Inorganic Chemistry
Communication
pubs.acs.org/IC

# Self-Assembly of Polyhedral Indium–Organic Nanocages

Jinjie Qian,[†,‡] Feilong Jiang,[†] Kongzhao Su,[†,‡] Qipeng Li,[†,‡] Daqiang Yuan,[†] and Maochun Hong*,[†]

[†]Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

[‡]University of the Chinese Academy of Sciences, Beijing 100049, China

Ⓢ *Supporting Information*

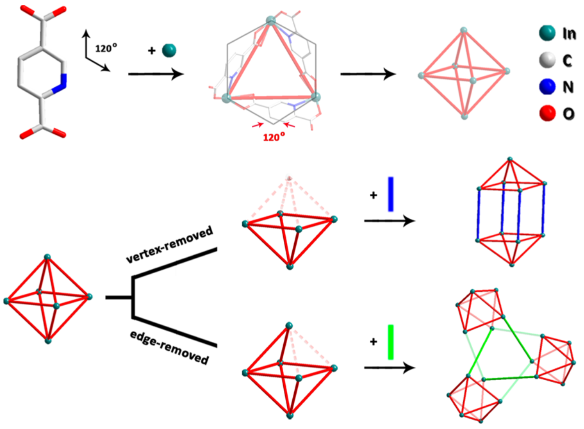
**ABSTRACT:** A synthetic strategy to construct discrete indium–organic polyhedra has been illustrated based on small three-membered windows from a 2,5-pyridinedicarboxylate (PDC) ligand with an angle of 120°. $[Et_2NH_2]_6[In_6(PDC)_{12}]$ (**InOF-10**) is a high-symmetry octahedron with eight three-membered windows, and $[Et_2NH_2]_{18}[In_{18}(BPDC)_6(PDC)_{30}]$ (**InOF-11**) is a complex polyhedron derived from 3-edge-removed octahedra with an auxiliary biphenyl-3,3′-dicarboxylate (BPDC) ligand. Moreover, the sorption behavior of the latter is also well investigated.

As one aspect of crystal engineering, the rational design and synthesis of metal–organic polyhedra (MOPs) have attracted enormous attention owing to not only their intriguing architectures[1] but also their promising applications, such as gas separation and storage,[2] nanoscale catalysis,[3] chemical sensing,[4] and host–guest interaction and recognition.[5] As the name implies, MOPs are discrete polyhedra constructed from metal cations/clusters with polytopic organic linkers.[6] From a predesign perspective, high-symmetry polyhedral cages are of growing interest because they are structurally simple and interesting and serve as platforms for the systematic study of their structures and functions. Although a large number of coordination cages with various sizes and geometries with high symmetry (tetrahedron, cube, octahedron, and dodecahedron) have been successfully developed,[7] there is still no synthetic approach to constructing an octahedron and/or octahedron-derived polyhedron, which remains a great challenge.

Previously reported by both the Zaworotko and Yaghi groups,[8] the cuboctahedron $[Cu_{24}(BDC)_{24}(DMF)_{14}(H_2O)_{10}]$ (BDC = 1,3-benzenedicarboxylate) can be assembled from the dicopper paddlewheel secondary building units (SBUs), where each BDC ligand bears a 120° bend angle suitable for constructing a truncated cuboctahedron structure with 12 $Cu_2(CO_2)_4$ SBUs and 24 BDC ligands. In this case, the bend angle of BDC is crucial in deciding large molecular cuboctahedra. Thereafter, isostructural cuboctahedra can be prepared from $Cu_2(CO_2)_4$ SBUs and functionalized BDC ligands, such as $NH_2$–BDC and OH–BDC.[9] Very recently, a series of examples are reported on three-dimensional metal–organic frameworks (MOFs) from these discrete nanoscale MOPs by auxiliary linear linkers.[10]

Inspired by this design principle, we propose in this Communication a strategy for constructing new MOPs by utilizing the smallest three-membered window[11] supported by the 120° angle organic ligand (Scheme 1), which are some of the most ideal SBUs because they can be further extended to form finite three-membered window-based octahedra and octahedron-derived polyhedra.

**Scheme 1. Schematic Route to Constructing Indium–Organic Coordination Cages from the 120° Angle PDC Ligand with Extra Auxiliary Ligands**



Despite the fact that a number of crystalline MOF materials are solvothermally obtained by the main-group element indium (In), there are very few reports on discrete indium–organic polyhedra (InOPs). Our group is particularly interested in seeking the design and synthesis of new solid indium–organic hybrid materials.[12] Presented here is a synthetic strategy for constructing octahedron and its derivative InOPs, namely, $[Et_2NH_2]_6[In_6(PDC)_{12}]$·Guest (**InOF-10**) and $[Et_2NH_2]_{18}[In_{18}(BPDC)_6(PDC)_{30}]$·Guest (**InOF-11**) ($H_2BPDC$ = biphenyl-3,3′-dicarboxylic acid; $H_2PDC$ = 2,5-pyridinedicarboxylic acid). **InOF-11** is kind of a serendipitous product because we also tried elongated carboxylic ligands to construct new InOPs without success. Herein, the syntheses, single-crystal structures, and sorption behaviors of these two novel indium-based polyhedra are discussed in detail as follows.

Colorless cubic crystals of **InOF-10** were obtained under solvothermal reaction conditions by heating a mixture of $In(NO_3)_3$ and $H_2PDC$ in a 1:2 molar ratio in a DEF/$HNO_3$ solvent (5:0.1, v/v; DEF = *N*,*N*′-diethylformamide; 65 wt % $HNO_3$) in a 23 mL vial at 85 °C for 5 days. For rhombic **InOF-11**, colorless crystals were similarly obtained by heating a mixture

**Received:** July 18, 2014
**Published:** November 13, 2014

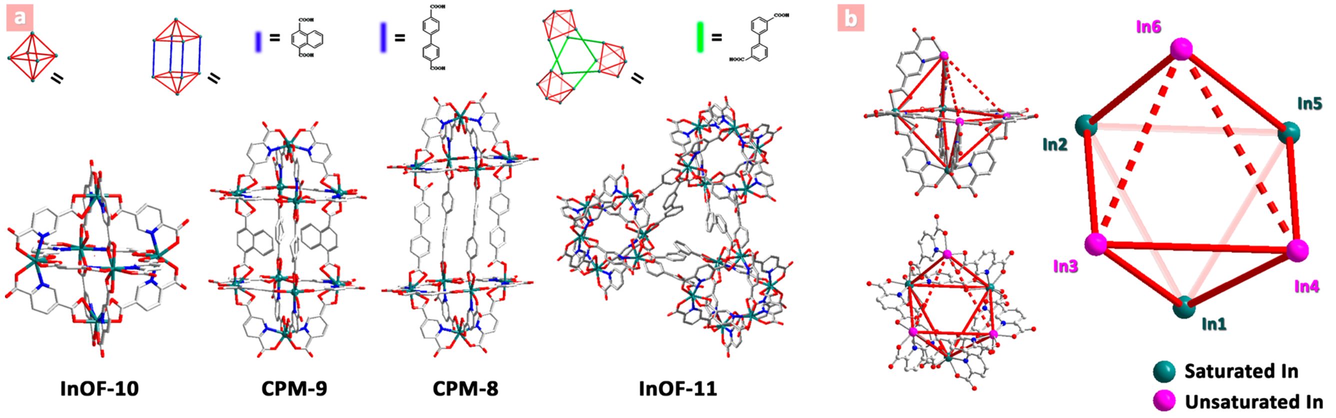


**Figure 1.** (a) $In_6(PDC)_{12}$ octahedron, $In_{10}(NDC)_4(PDC)_{16}$ and $In_{10}(BPDC)_4(PDC)_{16}$ dodecahedra, and $In_{18}(BPDC)_6(PDC)_{30}$ polyhedron. (b) Hexanuclear $In_6PDC_{10}$ SBB.

of $In(NO_3)_3$, $H_2BPDC$, and $H_2PDC$ in a 3:1:5 molar ratio in a DEF/EtOH/$HNO_3$ mixed solvent (3:3:0.1, v/v/v) at 110 °C for 7 days. The phase purity of the bulk products was confirmed by powder X-ray diffraction (PXRD) analysis (Figure S9 in the Supporting Information, SI). Their final formulas with guest solvent molecules were calculated from the SQUEEZE results combined with thermogravimetric analysis (TGA) and elemental analysis data. For more details about synthesis conditions, see the SI.

Single-crystal X-ray diffraction analysis reveals that **InOF-10** is crystallized in the cubic space group $Ia\overline{3}$ with cell parameters $a = b = c = 31.1940(1)$ Å and $V = 30354.0(2)$ Å$^3$ (refer to Table S1 in the SI). In its asymmetry unit, this compound is composed of one In(III) ion, 2 $PDC^{2-}$ ligands and 1 charge-balancing $Et_2NH_2^+$ cations with the removal of other disordered guest solvent molecules, leading to the formation of one indium-organic octahedron with the formula of $[Et_2NH_2]_6[In_6(PDC)_{12}]$[13] (Figure 1a, S1).

Structurally speaking, each indium(III) cation is eight-coordinated to two nitrogen atoms and six oxygen atoms from four separate $PDC^{2-}$ ligands to constitute a $[InN_2(CO_2)_4]$ moiety (Figure S2 in the SI), which is connected to others by bridging ligands to construct an anionic indium−organic octahedron $[In_6(PDC)_{12}]^{6-}$. Meanwhile, these $Et_2NH_2^+$ cations lying inside the open space are the byproduct of in situ decomposition of DEF molecules, thus leading to charge equilibrium. In the structure of **InOF-10**, each $[In_6(PDC)_{12}]^{6-}$ consists of six indium(III) ions occupying six vertexes of the octahedron bridged by 12 $PDC^{2-}$ ligands acting as the edges, with the In−N and In−O bond lengths in the ranges of 2.324(4)−2.367(4) and 2.168(4)−2.595(6) Å (Figure S3 in the SI), respectively.

Previously reported by the Bu group, $[Me_2NH_2]_{10}[In_{10}(NDC)_4(PDC)_{16}]$ (**CPM-8**) and ($[Me_2NH_2]_{10}[In_{10}(BPDC)_4(PDC)_{16}]$ (**CPM-9**)[14] belong to the Johnson-type solid family[15] derived from the vertex-removed octahedron and consist of 10 indium(III) ions, 16 $PDC^{2-}$ ligands, and 4 linear $NDC^{2-}$/$BPDC^{2-}$ ligands. In the well-refined crystal structure, indium ions can be treated as vertexes and the linear carboxylate ligands as edges; thus, they are described as elongated square bipyramids.

Single-crystal X-ray diffraction analysis reveals that **InOF-11** is crystallized in the trigonal space group $R\overline{3}$ with cell parameters $a = b = 48.4679(5)$ Å, $c = 44.1057(6)$ Å, and $V = 89729.3(4)$ Å$^3$ (Table S1 in the SI), structurally featuring a complex nanosized indium−organic coordination polyhedron never reported previously with the formula $[Et_2NH_2]_{18}[In_{18}(BPDC)_6(PDC)_{30}]$. There are 6 indium(III) ions, 2 *anti*-$BPDC^{2-}$ ligands, and 10 $PDC^{2-}$ ligands in the asymmetry unit (Figure S4 in the SI). In this case, these charge-balancing $Et_2NH_2^+$ cations are disordered and also the byproducts of in situ decomposition of the DEF solvents.[16]

As shown in Figure S5 in the SI, a basic three-membered $[In_3(PDC)_3]^{3+}$ window is constructed from the combination of three indium(III) ions and three $PDC^{2-}$ ligands with a 120° bend angle. With the removal of two neighboring $PDC^{2-}$ edges from a complete $In_6PDC_{12}$ octahedron, five such $[In_3(PDC)_3]^{3+}$ windows tend to constitute an edge-removed hexanuclear $In_6PDC_{10}$ secondary building block (SBB) with three saturated indium(III) ions only coordinated by $PDC^{2-}$ ligands (In1, In2, and In5) and three unsaturated indium(III) ions coordinated by both $PDC^{2-}$ and auxiliary $BPDC^{2-}$ ligands (In3, In4, and In6) (Figure 1b). In this $In_6PDC_{10}$ SBB, we can see that each saturated indium(III) ion adopts a seven/eight-coordinated geometry via binding to nitrogen/oxygen centers from four bent $PDC^{2-}$ ligands to give a 4-connected node, while the unsaturated In3 and In4 ions are connected to three $PDC^{2-}$ and one $BPDC^{2-}$ ligands, and the unsaturated In6 is coordinated by two $PDC^{2-}$ and two $BPDC^{2-}$ ligands (Figure S6 in the SI). Meanwhile, each $PDC^{2-}$ ligand takes its carboxylate groups and pyridyl nitrogen atoms to link two separate indium(III) centers, and each $BPDC^{2-}$ ligand acts as the bridging linker to connect two indium(III) ions from two independent SBBs with all In−N and In−O bond lengths in the ranges of 2.276(7)−2.399(6) and 2.095(6)−2.569(6) Å, respectively.

We note that **InOF-11** is a discrete nanosized polyhedron symmetrically constituted from three $In_6PDC_{10}$ SBBs and six $BPDC^{2-}$ ligands. Upon extraction from the middle of the polyhedron of three indium(III) atoms from one opening orientation and three carbon atoms from another one, the cavity consists of two kinds of window sizes along the *c* axis, where the small three-membered carbon window has a side-length value of 3.86 Å, while the large three-membered indium window is 13.90 Å (Figure 2). There is an irregular reverse triangular prism in the cavity of the molecular polyhedron **InOF-11**, and careful examination of the model reveals that there is enough interspace left from the space-filling environment (Figure S7 in the SI).

The free volume of **InOF-11** with removal of disordered solvent molecules is calculated to be 60% (solvent area volume 53943 Å$^3$; unit cell volume 89729 Å$^3$). To confirm the

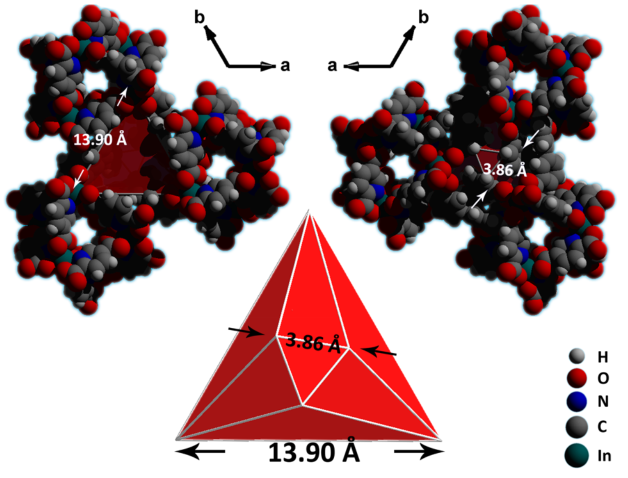


**Figure 2.** Two types of three-membered window sizes in the single-crystal structure for InOF-11.

architectural rigidity and permanent porosity, the $N_2$ sorption isotherms of desolvated samples at 77 K are determined with a saturated $N_2$ uptake of 115.5 $cm^3\ g^{-1}$ (Figure 3), corresponding to Brunauer−Emmett−Teller and Langmuir surface areas of 374 and 473 $m^2\ g^{-1}$, respectively. Meanwhile, we also investigate the volumetric $H_2$ uptake at 77 and 87 K. Both $H_2$ isotherms exhibit rapid kinetics and good reversibility without any hysteresis (Figure 3). The $H_2$ uptake capacity is up to 79.9 $cm^3\ g^{-1}$ (0.71 wt %) at 77 K and 1.0 bar and 58.6 $cm^3\ g^{-1}$ (0.52 wt %) at 87 K and 1.0 bar. Moreover, the isosteric heat of $H_2$ is simulated by the Clausius−Clapeyron equation, which is ∼7.17 kJ $mol^{-1}$ at zero coverage and increases slowly with incessant $H_2$ loading (Figures S11 and S12 in the SI).

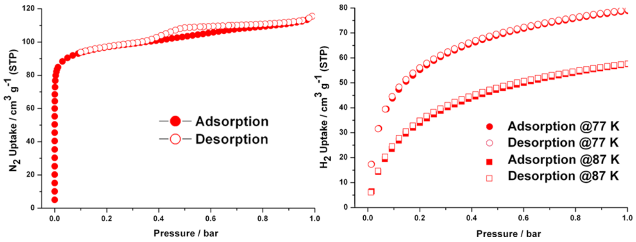


**Figure 3.** Experimental $N_2$ sorption isotherm at 77 K for **InOF-11**: (●) adsorption; (○) desorption. $H_2$ sorption isotherms are at 77 and 87 K.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Synthesis, crystallographic data in CIF format, supplementary figures, and TGA data, PXRD patterns, and gas sorption data of both compounds and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: hmc@fjirsm.ac.cn.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was financially supported by the 973 Program (Grant 2011CB932504), National Nature Science Foundation of China (Grant 21390392), "Strategic Priority Research Program" of the Chinese Academy of Sciences (Grant XDA09030102), and the CAS/SAFEA International Partnership Program for Creative Research Teams.

## ■ REFERENCES

(1) (a) Black, S. P.; Stefankiewicz, A. R.; Smulders, M. M. J.; Sattler, D.; Schalley, C. A.; Nitschke, J. R.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5749−5752. (b) Clingerman, D. J.; Kennedy, R. D.; Mondloch, J. E.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. K.; Mirkin, C. A. *Chem. Commun.* **2013**, *49*, 11485−11487.

(2) (a) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Côté, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110−7118. (b) Yan, Y.; Lin, X.; Yang, S.; Blake, A. J.; Dailly, A.; Champness, N. R.; Hubberstey, P.; Schroder, M. *Chem. Commun.* **2009**, 1025−1027.

(3) (a) Lu, W.; Yuan, D.; Yakovenko, A.; Zhou, H.-C. *Chem. Commun.* **2011**, *47*, 4968−4960. (b) Wu, R.; Qian, X.; Zhou, K.; Liu, H.; Yadian, B.; Wei, J.; Zhu, H.; Huang, Y. *J. Mater. Chem. A* **2013**, *1*, 14294−14299.

(4) (a) Yaghi, O. M.; Czaja, A. U.; Wang, B.; Furukawa, H.; Galatsis, K.; Wang, K. L. Google Patents, 2013. (b) Dutta, S.; Biswas, P. *Polyhedron* **2012**, *40*, 72−80.

(5) (a) Desmarets, C.; Ducarre, T.; Rager, M. N.; Gontard, G.; Amouri, H. *Materials* **2014**, *7*, 287−301. (b) Whitehead, M.; Turega, S.; Stephenson, A.; Hunter, C. A.; Ward, M. D. *Chem. Sci.* **2013**, *4*, 2744−2751.

(6) (a) Zhou, X. P.; Wu, Y.; Li, D. *J. Am. Chem. Soc.* **2013**, 16062−16065. (b) Reichel, F.; Clegg, J. K.; Gloe, K.; Gloe, K.; Weigand, J. J.; Reynolds, J. K.; Li, C.-G.; Aldrich-Wright, J. R.; Kepert, C. J.; Lindoy, L. F.; Yao, H.-C.; Li, F. *Inorg. Chem.* **2014**, *53*, 688−690. (c) Su, K.; Jiang, F.; Qian, J.; Wu, M.; Gai, Y.; Pan, J.; Yuan, D.; Hong, M. *Inorg. Chem.* **2014**, *53*, 18−20. (d) Su, K.; Jiang, F.; Qian, J.; Gai, Y.; Wu, M.; Bawaked, S. M.; Mokhtar, M.; Al-Thabaiti, S. A.; Hong, M. *Cryst. Growth Des.* **2014**, *14*, 3116−3123.

(7) (a) Liu, G.; Ju, Z.; Yuan, D.; Hong, M. *Inorg. Chem.* **2013**, *52*, 13815−13817. (b) Smulders, M. M.; Jiménez, A.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 6681−6695. (c) Xiong, K.; Jiang, F.; Gai, Y.; Yuan, D.; Chen, L.; Wu, M.; Su, K.; Hong, M. *Chem. Sci.* **2012**, *3*, 2321−2325. (d) Li, X. J.; Jiang, F. L.; Wu, M. Y.; Zhang, S. Q.; Zhou, Y. F.; Hong, M. C. *Inorg. Chem.* **2012**, *51*, 4116−4122.

(8) (a) Moulton, B.; Lu, J. J.; Mondal, A.; Zaworotko, M. J. *Chem. Commun.* **2001**, 863−864. (b) Eddaoudi, M.; Kim, J.; Wachter, J.; Chae, H.; O'Keeffe, M.; Yaghi, O. *J. Am. Chem. Soc.* **2001**, *123*, 4368−4369.

(9) Abourahma, H.; Coleman, A. W.; Moulton, B.; Rather, B.; Shahgaldian, P.; Zaworotko, M. J. *Chem. Commun.* **2001**, 2380.

(10) (a) Wang, H. N.; Liu, F. H.; Wang, X. L.; Shao, K. Z.; Su, Z. M. *J. Mater. Chem. A* **2013**, *1*, 13060−13063. (b) Wang, H. N.; Meng, X.; Yang, G.-S.; Wang, X. L.; Shao, K. Z.; Su, Z.-M.; Wang, C. G. *Chem. Commun.* **2011**, *47*, 7128−7130. (c) Li, J. R.; Timmons, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2009**, *131*, 6368−6369.

(11) (a) Hase, H. L.; Müller, C.; Schweig, A. *Tetrahedron* **1978**, *34*, 2983−2993. (b) Kostakis, G. E.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *253*, 2686. (c) Bu, F.; Xiao, S.-J. *CrystEngComm* **2010**, *12*, 3385−3387.

(12) (a) Qian, J. J.; Jiang, F. L.; Yuan, D. Q.; Li, X. J.; Zhang, L. J.; Su, K. Z.; Hong, M. C. *J. Mater. Chem. A* **2013**, *1*, 9075−9082. (b) Qian, J. J.; Jiang, F. L.; Yuan, D. Q.; Wu, M. Y.; Zhang, S. Q.; Zhang, L. J.; Hong, M. C. *Chem. Commun.* **2012**, *48*, 9696−9698.

(13) Liu, Y. L.; Kravtsov, V. C.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266−7267.

(14) Zheng, S. T.; Zuo, F.; Wu, T.; Irfanoglu, B.; Chou, C. S.; Nieto, R. A.; Feng, P. Y.; Bu, X. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 1849−1852.

(15) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972−983.

(16) (a) Huh, S.; Kwon, T. H.; Park, N.; Kim, S. J.; Kim, Y. *Chem. Commun.* **2009**, 4953−4955. (b) Zheng, S. T.; Bu, J. J.; Wu, T.; Chou, C. T.; Feng, P. Y.; Bu, X. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 8858−8862.