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Multiroute Synthesis of Porous Anionic Frameworks and Size-Tunable Extraframework Organic Cation-Controlled Gas Sorption Properties

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Porous materials are of great interest as adsorbents for applications such as hydrogen storage and carbon dioxide sequestration.[1−11] In efforts to develop better porous metal−organic framework (MOF) materials for such applications, a number of structural features such as pore size and shape, surface area, and pore volume have been found to play important roles in the sorption energetics and uptake capacity.[1a,4,5] Studies have also shown that a large pore size is not necessarily advantageous for storing small gas molecules. For example, an increase in the pore size can lead to a decrease in the volumetric H_2 uptake.[4a] Thus, synthetic strategies that allow the control of the pore size and pore geometry are particularly important. Catenation has been used as a method for reducing the pore size and partitioning the pore space; however, its occurrence during self-assembly processes can be difficult to control, and some types of framework topologies are not prone to form catenated structures.[5b,d]

Recently, many efforts have been focused on deliberate enhancement of the adsorbent−adsorbate interactions in order to improve gravimetric and volumetric energy storage density under noncryogenic conditions.[9c] Among the various methods used, the design of open metal sites on the framework has enjoyed particular success.[4b,d,8,9d] There has also been increased research on the effects of anionic frameworks and the associated extraframework cations on the gas sorption properties. This is in part because cationic extraframework species and anionic frameworks may enhance the adsorbent−adsorbate interactions through charge-induced forces. However, other than the variation of simple extraframework inorganic cations (usually through ion exchange),[4d,7,8,9b,e] little research has been done on the variation of extraframework *organic cations* in MOFs and its effect on the gas sorption properties.

In this contribution, we report a microporous anionic (3,4)-connected C_3N_4-type framework, $[In_3(btc)_4]_n^{3n-}$, which is quite unusual because it can be synthesized under diverse and dramatically different chemical environments, including (1) solvothermal assembly in molecular solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), and triethanolamine (TEOA); (2) an ionic liquid, tris(2-hydroxyethyl)methylammonium methylsulfate (TEMA Ms); and (3) a deep eutectic solvent (DES) made from choline chloride and ethyleneurea (compounds **1**−**7**; see Table 1, Scheme 1, and Scheme S1 in the Supporting Information).[12] To our knowledge, no MOF materials of a given topological type have been synthesized using such a set of chemically diverse environments.

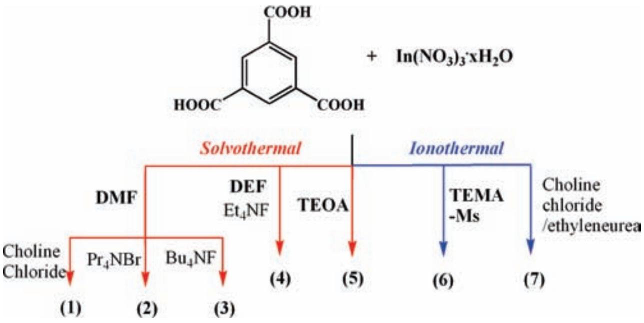
These solvents exhibit different roles. The solvothermal assembly in DMF or DEF leads to four compounds (**1**−**4**) with different organic cations (Scheme 2). Unlike DMF and DEF, TEOA not only serves as the solvent but in its protonated form is also incorporated into compound **5** as extraframework charge-balancing species. Of particular interest is the formation of the $[In_3(btc)_4]_n^{3n-}$ frameworks by ionothermal synthesis using the ionic liquid TEMA Ms and the DES choline chloride/ethyleneurea, leading to compounds **6** and **7**, respectively. The rich ionic environments of the ionic liquid and DES may be particularly helpful in the formation of the anionic $[In_3(btc)_4]_n^{3n-}$ framework.

Table 1. Summary of Crystal Data and Refinement Results

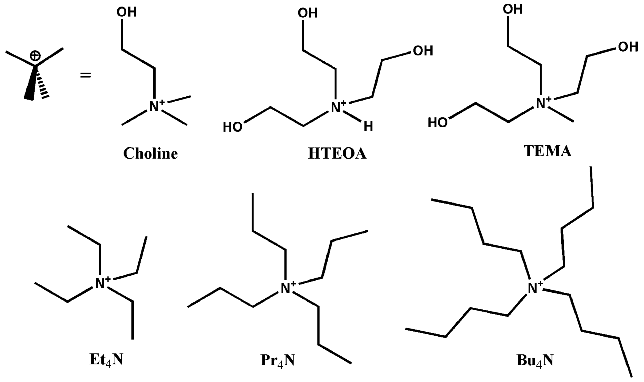
	formula[a]	space group	*a*, *b* (Å)	*c* (Å)	R(*F*)
1	$(choline)_3[In_3(btc)_4]\cdot 2DMF$	$I\bar{4}3d$	20.3980(1)	20.3980(1)	0.0420
2	$(Pr_4N)_3[In_3(btc)_4]$	$R3c$	29.1453(1)	16.9910(2)	0.0307
3	$(Bu_4N)_3[In_3(btc)_4]$	$R3c$	29.155(2)	17.367(3)	0.0584
4	$(Et_4N)_3[In_3(btc)_4]\cdot DEF$	$I\bar{4}3d$	20.4310(1)	20.4310(1)	0.0547
5	$(HTEOA)_3[In_3(btc)_4]$	$I\bar{4}3d$	20.4639(1)	20.4639(1)	0.0590
6	$(TEMA)_3[In_3(btc)_4]$	$I\bar{4}3d$	20.4029(8)	20.4029(8)	0.0482
7	$(choline)_3[In_3(btc)_4]\cdot eurea$	$I\bar{4}3d$	20.3878(4)	20.3878(4)	0.0385

[a] btc = 1,3,5-benzenetricarboxylate; choline = $[(CH_3)_3NCH_2CH_2OH]^+$; Pr_4N = tetrapropylammonium; Bu_4N = tetrabutylammonium; TEOA = triethanolamine; TEMA = tris(2-hydroxyethyl)methylammonium; eurea = ethyleneurea.

Scheme 1. Synthetic Conditions for the Seven Compounds



Scheme 2. Six Different Organic Cations



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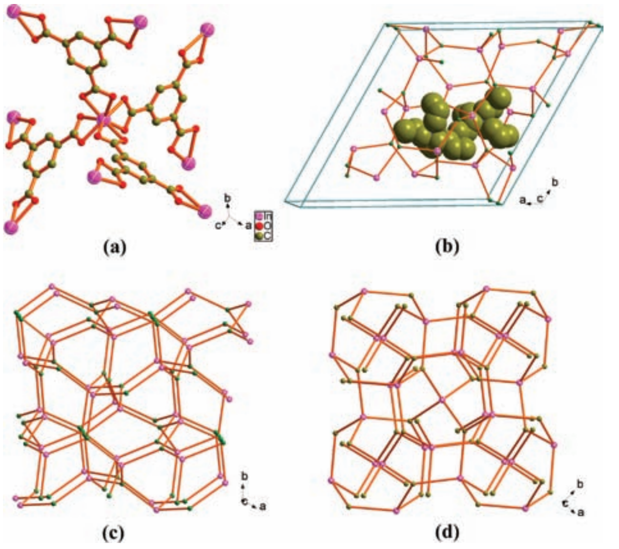

Figure 1. (a) Coordination environment and the (3,4)-connected mode in **3**. (b) Incorporation of guest Bu_4N^+ ions (space-filling mode) in the C_3N_4-type framework of **3**. (c) Topological representation of the C_3N_4 net in **3**, which is more distorted than (d) the C_3N_4 net in **1**.

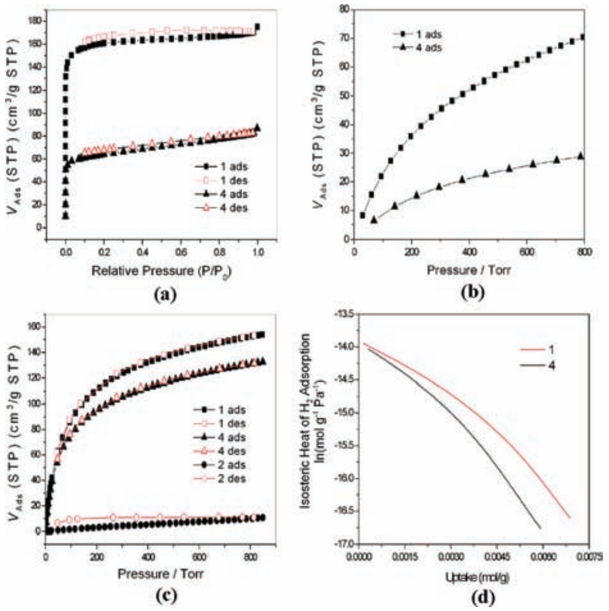

Figure 2. Adsorption isotherms: (a) N_2; (b) CO_2; (c) H_2. (d) Variation of isosteric heat of adsorption with amount of adsorbed H_2 in **1** and **4**.

More importantly, such diverse synthetic conditions allowed us to synthesize a series of anionic framework materials that have the same framework composition and topology but differ in the type of extraframework charge-balancing species. Through direct synthesis, six different organic cations (Scheme 2) were included into the pore space of the anionic framework. This created a unique opportunity to study the effect of size-tunable extraframework organic cations on gas adsorption properties.

In all of the structures, the basic coordination chemistry at the metal site is the same. Each In^{3+} site is 4-connected despite its eight-coordinate geometry, because each In^{3+} site is bonded to four carboxylate ligands and each carboxylate group chelates to just one In^{3+} site (Figure 1a). Such structural features are also found in some other indium MOFs.[11c,13]

The integration of the planar 3-connected btc ligand with the 4-connected $In(COO)_4$ unit generates the C_3N_4-type (3,4)-connected framework materials with high porosity. Even though the C_3N_4-type net contains no straight channels, a large extraframework pore volume is present. The free volume accessible to solvents and charge-balancing cations in **1** is 5617.1 Å^3 per unit cell, and the pore volume ratio is 66.2% as calculated with the PLATON program.[14] Such a large pore space is occupied by charge-balancing cations to different degrees in the structures reported here, depending on the sizes of the organic cations (Figure 1b). When the charge-balancing cations are relatively small, neutral solvent molecules are also present in the as-synthesized forms.

It is interesting to note that the relatively smaller organic cations (such as choline, DMF, and urea) are disordered in the structures because they do not fit snugly in the large pore space as a result of their small size. In comparison, the larger organic cations (Pr_4N^+, Bu_4N^+, and $HTEOA^+$) provide a better fit within the pore space and are thus crystallographically ordered. The ordering of large Pr_4N^+ and Bu_4N^+ cations also lowers the symmetry of the C_3N_4 network from cubic (**1**, **4**−**7**) to rhombohedral (**2** and **3**) (Figure 1c,d).

It is worth noting that the thermal properties of these materials are also affected by guest cations, as shown by thermal gravimetric analysis (TGA) of **1**, **2**, and **4** (Figure S2 in the Supporting Information). For compound **1,** there is a continual weight loss (due to the removal of DMF) from 80 to 300 °C, whereas for **4,** the weight loss occurs in two steps, with the first step corresponding to the loss of neutral solvent molecules (DEF in **4**). Compound **2** with ordered Pr_4N^+ cations shows only a one-step weight loss starting at ~400 °C.

Gas adsorption measurements (N_2, H_2, and CO_2) were performed on a Micromeritics ASAP 2010 surface area and pore size analyzer. The sample of **1** was degassed at 100 °C prior to the measurement, while the samples of **2** and **4** were degassed at 200 °C. Powder X-ray diffraction further confirmed that the frameworks do not change at the degassing temperature. The N_2 adsorption/desorption studies of **1** and **4** revealed that both have reversible type-I isotherms, indicating that they are microporous (Figure 2a). The Brunauer−Emmett−Teller and Langmuir surface areas for **1** are 507.8 and 711.8 m^2 g^{-1}, respectively, and those for **4** are 206.9 and 291.8 m^2 g^{-1}, respectively. Although compound **2** showed small H_2 adsorption, no significant N_2 or CO_2 adsorption was observed.

Notably, the CO_2 uptake capacity of compound **1** reached as high as 70.6 cm^3 g^{-1} (or 82 L per L) at 1 atm and 273 K, which is comparable to some of the highest values reported to date under the same measurement conditions (Figure 2b).[3b] Impressively, such a high CO_2 uptake capacity is achieved even when the pores are occupied with extraframework charge-balancing cations (choline in this case). One possible reason for such a high CO_2 adsorption may be the increased interaction between CO_2 and hydroxyl groups on the choline cations, similar to the recently reported interaction between $-NH_2$ groups and CO_2.[4c] In comparison, the CO_2 adsorption isotherm of **4** at 273 K and 1 atm shows an adsorption capacity of 28.9 cm^3 g^{-1}.

The studies of H_2 adsorption/desorption in **1**, **2**, and **4** at 77 K and 1 atm revealed that the H_2 uptake capacities follow the sequence **1** > **4** > **2** (Figure 2c). The amounts of H_2 uptake at 77 K and 1 atm are 151.1 cm^3 g^{-1} (1.36 wt %) for **1**, 129.6 cm^3 g^{-1} (1.16 wt %) for **4**, and 9.5 cm^3 g^{-1} (0.09 wt %) for **2**.

The H_2 adsorption data for **1** and **4** were analyzed using virial methods based upon the equation $\ln(n/P) = A_0 + A_1 n + A_2 n^2 + ...$, where P is the pressure, n is the total amount adsorbed, and A_0, A_1, etc., are virial coefficients (Figure 2d).[9d,15] **1** has $A_0 = -13.68$ and $A_1 = -401.52$ g mol^{-1}, while **4** has $A_0 = -13.62$ and $A_1 = -512.26$ g mol^{-1}. They have similar Henry's law constants $K_H = \exp(A_0)$,

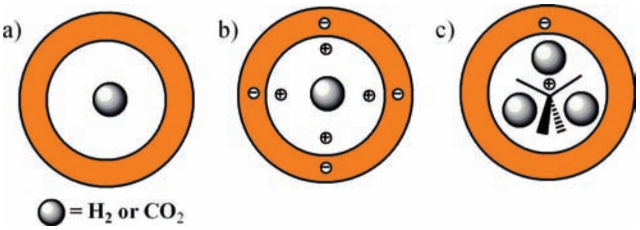

Figure 3. Schematic illustrations of possible locations of gas molecules in relation to extraframework species: H_2 or CO_2 in (a) a guest-free small neutral pore, (b) a pore containing small cations attached to the wall, and (c) a large pore occupied by a tetraalkylammonium cation.

indicating similar adsorbate−adsorbent interactions. However, the more negative A_1 value for **4** suggests a stronger H_2−H_2 interaction inside the framework and a narrower porosity than in **1**.

The above comparative study of gas sorption properties using N_2, H_2, and CO_2 clearly demonstrates the size effect of organic cations on the adsorption. The different adsorption properties can be simply explained as due to the different degrees of pore blockage by organic cations of different sizes. However, it is not totally impossible to have a pore partition effect in large-cavity structures containing organic cations. Unlike simple inorganic cations that tend to be attached to the wall of the anionic framework, organic alkylammonium cations are more likely to be located at or near the pore center, which is of course affected by hydrophilic and hydrophobic properties of the framework surface and organic cations. Properly designed partitioning of the pore space, whether through interpenetration or the size and shape of the guest species, could allow for more efficient use of the pore space to enhance the storage capacity for small gas molecules (Figure 3).

In summary, in diverse chemical environments that include organic solvents, an ionic liquid, and a deep eutectic solvent, we have prepared a series of porous anionic C_3N_4-type ($[In_3(btc)_4]_n^{3n-}$) framework materials that contain size-tunable and ion-exchangeable extraframework organic cations. The direct syntheses of porous materials with various-sized extraframework cations in MOFs, coupled with possible postsynthesis ion-exchange, provide a unique ability to tune the pore metrics and associated properties such as gas sorption. Gas sorption studies using N_2, H_2, and CO_2 clearly demonstrated the size effect of various organic cations on the sorption properties. Notably, even with a large fraction of the pore space being occupied with extraframework cations such as choline, a CO_2 uptake capacity as high as 70.6 cm^3/g (or 82 L per L) at 1 atm and 273 K can still be achieved. We believe that further extension of this synthetic method using extraframework guest species to tune the pore space for gas storage holds great promise for the development of porous materials for applications such as fuel storage, gas purification, and separation.

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Supporting Information Available: Experimental details, TGA and powder X-ray diffraction data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Typical synthesis of $(choline)_3[In_3(btc)_4]\cdot 2DMF$ (**1**): 1,3,5-Benzenetricarboxlic acid (H_3btc, 0.1259 g, 0.6 mmol), choline chloride (0.1170 g, 1 mmol), and $In(NO_3)_3\cdot xH_2O$ (0.1278 g, 0.4 mmol) in DMF solvent (6.0063 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 4 days, cooled to room temperature, and then washed with ethanol; this afforded colorless crystals in ~90% yield based on In. Anal. Calcd for $C_{54}H_{62}In_3N_5O_{29}$: C, 40.80; N, 4.41; H, 3.93. Found: C, 40.52; N, 4.61; H, 4.12. Typical synthesis of $(Et_4N)_3[In_3(btc)_4]\cdot DEF$ (**4**): H_3btc (0.072 g, 0.33 mmol), Et_4NBr (0.0623 g, 0.21 mmol), and $In(NO_3)_3\cdot xH_2O$ (0.0707 g, 0.25 mmol) in DEF solvent (2.5342 g) were placed in a 20 mL vial. The sample was heated at 120 °C for 4 days, cooled to room temperature, and then washed with ethanol; this afforded colorless crystals in ~95% yield (0.129 g, 0.23 mmol) based on In. Anal. Calcd for $C_{65}H_{83}In_3N_4O_{24}$: C, 47.35; N, 3.40; H, 5.07. Found: C, 47.50; N, 3.28; H, 5.36.

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