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Solvent-Controlled Assembly of ionic Metal-Organic Frameworks Based on Indium and Tetracarboxylate Ligand: Topology Variety and Gas Sorption Properties

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Abstract

Four Metal-Organic Frameworks (MOFs) based on Indium and tetracarboxylate ligand have been synthesized through regulation of the solvent conditions, the resulted compounds not only exhibited rich structural topologies (pts, soc and unique topologies), but also interesting charge reversal framework features. By regulating the solvent, different building units (indium monomer, trimer) have been generated in situ, and they are connected with the ligand to form ionic frameworks **1-4**, respectively. Among the synthesized four ionic frameworks, compounds **3** and **4** could keep their crystallinity upon heating temperature up to 300°C after fully removal of solvent guest molecules, they also exhibit the charge reversal framework features (**3** adopts an overall cationic framework, while **4** has an anionic framework). Both compounds **3** and **4** exhibit significant uptake capacity for CO₂ and H₂, besides that, compounds **3** and **4** also present excellent selective adsorption of CO₂ over N₂ and CH₄.

Introduction

Hydrogen storage and carbon dioxide capture have attracted lots of attention in recent years, since hydrogen is one of the most promising candidates for the replacement of current carbon-based energy source, and carbon dioxide is one of the main compounds of greenhouse gases, exploring high efficient adsorbents have been the keys. Various porous materials,¹⁻³ such as activated carbon, microporous organic polymers and zeolites have been extensively studied as adsorbents for these two gases, the common shortages of these traditional materials are either low capacities or difficult regeneration processes. Metal-organic frameworks (MOF), as an emerging class of porous materials, have been known for their intriguing structural diversities of architecture⁴⁻⁷ and promising potential applications in large areas,⁸⁻¹⁹ especially in gas sorption and separation.²⁰⁻²⁹ In order to develop MOFs for H₂ and CO₂ sorption, people once tried to design and synthesis elongated ligands to obtain frameworks with large surface area.³⁰⁻³² However, some research results show that large surface area is not necessarily advantageous for storing gas molecules in any conditions.^{33,34} According to the reported, the adsorption properties of H₂ and CO₂ in MOFs are varied with pressures. Generally, gas capacities depend on surface areas and pore volumes of the MOFs at high pressures, while at low pressure, the capacities mainly depend on the heats of adsorption for gas molecules adsorbed in MOFs, therefore, increasing the interaction strength between gas molecules and MOFs can be helpful for adsorption properties of MOFs.

As far as we know, there have been several strategies about enhancing interactions between gas molecules and MOFs, among these, the design of active sites on MOF structure has enjoyed great success,³⁵⁻³⁷ since at low pressure, both H₂ and CO₂ preferentially bind on the active sites that have large affinity. In addition, low-pressure gas adsorption can be also affected by catenation and interpenetration of framework.³⁸⁻⁴⁰ Recently, the charge-induced force in MOFs has been found have some influence for gas molecules and frameworks. However, the reported work are mainly anionic frameworks or introducing cations into MOFs by post-synthetic.^{41,42} Little research has been done on directly design and synthesis MOFs with charge reversal frameworks by using the same metal source and ligands, which should be contributed to the MOF structures mainly depends on the self-assemble of metal ions and organic ligands. Fortunately, solvent can also affect the conformation of frameworks.

In fact, solvent exhibits important roles for MOF synthesis,⁴³⁻⁴⁸ it not only can dissolve the reactants and promote the reaction work smoothly, but also act as template for conducting framework. Besides that, solvent has a large amount of species with different molecular polarity, which make it customary to screen a large number of solvents or solvent mixtures to find the best conditions for reactions. Since MOF is one kind of well-known crystalline material, solvent can not only greatly influence the mechanism of crystal growth but also incorporate into the crystalline lattice. If a solvent is in the pores or coordinated at the metal ion of the framework, the sorption properties would be also greatly affected not

only by the structure of the MOF but also the chemical environment of the pore surface. Here, four indium-organic frameworks have been successfully obtained by simple changing the solvent under the similar synthetic conditions. By regulating the solvent, different building units (indium monomer, trimer) have been generated in situ, and they are connected with the ligand to form ionic frameworks with pts, soc and unprecedented topologies

Experimental section

Materials and Methods.

The ligand H₄EBDC was prepared according to the literature.⁴⁹ All the other reagents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (XRD) data were collected on a Rigaku D/max-2550 diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The infrared (IR) spectra were recorded within the 4000-400 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The peak intensities are described in each spectra as very strong (vs), strong (s), medium (m), weak (w), and broad (br). The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The thermal gravimetric analyses (TG) were performed on NETZSCH STA 449C thermogravimetric analyzer used in air with a heating rate of $10^\circ\text{C min}^{-1}$. Low pressure gas sorption measurements were performed on a fully automated micropore gas analyzer Autosorb-1C (Quantachrome Instruments) at relative pressure up to 1 atm. The cryogenic temperatures were controlled using liquid nitrogen and liquid argon baths at temperatures of 77 K and 87 K, respectively.

Preparation of Compound 1: $[(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{EBDC})] \cdot 2\text{DMF} \cdot 2\text{DMSO} \cdot \text{H}_2\text{O}$

5,5'-(1,2-ethynediyl)bis(1,3-benzenedicarboxylic acid) (H_4EBDC) (10.0 mg, 0.0285 mmol), $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (40.0 mg, 0.102 mmol), DMF (1.0 mL), DMSO (1.0 mL), and HNO_3 (0.10 mL, 2.7M in DMF) were added to a vial, and the solution was heated to 85 °C for 36 h. Colorless polyhedral crystals were collected and air-dried (17.6 mg, 74% yield based on H_4EBDC). Elemental analysis calcd (%) for 1, $\text{C}_{30}\text{H}_{42}\text{N}_3\text{S}_2\text{O}_{13}\text{In}$: C 43.33, H 5.09, N 5.05, S 7.71; found: C 42.83, H 4.78, N 4.72, S 7.54.

IR spectrum (KBr, cm^{-1}): 3059(br), 2927(w), 2774(br), 2453(br), 1662(s), 1594(s), 1547(s), 1439(s), 1377(s), 1307(s), 1144(m), 1113(m), 1029(m), 939(s), 831(s), 783(s), 745(s), 603(w), 551(w), 480(m).

Preparation of compound 2: $[(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{EBDC})] \cdot \text{DMF}$

H_4EBDC (5.0 mg, 0.0143 mmol), $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (10.0 mg, 0.025 mmol), DMF (1 mL), and HNO_3 (0.2 mL, 2.7M in DMF) were added to a vial, and the solution was heated to 85°C for 36 h. Colorless cubic crystals were collected and air-dried (11.5 mg, 69% yield based on H_4EBDC)

Elemental analysis calcd (%) for 2, $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_9\text{In}$: C 47.28, H 3.62, N 4.79; found: C 48.09, H 3.76, N 4.62.

IR spectrum (KBr, cm^{-1}): 3072(br), 2774(br), 2431(br), 1639(s), 1578(s), 1433(s), 1388(s), 1296(s), 1273(m), 1190(w), 1106(w), 1013(m), 923(w), 824(w), 770(s), 725(m), 725(w), 664(w), 490(w).

Preparation of compound 3: $[\text{In}_3\text{O}(\text{EBDC})_{1.5}(\text{H}_2\text{O})_3]$

H₄EBDC (10.0 mg, 0.0285 mmol), In(NO₃)₃·5H₂O (40.0 mg, 0.102 mmol), DMF (1.0 mL), CH₃CN (1.0 mL), and HNO₃ (0.20 mL, 2.7M in DMA) were added to a vial, and the solution was heated to 85°C for 36 h. Colorless polyhedral crystals were collected and air-dried (25.2 mg, 67% yield based on H₄EBDC).

Elemental analysis calcd (%) for 3, C₄₀H_{43.5}N₆O_{22.75}In₃ : C 36.49, H 3.33, N 6.38; found: C 35.61, H 3.45, N 6.72.

IR spectrum (KBr, cm⁻¹): 3415(br), 3072(w), 2927(w), 2465(br), 1642(s), 1586(s), 1433(s), 1366(s), 1092(m), 1009(m), 920(m), 783(s), 725(s), 633(s), 551(m), 501(m), 436(m).

Preparation of compound 4:

H₄EBDC (10.0 mg, 0.0285 mmol), In(NO₃)₃·5H₂O (40.0 mg, 0.102 mmol), DMA (1.0 mL), CH₃CN (1.0 mL), and HNO₃ (0.10 mL, 2.7M in DMA) were added to a vial, and the solution was heated to 85°C for 36 h. Colorless trigonal crystals were collected and air-dried (15.8mg, 71% yield based on H₄EBDC).

Elemental analysis calcd (%) for 4, C₁₆₈H₁₈₇N₂₂O₇₄In₉ : C 42.64, H 3.98, N 6.51; found: C 40.59, H 3.48, N 6.32.

IR spectrum (KBr, cm⁻¹): 3384br, 3207br, 3072w, 2934w, 2774w, 2431w, 1639s, 1578s, 1433s, 1388s, 1296s, 1273m, 1190w, 1106w, 1013m, 923w, 824m, 770s, 725s, 673w, 634m, 612br, 551w, 490m, 436m.

The as-synthesized compounds **1-4** were insoluble in water and common organic

solvents. The phase purity of as-synthesized samples was confirmed by the evident similarities between the calculated and the experimental X-ray powder diffraction patterns (see Supporting Information Figure S1).

X-ray structure determinations.

Suitable single-crystals of **1-4** were selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Bruker Smart CCD diffractometer for **1-3** and a Bruker SMART Apex 2 diffractometer for **4** by using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT processing program and the structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL program. The solvent molecules in compounds **1**, **2** and **4** are highly disordered, and attempts to locate and refine the solvent peaks were not reasonable. SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules. The resulting new files were used to further refine the structures.

The guest molecular formulas of **1-4** are ascertained from elemental analysis, thermogravimetric analysis, and IR spectroscopy, the formulas are suggested to be $[(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{EBDC})]\cdot 2\text{DMF}\cdot 2\text{DMSO}\cdot \text{H}_2\text{O}$ for **1**, $[(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{EBDC})]\cdot 2\text{DMF}$ for **2**, $[\text{In}_3\text{O}(\text{EBDC})_{1.5}(\text{H}_2\text{O})_3][\text{NO}_3]\cdot 2\text{DMF}\cdot 2(\text{CH}_3\text{CN})\cdot 0.75(\text{H}_2\text{O})$ for **3**, and $[(\text{CH}_3)_2\text{NH}_2][\text{In}_3\text{O}(\text{EBDC})_{1.5}(\text{H}_2\text{O})_3]_2[\text{In}(\text{EBDC})]_3\cdot 8\text{DMF}\cdot 13(\text{CH}_3\text{CN})\cdot 10(\text{H}_2\text{O})$ for **4**. The CCDC-860713-860716 containing the supplementary crystallographic data for this manuscript can be obtained free of charge from the Cambridge Crystallographic

Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Additional details are presented in Table 1.

Results and discussion

Here, a solvent-controlled synthesis of crystalline MOFs has been described (Scheme 1), indium nitride and a tetracarboxylate ligand have been chosen as the metal node and linker, respectively. By regulation of the solvent conditions, four MOFs with different structures have been constructed, the resulted compounds are anionic or cationic frameworks, and exhibiting pts, soc and unprecedented topologies. The structures of the frameworks have been characterized in details, together with their gas sorption and separation properties.

Crystal Structure of 1. As shown in Fig.1, reaction between 5,5'-(1,2-ethynediyl)bis(1,3-benzenedicarboxylic acid) (H_4EBDC) and $In(NO_3)_3 \cdot 5H_2O$ in a N,N -dimethylformamide (DMF)/Dimethylsulfoxide (DMSO) solution in the presence of HNO_3 yields a homogeneous microcrystalline material, characterized and formulated by elemental analysis and single-crystal X-ray diffraction (SCD) studies as $[(CH_3)_2NH_2][In(EBDC)] \cdot 2DMF \cdot 2DMSO \cdot H_2O$ (Compound 1). In the crystal structure of 1, each In^{3+} centre is eight-coordinated to oxygen atoms of four carboxylate groups from four $EBDC^{4-}$ ligands. Each ligands binds to four separate In^{3+} centres. Accordingly, the inorganic ($[In(O_2C)_4]^-$) and organic ($EBDC^{4-}$) MBBs (molecular-building-block) can be rationalized as having tetrahedral and square-planar geometry, respectively (Fig 1a). The anionic framework

in **1** has pts topology and contains two types of intersecting channels along the *c* and *b* axis, with an approximate diameter of 6.655×5.567 Å and 5.567×5.567 Å (point-to-point and including van der Waals radii, Fig. 1b and 1c). Since both the inorganic ($[\text{In}(\text{O}_2\text{C})_4]^-$) and organic (EBDC^{4-}) MBBs can be simplified into 4-connected node, the resulting structure of **1** is a (4,4)-connected pts network (Figure 1d) with $[4^2.8^4]$ tile (Figure 1e). It is worth noting that the charge is balanced by $[(\text{CH}_3)_2\text{NH}_2]^+$ counter ions, which are from the decomposition of the DMF solvent.

Crystal Structure of 2. Similarly reaction of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and H_4EBDC but only using DMF as solvent, permitted the construction of the unprecedented, novel MOF, formulated by elemental analysis and SCD analysis as $[(\text{CH}_3)_2\text{NH}_2][\text{In}(\text{EBDC})] \cdot \text{DMF}$ (Compound **2**). The 3-periodic anionic MOF consists of two crystallographically independent In^{3+} atoms and two EBDC^{4-} units. Each In^{3+} atom is coordinated by four bidentate chelating carboxylate groups from four EBDC^{4-} ligands to form a tetrahedral node. Each ligand binds to four separate In^{3+} centres to form a square-planar node. The assembly of these two types of nodes generates a distinctive 3D framework (Fig 2a and table S1), which is the first report so far to the best of our knowledge. Compound **2** contains two types of channels, i.e. rectangular and triangular in shape and measure approximately of 6.366×4.420 Å and 5.174×5.174 Å, respectively (point-to-point and including van der Waals radii, Fig. 2b and 2c). The simplified two 4-connected nodes alternately connected to form a new topology (Fig.2d) and with unique tile shown in Fig. 2e.

Crystal Structure of 3. Similar reaction conditions as for **2** in the presence of 1mL

CH₃CN and 0.2 mL HNO₃ in DMA (2.7M) give polyhedral crystals formulated as [In₃O(EBDC)_{1.5}(H₂O)₃] [NO₃]₂·2DMF·2(CH₃CN)·0.75(H₂O) (Compound **3**). The crystallographic analysis of **3** revealed that it crystallizes in the cubic space group Pm-3n and its structure contains indium trimer building blocks, [In₃O(O₂C)₆(H₂O)₃]⁺, whereby each indium cation adopts an octahedral [InO₅(H₂O)] coordination environment. Each trimer unit is linked by six separate organic linkers to produce a novel 3D structure. The indium trimeric building units can be rationalized as a 6-connected trigonal prismatic building unit and can be regarded as a pseudo-octahedron. The organic H₄EBDC linker can be simplified as 4-connected rectangular-planar node. Accordingly, the assembly of such 4- and 6-connected nodes results in the formation of an edge-transitive 3-periodic network with **soc** topology (Fig 3a). To date, only two examples of trimeric building unit based MOFs with **soc** topology have been reported.⁵⁰ The overall framework of compound **3** is cationic and the charge balance is provided by disordered [NO₃]⁻ anions. Compound **3** exhibits an interesting pore system because it contains two well-defined types of infinite channels, namely an intersecting hydrophobic and hydrophilic channel system. The relative span of the cage is estimated to be 14.96 Å, while the channels measure approximately 7.66 Å (point-to-point and including van der Waals radii, Fig. 3b). The simplified 4- and 6-connected nodes alternately connected to form (4, 6)-connected network (Fig.3c), with two distinct tiles: [4⁴.6²] and [4⁶.8⁹] (Fig. 3d).

Crystal Structure of 4. Under similar reaction conditions for **3**, just changing the DMF solvent to DMA, led to the formation of a novel MOF with the formula

(Compound **4**). Compound **4** crystallizes in the chiral space group R32, and contains two distinctly different In^{3+} configurations: the monomeric $[\text{In}(\text{O}_2\text{C})_4]^-$ site and the trimeric $[\text{In}_3\text{O}(\text{O}_2\text{C})_6(\text{H}_2\text{O})_3]^+$ clusters. Each H_4EBDC ligand is linked by two monomeric In^{3+} centres and two trimeric building units in a cis configuration to generate a novel 3D anionic network (Fig 4a). Compound **4** contains three types of channels, the space-filling representations of the framework showing the channels along [100], [110] and [111] directions, respectively (Fig. 4b, c, d). If the monomeric $[\text{In}(\text{O}_2\text{C})_4]^-$ building unit is simplified as 4-connected tetrahedral node, the trimer as 6-connected node, and the H_4EBDC ligand served as 4-connected square node, the 3D framework of **4** can be simplified as a rare, ternary (4,4,6)-connected net (Fig.4e) with four distinct tiles: $[6^3]$, $[6^4]$, $[6^6]$ and $[4^6 \cdot 6^8]$ (Fig. 4f). To the best of our knowledge, only one example of In-MOF contains both indium monomer and trimer units have been reported.⁵¹

If we kept the monomer $[\text{In}(\text{O}_2\text{C})_4]^-$ and trimer $[\text{In}_3\text{O}(\text{O}_2\text{C})_6(\text{H}_2\text{O})_3]^+$ as still 4 or 6 connected nodes, while the tetracarboxylate ligand is simplified as two 3-*c* branch points, which is according to the latest topological analysis method,⁵² the topologies of compounds **1-4** would be totally different (see Fig S5-8), the 3D frameworks of **1-2** can be simplified as (3,4)-connected net with Schläfli symbol of $\{6^2 \cdot 8^4\}\{6^2 \cdot 8\}_2$ and $\{6 \cdot 8^2\}_2\{6 \cdot 8^5\}\{6^2 \cdot 8^4\}\{6^2 \cdot 8\}_2$, respectively, while compound **3** can be simplified as (3,6)-connected net with Schläfli symbol of $\{5^3\}_3\{5^6 \cdot 8^6 \cdot 9^3\}$, and compound **4** is (3,4,6)-connected net with Schläfli symbol of $\{6 \cdot 7^2\}_{12}\{6^3 \cdot 7^{12}\}_2\{7^5 \cdot 8\}_3$. The

calculated result by TOPOS for the linker simplified as 3 or 4 connected node have been illustrated in table S2.

Thermogravimetric Analysis.

The thermal stability of compounds **1-4** have been evaluated in the temperature range of 35-700°C under an air atmosphere (Supporting Information Figure S3). Thermogravimetric analysis for compound **1** shows a weight loss of 43.84 % (calcd: 44.08 %) between 35 and 300°C which corresponding to the loss of C₃H₇ON, H₂O, C₂H₆SO and (CH₃)₂NH₂ guest in the cavity. the further weight loss of 39.50% between 300 and 500 °C should be attributed to the release of organic H₄EBDC ligands (calcd: 39.23%). XRD studies indicated that the final product, upon calcinations above 500°C, is a main phase of In₂O₃ (JCPDS: 65-3170).

Thermogravimetric analysis for compound **2** shows a weight loss of 20.55 % (calcd: 20.40 %) between 35 and 160°C which corresponding to the loss of C₃H₇ON and (CH₃)₂NH₂ guest in the cavity. On further heating, a two-step weight loss of 55.57% between 160 and 500 °C should be attributed to the release of organic H₄EBDC ligands (calcd: 55.84%). XRD studies indicated that the final product, upon calcinations above 500°C, is a main phase of In₂O₃ (JCPDS: 65-3170).

For compound **3**, Thermogravimetric analysis shows a weight loss of 32.98 % (calcd: 32.73%) between 35 and 380°C, which corresponding to the loss of C₃H₇ON, CH₃CN, H₂O, and NO₃⁻ guest in the cavity. The further weight loss of 35.42% between 380 and 500 °C should be attributed to the release of organic H₄EBDC ligands (calcd:

35.64%). The different temperature XRD studies show the framework of compound **3** was stable to 300°C. XRD studies indicated that the final product, upon calcinations above 500°C, is a main phase of In₂O₃ (JCPDS: 65-3170).

Thermogravimetric analysis for compound **4** shows a weight loss of 33.20% (calcd: 33.07 %) between 35 and 350°C, which corresponding to the loss of C₄H₉ON, CH₃CN, H₂O, and (CH₃)₂NH₂ guest in the cavity. The further weight loss of 41.35% between 350 and 520 °C should be attributed to the release of organic H₄EBDC ligands (calcd: 40.52%). XRD studies indicated that the final product, upon calcinations above 500°C, is a main phase of In₂O₃ (JCPDS: 65-3170).

Gas Adsorption Properties.

The total solvent-accessible volumes for **1**, **2**, **3**, and **4** were estimated to be ~73.1%, ~72.5%, ~64.7%, and ~67.1%, respectively, by summing voxels more than 1.2 Å away from the framework using PLATON software. Though compounds **1** and **2** have large solvent-accessible volumes in theory, neither of them have any adsorption for N₂ at low temperature, which should be due to the framework collapsed after removing the solvents in the pores. In contrast to compounds **1** and **2**, it is worth noting that both compounds **3** and **4** could maintain their crystallinity upon heating temperature up to 300°C after full removal of solvent guest molecules (Fig. S2). The Argon adsorption/desorption studies of **3** and **4** revealed that both have reversible type I isotherms (Fig. 5), indicating that they are microporous. The Langmuir and BET surface area for **3** were estimated to be 1548 and 1285 m²/g. The calculated pore

volume was estimated to be $0.53 \text{ cm}^3/\text{g}$. The Langmuir and BET surface area, and free pore volume for **4**, estimated at 1355, $1129 \text{ m}^2/\text{g}$ and $0.49 \text{ cm}^3 \text{ g}^{-1}$. The surface area of **4** is higher than most of known anionic In-MOFs ($190\text{--}1441 \text{ m}^2/\text{g}$).^{51, 53-55}

Due to the charge reversal framework features of **3** and **4** (**3** adopts an overall cationic framework, while **4** has an anionic framework), it is interesting to evaluate the impact of the pore size, shape and the charge on the uptake and sorption energetics of H_2 and CO_2 gases. **3** and **4** exhibit significant uptake capacity for CO_2 and H_2 . The CO_2 uptake at 273 K and 1 atm for **3** and **4** are $91.0 \text{ cm}^3/\text{g}$ and $82.5 \text{ cm}^3/\text{g}$, respectively (Fig. 6). Although abundant MOF structures have been reported, MOFs with CO_2 uptake $>90 \text{ cm}^3/\text{g}$ at 273 K and 1 atm are still rare.⁵⁶ In the case of H_2 , **3** and **4** revealed a storage capacity of 1.84 wt % and 1.45 wt % at 77 K and 1 atm, respectively (Fig. 7). The Q_{st} for CO_2 was found to be higher in the entire studied range for **4** with a more pronounced difference at low loading, 35.2 kJ mol^{-1} vs. 29.7 kJ mol^{-1} for **3** (Fig. 8a).

Since the isosteric heats of CO_2 adsorption (Q_{st}) represents the strength of the interactions between CO_2 molecules and the framework lattice, there are two different inorganic MBBs in compound **4**, which would provide more open metal sites, besides that, some Lewis basic amines also occupied in the pores, compound **4** has smaller pores but the pores are large enough for adsorption CO_2 , all these might result stronger interactions between the framework and adsorbed CO_2 , and then resulted higher Q_{st} for compound **4** compared to **3**.

And for H_2 , the isosteric heat of adsorption (Q_{st}) of **4** was also found to be higher than

3 (7.2 vs. 6.7 kJ mol⁻¹ at low loading) (Fig. 8b). These observed improvements on the H₂ and CO₂ sorption energetics in the case of **4** is likely attributed to the narrow pore size and charge effect. CO₂, N₂ and CH₄ adsorption isotherms for compounds **3** and **4** have been also measured. As shown in Fig. 9, both compounds **3** (a) and **4** (b) exhibit a higher affinity and capacity for CO₂ than for other gases. The CO₂ uptake at 8000 mbar and 298 K for compounds **3** and **4** are 6.92 and 8.41 mmol g⁻¹, respectively, and very little N₂ uptake capacity (1.25 and 1.02 mmol g⁻¹, respectively). On the basis of CO₂, CH₄ and N₂ adsorption isotherms measured at 298 K, initial slopes of adsorption isotherms were estimated and then used to estimate the CO₂/CH₄ and CO₂/N₂ selectivities (as ratios of the initial slopes) (Fig. 9). As a result, the CO₂/N₂ selectivity of compounds **3** and **4** are 17:1 and 21:1, respectively. The CO₂/CH₄ selectivity are 4:1 and 6:1 respectively. To our knowledge, the CO₂/N₂ and CO₂/CH₄ selectivities are comparable to ZIF-68 and porous carbon monolith.^{57,58}

Conclusions

In summary, four indium-organic frameworks have been successfully synthesized by simple changing the solvent under the similar synthetic conditions. These materials exhibit rich structural chemistry and topologies. Both compounds **3** and **4** exhibit significant uptake capacity for CO₂ and H₂, and compound **4** displays improved sorption energetics due to its narrow pore size and charge effect compared to **3**. The ability to generate different building units (indium monomer, trimer, combination of monomer and trimer) in situ, by controlling the solvent system, presents a fruitful

route for the design of novel porous MOF materials with different topologies and ionic frameworks.

ASSOCIATED CONTENT

Supporting Information Available

Crystallographic data in CIF format, Powder XRD patterns, IR spectra, and TG curves, as well as some structure views of the compounds. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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Caption of Figures:

Scheme 1. Four indium-organic frameworks have been synthesized by changing the solvent under similar synthetic conditions.

Figure 1. A description of the structure of **1**: (a) each In^{3+} centre is eight-coordinated to oxygen atoms of four carboxylate groups from four EBDC^{4-} ligands, each ligand binds to four separate In^{3+} centres, the inorganic ($[\text{In}(\text{O}_2\text{C})_4]^-$) node and organic (EBDC^{4-}) node are rationalized as having tetrahedral and square-planar geometry, respectively, these two types of nodes alternately connected to form pts topology framework; (b) and c) Space-filling views for **1** showing the channels along $[010]$ and $[001]$ directions, respectively; (d) Ball-and-stick representation of **1** with the indium tetrahedral node shown in green and the square planar EBDC node shown in red; (e) Natural tiling representation of **1**. Color code: In, green; C, gray; O, red.

Figure 2. A description of the structure of **2**: (a) the inorganic ($[\text{In}(\text{O}_2\text{C})_4]^-$) node and organic (EBDC^{4-}) node are rationalized as having tetrahedral and square-planar geometry, respectively, the two types of nodes alternately connected to form a new type of topology framework; (b) and (c) Space-filling representations of the framework of compound **2** showing the channels along $[001]$ and $[110]$ directions, respectively; (d) Ball-and-stick representation of **2** with the indium tetrahedral node shown in green and the square planar EBDC node shown in red; (e) Natural tiling representation of **2**. Color code: In, green; C, gray; O, red.

Figure 3. A description of the structure of **3**: (a) the inorganic indium trimer node $[\text{In}_3\text{O}(\text{O}_2\text{C})_6(\text{H}_2\text{O})_3]^+$ and organic (EBDC^{4-}) node are rationalized as having pseudo-octahedron and square-planar geometry, respectively, the two nodes

alternately connected to result in the formation of an edge-transitive 3-periodic network with soc topology; (b) Space-filling representations of the framework of compound **3** showing the channels along [100] direction; (c) Schematic and Ball-and-stick representations of **3** with **soc** topology; (d) Natural tiling representation of **soc** net.

Figure 4. A description of the structure of **4**: (a) the inorganic monomeric $[\text{In}(\text{O}_2\text{C})_4]^-$ node and the trimeric $[\text{In}_3\text{O}(\text{O}_2\text{C})_6(\text{H}_2\text{O})_3]^+$ node can be rationalized as tetrahedral and pseudo-octahedron geometry, respectively, the organic (EBDC^{4-}) is still rationalized as square-planar geometry, each EBDC ligand is linked by two monomeric In^{3+} nodes and two trimeric nodes in a *cis* configuration to generate a novel topological network; (b), (c) and (d) Space-filling representations of the framework of compound **4** showing the channels along [100], [110] and [111] directions, respectively; (e) Ball-and-stick representation of **4** with the indium tetrahedral nodes shown in green, indium trigonal prism nodes shown in green, and the square planar EBDC^{4-} nodes shown in red; (f) Natural tiling representation of **4**.

Figure 5. Argon gas sorption isotherms and pore size distribution analysis for compounds **3** (a and b) and **4** (c and d) by using the cylindrical NLDFT model.

Figure 6. CO_2 adsorption isotherms of compounds **3** (a) and **4** (b)

Figure 7. H_2 adsorption isotherms of compounds **3** (a) and **4** (b)

Figure 8. Variation of the thermodynamic parameters of isosteric heat of adsorption (Q_{st}) for CO_2 and H_2 uptakes in compounds **3** (a) and **4** (b).

Figure 9. CO_2 , N_2 and CH_4 adsorption isotherms for compound **3** (a) and compound **4**

(b) at 298K; Initial slope calculation for CO₂, N₂ and CH₄ isotherms collected at 298K for compound **3** (c) and compound **4** (d). (CO₂: red squares; CH₄: green circles; N₂: blue triangles).

Table 1. Crystal data and structure refinement for compounds **1-4**.

	1	2	3	4
empirical formula	C ₃₀ H ₄₂ InN ₃ O ₁₃ S ₂	C ₂₃ H ₂₁ InN ₂ O ₉	C ₄₀ H _{43.50} In ₃ N ₆ O _{22.75}	C ₁₀₈ H ₃₆ In ₉ O ₅₆
formula weight	831.61	584.24	1316.77	3262.75
temperature (K)	296(2)	293(2)	293(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	Tetragonal	Orthorhombic	Cubic	Hexagonal
space group	P4 ₂ /mmc	Pbam	Pm-3n	R3 ₂
<i>a</i> (Å)	9.9798(2)	25.161(5)	22.6230(4)	22.1811(12)
<i>b</i> (Å)	9.9798(2)	35.988(7)	22.6230(4)	22.1811(12)
<i>c</i> (Å)	23.1921(8)	10.021(2)	22.6230(4)	41.961(5)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	120
<i>V</i> (Å ³)	2309.85(10)	9074(3)	11578.5(4)	17879(3)
<i>Z</i>	2	8	8	3
<i>D</i> _{calc} (g/cm ³)	1.196	0.855	1.511	0.909
μ (mm ⁻¹)	0.653	0.550	1.260	0.902
<i>F</i> (000)	856	2352	5236	4719
θ range (deg)	1.76 - 25	1.62 – 28.38	1.80 – 25.68	1.17 – 28.30
Reflections collected	12713	65514	64666	43519
Reflections unique (<i>R</i> _{int})	1182 (0.0288)	11948 (0.0824)	1935 (0.1768)	9788 (0.1132)
Goodness-of-fit on <i>F</i> ²	1.371	1.088	1.074	0.956
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0667, 0.2629	0.0879, 0.2669	0.0809, 0.1972	0.0952, 0.2262
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0753, 0.2687	0.1388, 0.3065	0.1454, 0.2571	0.1208, 0.2439

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

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Solvent-Controlled Assembly of ionic Metal-Organic Frameworks Based on Indium and Tetracarboxylate Ligand: Topology Variety and Gas Sorption Properties

Bing Zheng,^{a,d} Xiaodong Sun,^a Guanghua Li,^a Amy J. Cairns,^b Victor Ch. Kravtsov,^c Qisheng Huo,^a Yunling Liu,^{*a} and Mohamed Eddaoudi^{*b}

Four metal-organic frameworks (MOFs) based on indium and tetracarboxylate ligand have been synthesized through regulation of the solvent conditions, the resulted compounds are anionic or cationic frameworks with pts, soc and unprecedented topologies and exhibiting high H₂ and CO₂ uptake capacity.