Metal–Organic Frameworks

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Multiple Functions of Ionic Liquids in the Synthesis of Three-Dimensional Low-Connectivity Homochiral and Achiral Frameworks**

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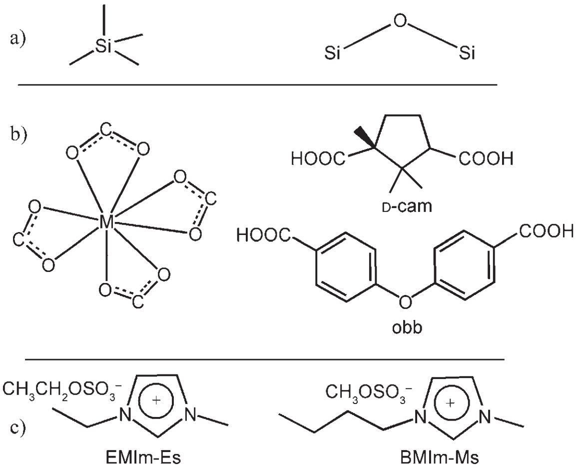
Low connectivity of framework building blocks (that is, with 4 or 3 connections) is closely associated with open architecture and porosity in three-dimensional (3D) framework materials. The importance of materials with low connectivity is shown by the large-scale industrial applications of zeolites (4-connected) in catalysis, gas separation, etc.[1] The synthetic development of low-connectivity frameworks with new composition and topology continues to attract much attention, as applications of such materials depend on the unique composition or framework topology of each individual material.[2–6]

Despite tremendous success in the synthesis of low-connectivity framework materials in the past several decades, 3D chiral low-connectivity framework materials, and particularly those with bulk homochirality, are still rare. Traditional zeolites are typically achiral. Even those with chiral topology (e.g., zeolite β) have not been prepared in the enantiopure form. Recent progress with metal–organic framework materials have opened up new routes toward the synthesis of homochiral solids.[7–9] However, a generalized synthetic approach is lacking for the preparation of 3D homochiral low-connectivity framework materials that are stoichiometrically and topologically similar to zeolites.

We seek to develop a generalized method to synthesize homochiral zeolite-like low-connectivity framework materials. Although the method is equally successful with the achiral system and in molecular solvents, herein we focus on the applicability of this method for the synthesis of homochiral materials and the multiple roles of ionic liquids.

The low-connectivity (3 or 4) is generated through the formation of bidentate chelating bonds between metals and dicarboxylates (Scheme 1). Such a bonding mode is well known in the literature. The simplest example is tin(IV) acetate, in which each acetate ligand chelates to a central tin(IV) ion.[10] Other metals that have such a bonding pattern include zirconium(IV), cadmium(II), and indium(III).[11,12] However, to serve as a general synthetic method to create homochiral 3D zeolite-like tetrahedral framework materials, the selection of metals and ligands has to be coupled with the templated synthesis approach, similar to the templated synthesis of zeolites. To this end, few examples exist in which such highly coordinated metal centers are joined into homochiral 3D tetrahedral frameworks by a templated synthesis.



Scheme 1. A comparison of the structural building blocks in zeolites (a) with those in this work (b), and two ionic liquids used for synthesis (c).

To test our synthetic method and to illustrate the generality of this method for the synthesis of both chiral and achiral materials, we employed enantiopure D-camphoric acid (D-H_2cam), and achiral 4,4′-oxybis(benzoic acid) (H_2obb) in two different ionic liquids, EMIm-Es (1-ethyl-3-methylimidazolinium ethylsulfate) and BMIm-Ms (1-butyl-3-methylimidazolinium methylsulfate). The ionothermal synthesis resulted in a number of open-framework materials that contain eight-coordinated indium(III) sites as the tetrahedral node (Scheme 1, Figure 1, and Table 1). Both 4-connected and less common 3-connected homochiral framework materials were synthesized.

Also of interest is the demonstration the triple roles of ionic liquids (Figure 2), namely as: 1) solvent and cationic structure-directing agent, 2) solvent only, and 3) solvent and cationic/anionic structure-directing agents. The first role, as observed for ALF-1 (ALF = anionic low-connectivity framework), ALF-4, and ALF-5, is to function as a solvent and as the cationic structure-directing agent. This dual role, which is well known in the literature, particularly through the seminal work of Morris et al,[3] has the advantage of eliminating competing effects between the solvent and the separate structure-directing agent;[3,4a] however, it has a limitation in

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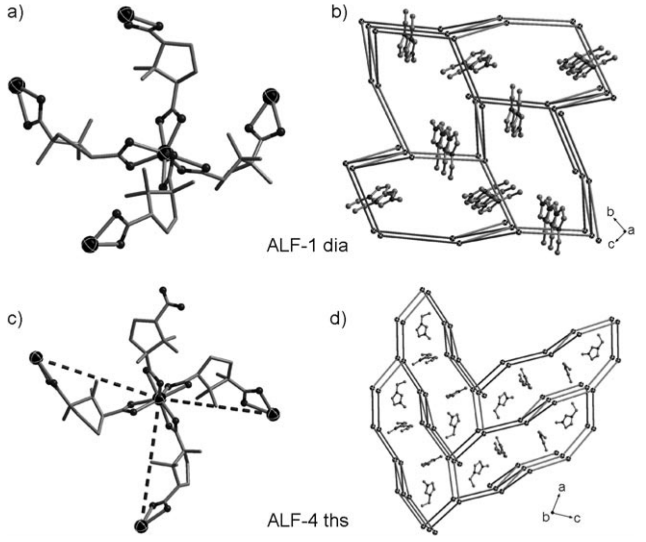

Figure 1. The basic 4-connected building block (a) and diamond-type framework filled by guest EMIm cations of ALF-1 (b), and the basic 3-connected building block (c) and ths-type framework filled by guest EMIm cations of ALF-4 (d).

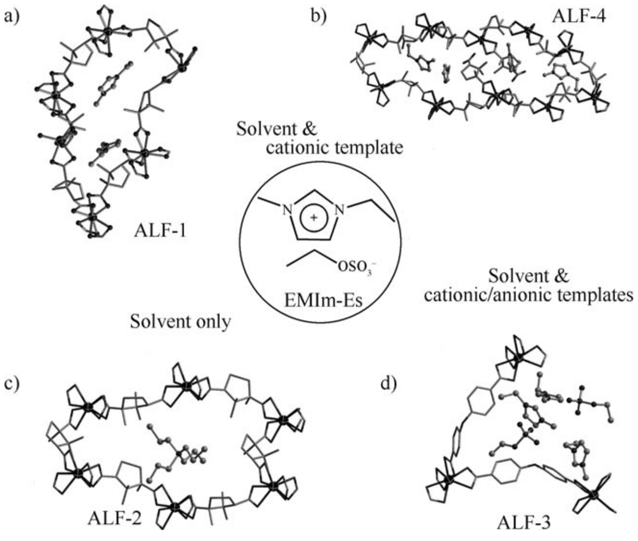

Figure 2. Three different roles of the EMIm-Es ionic liquids. a,b): EMIm-Es acting as both solvent and cationic structure-directing agents, leading to 4-connected homochiral ALF-1 with the diamond-type net (a) shown as the 6-membered ring, and 3-connected homochiral ALF-4 with the $ThSi_2$-type net (b) shown as the 10-membered ring. c) EMIm-Es acting as the solvent only; tetrapropylammonium cations serve as the cationic structure directing agent, leading to the formation of homochiral ALF-2 with the diamond-type net (the 6-membered ring is shown). d) Both cations and anions of EMIm-Es are trapped in the cavity of 4-connected framework with the $CdSO_4$-type topology.

the phase control because a new ionic liquid, which can be expensive and limited in selection, would be required to exert different structure-directing effects. It can be advantageous for the ionic liquid to serve just as the solvent and use other compounds as the structure-direct agents, the choice of which would be far less restricted. This second role of the ionic liquid is shown by ALF-2 and ALF-2r (r denotes racemic) in which tetrapropylammonium cations serve as the cationic structure-directing agent and suppress the structure-directing effect of the ionic liquid. Finally, a very interesting observation found in ALF-3 is the encapsulation of the whole ionic liquid (both cations and anions in the 3:2 ratio) within the cavity of a material with the 4-connected $CdSO_4$-type topology, a feature rarely observed in the synthesis of 4-connected open-framework materials.

The structures of these anionic low-connectivity frameworks were determined from single-crystal X-ray diffraction data. In all ALFs, the negative framework charge is balanced by extra-framework organic cations (tetraalkylammonium cations, immidazolium cations). In all structures, the basic coordination chemistry at the metal site is the same. Each 8-coordinate In^{3+} site is bonded to four carboxylate ligands (similar to Si^{4+} or Al^{3+} in zeolites) and in ALF-1 to ALF-3 each carboxylate ligand bonds to two In^{3+} sites (similar to O^{2-} in zeolites; Scheme 1, Figure 1 a,c). The framework features of ALF-1 to ALF-3 are characteristic of the 4-connected net with the AX_2 formula. The simple 4-connected frameworks of ALF-1 to ALF-3 have diamond (dia, for ALF-1, ALF-2 and 2r; Figure 1 b) or $CdSO_4$ (cds for ALF-3) topologies.

In addition to 4-connected frameworks in ALF-1 to ALF-3, 3D homochiral frameworks (ALF-4 and ALF-5) based on 3-connected nodes were prepared by reducing the amount of organic base, 1,4-diazabicyclo[2.2.2]octane (DABCO), in the synthesis, and therefore lowering the basicity, which leads to the partial protonation of camphoric acid and a decreased connectivity from 4 to 3. This demonstrates that even in the ionothermal synthesis, the acidity/basicity of the synthesis mixture can play a crucial role on the framework formation.

Both ALF-4 and ALF-5 have the ths ($ThSi_2$-type) topology. It is worth noting that although 3-connected nodes are common in layered materials (e.g., graphite), templated 3D framework materials based on only 3-connected nodes are

Table 1: A Summary of Crystal Data and Refinement Results.[a]

	Formula	Space Group	a [Å]	b [Å]	c [Å]	R(F)	Flack	Nets[c]	T/V[d] [nm^{-3}]
ALF-1	(EMIm)[In(D-cam)$_2$]	$P2_12_12_1$	12.3398(2)	13.4958(3)	16.9799(3)	0.0380	−0.04(2)	dia	1.41
ALF-2	(Pr$_4$N)[In(D-cam)$_2$]	$I2_12_12_1$	10.7086(9)	18.0006(13)	18.0493(12)	0.0555	0.01(6)	dia	1.14
ALF-2r	(Pr$_4$N)[In(DL-cam)$_2$][b]	$I\bar{4}2d$	17.9054(4)	17.9054(4)	10.7305(5)	0.0470	−0.08(8)	dia	1.14
ALF-3	(EMIm)$_3$[In(obb)$_2$]·(Es)$_2$·(H$_2$O)[b]	Cc	22.748(2)	15.847(1)	15.113(1)	0.0426	0.00(9)	cds	0.73
ALF-4	(EMIm)$_2$[In$_2$(D-cam)$_3$(D-Hcam)$_2$]	$P4_32_12$	13.7393(1)	13.7393(1)	37.2281(5)	0.0798	−0.03(7)	ths	1.14
ALF-5	(BMIm)$_2$[In$_2$(D-cam)$_3$(D-Hcam)$_2$]	$P4_32_12$	13.7548(2)	13.7548(2)	38.1612(8)	0.0767	−0.02(8)	ths	1.14

[a] D-H_2cam = D-camphoric acid, EMIm = 1-ethyl-3-methyl imidazolium, BMIm = 1-butyl-3-methyl imidazolium, Pr_4N = tetra-*n*-propylammonium, H_2obb = 4,4′-oxybis(benzoic acid), Es = ethylsulfate. [b] Non-enantiomorphous and non-centrosymmetric space group. [c] dia = diamond, cds = $CdSO_4$, ths = $ThSi_2$ topology. [d] T/V is the density of metal atoms per unit volume.

quite rare. Herein, the metal–ligand building block (ML_4) could function as the 3-connected node when one of four ligands becomes a pendant ligand. This was achieved by using two different ionic liquids that serve as both solvent and cationic structure-directing agents. The replacement of $EMIm^+$ in ALF-4 by $BMIm^+$ in ALF-5 results in a slightly larger unit cell. The non-interpenetrating ths-type $\{In_2(D\text{-}cam)_3(D\text{-}Hcam)_2\}_n^{2n-}$ framework has large channels along *a* or *b* axis that are filled by guest cations (Figure 1 d).

By adding a separate structure-directing agent, Pr_4NBr, a new compound, ALF-2, was obtained. A prominent structural feature in ALF-2 is that the Pr_4N^+ cations were selected into the 4-connected diamond framework, while the EMIm-Es ionic liquid only serves as the solvent. In other words, the cationic structure-directing effect of the ionic liquid is suppressed and superseded by the addition of a second structure-directing agent.

The diamond net (space group: $Fd\bar{3}m$) is achiral and yet ALF-1 and ALF-2 are homochiral because of the incorporation of enantiopure camphorate ligands. ALF-2r is synthesized from racemic DL-camphoric acid, and has essentially the same crystal structure as ALF-2, with the only difference being the opposite handedness in 50 % of the chiral ligand. This feature is also quite unusual because the packing of chiral molecules generally differ for pure enantiomers and for racemates as a consequence of differing symmetry requirements during the crystallization. The reason for the nearly identical packing in ALF-2 and ALF-2r is probably due to the dilution of chirality by achiral species (in this case In^{3+} and extra-framework Pr_4N^+).

The low connectivity, together with the large bridging ligands in the materials reported, leads to a low framework density defined as the number of tetrahedral vertices per unit volume. The concept of the framework density was introduced to characterize the openness of the zeolite-type structures. The lowest framework density is 5.2 nm^{-3} among the tabulated 4-connected structures.[13] The density of these ALFs ranges from 1.41 nm^{-3} (ALF-1) to 0.73 nm^{-3} (ALF-3) (Table 1).

In summary, a versatile synthetic method has been presented that goes beyond the traditional practice that relies on 4-coordinated elements (e.g., Si^{4+} and Al^{3+}) to create 4- and 3-connected frameworks. The method makes it possible to create 3D low-connectivity (3- or 4-connected) and low-density (as low as 0.73 nodes/nm^3) frameworks from high-coordination elements (coordination number ≥ 8). Of particular significance is the application of this method for the synthesis of 4- and 3-connected homochiral framework materials. The three different functions of the ionic liquid further extend the applicability of this method and make it possible to create a diversity of homochiral and achiral framework materials with various compositions and topologies.

Experimental Section

$(EMIm)[In(D\text{-}cam)_2]$ (ALF-1): D-Camphoric acid (0.1173 g), 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.1123 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.0829 g) in 1-ethyl-3-methylimidazolium ethylsulfate (EMIm-Es, 1.9080 g) were mixed in a 23 mL teflon cup, and the mixture was stirred for 20 min. The vessel was then sealed and heated at 160 °C for 5 days. The autoclave was subsequently allowed to cool to room temperature. Transparent colorless crystals were obtained.

$(Pr_4N)[In(D\text{-}cam)_2]$ (ALF-2): D-Camphoric acid (0.1051 g), tetrapropylammonium bromide (Pr_4NBr, 0.2519 g, 1 mmol), DABCO (0.0632 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.1136 g, 0.3 mmol) in EMIm-Es, (1.8211 g) were placed in a 20 mL vial. The sample was heated at 160 °C for 5 h, and then cooled to room-temperature. After washing with ethanol and distilled water, colorless crystals were obtained.

$(Pr_4N)[In(DL\text{-}cam)_2]$ (ALF-2 r): DL-Camphoric acid (0.1001 g, 0.5 mmol), tetrapropylammonium bromide (Pr_4NBr, 0.1234 g), DABCO (0.0632 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.1123 g, 0.3 mmol) in EMIm-Es, (Ei-Es, 1.67 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 48 h, and then cooled to room-temperature. After washing with ethanol and distilled water, colorless crystals were obtained.

$(EMIm)_3[In(obb)_2]{\cdot}(Es)_2{\cdot}(H_2O)$ (ALF-3): 4,4′-oxybis(benzoic acid) (0.1136 g), DABCO (0.0603 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.0736 g) in EMIm-Es (1.4819 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 4 days, and then cooled to room-temperature. After washing with ethanol and distilled water, colorless crystals were obtained.

$(EMIm)_2[In_2(D\text{-}cam)_3(D\text{-}Hcam)_2]$ (ALF-4): D-Camphoric acid (0.1077 g), DABCO (0.0546 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.0917 g) in EMIm-Es (1.5635 g) were placed in a 20 mL vial. The sample was heated at 160 °C for 4 days, and then cooled to room-temperature. After washing with ethanol and distilled water, colorless crystals were obtained.

$(BMIm)_2[In_2(D\text{-}cam)_3(D\text{-}Hcam)_2]$ (ALF-5): D-Camphoric acid (0.109 g), DABCO (0.0602 g) and $In(NO_3)_3{\cdot}x\,H_2O$ (0.093 g) in 1-butyl-3-methylimidazolium ethylsulfate (BMIm-Es, 1.436 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 3 days, and then cooled to room-temperature. After washing with ethanol and distilled water, colorless crystals were obtained.

CCDC-671541, CCDC-671542, CCDC-671543 (ALF-1, 2, and 2r), CCDC-671554 (ALF-4), CCDC-671555 (ALF-5), and CCDC-671556 (ALF-3) contain 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.

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