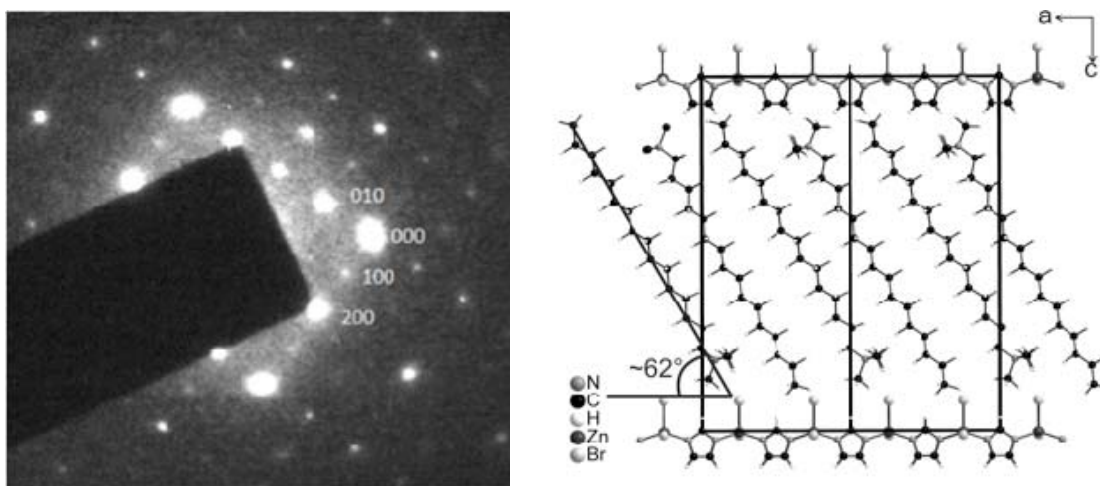


Figure 2: Left: SAED image of MIF-1, taken parallel to the c -axis. Due to the beam sensitivity of the sample only short acquisition times could be realized, resulting in noisy patterns. Right: Structural model of MIF-2 viewed along $[010]$, constructed with the *Visualizer* tool of the program *Materials Studio*. An AAA-type stacking model is used for simplicity. Copyright ©2012 by John Wiley & Sons, Inc.

Figure 2 (right) shows a tentative model for the structure of MIF-2 (MIF-1 may be constructed analogously), put together with the software package *Materials Studio* based on the spectroscopic, EA and diffraction results and assuming orthorhombic metrics. According to EA, we infer that $[\text{ZnBr}_2(\text{IM})_{2/2}]_n$ chains rather than $[\text{Zn}(\text{IM})_{4/2}]_n$ nets constitute the “inorganic” slabs. The metrics of the unit cell was extracted from XRD and TEM, respectively, yielding $a = 10.98 \text{ \AA}$ and $b = 8.95 \text{ \AA}$, and $c = 26.33 \text{ \AA}$. The metrics of the ab -plane is consistent with two $[\text{ZnBr}_2\text{IM}]_n^-$ zigzag-chains

running along the a axis, while the b parameter is given by the spacing of adjacent chains.[3] As for the organic slab, we assume an interdigitated monolayer arrangement with antiparallel stacking of surfactant cations, which are inclined with respect to the c axis by $\approx 62^\circ$ as similarly found in crystalline CTAB, rather than a tail-to-tail bilayer arrangement. Although we cannot distinguish between an AAA-type stacking of the surfactants with a basal spacing of 26.3 Å ($00l: l=n$) and an ABAB-type stacking with a doubled basal spacing of 52.6 Å and extinction of the $l=2n$ reflections, an AAA-type stacking is used here as working model. The SAED images imply perfect registry between the organic and inorganic slabs, which is rarely observed in lamellar mesophases.

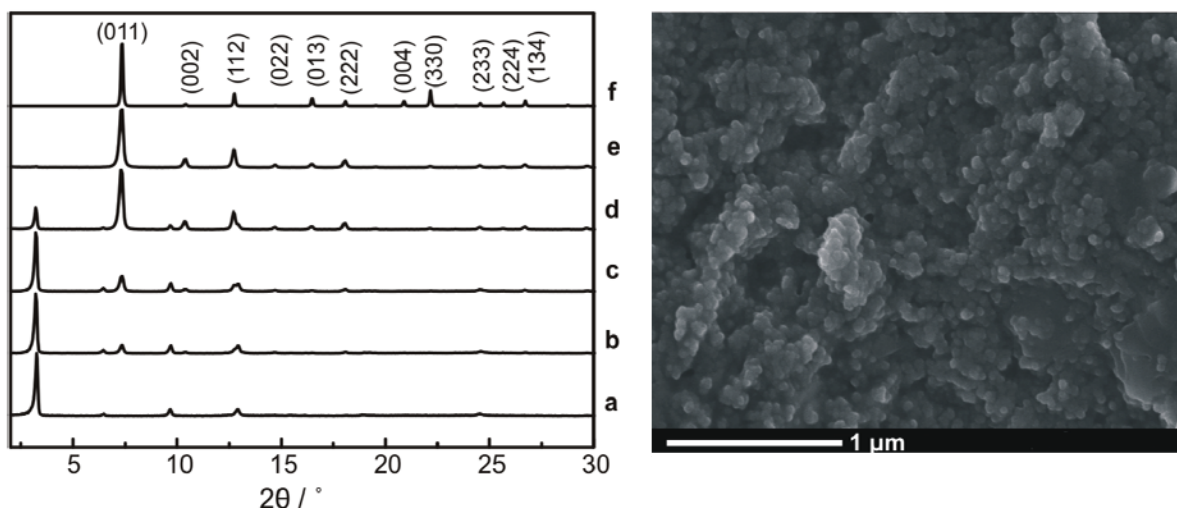


Figure 3: Left: XRD patterns illustrating the structural evolution of ZIF-8 after refluxing MIF-1 in EtOH at 100 °C for different times. a) Untreated, b) 5 min, c) 10 min, d) 1 h, e) 2 h, and f) simulated powder pattern of ZIF-8. Right: SEM image of MIF-1 treated with EtOH at 100 °C for 2 h. ZIF-8 nanoparticles of roughly 100 nm are visible, corresponding to diffraction pattern e) in Figure 3 (left). Copyright ©2012 by John Wiley & Sons, Inc.

Besides their high thermal stability of up to 300 °C, the behaviour of MIFs upon extraction of the surfactants is remarkable. When MIF-1 is treated with ethanol at 100 °C, it is converted into pure nanocrystalline ZIF-8 within minutes. Figure 3 (left) demonstrates the gradual formation of ZIF-8, which is presumed to proceed by heterogeneous growth and direct conversion of MIF-1 rather than dissolution of MIF-1 and growth of the new phase. The conversion process was followed by scanning electron microscopy imaging and reveals the coexistence of a lamellar structure (MIF-1) with ZIF-8 nanoparticles at intermediate growth stages, while after 2 h only agglomerates of ZIF-8 nanoparticles with sizes around 100 nm are observed (Fig. 3, right) [2].

The facile transformation of MIF-1 into ZIF-8 indicates a close topological relationship between the two materials, although the exact structure of the MIFs needs to be further ascertained. With the presented zinc imidazolate mesophases we have transferred the concept underlying mesostructured silica materials such as the MCM phases (mobile compound of matter) to zinc imidazolates, which may be rationalized by the similar Si-O-Si and Zn-IM-Zn bonding geometries. Thus, the structural analogy between microporous ZIFs and zeolites has been extended to mesostructured silica materials on the one hand, and mesostructured zinc imidazolates on the other hand.

References:

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