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COMMUNICATION

Supramolecular imidazolium frameworks: direct analogues of metal azolate frameworks with a charge-inverted node-and-linker structure

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While azolate anions have been extensively used as anionic linkers in framework design, we now demonstrate the synthesis of square-grid networks that utilise their cationic analogues, imidazolium ions, as linkers. The resulting imidazolium frameworks are direct hydrogen-bonded analogues of square-grid metal azolates and the first examples of an inverted polarity framework design based on anionic nodes and cationic linkers.

The development of designs for the synthesis of network solids is a central area of solid-state chemistry and materials science.^{1,2} Traditionally dominated by inorganic solids³ (silicates, zeolites), this area is now expanded by coordination polymers⁴ (including metal-organic frameworks),⁵ and covalent organic frameworks.⁶ Such development is attributable to the systematic application of geometrical analysis to framework synthesis, specifically the *node-and-linker* approach^{4,7} which predicts framework formation based on judicious choice of building blocks with suitable geometry and connectivity. This approach has had less success⁸ for molecular solids due to the flexibility of underlying supramolecular interactions (e.g. hydrogen and halogen bonds), which makes crystal structures of molecular solids highly sensitive to variations in constituent building blocks.^{9,10} Instead, the design of open frameworks in molecular solids relies mostly on the self-assembly of shape-designed molecules or molecular clusters, or the use of strong charge-assisted hydrogen bonds centred on a particular type of organoammonium cation.^{8,11-14}

We now report a reliable node-and-linker design for open, hydrogen-bonded (4,4)-nets. The design uses tetrahedral sulfate or selenate anions as nodes and substituted imidazolium cations as linkers, providing the first examples of reliable framework synthesis involving negatively charged nodes and positive linkers. The resulting self-assembled imidazolium frameworks are direct analogues¹⁵ of square grid metal azolate frameworks (MAFs)¹⁶ but with inverted polarity of nodes and linkers.

Benzimidazolium sulfate was synthesized from benzimidazole (HBim) and H₂SO₄ in acetonitrile.¹⁷ X-ray diffraction on single crystals grown from methanol (MeOH) revealed hydrogen-bonded sheets involving SO₄²⁻ anions as

four-connected nodes and H₂Bim⁺ cations as 1,3-connected linkers.[†] The result is an open, non-interpenetrated net of (4,4)-topology (also: square grid, **sql**-topology) in which each node is shared

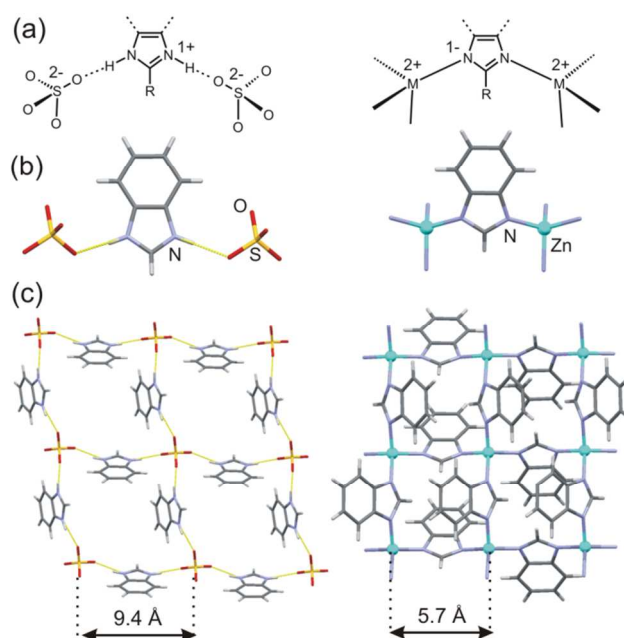


Figure 1. Comparison of the crystal structures of the supramolecular imidazolium framework (H₂Bim)₂SO₄ (left) and the MAF **sql**-Zn(Bim)₂ (CCDC KOLYAM) (right): (a) schematic and (b) capped stick representation of the arrangement of nodes and linkers; (c) a single sheet of (4,4)-topology.

between four 4-rings. Linker protonation was confirmed by solid-state ¹⁵N CP-MAS NMR, and powder X-ray diffraction (PXRD) was used to confirm that bulk material was identical to the single crystals (see ESI).[‡] The net in (H₂Bim)₂SO₄ resembles that found in **sql**-zinc benzimidazolate (Zn(Bim)₂, CCDC KOLYAM) and nickel(II)imidazolate (CCDC ALIDUU). The direct analogy between Zn(Bim)₂ and (H₂Bim)₂SO₄ structures is summarised by factors of geometry

and stoichiometry: (i) structural similarity of SO_4^{2-} to the tetrahedrally coordinated Zn^{2+} ; (ii) geometrical similarity of imidazolite anions and imidazolium cations as linkers and (iii) 1:2 stoichiometry of nodes and linkers. In this analogy the $\text{Zn}\cdots\text{N}$ bonds of $\text{Zn}(\text{Bim})_2$ are replaced by $\text{N}\cdots\text{H}^+\cdots\text{O}^-$ hydrogen bonds in $(\text{H}_2\text{Bim})_2\text{SO}_4$, resulting in a grid spacing of ~ 1 nm. Each 4-ring creates a ca. 20 \AA^3 void, too small to accommodate guests, as confirmed by thermogravimetric analysis (TGA) and nitrogen sorption measurements (see ESI).

Description of $(\text{H}_2\text{Bim})_2\text{SO}_4$ as a (4,4)-net of anionic nodes and cationic linkers led us to explore the robustness of this framework to linker modifications. Attempts to use 2-H or 2-methylimidazole as linkers gave hydrates or crystals too deliquescent for handling. However, 2-ethylimidazole (**HEtim**, Figure 2a) gave crystals that, although deliquescent, were suitable for structure determination by X-ray diffraction.[†] Structure of $(\text{H}_2\text{Etim})_2\text{SO}_4$ consists of layers with distorted square grid topology, confirming the ability of imidazolium cations to assemble with SO_4^{2-} into a (4,4)-net (Figure 2b). Distortion of the square grid can be quantified by ϕ , the acute angle formed by three nearest-neighbour anions in a sheet. While an ideal square grid would have $\phi=90^\circ$, in $(\text{H}_2\text{Etim})_2\text{SO}_4$ this value is 62° (Figure 2b). The sheets of $(\text{H}_2\text{Etim})_2\text{SO}_4$ exhibit voids of ca. 6 \AA diameter, occupied by ethyl residues from neighbouring sheets (see ESI). Tolerance of the benzimidazolium sulfate (4,4)-net to substitution was explored by using 2-phenylbenzimidazole (**HPhBim**) and 2-methylbenzimidazole (**HMeBim**) as linkers (Figure 2a).[†] Crystallisation of $(\text{H}_2\text{PhBim})_2\text{SO}_4$ from either MeOH or ethanol (EtOH) gave isostructural solvates in which cations and anions assembled into a (4,4)-net, with solvent attached to each sheet by $\text{O}\cdots\text{H}\cdots\text{O}$ bonds (Figure 2c,d).[‡] These solvates show that the assembly of square grid imidazolium frameworks tolerates hydrogen bonding to protic solvents. Only with $(\text{H}_2\text{MeBim})_2\text{SO}_4$ was the synthesis of the (4,4)-net unsuccessful: all crystallisation attempts gave the SiS_2 -type structure in which cations and anions retain respective bridging and tetrahedral geometries, but form chains of 2-rings with shared nodes (Figure 2d).^{18,19}

Next, we explored the selenate ions as larger framework nodes with intramolecular $\text{O}\cdots\text{O}$ distance of 2.70 \AA , compared to 2.40 \AA in SO_4^{2-} . The salts were prepared by reacting benzimidazoles with a solution of concentrated aqueous H_2SeO_4 in acetonitrile.[†] Structural analysis[†] of $(\text{H}_2\text{Bim})_2\text{SeO}_4$ revealed square grid sheets similar to those in $(\text{H}_2\text{Bim})_2\text{SO}_4$ (Figure 3a). Both **HPhBim** and **HMeBim** selenate salts also afforded (4,4)-nets. Unlike the corresponding sulfate, $(\text{H}_2\text{PhBim})_2\text{SeO}_4$ could be crystallised in a non-solvated form by using N,N -dimethylformamide as a solvent, yielding a structure based on corrugated sheets of alternating 4-rings with $\phi=45^\circ$ and $\phi=88^\circ$ (Figure 3b).[†] Crystallisation of $(\text{H}_2\text{PhBim})_2\text{SeO}_4$ from MeOH gave a solvate isostructural to that of $(\text{H}_2\text{PhBim})_2\text{SO}_4$,[†] with square grid sheets lined by MeOH molecules.

Crystallisation of $(\text{H}_2\text{MeBim})_2\text{SeO}_4$ from a MeOH/acetone solvent mixture produced square grid layers of H_2MeBim^+ and SeO_4^{2-} , separated by alternating layers of water and MeOH molecules (Figure 3c,d).^{†,‡} The herein described solvates of $(\text{H}_2\text{PhBim})_2\text{SO}_4$, $(\text{H}_2\text{PhBim})_2\text{SeO}_4$ and $(\text{H}_2\text{MeBim})_2\text{SeO}_4$ highlight the robustness of the (4,4)-net to changes in anion size and hydrogen bonding with protic solvents.

In conclusion, we demonstrated the first reliable design for open square-grid frameworks using a charge-inverted node-and-linker design. The structures of the presented salts

demonstrate the unique versatility of imidazoles to generate geometrically similar anionic and cationic framework linkers: the assembly of tetrahedral sulfate or selenate anions with imidazolium linkers yields structures that are direct analogues to MAFs, based on stoichiometry and geometry of nodes and linkers. Although the obtained (4,4)-nets are not microporous, we believe imidazolium frameworks illustrate an attractive new design for open supramolecular frameworks. The generality of this design is

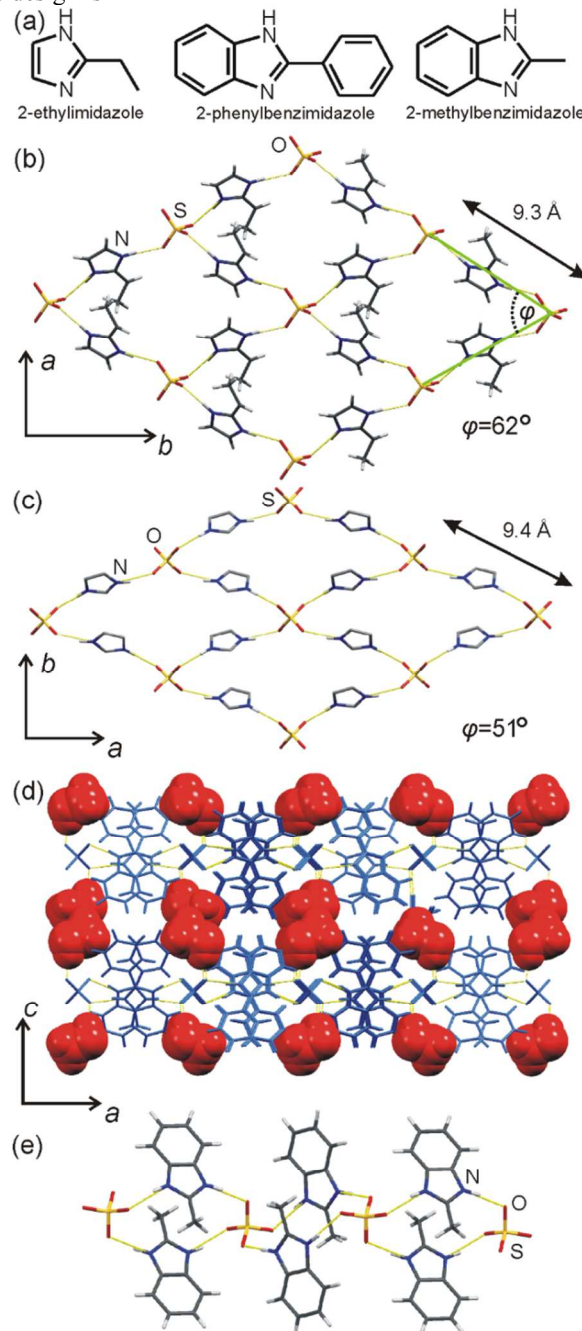


Figure 2. (a) Molecular structures of **HEtim**, **HPhBim** and **HMeBim**; (b) a hydrogen-bonded sheet in $(\text{H}_2\text{Etim})_2\text{SO}_4$; (c) a hydrogen-bonded sheet of $(\text{H}_2\text{PhBim})_2\text{SO}_4$ in the corresponding MeOH solvate, with solvent molecules and phenyl substituents omitted; (d) two hydrogen-bonded sheets of $(\text{H}_2\text{PhBim})_2\text{SO}_4$ (blue) with MeOH molecules shown (red); (e) a SiS_2 -type chain in $(\text{H}_2\text{MeBim})_2\text{SO}_4$.

reflected in its robustness to variations in nodes and linkers components, as well as to competitive hydrogen bonding with protic solvents. While $(\text{H}_2\text{MeBim})_2\text{SeO}_4$ did not form a (4,4)-net, the cations and anions retained their binding geometries to form a SiS_2 -type structure, suggesting that further exploration might reveal other charge-inverted analogues to MAFs or silica-like materials. With that in mind, we are now exploring imidazolium salts of other anions.

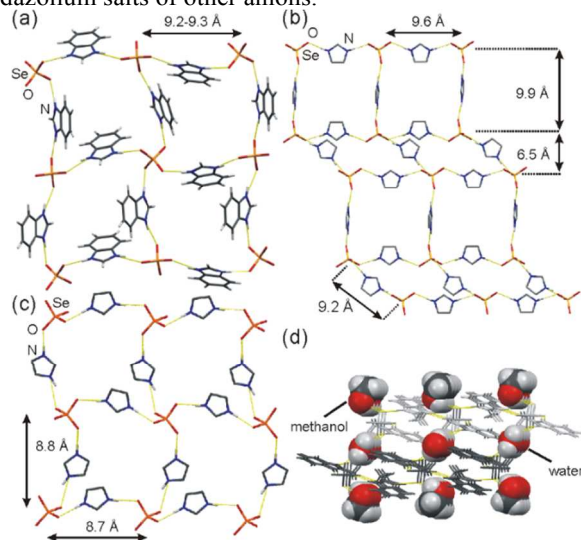


Figure 3. (a) The (4,4)-topology sheet in $(\text{H}_2\text{Bim})_2\text{SeO}_4$; (b) corrugated sheet of (4,4-topology in non-solvated $(\text{H}_2\text{PhBim})_2\text{SeO}_4$; (c) (4,4)-net in the MeOH and water solvate of $(\text{H}_2\text{MeBim})_2\text{SeO}_4$ with phenyl substituents omitted for clarity; (d) sheets of $(\text{H}_2\text{MeBim})_2\text{SeO}_4$ intercalated by layers of MeOH and water (space-filling).

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Notes and references

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†Crystallographic data: $(\text{H}_2\text{Bim})_2\text{SeO}_4$, CCDC 1050268, orthorhombic $Fdd2$, $a=14.6766(8)$ Å, $b=18.8388(14)$ Å, $c=11.8862(7)$ Å, $V=3286.4(4)$ Å³, $Z=8$, $R_1=0.0308$, $wR_2=0.0819$ ($I>2\sigma_1$), $S=1.069$; $(\text{H}_2\text{EtBim})_2\text{SeO}_4$, CCDC 1050267, monoclinic $C2/c$, $a=9.642(11)$ Å, $b=15.986(17)$ Å, $c=9.334(10)$ Å, $\beta=92.708(12)^\circ$, $V=1437.11(6)$ Å³, $Z=4$, $R_1=0.0472$, $wR_2=0.1378$ ($I>2\sigma_1$), $S=1.081$; $(\text{H}_2\text{PhBim})_2\text{SeO}_4 \cdot 2\text{MeOH}$, CCDC 1050271, orthorhombic $Pbcn$, $a=16.933(4)$ Å, $b=8.0337(18)$ Å, $c=19.688(4)$ Å, $V=2678.25(10)$ Å³, $Z=4$, $R_1=0.0650$, $wR_2=0.1590$ ($I>2\sigma_1$), $S=1.045$; $(\text{H}_2\text{PhBim})_2\text{SeO}_4 \cdot \text{EtOH}$, CCDC 1050270, orthorhombic $Pbcn$, $a=16.620(4)$ Å, $b=8.218(2)$ Å, $c=19.159(5)$ Å, $V=2616.8(11)$ Å³, $Z=4$, $R_1=0.1023$, $wR_2=0.1497$ ($I>2\sigma_1$), $S=1.095$; $(\text{H}_2\text{MeBim})_2\text{SeO}_4$, CCDC 1050269, monoclinic $C2/c$, $a=17.398(3)$ Å, $b=7.4436(11)$ Å, $c=14.051(2)$ Å, $\beta=105.3800(10)^\circ$, $V=1754.5(4)$ Å³, $Z=4$, $R_1=0.0411$, $wR_2=0.1338$ ($I>2\sigma_1$), $S=1.069$; $(\text{H}_2\text{Bim})_2\text{SeO}_4$, CCDC 1050272, tetragonal $P4_32_1$, $a=18.5107(19)$ Å, $c=18.953(2)$ Å, $V=6494.2(12)$ Å³, $Z=16$, $R_1=0.0290$, $wR_2=0.0605$ ($I>2\sigma_1$), $S=1.034$; $(\text{H}_2\text{PhBim})_2\text{SeO}_4$, CCDC 1050274, triclinic $P\bar{1}$, $a=9.611(4)$ Å, $b=10.852(4)$ Å, $c=11.918(5)$ Å, $\alpha=83.339(6)^\circ$, $\beta=72.175(5)^\circ$, $\gamma=88.808(5)^\circ$, $V=1175.2(8)$ Å³, $Z=2$, $R_1=0.0631$, $wR_2=0.1337$ ($I>2\sigma_1$), $S=1.003$; $(\text{H}_2\text{PhBim})_2\text{SeO}_4 \cdot 2\text{MeOH}$, CCDC 1050275, orthorhombic $Pbcn$, $a=17.3442(12)$ Å, $b=8.0712(6)$ Å, $c=19.5768(14)$ Å, $V=2740.5(3)$ Å³, $Z=4$, $R_1=0.0376$, $wR_2=0.0772$ ($I>2\sigma_1$), $S=1.043$; $(\text{H}_2\text{MeBim})_2\text{SeO}_4 \cdot \text{MeOH} \cdot \text{H}_2\text{O}$, CCDC 1050273, monoclinic

$C2/c$, $a=25.917(2)$ Å, $b=8.7717(7)$ Å, $c=17.5915(14)$ Å, $\beta=100.377(1)^\circ$, $V=3933.8(5)$ Å³, $Z=8$, $R_1=0.0387$, $wR_2=0.0850$ ($I>2\sigma_1$), $S=1.046$.

‡Bulk analysis of solvates by PXRD or TGA was prevented by rapid and visible deterioration of crystals once outside of solution. Consequently, we determined the unit cell parameters for ten crystals from each batch as a means to confirm phase purity (see ESI).

¶ Heat should be avoided in the preparation and recrystallisation of selenate salts, due to easy reduction of selenate anions, see ESI.

Electronic Supplementary Information (ESI) available: crystallographic data in CIF format, selected PXRD, infrared and solid-state NMR spectroscopy, and TGA data. See DOI: 10.1039/c000000x/

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