

Molecular building blocks approach to the assembly of zeolite-like metal–organic frameworks (ZMOFs) with extra-large cavities

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Two novel porous anionic zeolite-like metal–organic frameworks, *rho*-ZMOF and *sod*-ZMOF, have been synthesized by metal-ligand-directed assembly of rigid and directional tetrahedral building units, InN_4 synthesized *in situ*, and doubly deprotonated bis(bidentate) imidazolecarboxylic acid ligands (HImDC) in the presence of different structure directing agents (SDAs).

Zeolites, purely inorganic microporous crystalline solids constructed from tetrahedral building units sharing corners, are an important class of solid-state materials and are of major economic significance owing to the homogeneously sized and shaped openings and voids.¹ These confined spaces permit their conventional use *par excellence* as shape- and size-selective catalysts, ion exchangers and adsorbents. These properties are closely related to the framework's structural features such as the size of the pore openings and cavities. Difficulties in altering the zeolite i) structural features in order to enclose extra-large cavities beyond the 1 nm prison² and/or ii) composition to contain a periodic array of intra-framework organic functionality³ have thus far restricted their application to small molecules. Rational construction of tetrahedrally connected porous materials, related in their topological properties to zeolites, with extra-large cavities and periodic intra-framework organic functionality, is an ongoing synthetic challenge, and it is of exceptional scientific and technological interest, offering great potential for innovative applications pertaining to large molecules, nanotechnology, optics, sensor-technology, medicine, *etc.*⁴

Decoration and/or expansion of tetrahedrally connected open networks, zeolite-like nets, using the molecular building blocks (MBBs) approach provides the material designer with a prospective method to systematically construct functionalized porous materials with tunable and enlarged cavities by substituting the tetrahedral vertices with larger supertetrahedra,⁵ decorating the net, and/or expanding the edges with a longer linker.

The latter, less-explored strategy toward expanded zeolite-like networks, but the one that we consider here, is based on replacing the oxygen (O^{2-}) that bridges the tetrahedral building units (TBUs) with a longer ditopic organic linker. This process, called edge expansion, offers great potential toward the design and synthesis of very open zeolite-like metal–organic frameworks

(ZMOFs), and its successful implementation will permit the introduction of a periodic array of tunable organic functionalities in the to-be-generated extra-large cavities.

Metal-ligand-directed assembly, using the MBBs approach, has permitted the logical design and synthesis of MOFs based mainly on the expansion and decoration of typical dense nets.⁶ Accordingly, MOFs based on the decoration and/or expansion of the cubic diamond topology are extensively predominant for the assembly of simple TBUs.⁷ Therefore, non-default structures for the assembly of TBUs, such as zeolites, can be targeted by judicious selection of the appropriately shaped rigid MBBs and linkers. Readily accessible, rigid and directional TBUs can be formed by means of our recently introduced approach founded on the utilization of single-metal-ion-based MBBs where each hetero-coordinated single metal ion, formed *in situ*, is rendered rigid and directional using ligands that permit the completion of the metal ion coordination sphere *via* a hetero-chelating functionality.⁸

To make very open ZMOFs using our approach, some conditions should be met: (i) The metal ion coordination sphere should permit the formation of MN_4O_2 or MN_4O_4 MBBs (MN_4 , TBUs) and should have a minimum coordination number of six and maximum of eight. (ii) The linker to be employed, substituting the oxygen atom that originally occupies the edges of zeolite nets, should be rigid and concurrently contain the chelating and bridging functionality. The ligand should include both carboxylate and nitrogen groups as plausible coordinating moieties. The nitrogen groups must be an integral part of an aromatic ring, and the carboxylates must be located in the α -position relative to nitrogen. The nitrogen groups will need to be coordinated to the metal, and thus direct the framework topology, as the carboxylate groups will secure the geometry of the metal by locking it into its position through the formation of rigid five-membered rings *via* N-, O- hetero-chelation. Another important attribute is the ability of the ligand to position the TBUs (MN_4) at an angle comparable to the 145° average T–O–T angle observed in inorganic zeolites.^{9,10} (iii) The synthesis must be performed under mild conditions, permitting the conservation of the structural integrity of the organic components. The constructed framework has to be crystalline to permit complete characterization. Preferably, anionic ZMOFs will be targeted, allowing for the utilization of different SDAs.

Accordingly, we opt to use the ligand 4,5-imidazolecarboxylic acid (H_3ImDC) as the bridging linker and indium, a group 13 element, as the metal ion source. The preferred oxidation state of indium is +3, which permits the formation of high coordination complexes (coordination number between 6 and 8) and the construction of anionic frameworks when saturated with the

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desired ligand. It should also be mentioned that MOFs based on In(III) are rare, adding interest to its use.

Indeed, reactions of H_3ImDC and $\text{In}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ in an N,N -dimethylformamide (DMF)/acetonitrile (CH_3CN) solution in the presence of different SDAs have yielded two homogeneous microcrystalline materials (referred to as *rho*-ZMOF and *sod*-ZMOF).[‡] The as-synthesized compounds were characterized and formulated by elemental microanalysis and single-crystal X-ray diffraction studies as:§ $\text{In}_{48}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)_{96}(\text{C}_7\text{N}_3\text{H}_{15})_{24}(\text{DMF})_{36}(\text{H}_2\text{O})_{192}$ (*rho*-ZMOF, HPP) and $\text{In}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)_2(\text{C}_3\text{N}_2\text{H}_5)(\text{DMF})_4(\text{CH}_3\text{CN})(\text{H}_2\text{O})_4$ (*sod*-ZMOF, HIm). These ZMOFs were insoluble in water and common organic solvents. The purity of each compound was confirmed by similarities between simulated and experimental X-ray powder diffraction (XRPD).

In the crystal structure of *rho*-ZMOF (Fig. 1), each indium metal ion is coordinated to four nitrogen atoms and four oxygen atoms of four separate HImDC ligands, respectively, to form an eight-coordinated (dodecahedron geometry) MBB, $\text{InN}_4(\text{CO}_2)_4$, (Fig. 1a), which can be regarded as a TBU, InN_4 (Fig. 1b). Each independent HImDC is coordinated to two In(III) metals by forming two rigid five-membered rings *via* N-, O- hetero-chelation, where the In–N bonds direct the topology. The assembly of the 4-connected nodes results in the generation of truncated cuboctahedra (containing 48 In ions) which link together through double-eight-membered rings (D8R) to form a metal–organic framework with a zeolite *rho* topology (Fig. 1d).^{9,11} *rho*-ZMOF represents the first example of a 4-connected metal–organic framework based on the zeolite *rho* topology. The *rho*-ZMOF structure consists of a body centered cubic arrangement of truncated cuboctahedra (α -cages) linked *via* D8R which exist only in *rho*, merlinoite, paulingite, tschörtnerite and UCSB-8.⁹ Edge expansion of the *rho*-zeolite net (organic linker instead of oxygen) has generated a very open structure with extra-large cavities; a sphere of 18.2 Å in diameter can fit inside each cavity.

The *rho*-ZMOF unit cell contains 48 indium metal ions and 96 ligands to give an overall framework formula of $[\text{In}_{48}(\text{HImDC})_{96}]^{48-}$, where the negatively charged framework is neutralized by 24 doubly protonated HPP molecules. The unit cell volume of the first *rho*-ZMOF is 8 times larger than the

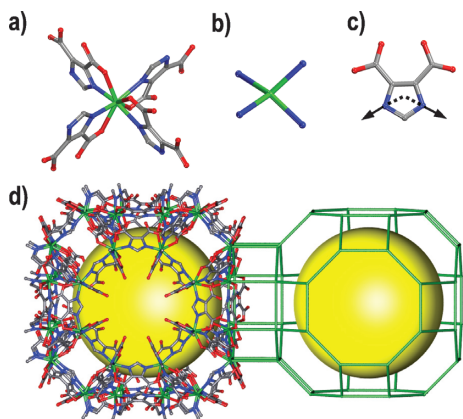


Fig. 1 Single-crystal structure of *rho*-ZMOF composed of (a) eight-coordinated MBBs which can be viewed as (b) 4-connected TBUs, (c) the angle in the HImDC ligand. (d) A fragment of the *rho*-ZMOF, where the yellow spheres represent the largest sphere that would fit in the α -cavities without touching the van der Waals atoms of the framework.

alumino-silicate analogue, since the unit cell edge is doubled (3.10 nm vs. 1.51 nm).

In the as-synthesized *rho*-ZMOF material, the negatively charged cavities, α -cages and D8R, are occupied by at least 36 DMF, 24 doubly protonated HPP and 192 water guests per unit cell. The space occupied by guest molecules alone represents 56% of the cell volume or $16,718 \text{ \AA}^3$ per unit cell.

In the crystal structure of *sod*-ZMOF (Fig. 2), each indium metal ion is coordinated to four nitrogen atoms and two oxygen atoms of four individual HImDC ligands, respectively, to form a six-coordinated MBB, $\text{InN}_4(\text{CO}_2)_2$, which can be regarded as a TBU, InN_4 . The structure of *sod*-ZMOF is anionic and it is based on the expansion of the sodalite net. To the best of our knowledge, only a few metal–organic frameworks with the sodalite topology have been reported, all of which possess neutral or cationic frameworks.⁷ The *sod*-ZMOF represents the first example of a MOF with an anionic framework based on the sodalite topology.

Comparable to the conventional inorganic zeolites, our ZMOFs are anionic and exhibit facile ionic exchange capacity. Ion exchange studies indicate that the organic cations in the cavities can be fully exchanged at room temperature after 24 hours, as proven by elemental microanalysis and atomic absorption studies. The exchanged compounds retain their morphology and crystallinity, as proven by optical microscopy and the preservation of their XRPD patterns. Unlike inorganic *rho* zeolite and other *rho* analogues, framework compositions of aluminosilicate or aluminophosphate, *rho*-ZMOF requires twice as many positive charges, 48 vs. 24, to neutralize the anionic framework. For Na^+ -exchanged *rho*-ZMOF, formulated as $[\text{Na}^+_{48}(\text{H}_2\text{O})_{282}[\text{In}_{48}(\text{C}_5\text{N}_2\text{O}_4\text{H}_2)_{96}]]$, the concentration of charge carriers is higher than a typical *rho* zeolite (*i.e.*: $[(\text{Na}^+, \text{Cs}^+)_{12}(\text{H}_2\text{O})_{44}[\text{Al}_{12}\text{Si}_{36}\text{O}_{96}]]\text{-RHO}$). The elevated concentration of charge carriers present in *rho*-ZMOF could augment the ionic conductivity.

The thermogravimetric analysis for the Na^+ -exchanged *rho*-ZMOF showed that all residential water guest molecules can be completely evacuated around $105 \text{ }^\circ\text{C}$ (calcd. 26.9%). The N_2 adsorption/desorption study for *rho*-ZMOF revealed a reversible type I isotherm, characteristic of microporous materials (Fig. 3). The isotherm shows no hysteresis on desorption of gas from the pores. The apparent Langmuir surface area is estimated to be $1067 \text{ m}^2/\text{g}$.

The anionic character and the large accessible voids of *rho*-ZMOF have allowed the full exchange of HPP cations with various organic and inorganic cations. This ability has led us to investigate the encapsulation of cationic probes (*i.e.* acridine chromophores, *etc.*) to sense neutral molecules. Acridine orange

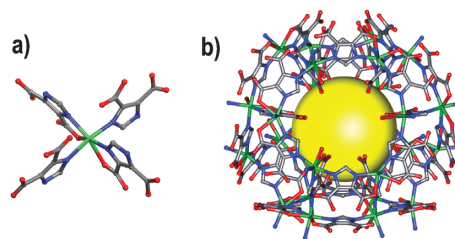


Fig. 2 Single-crystal structure of *sod*-ZMOF composed of (a) six-coordinated MBBs which can be regarded as TBUs, InN_4 , and (b) a fragment of the *sod*-ZMOF, the β -cage.

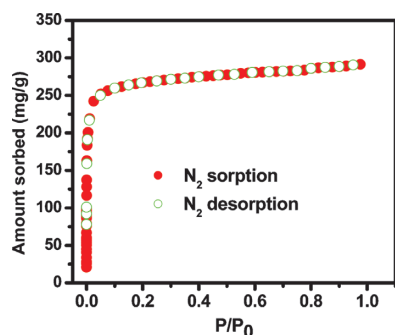


Fig. 3 Nitrogen sorption isotherm for Na⁺ rho-ZMOF at 78 K.

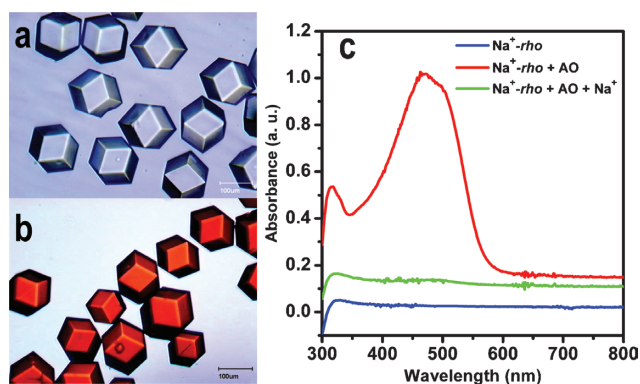


Fig. 4 Optical images obtained on an Olympus MIC-D optical microscope: (a) as-synthesized rho-ZMOF crystals, (b) rho-ZMOF crystals after AO exchange and (c) solid-state UV-vis spectra of rho-ZMOFs.

(AO, *N,N,N',N'*-tetramethyl-3,6-acridinediamine) is smaller than the window dimensions of the rho-ZMOF (0.9 nm), consequently these molecules may freely diffuse into the larger cavities. Electrostatic interactions between the cationic AO and the negatively charged cavities of the rho-ZMOF preclude further diffusion of AO out of the cavities once encapsulated (anchored). Incubation of rho-ZMOF in an ethanolic solution of AO results in a red material with absorption and emission spectra similar to AO contained in n-heptane–sodium 1,4-bis(2-ethylhexyl)sulfosuccinate (AOT)–water reverse micelles, (Fig. 4).¹²

The extra-large cavities of rho-ZMOF can accommodate neutral molecules in addition to the cationic guest molecules that can only be exchanged with other cations. These features permit the exploration of this system to sense neutral molecules upon exchange with a cationic probe. Incubation of the AO–rho-ZMOF with solutions containing methyl xanthenes or DNA nucleoside bases results in a change in both steady state emission and lifetime of the encapsulated AO that is dependent upon the nature of the second guest. These preliminary results demonstrate the ability of the ZMOF to serve as a (host–guest)–guest sensor where the ZMOF offers a periodic nanospace for fluorescent cations, which can then serve as the sensor unit.

Here we have reported a novel strategy to construct ZMOFs with extra-large cavities and a periodic array of intra-framework organic functionality. Work is in progress i) to explore the unique sorption, inclusion and catalytic properties of ZMOFs and ii) to construct novel ZMOFs by employing different SDAs and/or similar ligands.

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Notes and references

‡ *Synthesis of rho-ZMOF*: 4,5-Imidazolecarboxylic acid (0.014 g, 0.087 mmol), In(NO₃)₃·2H₂O (0.015 g, 0.0435 mmol), DMF (1 mL), CH₃CN (1 mL), 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (HPP) (0.2 mL, 0.42 M in DMF), and HNO₃ (0.125 mL, 3.5 M in DMF) were added respectively to a 20-mL vial, which was sealed and heated to 85 °C for 12 h and 100 °C for 14 h, then cooled to room temperature. The colorless polyhedral crystals were collected and air-dried, yielding 0.0175 g (64% based on In(NO₃)₃·2H₂O). CHN elemental analysis (%) for rho-ZMOF, In₄₈(C₅N₂O₄H₂)₉₆(C₇N₃H₁₅)₂₄(DMF)₃₆(H₂O)₁₉₂. Calcd. C, 30.49; H, 4.02; N, 14.11. Found C, 29.82; H, 4.08; N, 14.06. FT-IR (4000–600 cm⁻¹): 3416(br), 1657(w), 1571(m), 1474(s), 1400(m), 1323(w), 1302(w), 1252(m), 1108(s), 1015(w), 980(w), 836(m), 781(s).

Na⁺-exchanged rho-ZMOF: In₄₈(C₅N₂O₄H₂)₉₆Na₄₈(C₂H₅OH)₉₆(H₂O)₁₉₂. Calcd. C, 27.56; H, 3.96; N, 9.18. Found C, 27.36; H, 3.65; N, 9.14.

Atomic absorption result: Calcd. Na, 3.77%. Found Na, 3.9%.

Synthesis of sod-ZMOF: 4,5-Imidazolecarboxylic acid (0.021 g, 0.1305 mmol), In(NO₃)₃·2H₂O (0.015 g, 0.0435 mmol), DMF (1.5 mL), CH₃CN (0.5 mL), imidazole (0.2 mL, 1.5 M in DMF), and HNO₃ (0.3 mL, 3.5 M in DMF) were added respectively to a 20-mL vial, which was sealed and heated to 85 °C for 12 h and 105 °C for 23 h. The colorless polyhedral crystals were collected and air-dried, yielding 0.021 g (54% based on In(NO₃)₃·2H₂O). CHN elemental analysis (%) for sod-ZMOF, In(C₅N₂O₄H₂)₂(C₃N₂H₅)(DMF)₄(CH₃CN)(H₂O)₄. Calcd. C, 36.13; H, 5.39; N, 17.17. Found C, 37.07; H, 4.92; N, 17.18.

§ *Crystal data for rho-ZMOF*. C₁₀H₄InN₄O₄: Cubic, *Im-3m*, *a* = 31.0622(7) Å, *V* = 29970.7(12) Å³, *Z* = 48, Final *R* = 0.0590, *wR*₂ = 0.1512 (for 878 unique reflections assumed as observed with *I* > 2σ(*I*)).

Crystal data for sod-ZMOF. C₁₀H₄InN₄O₈: Cubic, *Fd-3c*, *a* = 36.0435(11) Å, *V* = 46825(2) Å³, *Z* = 96, Final *R* = 0.0872, *wR*₂ = 0.2334 (for 1174 unique reflections assumed as observed with *I* > 2σ(*I*)).

CCDC Reference number for rho-ZMOF is 294663 and that for sod-ZMOF is 294664. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600188m

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