Metal–Organic Frameworks

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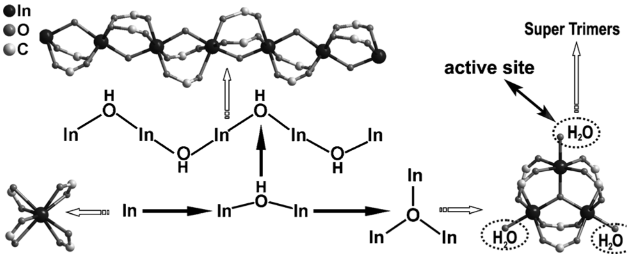
Porous Indium–Organic Frameworks and Systematization of Structural Building Blocks**

Shou-Tian Zheng, Jennifer J. Bu, Tao Wu, Chengtsung Chou, Pingyun Feng,* and Xianhui Bu*

Metal–organic frameworks (MOFs) have attracted lots of interest because their diverse compositions and framework architectures allow for a high degree of control over their properties.[1] Intensive synthetic efforts are underway to develop new types of porous materials with enhanced properties to meet the needs of various applications. Clearly, the success of such efforts depends, to a large degree, on the availability of chemical building blocks. Given the scarcity (compared to the variety of organic ligands) of metallic elements in the periodic table, it is no wonder that there is a strong desire for new pseudo-elements in the form of metal clusters (also called secondary building units or SBUs), which in effect expand the periodic table as far as the coordination chemistry is concerned.

Compared to single metal ions, SBUs usually have predefined and often rigid coordination geometries, which not only helps to enhance pore properties (e.g., through unsaturated coordination sites) and robustness of the resulting frameworks (owing to the increased number of links) but also provides a versatile pool of connectors for the rational synthesis of targeted MOFs.[2–4] Unfortunately, the discovery of new SBUs proves challenging and is usually through trial and error.

Occasionally, the synthetic search for new SBUs may entail a certain degree of purposefulness, because new SBUs may be inferred from known ones based on chemical or geometric considerations. For example, there may exist new SBUs intermediate between two known ones or a super-SBU may be formed from two or more known SBUs. Among p-block metals, indium(III) is known to form monomers (e.g., $\{In(O_2CR)_4\}$),[5,6] $\{In(OH)\}_\infty$ chains,[7] or trimers (e.g., $\{In_3O(O_2CR)_6(H_2O)_3\}$).[8] More interestingly, some combinations of these SBUs are known to co-exist in MOFs (i.e., monomer/trimer or monomer/chain),[9] thus revealing possible solution equilibria involving these SBUs. From these known SBUs, it is clear that there should be a hydroxy-bridging V-type binuclear SBU (i.e., $In_2(OH)$), which is a necessary intermediate during the evolution process from monomer to either trimer or to chain (Scheme 1). The actual synthetic trapping of such a dimeric intermediate in MOFs has, however, eluded all previous synthetic efforts. Additionally, through the discovery of two super-trimeric units herein, two analogous series of SBUs with In^{3+} monomer and In^{3+} trimer as the parent SBU, respectively, have been identified, which helps to systematize SBUs in the indium system. The first series involves In^{3+} monomer, OH^- bridged $In_2(OH)$ dimer, and $[In(OH)]_\infty$ polymeric chain, which are in strict analogy with single $\{In_3O(O_2CR)_6(H_2O)_3\}$ trimer, $HCOO^-$ bridged di-trimer, and infinite polymeric trimer in the second series.



Scheme 1. Evolutionary process from indium momoner to more complex building units.

Herein, we report five InOFs (denoted as CPM-10, 11, 12, 13, and 14, CPM = crystalline porous materials) that contain novel dimeric $\{In_2(OH)\}$ (for CPM-10, 11, and 12) and super-trimeric indium clusters (for CPM-13 and CPM-14; Table 1). One of these materials (CPM-13) has perhaps the highest Langmuir surface area among indium-based anionic framework materials (1441 $m^2 g^{-1}$, Table S1 in the Supporting Information). It is worth noting that even though surface areas as high as 10000 $m^2 g^{-1}$ are known for neutral MOFs,[2f] it remains a significant challenge to obtain high surface areas for anionic framework materials. CPM-13 also has one of the highest surface areas among chiral porous frameworks constructed from achiral building blocks.

Three synthetic strategies contribute to our successful trapping of highly elusive dimers. One is the exclusive use of a ligand bearing a single negative charge (in this case, nicotinate) with In^{3+}. Prior to this work, indium carboxylate frameworks generally contain ligands bearing two, three, or four negative charges. The second is the use of two size-complementary tricarboxylates (i.e., btc and btb, see Table 1). While the combination of di- and tricarboxylates (or two

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[*] Dr. S.-T. Zheng, C. Chou, Prof. Dr. X. Bu
Department of Chemistry and Biochemistry
California State University, Long Beach, CA 90840 (USA)
E-mail: xbu@csulb.edu

J. J. Bu, T. Wu, Prof. Dr. P. Feng
Department of Chemistry
University of California, Riverside, CA 92521 (USA)
E-mail: pingyun.feng@ucr.edu

J. J. Bu
J. W. North High School, Riverside (USA)

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Table 1: Summary of crystal data and refinement results.[a]

Name	Formula	Space Group	*a* [Å]	*b* [Å]	*c* [Å]	α/β [°]	γ [°]	*R*(F)
CPM-10	$[In_2(OH)(nic)_5]\cdot 2\,CH_3CN$	$P6_522$	12.3651(5)	12.3651(5)	37.4849(5)	90	120	0.0420
CPM-11	$[CH_3NH_3]_2[In_2(OH)(btc)_{7/3}]\cdot$solvent	*Pnma*	29.7560(9)	14.5284(4)	29.7388(9)	90	90	0.0816
CPM-12	$[(C_2H_5)_2NH_2]_2[In_2(OH)(btc)_{5/3}(btb)_{2/3}]\cdot$solvent	$P\bar{3}$	24.7273(2)	24.7273(2)	14.3812(3)	90	120	0.0818
CPM-13	$[CH_3NH_3][In_3O(bbdc)_3(HCO_2)_{3/2}(H_2O)]_2\cdot$solvent	$P4_32_12$	22.1386(6)	22.1386(6)	36.2651(18)	90	90	0.0480
CPM-14	$[In_3O(obb)_3(HCO_2)(H_2O)]\cdot$solvent	*R*32	23.3120(4)	23.3120(4)	26.6650(9)	90	120	0.0496

[a] Hnic = nicotinic acid, H_3btc = 1,3,5-benzenetricarboxylic acid, H_3btb = 1,3,5-tri(4-carboxyphenyl)benzene, H_2bbdc = 4,4′-biphenyldicarboxylic acid, H_2obb = 4,4′-oxybis(benzoic acid).

dicarboxylates) has been exploited in the synthesis of MOFs, mixed size-complementary tricarboxylates, have been little examined. The third is the use of a novel solvent, *N*-methylformamide (NMF), in contrast with commonly used solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), or *N*,*N*-dimethylacetamide (DMA). Note that these amide solvents not only serve as reaction media but also decompose to provide charge-balancing cations. The decomposition product of NMF ($H_3NCH_3^+$) is smaller than those of DMF, DEF, and DMA, which contributes to the high surface area of CPM-13, compared to the surface area of other anionic frameworks.

In CPM-10, 11, and 12, each $\{In_2(OH)\}$ dimer has a V-type shape with an In–In distance of approximately 3.8 Å and In-OH-In angle of ca. 135°. Unlike well-known paddlewheel $M_2(CO_2)_4$ motifs in which four carboxylate ligands are nearly perpendicular to each other,[3] the V-shaped $\{In_2(OH)\}$ dimer directs carboxylate ligands to arrange in parallel in pairs, leading to the formation of larger rigid motifs, such as $\{[In_2(OH)]_2(nic)_2\}$ four-membered ring (i.e., four metal sites in a ring) in CPM-10 and $\{[In_2(OH)]_3(btc)_2\}$ triangular prism in CPM-11 and CPM-12.

CPM-10 crystallizes in the chiral space group $P6_522$ and contains interesting chiral tubular channels (Figure 1a and Figure S1 in the Supporting Information). Each channel is constructed from two types of ladder-like coaxial left-handed helical chains interlinked through nicotinate (nic) ligands. On the basis of the distance from the channel center, these two kinds of helical chains can be distinguished as inner and outer helices. Both chains contain one type of $\{[In_2(OH)]_2(nic)_2\}$ four-membered ring built from two $\{In_2(OH)\}$ SBUs linked by two nic ligands (Figure 1d). In the four-membered ring, the two nic ligands are nearly parallel and thus further stabilize the ring configuration through a $\pi\cdots\pi$ stacking interaction of approximately 3.6 Å, which likely plays a key role in the stabilization of the $\{In_2(OH)\}$ dimer. The inner helix is made up of four-membered $\{[In_2(OH)]_2(nic)_2\}$ rings connected through shared $\{In_2(OH)\}$ dimers (Figure 1b), while the outer helix is constructed from four-membered $\{[In_2(OH)]_2(nic)_2\}$ rings linked through additional nic ligands (Figure 1c). Viewed along the *c* axis, the inner and outer helices exhibit pseudo-12-ring and pseudo-24-ring configurations, respectively. Interestingly, using TOPOS,[10] the 3D framework of CPM-10 can be simplified as a rare chiral 5-connected **wjs** net (Figure S14 in the Supporting Information).

The discovery of CPM-11 and its dimeric $In_2(OH)$ cluster in the well-studied In/btc system is an exciting development, considering that many previous syntheses in this system showed no trace of the dimer. We attribute our success to the use of a novel solvent system, NMF/H_2O. In fact, our systematic studies in this In/btc/NMF/H_2O system show that by varying the concentration of In^{3+} and H_3btc and the ratio between NMF and H_2O, multiple forms of indium SBUs (monomer, dimer, trimer, and chain, or their different combinations) can be generated.

Specifically, without the cosolvent H_2O (0.12 g $In(NO_3)_3\cdot x\,H_2O$, 0.12 g H_3btc, 5.0 g NMF), pure CPM-6 (containing both monomer and trimer)[9b] is readily obtained (Figure S2 in the Supporting Information). Under the same conditions, but with a mixed solvent (4.0 g H_2O, 1.0 g NMF), MIL-96 (containing both monomer and chain) is obtained (Figure S3 in the Supporting Information).[9a] An increase in the concentration (0.20 g $In(NO_3)_3\cdot x\,H_2O$, 0.17 g H_3btc, 4.0 g H_2O, 1.0 g NMF), however, led to the synthesis of CPM-11 with only dimer (Figure S4 in the Supporting Information). A mixture of CPM-6 and CPM-11 typically results under other conditions (Figure S5 in the Supporting Information), thus suggesting the possible solution-phase co-existence of monomer, dimer, and trimer. It is likely that the dimer is intimately associated with other SBUs in the solution, and the delicate equilibria shift to favor one or more types of SBUs in response to solvent properties and solute concentrations.

In CPM-11, $\{In_2(OH)\}$ dimers are connected by btc to generate two larger motifs: $\{[In_2(OH)]_3(btc)_2\}$ triangular prisms and $\{In_2(OH)(btc)\}_\infty$ belt-like chain (Figure 1f,g). Similar to the $\{[In_2(OH)]_2(nic)_2\}$ square ring in CPM-10, $\pi\cdots\pi$ stacking interaction can also be found in the $\{[In_2(OH)]_3(btc)_2\}$ triangular prism, in which two btc ligands are parallel with an interfacial distance of approximately 3.7 Å. The $\{[In_2(OH)]_3(btc)_2\}$ triangular prisms are further stacked in parallel to form $\{[In_2(OH)]_3(btc)_2\}_\infty$ triangular columns running along the *b* axis. By sharing $\{In_2(OH)\}$ SBUs (Figure 1e), the $\{[In_2(OH)]_3(btc)_2\}_\infty$ triangular columns and $\{In_2(OH)(btc)\}_\infty$ belt-like chains are joined together to form a porous 3D framework with three distinct tubular channels running along the *b* axis, including large tetragonal channel A, medium-sized tetragonal channel B, and small trigonal channel C (Figure S6 in the Supporting Information). The diameters of the largest sphere that can fit into channels A, B, and C without touching the van der Waals surfaces of frameworks are approximately 7.2, 6.4, and 5.6 Å, respectively. Such multiporous tubular frameworks (those with distinct channels) are uncommon, but they are attracting attention for some novel applications, such as co-storage of chemically incompatible materials.[11]

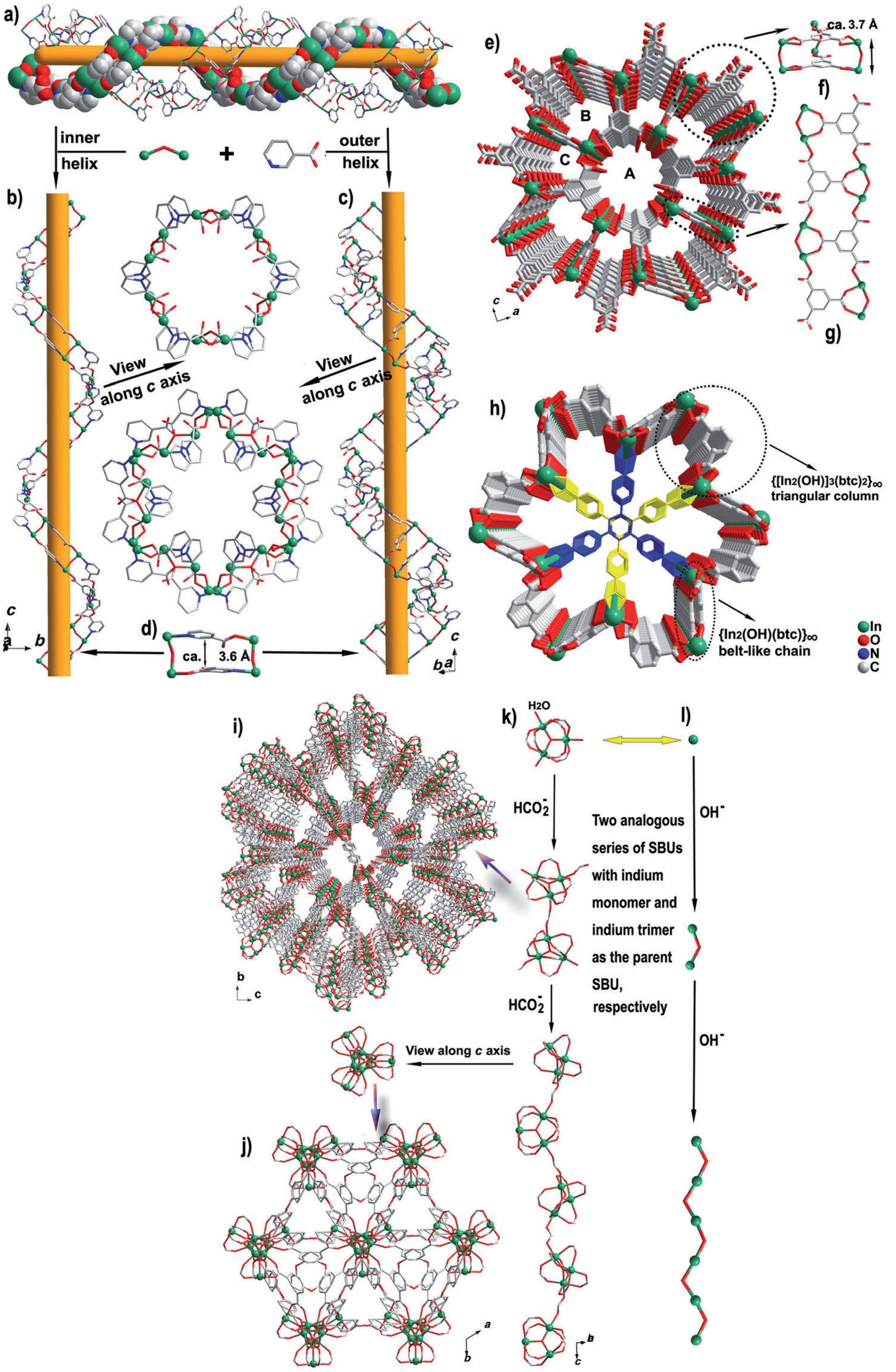

Figure 1. a) Nanotubular channel in CPM-10. The bridging nic ligands between inner and outer helices are omitted for clarity. b–d) View of inner helix, outer helix, and square $\{[In_2(OH)]_2(nic)_2\}$ ring, respectively. e–g) Structures of 3D tubular framework, $\{[In_2(OH)]_3(btc)_2\}$ triangular prism, and $\{In_2(OH)(btc)\}$ chain in CPM-11, respectively. h) Hexagram-shaped tubular structure in CPM-12. i, j) View of 3D structures of CPM-13 and CPM-14, respectively. k, l) View of structure evolution from indium trimer to trimer chain and from indium monomer to chain, respectively.

CPM-12 is a rare example of a porous framework constructed from the size-complementary L^{3-}/L^{3-} ligands in which one ligand is a scaled-up version of the other. This situation is in contrast to the widely used strategy involving mixed ligands with complementary bonding geometry (e.g., 120° and 180° ditopic ligands) or charge (e.g., L^0/L^{1-}, L^0/L^{2-}, L^{2-}/L^{3-}, etc.). Interestingly, CPM-12 consists of the same structural motifs, belt-like $\{In_2(OH)(btc)\}_\infty$ chain and triangular $\{[In_2(OH)]_3(btc)_2\}_\infty$ column, as CPM-11 but exhibits a different 3D tubular framework. As shown in Figure 1h, every six belt-like $\{In_2(OH)(btc)\}_\infty$ chains and six triangular $\{[In_2(OH)]_3(btc)_2\}_\infty$ columns interconnect though sharing $\{In_2(OH)\}$ SBUs to form a giant hexagram-shaped tubular channel along the *c* axis with nanosized window dimensions of 20.9 × 29.9 Å (measured between opposite atoms). Within such large channels reside the large btb ligands, arranged in parallel and in pair, to partition the pore space. Finally, every hexagram-shaped channel is surrounded by six neighboring channels through edge sharing to generate an overall 3D framework.

One of the most interesting features in the synthesis of CPM-13 is the four different roles of the amide solvent. In addition to serving as solvent and pore-filling species, both of its decomposition products ($NH_3CH_3^+$ and $HCOO^-$) control the framework formation and porosity. In CPM-13, as shown in Figure 1k, two terminal water sites of each $[In_3O(O_2CR)_6(H_2O)_3]^+$ trimer are replaced by two $HCOO^-$ groups, one acting as a terminal ligand and another acting to join together two trimers, which results in the formation of a new, negatively charged, di-trimeric SBU $[\{In_3O(O_2CR)_6(HCO_2)_{3/2}(\text{-}H_2O)_2\}_2]^-$, in distinct contrast to the positively charged single $[In_3O(O_2CR)_6(H_2O)_3]^+$ trimer. Each di-trimeric SBU is then linked to eight adjacent ones by 12 bbdc ligands to give rise to a 3D anionic architecture with channels along the *a* and *b* axes (Figure 1i and Figures S7 and S8 in the

Supporting Information). If each di-trimeric SBU is considered as an 8-connected node, the structure of CPM-13 can be simplified as the **bcu** net.

Apparently, in addition to the di-trimeric cluster, polytrimers can also form. In analogy with the formation of In(OH) chains from monomeric In^{3+} (Figure 1l), CPM-14 shows that trimeric $\{In_3O(O_2CR)_6(H_2O)_3\}$ clusters can also form an infinite $\{In_3O(O_2CR)_6(HCO_2)(H_2O)\}_\infty$ chain, which is clearly of a higher structural hierarchy than the simpler In(OH) chain. In contrast with the positively charged single trimer and the negatively charged di-trimer, the infinite polytrimer $\{In_3O(O_2CR)_6(HCO_2)(H_2O)\}_\infty$ chain is neutral. In CPM-14, each chain is linked by obb ligands along the *a* and *b* axis to six neighboring ones, thus generating a neutral 3D framework with 1D triangular channels along the *c* axis (Figure 1j). Such formation of super-trimeric units (di-trimers in CPM-13, polymeric trimer chains in CPM-14), coupled with the trapping of $In_2(OH)$ dimers in CPM-10, 11, and 12 reveals fascinating synthetic and structural chemistry of In MOFs which, even though rather diverse, shows strikingly systematic structural evolution and analogy in their structural building blocks.

PLATON calculations show that CPM-10, 11, 12, 13, and 14 have 14.8, 58.3, 49.8, 62.8, and 32.1%, respectively, potential guest-accessible volumes (solvent molecules and charge-balancing cations for negative frameworks).[12] CPM-12 and CPM-13 were selected to characterize the porosity. The thermal gravimetric analysis and powder X-ray diffraction show that the desolvated CPM-12 and CPM-13 retain their crystallinity up to about 200 and 250°C (Figure S9–S12 in the Supporting Information), respectively. CPM-12 was activated by soaking the crystals in methanol for one week to remove DEF and then degassed at 85°C for 24 h under vacuum prior to the gas adsorption measurement, while CPM-13 was directly degassed at 200°C for 24 h.

As shown in Figure 2, the N_2 sorption of CPM-13 exhibits a type I isotherm typical of materials of permanent microporosity. The Langmuir and BET surface areas of CPM-13 are 1441 and 904 $m^2 g^{-1}$, respectively, among the highest of all known anionic InOFs (Table S1 in the Supporting Information). A micropore volume of 0.487 $cm^3 g^{-1}$ (determined using the Horvath–Kawazoe method) and a median pore size of 7.02 Å were calculated. Furthermore, CPM-13 exhibits a significant uptake capacity for CO_2 and H_2. The CO_2 uptake at 273 K and 1 atm and H_2 uptake at 77 K and 1 atm reach 2.03 $mmol g^{-1}$ (45.4 $cm^3 g^{-1}$) and 5.00 $mmol g^{-1}$ (1.00 wt%), respectively. Further CH_4 sorption shows that CPM-13 selectively adsorbs CO_2 over CH_4 (0.42 $mmol g^{-1}$) at 273 K and 1 atm.

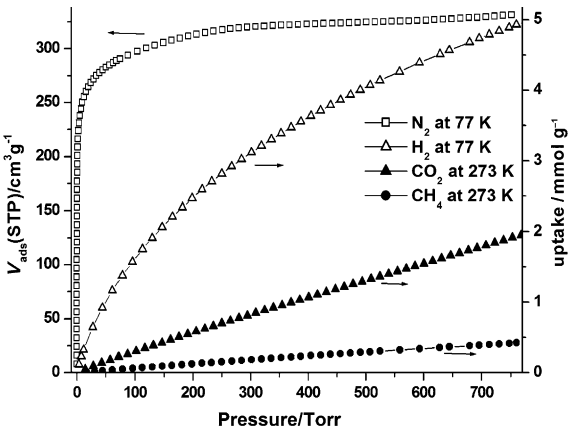

Figure 2. Gas sorption isotherms of CPM-13.

CPM-12 exhibits negligible uptake of N_2 at 77 K and 1 atm but quite high uptake of CO_2 at 273 K and 1 atm (78.6 $cm^3 g^{-1}$, Figure S13 in the Supporting Information), which is comparable with the highly porous framework ZIF-69 (70 $cm^3 g^{-1}$, Langmuir surface area 1070 $m^2 g^{-1}$) under the same conditions.[13] The selectivity of CPM-12 for CO_2 over N_2 is likely due to the partitioning effect of the pore space by btb ligands at the channel center.

In summary, the synthetic discovery of the indium dimer and two indium super-trimeric units in porous materials offers new insight into the rich synthetic and structural chemistry of indium–organic framework materials and has led to the systematization of six indium-based framework building units into two analogous series (i.e., the monomer series vs. the trimer series, Figure 1k,l). These framework building units, either alone or in combination with others, are capable of generating different novel 3D framework materials in response to simple changes in synthetic conditions. CPM-13 likely exhibits the highest surface area among anionic InOFs. CPM-12 exhibits high CO_2 uptake capacity and selectively adsorbs CO_2 over N_2. The tendency of these In MOFs to form chiral porous frameworks (three out of five are chiral) is worth noting and adds a new dimension to their possible applications.[14]

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