Zeolite CAN and AFI-Type Zeolitic Imidazolate Frameworks with Large 12-Membered Ring Pore Openings Synthesized Using Bulky Amides as Structure-Directing Agents

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(S) Supporting Information

ABSTRACT: Using bulky amides as the structure-directing agents (SDAs) is an alternative synthetic strategy for the exploration of crystalline large pore (≥12-membered ring) zeolitic imidazolate frameworks (ZIFs). Specifically, by using the bulky amides, dibutylformamide (DBF) and dipropylformamide (DPF) as solvent and imidazole (Im) as a ligand, two ZIFs mimicking the CAN and AlPO-5 (AFI) zeotypes with 12-membered ring (MR) pore openings were synthesized, and denoted as CAN-[Zn(Im)$_2$] and AFI-[Zn(Im)$_2$], respectively. These two materials are the first known examples of Zn(Im)$_2$ polymorphs with 12-MR pores and AFI-[Zn(Im)$_2$] has the largest pore apertures reported to date for ZIF materials. The concept that the bulky amides used were not simply acting as the solvent, but were in fact acting as SDAs or templates during the synthesis of the large pore ZIFs, was suggested by the closeness of the geometrical fit between the guest DBF and the *can* cages (composite building units) of the CAN-[Zn(Im)$_2$].

Zeolites are technologically important microporous materials, with more than 230 framework topologies known to date.[1] Attributed to the similarity of the coordination angle of the imidazolate linker and the Si−O−Si angle, imidazole (Im) and its derivatives/analogs have been utilized as linkers to create metal−organic frameworks (MOFs) with zeolitic topologies, which are typically referred to as zeolitic imidazolate frameworks (ZIFs),[2] metal azolate frameworks (MAFs),[3] tetrahedral imidazolate frameworks (TIFs),[4] boron imidazolate frameworks (BIFs)[5] or zeolite-like metal−organic frameworks (ZMOFs).[6−9] The past decade has witnessed ZIFs (this is more broadly utilized) hold great promise as porous materials for a variety of applications, driven by the prospect of the structures and properties arising from the combination of zeolites and MOFs.[10−12]

However, most of the ZIFs reported to date are 6-, 8- and 10-membered ring (MR) pore structures and only five ZIF topologies (zeolite GME[2b] and zeolite-like poz,[2c] moz,[2c] zea[4a] and zeb[4b]) contain large 12-membered ring (MR) pores when

compared to over 70 zeolite topologies with large/extra-large pore (≥12 MR pore openings constructed from ≥12 tetrahedrally coordinated atoms) structures observed in zeolites.[1,13] Large pore crystalline materials continue to be of particular significance in both academia and industry for their potential ability to process bulkier molecules.[13,14] Thus, although some hypothetical ZIF structures with known zeolite topology and large pores have been predicted, the designed synthesis of ZIFs materials featuring a large pore (≥12 MR) zeolite topology is still a great challenge.[15]

These large pore ZIFs containing large 12-MR channels have been synthesized using a ligand-directed strategy involving new and large-sized substituted Im ligands.[2,4] In addition, the substituted Im may also block the apertures and the largest reported pore aperture for any ZIFs is 13.1 Å (ZIF-70) (Table S1).[2b,d] In contrast, all of these novel large pore zeolites are the result of innovations in template design; however, the general strategy involves novel and bulky organic molecules as structure-directing agents (SDAs) which remain as extra-framework entities.[13,16] Thus, to make large pore ZIFs, it may seem logical to use large solvent molecules as the SDAs/templates and Im as a ligand.

For Zn(Im)$_2$ (Im = unsubstituted imidazolate) polymorphs as many as 13 different topologies have been experimentally obtained, which include 6-, 8- and 10-MR pore structures (Table S2).[2a,d,6b,17−19] Whereas, these Zn(Im)$_2$ compounds are typically prepared using small amides as the solvent, such as dimethylformamide. Very recently, high porosity of MER-Zn(Im)$_2$ featuring a 8-MR channel has been synthesized by employing a bulky macrocyclic template.[18b] We have recently synthesized a new Zn(Im)$_2$ compound featuring a 10-MR channel using a bulky amide as SDAs.[19] In addition, the bulky molecules, such as ionic liquids,[20a] caffeine[20b] and polyoxometalates,[20c] have played the template roles in the synthesis of MOFs. These observations inspired us to establish and develop a strategy for the preparation of large pore ZIFs (≥12 MR) based
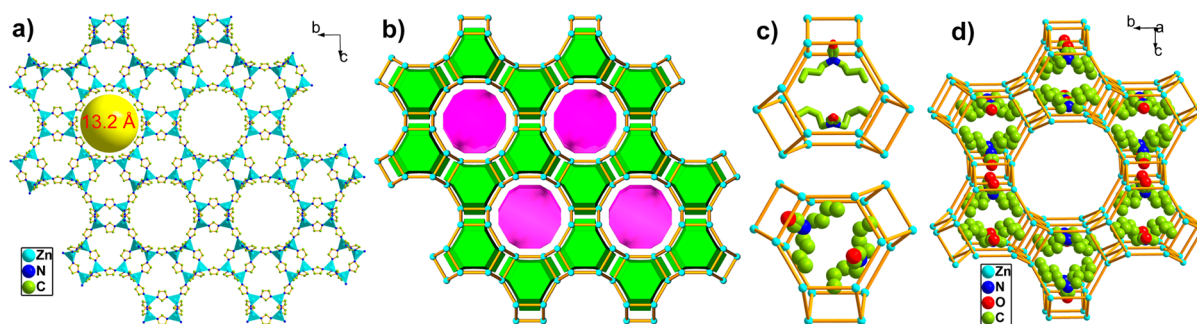
Figure 1. (a) Polyhedron representation of CAN-[Zn(Im)$_2$] (the guest DBF were removed) showing the 12-MR pore openings with a diameter of 13.2 Å; (b) topological structure and natural tiling of CAN-[Zn(Im)$_2$] (the *can* cages/tiles are shown in green, the *ato* tiles are shown in fushcia); (c) distribution of DBF (space filling and stick models) in the *can* cage; and (d) distribution of DBF (space filling models) in the fused *can* cages and 12-MR channels.

on the reasoning that the structure directing/template effects can be caused by using bulky and novel amide molecules.

In this Communication, by using the bulky and commercially available amides, dibutylformamide (DBF) and dipropylformamide (DPF) (Scheme S1), as solvent and Im as a ligand, two new large pore ZIF compounds with 12-MR pore openings were synthesized, which possessed the zeolite CAN and AFI topology, and termed CAN-[Zn(Im)$_2$] and AFI-[Zn(Im)$_2$], respectively. Interestingly, AFI-[Zn(Im)$_2$] has the largest pore aperture (15.6 Å) reported to date for ZIF materials and the 12-MR channel is not known in Zn(Im)$_2$ compounds prior to this work. In addition, bulky DBF as a template may be responsible for the formation of the *can* cages (composite building units) of CAN-[Zn(Im)$_2$].

CAN-[Zn(Im)$_2$] was prepared via a solvothermal synthesis between Zn(OAc)$_2$·2H$_2$O and Im in DBF at 40 °C. The as synthesized compound was characterized and formulated using single-crystal X-ray diffraction studies and elemental analysis as Zn$_3$(Im)$_6$·1.5DBF. The bulk purity of as-synthesized samples was confirmed by comparing its experimental powder X-ray diffraction (PXRD) pattern to that calculated based on the single crystal structure data (Figure S1). The crystal structure study revealed that CAN-[Zn(Im)$_2$] crystallizes in an orthorhombic structure with space group *Pnma*. There are three crystallographically unique zinc atoms, six different Im ligands in the asymmetric unit of CAN-[Zn(Im)$_2$] (Figure S2). All the Zn atoms are tetrahedrally linked by four N atoms from four different Im molecules to furnish a three-dimensional (3D) porous framework (Figure 1a).

The topological analysis indicates that CAN-[Zn(Im)$_2$] possesses a zeolite CAN framework, which has not been observed in ZIFs (Figure 1b). The secondary building units (SBUs) of CAN-[Zn(Im)$_2$] are 4-, 6- and 12-MR of zinc imidazolate. Being basic SBUs, the 4- and 6-MR lead to basic composite building units (CBUs): *can* cage (Figures 1b and S3b). Of particular interest is that the one-dimensional 12-MR channels with a pore aperture size of ca. 13.2 Å (the diameter of the largest sphere that will pass through the pore) are obtained when the (fused) *can* cages are connected around a 3-fold axis. The channels and *can* cages are connected through common zigzag chains and 6-MR. Based on the assembly of tiling (Figures 1b and S3c), the structure can also be described as being built from *ato* [6^{3}12^2] tiles forming channels of 12-MR parallel to the *a*-axis linked by the surrounding *can* [4^{6}6^5] tiles (=*can* cage). Prior to this work, only five ZIF topologies containing large 12-MR and no examples containing a 12-MR have been reported for Zn(Im)$_2$ polymorphs (Tables S1 and S2).

A further interesting point is that a very good geometrical fit between the guest molecule (DBF) and the *can* cage was observed in CAN-[Zn(Im)$_2$] (Figure 1c,d). The *can* cage was composed of six 4-MR and five 6-MR faces and there are two trapped DBF molecules per *can* cage. The amide group of one DBF molecule was located in the intersection of the two 4-MR with the two long alkyl chains stretching along the two 6-MR. In contrast, the amide group of another DBF molecule is vertical to the 6-MR windows with the two long alkyl chains stretching along one of the 6-MR and finally point to the intersection of the two 4-MR. Thus, it is logical to regard DBF as a template that favors the formation of the *can* cage. In addition, to join the *can* cage into the zeolite CAN-type structure, the disordered and large DBF molecules occupy the channel space of a 12-MR to maximize the short-range interactions occurring between the guest DBF and the 12-MR channel (Figure S4). Correspondingly, in the synthesis of CAN-[Zn(Im)$_2$], the organic DBF molecule acts as a template or SDA, which leads to the generation of *can* basic CBUs and large pore ZIFs. In fact, *can* cage also exist in many 12-MR zeolite (zeolite LTL, MOZ, OFF, SBS, SBT) as CBUs.[1] We expect that large pore ZIFs mimicking these zeotypes may also be achievable under appropriate conditions using DBF templates.

AFI-[Zn(Im)$_2$] was prepared via a solvothermal synthesis between Zn(OAc)$_2$·2H$_2$O and Im in DPF at 60 °C. The obtained crystals were not suitable for single crystallography due to their small size. The composition of AFI-[Zn(Im)$_2$] was determined to be Zn(Im)$_2$·0.8DPF using elemental analysis (Zn, 22.77; C, 45.76; H, 5.82; N, 21.95; O, 4.10). The thermogravimetric (TG) analysis (Figure S10) exhibits a mass loss of ca. 34.7 wt % from 30 to 300 °C, which was attributed to the loss of 0.8 DPF guests and was closest to the calculated values (34.2 wt %).

Fortunately, some hypothetical ZIF structures have been predicted.[15,21] Using the hypothetical structure model from AFI, the Rietveld refinement was successfully performed for AFI-[Zn(Im)$_2$] in the space group *P6/mcc* with the cell parameters $a = b = 26.437$ Å, $c = 16.632$ Å. Figure 2 shows a very good agreement between the observed and calculated PXRD patterns with reasonable R-factors (R_{wp} = 9.18% and R_p = 5.73%), taking into account the limited signal-to-noise ratio, especially for the data at a high angle. The results adequately confirm that AFI-[Zn(Im)$_2$] was a ZIF analogue of the AFI structure. Zeolite AFI is of great interest in the zeolite family because the AFI-type material AlPO-5 has been most extensively studied.[22]

The skeletal model of the refined framework is shown in Figure 3a. Like CAN-[Zn(Im)$_2$], 4-, 6- and 12-MR of zinc imidazolate also exist in AFI-[Zn(Im)$_2$] as SBUs. Being SBUs, the 4- and 6-rings lead to two basic CBUs: *afi* and *bog*, as shown in Figures 3b
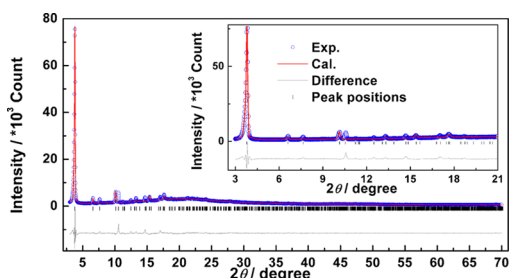
**Figure 2.** Observed and calculated XRD patterns of AFI-[Zn(Im)$_2$] as well as the difference profile.
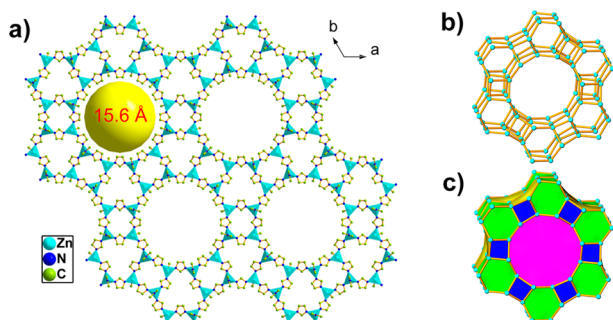
Figure 3. (a) Polyhedron representation of AFI-[Zn(Im)$_2$] showing the 12-MR pore openings that can accommodate a yellow sphere with a diameter of 15.6 Å; (b) topological net and (c) tiling of AFI-[Zn(Im)$_2$] (the *kah* tiles are shown in yellow, the *lov* tiles in blue, *afi* tiles in green and the *apf* tiles in fushcia).

and S5b, respectively. An attractive feature was the one-dimensional large 12-MR pore channels obtained when the *afi* and *bog* were cross-connected by shared 6-MR. The framework can be built using the assembly of four distinct tiles corresponding to *apf* [6^{6}12^2], *afi* [6^5](=CBUs *afi*), *lov* [4^{2}6^2] and *kah* [6^3] (Figures 3c and S5c). The large 12-MR has a window size of 15.6 Å (the diameter of the largest sphere that will pass through the pore). Thus, AFI-[Zn(Im)$_2$] has the largest pore apertures found in ZIFs to date (Tables S1 and S2). In fact, two basic *afi* and *bog* also exist in 14-MR zeolite AET and even 18-MR zeolite VFI as CBUs[1]. We expect that large pore ZIFs mimicking these zeotypes may also be achievable under appropriate conditions using DPF templates.

Next, ^{13}C MAS NMR (magic angle spinning nuclear magnetic resonance) spectrum (Figure 4) was used as a local probe to investigate the framework composition and the solvent molecules that were included in the framework. In the ^{13}C MAS NMR spectrum of CAN-[Zn(Im)$_2$], the peaks at δ = 125.6–126.1 ppm and δ = 142.1–143.4 ppm were observed and correspond to the deprotonated imidazole ligands. Nine peaks at δ = 162.2, 46.4, 41.5, 30.5, 29.7, 20.2, 19.4, 13.7 and 13.4 ppm belong to the carbonyl and methyl carbons of DBF (Figure 4a). In the ^{13}C MAS NMR spectrum of AFI-[Zn(Im)$_2$], the resonances at δ = 143.0/143.8 ppm and δ = 125.9 ppm correspond to the carbon atoms in the Im ring. The other additional peaks at δ = 162.7, 49.2, 43.9, 22.2, 21.1, 11.5 and 10.9 ppm were assigned to the carbonyl and methyl carbons of DPF (Figure 4b). These observations imply that during the formation process from raw materials to CAN-[Zn(Im)$_2$] and AFI-[Zn(Im)$_2$], the DBF and DPF solvent molecules act as structure-directing agents and therefore, were occluded inside the framework.

In fact, most of the Zn(Im)$_2$ polymorphs obtained to date are either too dense or collapse on the removal of the guest
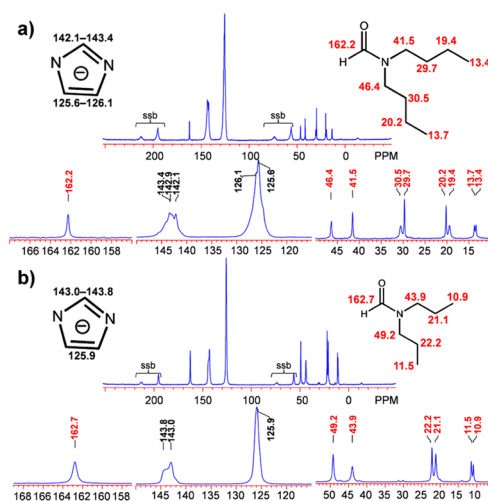
Figure 4. ^{13}C{^{1}H} MAS solid-state NMR spectrum of (a) CAN-[Zn(Im)$_2$] and (b) AFI-[Zn(Im)$_2$] (the ssb are the spinning side bands).

molecules.[2a,d,6b,17−19] Thus, only SOD-Zn(Im)$_{1.7}$(mIm)$_{0.3}$ (prepared via ligand exchange) and MER-Zn(Im)$_2$ exhibit high surface areas.[18] The as-synthesized AFI-[Zn(Im)$_2$] and CAN-[Zn(Im)$_2$] samples were immersed in a dried acetone for 48 h to remove the guest molecules and was subsequently activated under vacuum at 50 °C. The activated samples were measured by PXRD to confirm that they have the same structures as those of the as-synthesized samples (Figures S12 and S13). In addition, a remarkable plateau was observed for the activated samples at temperatures up to 300 °C in the TG curves (Figures S8 and S10) and the absence of peaks corresponding to guest molecules was observed in the ^{13}C MAS NMR spectroscopy (Figures S14 and S15), which showed that all the guest molecules in the cavities could be completely evacuated.

They were found to exhibit type I isotherms, indicating their microporous properties based on the N$_2$ sorption measurements (Figure 5). The Langmuir surface areas were measured as 1628
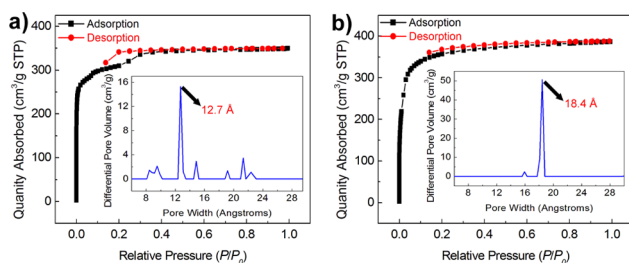
Figure 5. Isotherm obtained for N$_2$ adsorption at 77 K and pore size distribution (inset) of CAN-[Zn(Im)$_2$] (a) and AFI-[Zn(Im)$_2$] (b).

m^2 g^{-1} (BET: 1386 m^2 g^{-1}) and 1401 m^2 g^{-1} (BET: 1178 m^2 g^{-1}) for AFI-[Zn(Im)$_2$] and CAN-[Zn(Im)$_2$], respectively, with total pore volumes of 0.64 and 0.54 cm^3 g^{-1}, respectively. These numbers stand relatively high among the large 12-MR ZIFs (Table S1) and representative ZIFs (Table S3). The porosity distribution was calculated by a density functional theory model using the isotherm, which showed very a sharp peaks centered at 12.7 and 18.4 Å, respectively. These values are closest to those calculated from the crystal structure of CAN-[Zn(Im)$_2$] (13.2 Å) and AFI-[Zn(Im)$_2$] (15.6 Å), indicating the good crystallinity and purity of the activated samples.

In conclusion, using bulky amides as the SDAs or templates is an alternative synthetic strategy for the exploration of crystalline large pore (≥12 MR) ZIFs. We have shown the synthesis of the first $Zn(Im)_2$ polymorphs bearing a 12-MR pore channel, CAN-$[Zn(Im)_2]$ and AFI-$[Zn(Im)_2]$ using DBF and DPF as the solvent. AFI-$[Zn(Im)_2]$ has the largest pore apertures reported to date for ZIF materials. The bulky amides used were in fact acting as templates during the synthesis of the large pore ZIF, which can be attributed to the closeness of the geometrical fit between the guest DBF and the *can* cages of the CAN framework. In fact, the basic CBUs of CAN-$[Zn(Im)_2]$ and AFI-$[Zn(Im)_2]$ also exist in 12-, 14- and even 18-MR zeolite. We expect that large pore ZIFs mimicking these zeotypes may also be achievable. All these observations underline the rich synthetic and structural chemistry of large pore ZIFs, and work is in progress to construct large pore ZIFs (≥12 MR) by employing different bulky amides as SDAs.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11197.

Experimental details (PDF)

Crystallographic data for $C_{63}H_{93}N_{27}O_3Zn_6$ (CIF)

Crystallographic data for $C_{36}H_{36}N_{24}Zn_6$ (CIF)

Crystallographic data for $C_6H_6N_4Zn$ (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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