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Cooperative Assembly of 3-Ring-Based Zeolite-Type Metal-Organic Frameworks and Johnson-Type Dodecahedra

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Abstract

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Two birds with one stone One synthetic strategy led to the preparation of both 3-ring-based zeolite-type metal-organic frameworks (NPO-type) and Johnson-type metal-organic polyhedra. The strategy is based on the cooperative assembly of 4-connected indium nodes with two symmetry-complementary ligands (one serves to generate 3-rings and the other crosslinks 3-rings). Photocatalytic H₂ production experiments demonstrated these NPO-zeolite compounds behave as semiconductors and exhibit photocatalytic activity for the generation of dihydrogen from water under ultraviolet irradiation.

Keywords

metal-organic framework; metal-organic polyhedra; zeolite; 3-ring; mixed ligands

Large-scale industrial applications of zeolites in areas such as air separation and petrochemical processing have rendered the zeolite-type topology a prime target in new materials design.^[1] Zeolite structure types exemplified by commercially important zeolites A, X, and ZSM-5 are characterized by 4-connected open topologies and TL₂ framework compositions (T indicates tetrahedral and L is a bicoordinated species between two T-atoms). During the past decades, the synthesis of zeolite-type MOFs, ^[2–13] defined here as metal-organic frameworks (MOFs) with zeolite-type 4-connected topologies has attracted increasing interest.

Known zeolite-type MOFs are mostly synthesized by following a strategy based on the mimicking of the Si-O-Si bond angle of $\approx 145^\circ$ by T-L-T angles in MOFs through judicious choice of metal and ligand geometry. This strategy has led to the preponderance of imidazolate-type ligands (with or without auxiliary functional groups such as -COO⁻) in zeolite-type MOF chemistry,^[3–4, 7–11] while “pure” carboxylates (those with only -COO⁻ donor groups) that permeate most other aspects of MOF chemistry have played little roles in the design of zeolite-type MOFs, possibly because of their perceived “wrong” T-L-T angles.

On the other hand, it has long been recognized that zeolite-type nets can accommodate a large range of T-O-T angles. For example, in gallosilicates, gallogermanates, and zincoarsenates, an increase in the T-O bond distance (compared to silicates) leads to a decrease in the T-O-T angle to as low as 123.8° in a zincoarsenate sodalite.^[14] Furthermore, the longer T-O distance and the correspondingly smaller T-O-T angle also provide some advantages because they contribute to the formation of new topologies and also help to stabilize secondary building units (SBUs, e.g., 3-rings) that are strained and difficult to form in silicates.^[15]

In developing strategies for constructing new porous materials, the 3-ring, having the smallest possible ring size, is one of the most desirable SBUs because it can help to create new topological types with low framework density,^[3b, 16] and could also induce the concurrent formation of large ring sizes such as 14-rings (The ring size refers to the number of T-node in a ring and the smallest ring size in known zeolite structure types is rarely 3, often 4, and sometimes 5).^[2c] Additionally, the 3-ring is also one of the most effective SBUs for constructing metal-organic polyhedra (MOPs).^[17–19] For example, 3 out of 5 Platonic

solids and 9 out of 13 Archimedean solids contain triangles. Yet, 3-rings are uncommon in either traditional porous oxides or more recent MOFs.^[2c]

Thus, it becomes clear that the introduction of 3-rings could allow access to new zeolite-like MOFs and MOPs. In this work, we select In^{3+} ions as metal centers and mixed dicarboxylic linkers with 120 and 180° angles as complementary and cooperative linkers for the construction of 3-ring based zeolite-type nets (Scheme 1) and MOPs. Among metal ions, In^{3+} is of special interest, because it can form a 4-connected $\{\text{In}(\text{O}_2\text{CR})_4\}$ group, which is an appealing T-node for targeting zeolite-type MOFs and MOPs.^[12,13] The choice of the dicarboxylic linkers with 120° bent angle is because of their ability to induce the assembly of In_3 3-rings. The second dicarboxylic linker is chosen to provide the cross-links between 3-rings to generate an overall 3D architecture. Based on this strategy, we have been able to synthesize not only a series of isostructural 3-ring based zeolite-type MOFs (denoted as CPM-2-NH₂, CPM-2-OH, CPM-2-H, CPM-2-NH₂-Cs, and CPM-3) with large 12-ring pore size (Table 1, CPM = crystalline porous material), but also two Johnson-type MOPs (denoted as CPM-8 and CPM-9) with elongated square dipyramidal configuration.

CPM-2-NH₂ crystallizes in a highly symmetric and yet noncentrosymmetric trigonal space group *P*31c. The asymmetric unit (Figure S1) consists of three crystallographically independent In^{3+} ions, each of which is coordinated by four bidentate chelating carboxylate groups from two 5-aip and two bpdc ligands to form a T-node. These three indium sites exhibit only one type of loop configuration (Figure 1a) involving one 3-ring corresponding to a triangular $\{\text{In}_3(\text{aip})_3\}$ group (Figure 1b). The loop configuration is a simple graph showing how many 3- or 4-membered rings a given T-node is involved in.^[2c] The triangular $\{\text{In}_3(\text{aip})_3\}$ groups act as SBUs and each of them is connected to six neighboring ones through six linear bpdc ligands (Figure 1c), resulting in the formation of a 3D framework with the zeolite NPO topology (Figure 1d) originally discovered in a nitridophosphate.^[2c,20]

CPM-2-NH₂ exhibits two types of infinite channels along the *c*-axis. The first type has small 3-ring openings that can accommodate a sphere with a maximum free diameter of 4.6 Å. The 3-ring channel consists of one kind of nonanuclear $\{\text{In}_9(\text{aip})_6(\text{bpdc})_6\}$ cages built from two $\{\text{In}_3(\text{aip})_3\}$ 3-rings linked by three $\{\text{In}(\text{bpdc})_2\}$ groups (Figure 1e). The free diameter of the largest sphere that can fit into the cage is ~14.6 Å. By sharing 3-ring faces, adjacent cages are joined together to form infinite 3-ring channels. Interestingly, arrays of 3-ring channels form a hexagonal pattern and are interconnected through linear bpdc linkers to generate a 12-ring channel (Figure 1d). It is worth noting that unlike zeolites in which the aperture size is primarily determined by the ring size (i.e., the number of T-nodes), the aperture size in MOFs is generally determined by the ligand length. Zeolite-type MOFs with the large ring size such as 12-rings are rare.^[11] In CPM-2-NH₂, the 12-ring channel has the narrowest free diameter of 12.2 Å (Figure S2).

Different from zeolite-type MOFs that rely on heterocyclic ligands (e.g., imidazole derivatives), CPM-2-NH₂ is based on a pure metal-carboxylate framework with only -COO⁻ donors. Up to now, zeolite-type MOFs with pure metal-carboxylate frameworks remain rare. Compared with heterocyclic ligands such as imidazoles, pure dicarboxylates usually have longer distance between donor sites, which helps to increase the separation between adjacent

T-nodes. As a result, the framework density (FD) (0.33) of a single sublattice in CPM-2-NH₂ is very low compared to known zeolite-type MOFs (usually larger than 2.0) and inorganic zeolites (usually larger than 10.0). The FD is defined as the number of T-nodes per 1000 Å³.^[2c] Such an open net, however, resulted in the formation of a 3-fold interweaving structure in CPM-2 (Figure S3). Still, the overall structure is quite open with a total guest-accessible volume of 44% (8074 Å³ per unit cell). Even considering all triply interweaving nets, the overall FD (1.0) is still very low.

The presence of two symmetry-complementary ligands in CPM-2-NH₂ makes it possible to tune the framework composition by replacing either one of two ligands. By using two other bent dicarboxylates (i.e., 5-hip and 1,3-bdc), two more phases (denoted CPM-2-OH and CPM-2-H) were obtained. The functional groups (NH₂⁻ and OH⁻) in these structures are oriented towards the pore center of 12-ring channels and can lead to different interactions with guest molecules. Alternatively, the bpdc ligand that crosslinks 3-rings can also be replaced by other linear dicarboxylates. For example, the use of a longer linear dicarboxylate H₂sbc leads to CPM-3 with a guest-accessible volume of 11270 Å³ per unit cell (53.4 %). It is also possible to introduce inorganic cations (i.e., Cs⁺) into the pore space through direct synthesis by simply including a caesium source (e.g., CsCl) into the synthesis mixture with DEF as the solvent, leading to a Cs-containing phase, denoted as CPM-2-NH₂-Cs.

We then further examined the versatility of our synthetic method by expanding from the bent carboxylate system to the bent heterocyclic carboxylate system. In this work, the bent heterocyclic carboxylate selected is H₂pdc with the 120° bent angle, and ligands for crosslinking 3-rings are bpdc and 1,4-ndc (Table 1). The combination of two symmetry complementary ligands led to two discrete 3-ring-based MOPs, denoted as CPM-8 and CPM-9.

As shown in Figure 2, CPM-8 and CPM-9 consist of ten In³⁺ ions, sixteen bent pdc and four linear bpdc (or 1,4-ndc) ligands. The presence of pdc with 120° bent angle induces the formation of a basic {In₃(pdc)₃} 3-ring SBU (Figure 2a) and subsequently a penta-nuclear square pyramidal {In₅(pdc)₈} cluster. In the presence of the symmetry complementary dicarboxylates, two penta-nuclear pyramidal moieties are pillared into an expanded size-tunable cage structures comprising eight triangular and four quadrilateral windows (Figure 2b). With four linear bpdc ligands, the dimensions of CPM-8 are approximately 8.3 × 8.3 × 27.0 Å (atom-to-atom distance). With a shorter ndc ligand, an isostructural deca-nuclear In-MOP CPM-9, 8.3 × 8.3 × 22.8 Å in dimension was obtained.

When indium ions are viewed as vertices and the ligands as edges, CPM-8 and CPM-9 can be described as elongated square dipyrramids (Figure 2c, 2e), a Johnson solid. So far, a number of MOPs with various sizes and shapes have been reported.^[16–18] However, most of known MOPs belong to Archimedean or Platonic solids in which all the vertices are identical. In comparison, Johnson solids possess different kinds of vertices.^[17a]

Thermal gravimetric analysis of CPM-2-NH₂ shows that the removal of solvent molecules occurs in the temperature range of 60~220 °C (Figure S4). PXRD further confirms that the desolvated sample retains its crystallinity up to about 250 °C (Figure S5). The UV/vis

diffuse reflectance spectrum of CPM-2-NH₂ shows that its band gap is 3.0 eV (Figure S7). Photocatalytic H₂ production experiment was conducted in a sealed circulation system. 1% Pt was load as a cocatalyst by UV irradiation of the PtCl₄ aqueous solution. In a typical run, 0.100g of sample was suspended in 120 mL 25% methanol aqueous solution (containing 0.0017g PtCl₄) under magnetic stirring. Then a 300 W Xe lamp was applied to this mixture for 30 minutes, which led to the deposition of the Pt nanoparticles onto the sample surface as cocatalyst. After degassing the system for one hour, the 300 W Xe lamp was applied to execute the photocatalytic reaction. The products were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD). As shown in Figure S8, the photocatalytic reactions of CPM-2-NH₂ exhibit a stable H₂ release rate of 2.0 μ mol/h/0.1g, demonstrating that the sample has photocatalytic activity for the generation of H₂ gas from water under UV irradiation. The photocatalytic activity of CPM-2-NH₂ compares favorably against that of the In₂O₃ powder which gave a dihydrogen release rate of 2 μ mol/h/0.3g under the irradiation of 500W high pressure Hg lamp.^[21]

In summary, the utilization of bent dicarboxylates for directing the formation of 3-rings and linear dicarboxylates for crosslinking 3-rings has allowed the synthesis of 3-ring based zeolite-type MOFs and MOPs with tunable framework and extra-framework compositions. These new materials possess structural and topological features (such as 3-rings, large 12-ring channels, expanded MOP cages) that are the direct results of the synthetic strategy. The synthesis of CPM-2 and CPM-3 shows a new pathway for the creation of zeolite-type MOFs using only -COOH functionality, instead of the currently popular practices that rely on heterocyclic compounds. CPM-8 and CPM-9 are indium-based metal-organic polyhedra and belong to a family of Johnson-type solids that are uncommon among MOPs. As demonstrated by CPM-2-NH₂, these materials behave as semiconductors and can function as photocatalysts for the generation of dihydrogen from water.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

a) View of the loop configuration in CPM-2-NH₂. b) Structure of {In₃(aip)₃} 3-ring. c) Coordination relationship of {In₃(aip)₃} 3-ring with adjacent units. d-e) View of 3D NPO-zeolite framework and nonanuclear {In₉(aip)₆(bpdc)₆} cages, respectively. f) Structure of {In₃(pdc)₃} 3-ring. g-h) and i-j) Schematic representations of the MOPs in CPM-8 and CPM-9, respectively.

Scheme 1.

Illustration of the synthetic strategy for the construction of 3-ring based zeolite nets using two symmetry-complementary ligands.

Table 1

A Summary of Crystal Data and Refinement Results.^[a]

Compound	Formula	Sp. Gr.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	R(F)
CPM-2-NH ₂	[N(CH ₃) ₂] ₃ [In ₃ (aip) ₃ (bpd ₃) ₃] ₃ ·solvent	<i>P</i> 31 ₁ <i>c</i>	27.2959(7)	27.2959(7)	28.0896(16)	90	90	120	0.0852
CPM-2-OH	[N(CH ₃) ₂] ₃ [In ₃ (hip) ₃ (bpd ₃) ₃] ₃ ·solvent	<i>P</i> 31 ₁ <i>c</i>	27.6060(32)	27.6060(32)	28.1798(41)	90	90	120	[<i>b</i>]
CPM-2-H	[N(CH ₃) ₂] ₃ [In ₃ (m-bdc) ₃ (bpd ₃) ₃] ₃ ·solvent	<i>P</i> 31 ₁ <i>c</i>	27.2959(30)	27.2959(30)	28.0896(55)	90	90	120	[<i>b</i>]
CPM-2-NH ₂ -Cs	Cs[N(C ₂ H ₅) ₂] ₃ [In ₃ (aip) ₃ (bpd ₃) ₃] ₃ ·solvent	<i>P</i> 31 ₁ <i>c</i>	27.3449(3)	27.3449(3)	28.2554(7)	90	90	120	0.082
CPM-3	[N(CH ₃) ₂] ₃ [In ₃ (aip) ₃ (sdc) ₃] ₃ ·solvent	<i>P</i> 31 ₁ <i>c</i>	27.2340(2)	27.2340(2)	32.8706(7)	90	90	120	0.0946
CPM-8	[N(CH ₃) ₂] ₁₀ [In ₁₀ (pdc) ₁₆ (bpd ₃) ₄] ₃ ·solvent	<i>P</i> 21/ <i>c</i>	22.5221(10)	29.1986(12)	32.0959(11)	90	132.243(2)	90	0.1040
CPM-9	[N(CH ₃) ₂] ₁₀ [In ₁₀ (pdc) ₁₆ (ndc) ₄] ₃ ·solvent	<i>P</i> cca	39.7134(7)	17.4359(3)	46.3618(8)	90	90	90	0.0963

[*a*] H₂bpd₃ = 4,4'-biphenyl-dicarboxylic acid; H₂hip = 5-hydroxyisophthalic acid; H₂aip = 5-aminoisophthalic acid; m-H₂bdc = 1,3-benzenedicarboxylic acid; H₂sdc = 4,4'-stilbenedicarboxylic acid; H₂pdc = pyridine-2,5-dicarboxylic acid; H₂ndc = naphthalene-1,4-dicarboxylic acid.

[*b*] The unit cells of CPM-2-OH and CPM-2-H were obtained by single crystal X-ray diffraction. The bulk samples of CPM-2-OH and CPM-2-H were identified as isostructural to CPM-2-NH₂ using XPRD (Figure S6).