

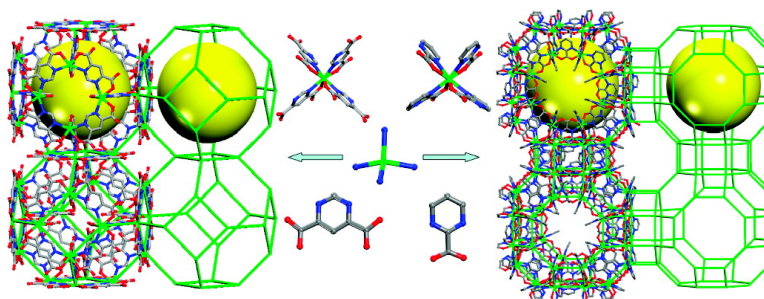
Communication

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Quest for Zeolite-like Metal–Organic Frameworks: On Pyrimidinecarboxylate Bis-Chelating Bridging Ligands

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In the ongoing quest for the design of functional materials, metal–organic materials (MOMs, e.g., metal–organic polyhedra, metal–organic frameworks (MOFs), or coordination polymers) have been identified as potential platforms for myriad applications: gas storage, ion exchange, encapsulation/sequestration/sensing of target molecules, catalysis, magnetism, nonlinear optics, etc.¹ The deliberate construction of porous periodic solids² can address pertinent scientific and societal needs via particular integrated functions and is of great interest across disciplines. Our group, among others, has successfully implemented rational design strategies for the synthesis of functional materials from single-metal-ion-based molecular building blocks (MBBs) where the desired functionality and directionality are embedded prior to the assembly process.³ We have utilized heterofunctional organic ligands that are rigid and directional, which allow the formation of rigid five-membered rings of chelation through N-,O- heterocoordination to a single metal ion, to facilitate the synthesis of intended MOMs. Accordingly, the judicious selection of organic linkers (e.g., imidazolecarboxylates) has allowed for the saturation of single metal ions to generate MBBs (MN₄O₂, MN₄O₄) regarded as rigid and directional tetrahedral building units (TBUs, MN₄) necessary for the construction of zeolite-like metal–organic frameworks (ZMOFs).^{1b,4}

ZMOFs represent a unique subset of MOFs that are topologically related to the purely inorganic zeolites and exhibit similar properties: (1) forbidden self-interpenetration which allows for the design of readily accessible extra large cavities; (2) chemical stability, where the structural integrity is maintained in water (not common in MOFs), permits potential ZMOF applications for heterogeneous catalysis, separations, and sensors, especially in aqueous media; (3) ion exchange capability permits (a) the ability to control and tune extraframework cations toward specific applications such as catalysis or gas storage and (b) the removal/sequestration of toxic metal ions. In addition, ZMOFs are constructed using metal–ligand directed assembly and encompass periodic arrays of organic functionality, allowing for the tunability of both inorganic and organic components, features that permit facile alteration of pore size and/or organic functionality and hence the expansion of zeolite applications to large molecules.^{1b} MOFs having zeolite-like topologies are atypical as a direct consequence of the intricate systematic design strategies necessary for their deliberate construction. That is, zeolite topologies are not the default structure for the assembly of simple TBUs (i.e., not rigid nor directional), which, in combination with flexible ditopic organic linkers, has consistently lead to MOFs having the default cubic diamond topology.⁵ Therefore, building information into the MBB is vital, and it is of broader interest to use the MBB approach based on rigid and directional single-metal-ion TBUs as a solid platform and basis for developing

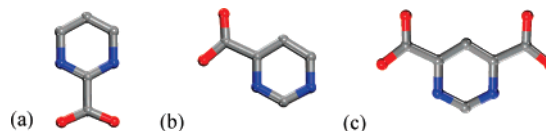


Figure 1. (a) 2-pyrimidinecarboxylate (2-PmC), (b) 4-pyrimidinecarboxylate (4-PmC), and (c) 4,6-pyrimidinedicarboxylate (4,6-PmDC).

new design strategies to construct and functionalize novel ZMOFs for specific applications.

Herein we present the utility of this strategy to synthesize novel ZMOFs by targeting rigid and directional TBUs built from suitable heterofunctional organic linkers, such as pyrimidine derivatives with carboxylate substituents in the 2-, 4-, or 4,6- positions (Figure 1). We report the synthesis of two novel ZMOFs, *sod*-ZMOF^{1b} derived from 4,6-pyrimidinedicarboxylate (4,6-PmDC)^{6a} (**1**), and *rho*-ZMOF^{1b} from 2-pyrimidinecarboxylate (2-PmC)^{6b} (**2**). To the best of our knowledge, this is the first report of a MOF constructed with 4,6-PmDC, even though previous work has been carried out with pyrimidine and some of its derivatives,⁷ including 2-PmC.⁸

Reaction between 4,6-PmDC and In(NO₃)₃·5H₂O in a solution of *N,N*-dimethylformamide (DMF) and water afforded pale yellow homogeneous crystals with polyhedral morphology, referred to as *sod*-ZMOF (**1**).⁹ The as-synthesized compound, stable and insoluble in water and common organic solvents, was characterized and formulated by single-crystal X-ray diffraction studies as [In-(C₆N₂O₄H₂)₂Na_{0.36}K_{1.28}](NO₃)_{0.64}(H₂O)_{2.1}.¹⁰

In the crystal structure of **1** (Figure 2), four bis(bidentate) 4,6-PmDC ligands fully saturate the coordination sphere of each indium metal ion through N- and O-bonds, forming a chelate ring that locks the metal in its position and reinforces the rigidity of the TBU. Hence, each ligand chelates two individual indium ions, forming two five-membered rings coplanar with the pyrimidine ring. The MBB is represented by InN₄(CO₂)₄ (Figure 2a), which translates into a four-connected node regarded as a TBU, InN₄ (Figure 2b). The building units assemble in a fashion that gives rise to the formation of truncated octahedra (β -cages) that are further connected through shared square windows, forming a net with sodalite topology.^{1b,7b,c} The as-synthesized **1**, *sod*-ZMOF, unit cell contains 12 indium metal ions, 24 ligands, 15 potassium cations disordered over 24 positions, 4 sodium cations disordered over 12 positions, 5 nitrate anions disordered over 16 positions, and approximately 25 disordered water molecules. The framework is anionic, where the overall charge is balanced by the K and Na cations. The approximate diameter of the largest sphere that can be fit inside the cage, considering the van der Waals radii of the nearest atoms, is 9.6 Å.

Reaction between 2-cyanopyrimidine (2-PmCN) and Cd(NO₃)₂·4H₂O in a solution of DMF and water yielded colorless polyhedral

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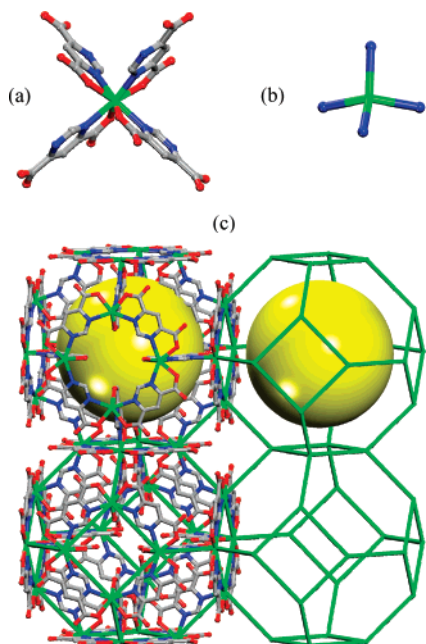


Figure 2. Single-crystal structure of **1** comprised of (a) eight-coordinated $\text{InN}_4(\text{CO}_2)_4$ MBB that can be regarded as (b) an InN_4 TBU and (c) fragment of the *sod*-ZMOF structure. Hydrogen atoms and guest molecules are omitted for clarity; In = green, C = gray, N = blue, O = red. The yellow sphere represents the largest sphere that can be fit inside the cage, considering the van der Waals radii.

crystals with dodecahedron morphology, referred to as *rho*-ZMOF (**2**).¹¹ The as-synthesized compound was characterized and formulated by X-ray crystallography diffraction studies as $\text{Cd}(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2 \cdot (\text{C}_4\text{N}_2\text{H}_{10})_{0.35}(\text{H}_2\text{O})_{5.36}$.¹² In the crystal structure of **2** (Figure 3), four independent bis(bidentate) 2-PmC ligands, generated in situ from 2-PmCN, heterocoordinate through N- and O- to the eight-coordinate cadmium metal ion. As a result, four chelating rings

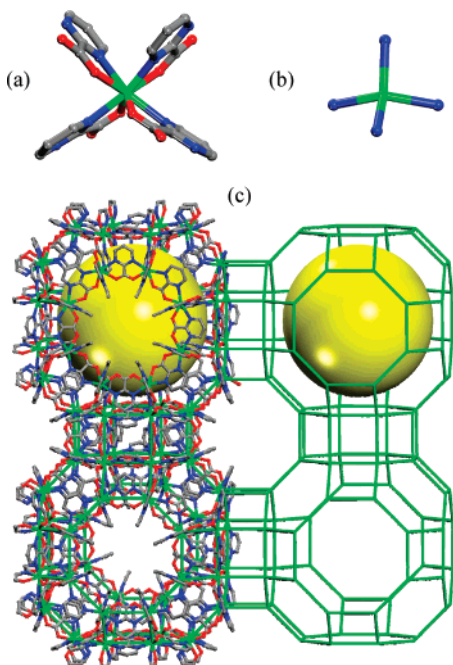


Figure 3. Single-crystal structure of **2** comprised of (a) eight-coordinated $\text{CdN}_4(\text{CO}_2)_4$ MBB, which can be regarded as (b) a CdN_4 TBU and (c) fragment of the *rho*-ZMOF structure. Hydrogen atoms and guest molecules are omitted for clarity; Cd = green, C = gray, N = blue, O = red. The yellow sphere represents the largest sphere that can be fit inside the cage, considering the van der Waals radii.

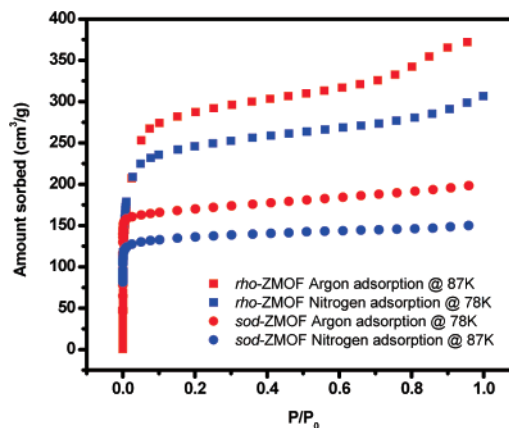


Figure 4. Nitrogen adsorption isotherm at 78 K and argon adsorption isotherm at 87 K on **1** and **2**.

are formed around the metal ensuring the rigidity of the MBB represented by $\text{CdN}_4(\text{CO}_2)_4$ (Figure 3a), regarded as a four-connected TBU, CdN_4 (Figure 3b).

Consequently, the periodic arrangement of these TBUs generate the formation of truncated cuboctahedra (α -cages) that are connected via double-eight-member rings to yield *rho*-ZMOF (Figure 3c), with analogous topological features to the inorganic *rho* zeolite net, which has been encountered only twice in the work carried out with MOMs.^{1b,13} Each α -cage consists of 48 cadmium ions and 96 2-PmC ligands, with piperazine and water guest molecules residing inside the cavity. Upon their removal, open channels are exploitable in all three directions, the diameter of the largest sphere that can be fit inside the cage without interacting with the van der Waals atoms of the framework being approximately 16.4 Å.

The total solvent-accessible volumes for **1** and **2** were obtained using PLATON software by summing voxels that are more than 1.2 Å away from the framework. In the case of **1**, the potential accessible free volume corresponds to approximately 46% of the unit cell volume, while for **2** this was estimated to be 58%.

In order to investigate the ion exchange capabilities of **1** and also to exploit its porous nature, we fully exchanged the K cations, present in the as-synthesized **1** that prevent pore access, with smaller Li cations, respectively; the process was carried out at room temperature for 24 h in aqueous media and was monitored by atomic absorption studies (page S5 of Supporting Information). Gas sorption experiments were performed on the Li-exchanged sample which was outgassed at room temperature for 12 h; it was proven that the Li^+ -exchanged and fully evacuated *sod*-ZMOF exhibits permanent microporosity, as evidenced by the reversible type I N_2 and Ar adsorption isotherms (Figure 4). The apparent Langmuir surface area is estimated to be $616 \text{ m}^2 \text{ g}^{-1}$, and the pore volume is determined using the Dubinin–Radushkevich (D–R) equation to be equal to $0.245 \text{ cm}^3 \text{ g}^{-1}$. Similarly, sorption studies (nitrogen and argon) were performed on the acetonitrile-exchanged, fully evacuated *rho*-ZMOF, **2**, and confirm permanent microporosity (Figure 4). The apparent Langmuir surface area is estimated to be $1168 \text{ m}^2 \text{ g}^{-1}$ with a corresponding pore volume of $0.474 \text{ cm}^3 \text{ g}^{-1}$, calculated by the D–R equation.

The dual character of ZMOFs, anionic frameworks and/or containing large accessible cavities, forms a suitable platform to evaluate the effect of pore size and/or intra-/extraframework charge density on the hydrogen uptake and its sorption energetics. Accordingly, hydrogen sorption studies were conducted on both compounds at 78 and 87 K and atmospheric pressure. The activation of the samples included guest exchange in acetonitrile at room temperature. It was revealed that **1** can store up to 0.9% weight H_2

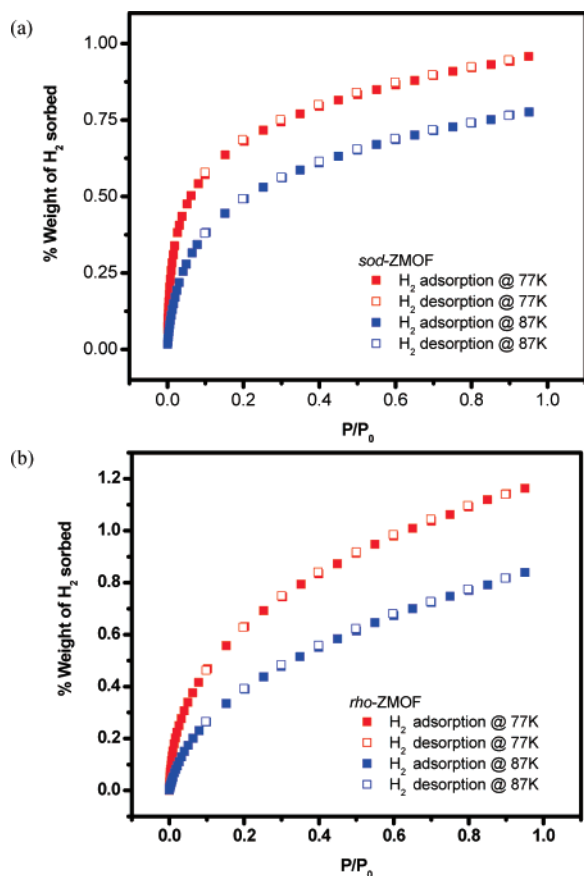


Figure 5. Hydrogen sorption isotherms on (a) **1** and (b) **2** at 78 and 87 K, at 78 K and 1 atm, (Figure 5a) with an associated isosteric heat of adsorption (q) estimated at lower loadings to be 8.4 kJ mol^{-1} (Figure S2a). In the case of **2**, uptakes up to 1.16% weight H_2 were obtained at 78 K and 1 atm (Figure 5b), where the isosteric heat of adsorption reaches a maximum value at lower loadings of $q = 8.7 \text{ kJ mol}^{-1}$ (Figure S2b).

The deliberate enhancement of the framework–hydrogen interactions is an ongoing challenge. Herein, it is important to emphasize that the isosteric heat of adsorption reveals relatively large values, in the context of MOFs, for both compounds, despite the fact that the hydrogen uptake is not considerably high. We have previously postulated that the pore dimensions (around 1 nm) and the presence of high local charge density, in combination with large surface areas, are key elements to enhance the H_2 uptake at moderate pressures and elevated temperatures.¹⁴ In the case of *sod*-ZMOF, anionic framework, the uptake at lower pressures is steepened compared to *rho*-ZMOF, neutral framework, as evidenced by the shape of the isotherm, which can be correlated to the charge effect and the pore size on the H_2 sorption. This is supported by the fact that in **1** the constancy of the isosteric heat of adsorption is maintained up to 0.4% H_2 sorbed (Figure S2a). For **2**, the isosteric heat of adsorption decreases more rapidly as a function of the H_2 loading, as expected, due to the fact that the framework is neutral and encompasses extra large cavities, allowing for a decrease in the overlap of potential energy fields of the pore walls.

Here we have delineated the potential of this strategy to synthesize ZMOFs assembled from rigid and directional TBUs using the single-metal-ion-based MBB approach, which may hold promise toward finding appropriate porous candidates for hydrogen storage at room temperature and moderate pressure. ZMOFs are unique porous materials that combine the ability to readily alter pore size, charge density, and surface area. Work is in progress to

explore (i) the effect of pore size and charge, (ii) the effect of various extraframework cations on the hydrogen isosteric heats of adsorption and uptakes, and (iii) the construction of novel ZMOFs based on functionalized pyrimidinecarboxylate ligands in combination with different metal ions and structure directing agents.

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Supporting Information Available: IR, XRPD, atomic absorption and gas sorption data, structure figures, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Preparation of **1**: 4,6-PmDC (0.016 g, 0.087 mmol), $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.017 g, 0.0435 mmol), DMF (0.75 mL), H_2O (1.5 mL), HNO_3 (0.2 mL, 3.5 M in DMF) were placed in a 20 mL scintillation vial and heated to 85 °C for 12 h, 105 °C for 23 h and 115 °C for 23 h. The pale yellow polyhedral crystals were collected and air-dried, with a 88% yield based on $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. The as-synthesized material is insoluble in water and common organic solvents.
- (10) Crystallographic data for **1**: $[\text{In}(\text{C}_6\text{N}_2\text{O}_4\text{H}_2)_2\text{Na}_{0.36}\text{K}_{1.28}(\text{NO}_3)_{0.64}(\text{H}_2\text{O})_{2.1}]$, cubic, $Im\bar{3}m$, $a = 18.761(4) \text{ \AA}$, $V = 6603.2(9) \text{ \AA}^3$, $Z = 96$, Final R indicates ($I > 2\sigma(I)$): $R_1 = 0.0436$, $wR_2 = 0.1252$.
- (11) Preparation of **2**: 2-PmCN (0.0092 g, 0.087 mmol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.0134 g, 0.0435 mmol), DMF (1 mL), H_2O (1 mL), piperazine (0.1 mL, 0.58 M in DMF) were added to a 20 mL glass scintillation vial and heated to 85 °C for 12 h. Colorless polyhedral crystals were collected and air-dried, with a 15% yield based on $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The as-synthesized material is insoluble in water and common organic solvents.
- (12) Crystallographic data for **2**: $\text{Cd}(\text{C}_3\text{H}_3\text{N}_2\text{O}_2)_2(\text{C}_4\text{N}_2\text{H}_{10})_{0.35}(\text{H}_2\text{O})_{5.36}$, cubic, $Im\bar{3}m$, $a = 30.070(7) \text{ \AA}$, $V = 27229(17) \text{ \AA}^3$, $Z = 96$, Final R indicates ($I > 2\sigma(I)$): $R_1 = 0.0771$, $wR_2 = 0.1900$.
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