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COMMUNICATION

A mixed ligand route for the construction of tetrahedrally coordinated porous lithium frameworks†

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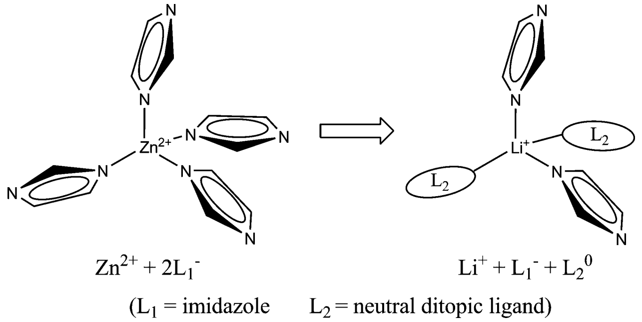
Reported here are two 4-connected 3D frameworks based on monomeric lithium nodes, which are synthesized through a mixed ligand route. By combining a negatively charged imidazole ligand and a neutral bis(imidazolyl)methane ligand (or one of its derivatives), neutral frameworks adopting chiral quartz-dual and diamond topologies have been obtained. These materials have low framework density and can reversibly adsorb hydrogen gas.

The synthesis of crystalline porous frameworks has long been of great interest because of their many possible applications.[1–5] Materials based on imidazolates, such as zeolitic imidazolate frameworks (ZIFs) which are a family of 3D porous crystalline materials, have caught the attention of many researchers in recent years.[6–11] Typically, ZIFs are simply built by using divalent metal cations (such as Zn^{2+}, Co^{2+}, or Cd^{2+}) with imidazolate bridges. In these materials, all the cations are tetrahedrally coordinated and the final 3D frameworks are neutral. The topology can be controlled by applying different substitution groups on the imidazolate module. In this way, about ten zeolitic topologies have been obtained and their gas sorption studies have showed some exciting results.

Introducing lightweight elements into the construction of metal–organic frameworks is one strategy to enhance the gas sorption properties by directly reducing the framework density.[12–18] Recently, a method based on the mixed tetrahedral nodes has been developed by utilizing tetrahedrally coordinated B^{3+} and Li^+.[18] Since the total charge of B^{3+} and Li^+ equals that of two Zn^{2+} ions, the resulting frameworks (known as boron imidazolate framework or BIF) are still neutral. These BIFs exhibit similar zeolitic topologies as ZIFs, however, the framework boron and lithium ions are much lighter than zinc.

The short B–N bond (≈1.5 Å) in BIFs, however, leads to a closer contact and stronger steric repulsion between imidazolate bridges, making it challenging to tune the framework topology by introducing imidazolates with various substituent groups (*e.g.*, benzimidazole). In this work, we aim to develop imidazolate frameworks with only 4-connected lithium nodes (Li–N bond ≈ 2.0 Å). However, we noticed that the total charge of the resulting 4-connected framework will become negative if B^{3+}/Li^+ is replaced with Li^+/Li^+ and no change is made on the imidazolate ligands.

Thus, we have developed the mixed ligand route to balance the charge of the framework (Scheme 1). By replacing half of the negatively charged imidazolate ligands with neutral ligands, the resulting 3D framework will be neutral. To execute this strategy, any neutral ditopic ligands can be examined. However, we are particularly interested in neutral ligands whose coordination geometry and bonding features closely mimic the imidazolate in a way similar to those in ZIFs and BIFs. In this work, we used a bis(imidazolyl)methane type ligand which contains an imidazole-like ring on each side, but is neutral in charge.



Scheme 1 Schematic illustration of the mixed valent ligand strategy to build a tetrahedrally coordinated lithium framework.

Here, we report the synthesis and structures of two 3D networks in LiL_1L_2 type (L_1 is a negatively charged imidazole type ligand and L_2 is a neutral bis(imidazolyl)methane type ligand) denoted as MVLIF-1 and MVLIF-2 with formula $Li(bim)[CH_2(im)_2]$ and $Li(im)[CH_2(mim)_2]$, respectively (MVLIF = Mixed Valent ligand Lithium Imidazolate Framework). In contrast to the inability to prepare 3D BIFs from benzimidazole, the 3D framework of benzimidazole-containing MVLIF-1 demonstrates the effect of the longer Li–N distance (as compared to the B–N distance).

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Bis(imidazolyl)methane ligands were synthesized through a liquid–liquid phase transfer reaction according to the literature report with minor modifications (Scheme S1, ESI†). In brief, a mixture of sodium hydroxide, tetraethyl-ammonium bromide (TEAB), and imidazole in a mixed solvent of methylene chloride and water was reacted under reflux conditions. After about 24 h, the final white powder product was obtained by extraction of the reaction mixture with methylene chloride, followed by rotating evaporation. To examine the structure-directing role of substitution groups on the ligands, the bis(2-methyl-imidazolyl)methane was also synthesized by the similar method. The identity and the purity of the products were confirmed by ^{1}H NMR spectroscopy (Fig. S1, ESI†).

The typical synthesis of the LiL_1L_2 compounds was performed by solvothermal reactions of excess Li_2S and equal molar amount of both types of ligands (HIm type and $CH_2(Im)_2$ type) in acetonitrile. Keeping the reaction mixture at 120 °C for 48 h leads to the formation of high quality colorless crystals for single-crystal X-ray diffraction measurement. The purity of the compounds was confirmed by the powder XRD patterns (Fig. S5 and S6, ESI†). In fact, the synthesis of such lithium compounds has proven to be challenging, mainly in two aspects: (1) the choice of the solvent and (2) the choice of the lithium source. As is well known, lithium has a strong affinity with oxygen-containing species. However, there are only Li–N bonds in our target structures, whose affinity is weaker than that between lithium and oxygen. Thus we chose acetonitrile as the solvent to eliminate the strong solvation effect that is likely with oxygen-containing solvents such as amides, alcohols, or water. Similarly, we used Li_2S as the metal source to exclude the possible affect from oxygen-containing anions. In addition, it is essential to maintain the basic environment by using excess Li_2S to fully deprotonate the imidazole ligand during the synthesis. Other salts such as $LiNO_3$ have been found to be ineffective.

The crystal structures of both compounds have been solved by single-crystal X-ray crystallography (Table S1, ESI†). In both compounds, lithium sites are tetrahedrally coordinated with four N atoms from different imidazole rings (Fig. 1). Specifically, the lithium ion is connected to two negatively charged benzimidazole ligands and two neutral bis(imidazolyl)methane ligands in MVLIF-1, while the lithium ion is connected by two negatively charged imidazole ligands and two neutral bis(2-methyl-imidazolyl)methane ligands in MVLIF-2. Such a bonding mode by mixed charge-complementary ligands follows exactly our original synthetic strategy. However, an obvious difference between the two structures is that, in MVLIF-1, two neutral ligands attached to the same Li site are oriented away from each other, while in MVLIF-2, the two neutral ligands are oriented towards each other (Fig. 1). In addition, unlike the typical case in which the M–N bond between the metal ion and imidazole is located within the imidazole plane, in MVLIF-1, the structure is slightly distorted with one of the Li–N bonds located off the benzimidazole plane.

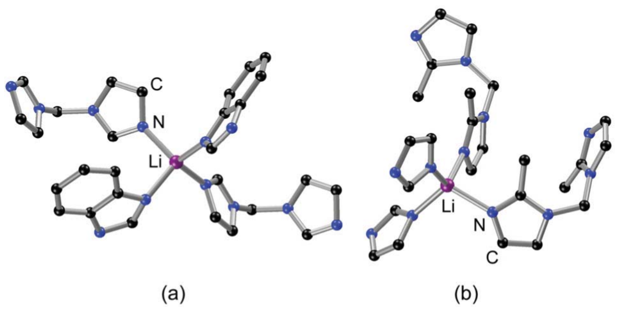

Fig. 1 Coordination environment of Li^+ in (a) MVLIF-1 and (b) MVLIF-2. (purple: Li; blue: N; black: C).

Similar to ZIFs and BIFs, the steric effects of substituent groups exhibit strong structure-directing effects. Through two unique combinations between neutral and charged ligands (bim and $CH_2(im)_2$ in MVLIF-1 *vs.* im and $CH_2(mim)_2$ in MVLIF-2), two totally different chiral frameworks (Fig. S2, ESI†) were obtained. The topological analysis shows that MVLIF-1 adopts the quartz dual (qzd) topology (Fig. 2c), which is an intrinsically chiral net. In

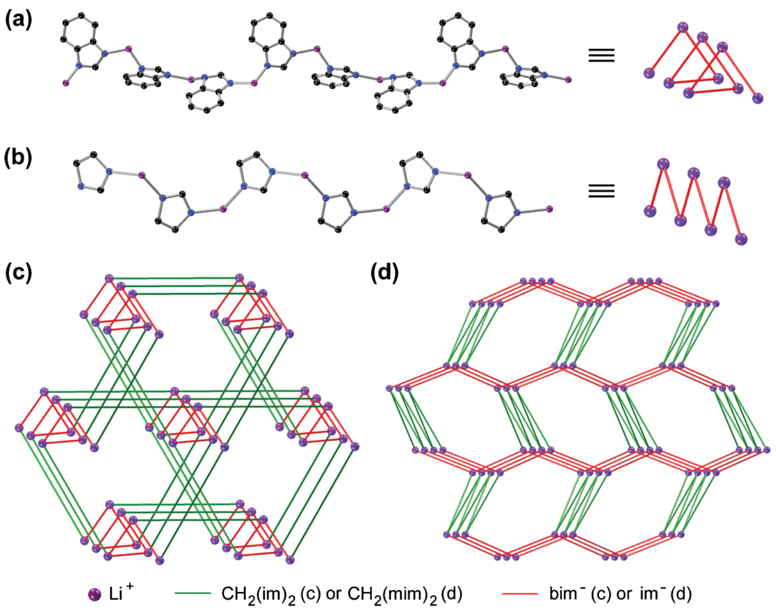

Fig. 2 (a) Segment of Li(bim) helical chain in MVLIF-1, (b) Segment of Li(im) zigzag chain in MVLIF-2, and illustration of framework topologies in MVLIF-1 (c) and MVLIF-2 (d).

comparison, MVLIF-2 adopts the single diamond (dia) topology (Fig. 2d), also with a chiral symmetry. The structure of MVLIF-1 can be understood as parallel helical chains of Li(bim) interconnected by the neutral bis(imidazolyl)methane (Fig. 2a). In MVLIF-2, zig-zag chains of Li(im) are further bridged by the neutral bis(2-methyl-imidazolyl)methane ligand (Fig. 2b) into the 3D framework.

The gas sorption properties of both compounds have also been studied, and both compounds showed the ability to reversibly adsorb hydrogen gas (Fig. 3). The volumetric uptake capacity is 31.4 cm^3 cm^{-3} and 39.4 cm^3 cm^{-3} at 1 atm and 77 K for MVLIF-1 and MVLIF-2, respectively. No significant N_2 adsorption was observed, likely due to the limitation of the pore size. To further enhance the gas sorption properties, the creation of porous materials with larger pore size and greater pore volume would be beneficial. The successful synthesis of MVLIF-1 and MVLIF-2 certainly demonstrates the feasibility for the synthesis of other members of the MVLIF family through the judicious choice of L1 and L2 ligands.

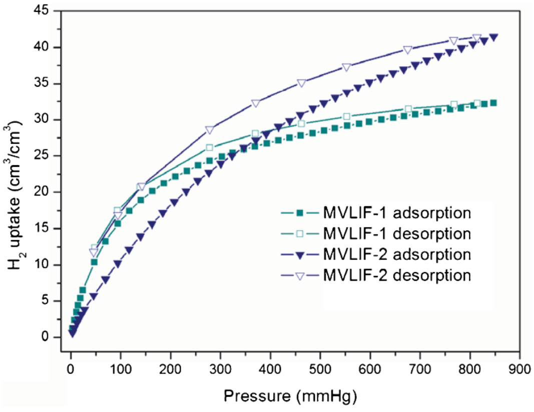

Fig. 3 H_2 uptake of MVLIF-1 and MVLIF-2 at 1 atm and 77 K.

In conclusion, two types of 3D imidazolate frameworks containing uninodal tetrahedrally coordinated lithium ions have been successfully realized by applying a mixed valent ligand synthetic route. The framework densities of MVLIF-1 and MVLIF-2 reach as low as 0.766 g cm^{-3} and 0.778 g cm^{-3}, respectively, which is a direct result of extremely lightweight elements (Li, C and N) used in the synthesis strategy. Both compounds can reversibly adsorb H_2. This work demonstrates a general method for constructing the mixed valent ligand lithium imidazolate frameworks. Further optimization in the ligand design could result in a family of more open architectures that could lead to promising gas sorption properties.

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