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Development of Composite Inorganic Building Blocks for Metal-Organic Frameworks

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Abstract

A general direction for diversifying metal-organic frameworks (MOFs) is demonstrated here through the synthesis of composite inorganic clusters between indium and elements from s-, d-, and f-blocks. These previously unseen heterometallic clusters, with various nuclearity, geometry, charge, and metal-to-metal ratios, have significantly expanded the pool of inorganic building blocks and are shown here to be highly effective for the construction of porous MOFs with high gas uptake capacity.

Crystalline porous materials (CPMs) comprise a broad range of solid-state materials with diverse compositions, structures, and properties.^[1–7] The most recent addition to this family of materials is metal-organic framework (MOF) materials.^[1–5] In the past decade, many advances in MOF are due to the availability of practically infinite number of organic building blocks. In comparison, much smaller number of inorganic building blocks are currently known.

One of the most promising routes to increase the number of inorganic components should be the creation of composite inorganic building units, because given dozens of chemical elements, the number of different ways to combine them (in various ratios) is just as infinite as the types of organic molecules. Here we focus on two general approaches that could lead to much increased diversity of inorganic building blocks. The first is the integration (in the same material) of two or more elements that were not known to co-exist (in 3D MOFs) prior to our work. For example, indium is rarely known to form 3D MOFs with another type of elements such as Mg, Mn, Co, Cu, and lanthanide (Ln) ions, even though each of these individual elements is well known as the building block for MOFs.

The second approach involves the creation of composite inorganic clusters as framework building blocks. This has remained a significant challenge in MOF chemistry, because a common occurrence in the attempted synthesis of heterometallic MOFs is the *macroscopic phase separation* of different metal ions into separate phases or the *molecular-level*

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Supporting Information. Details about sample preparation, TGA, XRD, cif files, and additional structural figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

separation of such metal ions by organic ligands.^[8–10] Prior to this work, heterometallic MOFs, especially those based on the combination of d- and f- block elements are well-known.^[8] However, until now, there are a much smaller number of examples in which heterometallic metals combine to form discrete clusters crosslinkable by organic ligands into 3D MOFs.^[11]

Herein, we report five series of MOFs, CPM-18-M (M=Nd, Sm), CPM-19-M (M=Nd, Pr), CPM-20, CPM-21-M (M=Mn, Co, Cu), and CPM-23 based on indium heterometallic clusters (Table 1). For the first time, the p-block indium is shown to be capable of co-assembling with metals from any other block of the periodic table to afford a pool of new heterometallic clusters for fabricating MOFs. These In-M clusters possess diverse configuration, nuclearity, metal-to-metal ratio, and charge, as shown by trimeric $[\text{InCo}_2(\text{OH})]^{6+}$, tetrameric *trans*- $[\text{In}_2\text{M}_2(\text{OH})_2]^{8+}$ (M = Mn, Co, Cu), tetrameric *cis*- $[\text{In}_2\text{Mg}_2(\text{OH})_2]^{8+}$, and tetrameric cube- $[\text{In}_3\text{M}(\text{OH})_4]^{8+}$ (M = Nd, Sm), and pentameric $[\text{In}_3\text{M}_2(\text{OH})_3\text{O}]^{10+}$ (M = Nd, Pr) (Fig. 1). To our knowledge, with the exception of tetrameric *trans*- $[\text{In}_2\text{M}_2(\text{OH})_2]^{8+}$ which is known in isolated In-M heterometallic complexes, all other In-M heterometallic oxide clusters are unknown prior to this work.^[12] One factor that increases the variety of such clusters is that for the same nuclearity, the ratio between heterometals can have different values (e.g., 3:1 or 2:2 for tetramers). Even though these clusters look quite different from each other, there appears to have an intrinsic relationship among them, because the overall charge of each cluster is exactly twice of its nuclearity.

CPM-18-Nd contains cubane-like 3:1 $[\text{In}_3\text{Nd}(\text{OH})_4]^{8+}$ cluster and crystallizes in a chiral space group $P2_13$ with three types of cages (Fig 2b–d). Two of them are constructed from the crosslinking of four $[\text{In}_3\text{Nd}(\text{OH})_4]^{8+}$ clusters by BTCs to form tetrahedral cages with maximum free diameters of ca. 6.2 Å and ca. 6.6 Å, respectively, while the third pore is composed of six cubane clusters bridged by BTCs to form an octahedral cage with a maximum free diameter of ca. 4.2 Å. The sharing of cubane clusters by adjacent cages leads to an overall anionic 3D framework (Figs. S1, S2).

In CPM-18-Nd, each $[\text{In}_3\text{Nd}(\text{OH})_4]^{8+}$ cube coordinates with nine carboxyl groups from nine BTC ligands (Fig S3). Among nine carboxyl groups, three adopt a bidentate mode by bridging a 6-coordinate In^{3+} ion and a 9-coordinate Nd^{3+} ion, while remaining six carboxyl groups only coordinate to one In^{3+} ion in a monodentate fashion leaving one uncoordinated oxygen atom per carboxyl group (Fig. 2a). As shown below by CPM-19-Nd, these uncoordinated oxygen atoms can bond with an additional metals ion to form new heterometallic clusters with higher nuclearity.

The structural correlation between CPM-18-Nd and CPM-19-Nd is of particular interest because it involves the cooperative action of six carboxyl groups to capture an additional Ln^{3+} to form a pentamer (Fig. 2a). Different from $[\text{In}_3\text{Nd}(\text{OH})_4]^{8+}$ cubes in CPM-18-Nd, CPM-19-Nd is constructed from pentameric $[\text{In}_3\text{Nd}_2(\text{OH})_3\text{O}]^{10+}$ clusters which can be derived from cubane-like clusters by just attaching an additional Nd^{3+} ion to one corner of the cube (Fig 2a). Because of the larger size of BTB, the free diameters of two tetrahedral cages and one octahedral cage in CPM-19-Nd are increased to 7.4 Å, 7.6 Å, and 9.4 Å, and

the solvent accessible volume (72.8 %) of CPM-19-Nd is also larger than that of CPM-18-Nd (41.3%).^[13]

One of the most interesting features demonstrated by CPM-18-Nd and CPM-19-Nd is the charge reversal of the framework. Through the incorporation of additional Nd³⁺ cations, CPM-19-Nd adopts an overall cationic framework, in contrast to its iso-reticular CPM-18-Nd that has an anionic framework. Such a charge reversal among isorecticular MOFs is quite unusual and demonstrates a new mechanism for altering framework charge properties by inserting or removing metal ions in a crystallographically ordered fashion.

In addition to In-Ln clusters shown above, the co-assembly of In³⁺ with Co²⁺ gives two types of In-Co clusters of different nuclearity: trimeric [InCo₂(OH)]⁶⁺ in CPM-20 and tetrameric [In₂Co₂(OH)₂]⁸⁺ in CPM-21-Co (Fig 1c,e). CPM-20 is quite unusual because it is both a mixed-metal and mixed-ligand MOF. Trinuclear [InCo₂(OH)]⁶⁺ clusters in CPM-20 are crosslinked by six 1,4-BDC ligands and three INA ligands to form a nine-connected net with the known ncb topology. (Fig S4).^[6c-d] It comprises two types polyhedral cages: tetrahedral {[InCo₂(OH)]₄(1,4-BDC)₆} cage and square antiprismatic {[InCo₂(OH)]₈(INA)₁₂(1,4-BDC)₂} cage (Fig 3).

Unlike the cube-like tetramer in CPM-18-Nd, “chair-like” [In₂Co₂(OH)₂]⁸⁺ tetramer in CPM-21-Co is derived by attaching an additional In³⁺ to the trimeric InCo₂(OH). One likely reason for the different geometry between cube-type In-Ln tetramers and chair-like Ln-Co tetramers is the fewer number of OH⁻ groups needed for the formation of M³⁺/M²⁺ tetramers (two OH⁻ groups), compared to the formation of M³⁺/M³⁺ tetramers (four OH⁻ groups), likely as a result of the lower Co²⁺ charge. The [In₂Co₂(OH)₂]⁸⁺ tetramer is called *trans*-[In₂Co₂(OH)₂]⁸⁺ because its two In³⁺ ions are oriented in a *trans* fashion with respect to the {Co₂(OH)₂} plane. In addition to cobalt, other 3d metals such as Mn and Cu can also form the same *trans* tetramer (Table 1).

In CPM-21-Co, the 3D framework is built up from a simple cubic packing of large octahedral cages {[In₂Co₂(OH)₂]₆(BTB)₈} (Fig 4a, 4c) containing twelve In³⁺ and twelve M²⁺ sites. At each corner of the octahedral cage is a tetrameric *trans*-[In₂Co₂(OH)₂]⁸⁺ cluster, and eight BTB ligands occupy the trigonal planes. The inner free diameter of these cages is ~ 15.5 Å. Furthermore, eight octahedral enclose a large cuboctahedral cage with a huge free diameter of ~ 22.5 Å (Fig 4b). Such an open net, however, resulted in the formation of a 2-fold interweaving structure. Nevertheless, the overall structure is still quite open with a total guest-accessible volume of 60.4%.

In addition to the In-Ln (the combinations between elements from p and f blocks) and In-Co/Mn/Cu (the p-d combinations) clusters discussed above, the first In-Mg (the p-s combination) cluster has also been created. As shown in Figure 1d, [In₂Mg₂(OH)₂]⁸⁺ clusters in CPM-23 can be viewed as formed by fusing together two [In₂Mg(OH)]⁷⁺ trimers by sharing the In...In edge, in contrast to *trans*-[In₂Co₂(OH)₂]⁸⁺ clusters which can be considered as formed by fusing two [InCo₂(OH)]⁶⁺ trimers through sharing the Co...Co edge. The [In₂Mg₂(OH)₂]⁸⁺ cluster is further different from the *trans*-[In₂Co₂(OH)₂]⁸⁺

cluster, because two Mg^{2+} ions are oriented in a *cis* fashion with respect to the central $\{\text{In}_2(\text{OH})_2\}$ plane.

In CPM-23, every *cis*- $[\text{In}_2\text{Mg}_2(\text{OH})_2]^{8+}$ cluster is connected by eight BTB ligands to generate a 3D framework. CPM-23 possesses a high solvent accessible volume (74.7 %). As shown in Figure 5, the accessible volume in the hexagonal channels are delimited by BTB ligands into two types of individual cavities with internal free diameters of $\sim 10.2 \text{ \AA}$ and $\sim 19.5 \text{ \AA}$. Both of these two cavities can be simplified as octahedral by considering *cis*- $[\text{In}_2\text{Mg}_2(\text{OH})_2]^{8+}$ clusters as nodes.

The thermal gravimetric analyses of CPM-19-Nd and CPM-20 show that the removal of solvent molecules occurs in the temperature ranges of $30 - 150 \text{ }^\circ\text{C}$ and $40 - 300 \text{ }^\circ\text{C}$ (Fig S5), respectively. PXRD further confirms that the crystals of CPM-19-Nd and CPM-20 retain their crystallinity up to about $200 \text{ }^\circ\text{C}$ and $300 \text{ }^\circ\text{C}$ (Figs S6, S7), respectively. Thus, CPM-19-Nd and CPM-20 were degassed at $150 \text{ }^\circ\text{C}$ and $260 \text{ }^\circ\text{C}$ for 24 h under vacuum prior to the measurement, respectively. As shown in Figures 6 and S8, the N_2 sorptions of both samples exhibit type I isotherm typical of materials of permanent micro-porosity. The BET and Langmuir surface areas of CPM-19-Nd are 272 and $370 \text{ m}^2/\text{g}$, respectively. A micropore volume of $0.133 \text{ cm}^3/\text{g}$ (using Horvath-Kawazoe method) and the median pore size of $9.38 \text{ \AA}$ were calculated. CPM-19-Nd can also adsorb a considerable amount of H_2 at 77 K and 1 atm ($1.32 \text{ wt\%}$, 6.60 mmol/g), which is comparable with the highly porous framework ZIFs (ZIF-8, $1.29 \text{ wt\%}$, ZIF-11, $1.37 \text{ wt\%}$, ZIF-20, $1.1 \text{ wt\%}$).^[14] Its uptake for CO_2 reaches $38.4 \text{ cm}^3/\text{g}$ at 273 K and 1 atm .

Compared to CPM-19-Nd, CPM-20 exhibits significantly higher BET surface area ($1009 \text{ m}^2/\text{g}$), Langmuir surface areas ($1134 \text{ m}^2/\text{g}$), micropore volume ($0.404 \text{ cm}^3/\text{g}$), and H_2 uptake at 77 K and 1 atm ($195.4 \text{ cm}^3/\text{g}$, $1.74 \text{ wt\%}$). Furthermore, CPM-20 exhibits a very high CO_2 uptake at 273 K and 1 atm and at 298 K and 1 atm , which reach $91.2 \text{ cm}^3/\text{g}$ and $47.7 \text{ cm}^3/\text{g}$, respectively. The higher uptake of CPM-20 may be due to the lack of extra-framework charge-balancing species in CPM-20. It is worth noting that even though numerous MOF structures have been reported, MOFs with CO_2 uptake of more than $90 \text{ cm}^3/\text{g}$ at 273 K and 1 atm are still scarce. Further N_2 sorption of CPM-20 at 273 K indicate little uptake over the entire pressure range ($2.28 \text{ cm}^3/\text{g}$ at 1 atm). The selectivity of CO_2/N_2 at 273 K is calculated to be $49:1$ at 0.16 atm and $40:1$ at 1 atm (or $77:1$ at 0.16 atm and $63:1$ at 1 atm by weight), indicating CPM-20 has a high CO_2/N_2 selective adsorption.^[15]

In summary, through the creation of a large family of MOFs reported here, we have demonstrated the feasibility and a general direction for greatly diversifying MOFs. It is shown that the p-block element (indium here) is capable of being co-assembled with elements from any other block of the periodic table (s-, d-, and f-blocks) to create a series of previously unseen composite inorganic building blocks with differing nuclearity (3 to 5), metal-to-metal ratios (i.e., 2:1, 3:1, 2:2, 3:2), geometry, and charge. These composite inorganic clusters, which are still quite rare among known MOFs, have significantly expanded the pool of inorganic building blocks and are clearly capable of serving as building blocks for the construction of porous MOFs with high gas uptake capacity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Five types of indium-containing clusters synthesized in this work. (a) $\text{In}_3\text{Nd}_2(\text{OH})_3\text{O}$, (b) $\text{In}_3\text{Nd}(\text{OH})_4$, (c) *trans*- $\text{In}_2\text{Co}_2(\text{OH})_2$, (d) *cis*- $\text{In}_2\text{Mg}_2(\text{OH})_2$, and (e) $\text{InCo}_2(\text{OH})$.

Figure 2.

Illustration of structural correlation between CPM-18 (left column) and CPM-19 (right column). a) Some carboxyl groups in CPM-18-Nd contain dangling oxygen atoms that cooperatively grab onto one lanthanide ion in CPM-19-Nd, leading to a change from tetrameric $[\text{In}_3\text{Nd}(\text{OH})_4]^{8+}$ in CPM-18-Nd to pentameric $[\text{In}_3\text{Nd}_2(\text{OH})_3\text{O}]^{10+}$ in CPM-19-Nd, and a switch from negative framework to positive framework. b)–d) and e)–g) Three types of polyhedral cages in CPM-18-Nd and CPM-19-Nd, respectively.

Figure 3.
a)–b) Two types of polyhedral cages in CPM-20.

Figure 4.
a)–b) Two types of polyhedral cages in CPM-21-Co. c) Its 3D framework.

Figure 5.
a)–b) View of two kinds of octahedral cages in CPM-22. c) Side views of 1D hexagonal pattern of CPM-22 along the c-axis.

Figure 6.
Gas adsorption isotherms of CPM-20.

Table 1

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

Name	Formula	Sp. Gr.	a/b(Å)	c(Å)	α/β (°)	γ (°)	R(F)
CPM-18-Nd	$[(CH_3)_2NH_2][In_3Nd(OH)_4(BTC)_3(DMF)_3] \cdot solvent$	$P2_13$	16.8753(13)	16.8753(13)	90	90	0.0531
CPM-18-Sm	$[(CH_3)_2NH_2][In_3Sm(OH)_4(BTC)_3(DMF)_3] \cdot solvent$	$P2_13$	16.8845(2)	16.8845(2)	90	90	0.0360
CPM-19-Nd	$[In_3Nd_2O(OH)_3(BTB)_3(H_2O)_6] \cdot NO_3 \cdot solvent$	$P2_13$	27.1319(3)	27.1319(3)	90	90	0.0772
CPM-19-Pr	$[In_3Pr_2O(OH)_3(BTB)_3(H_2O)_6] \cdot NO_3 \cdot solvent$	$P2_13$	27.1344(1)	27.1344(1)	90	90	0.0465
CPM-20	$[InCo_2(OH)(INA)_3(1,4-BDC)_{3/2}] \cdot solvent$	$I-43m$	21.9141(9)	21.9141(9)	90	90	0.0571
CPM-21-Mn	$[In_2Mn_2(OH)_2(BTB)_{8/3}(DMA)_2] \cdot solvent$	$R-3$	36.4998(4)	24.1865(7)	90	120	0.0660
CPM-21-Co	$[In_2Co_2(OH)_2(BTB)_{8/3}(DMF)_2] \cdot solvent$	$R-3$	36.3966(5)	23.9655(6)	90	120	0.0850
CPM-21-Cu	$[In_2Cu_2(OH)_2(BTB)_{8/3}(H_2O)_2] \cdot solvent$	$R-3$	36.2180(14)	23.6120(19)	90	120	0.0921
CPM-23	$[In_2Mg_2(OH)_2(BTB)_{8/3}(H_2O)_4] \cdot solvent$	$R-3$	32.2214(3)	92.4420(20)	90	120	0.0433

^[a] H₃BTC = 1,3,5-benzenetricarboxylic acid, H₃BTB = 1,3,5-tri(4-carboxyphenyl)benzene, HINA = isonicotinic acid, 1,4-H₂BDC = 1,4-benzenedicarboxylic acid.