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Two Stable 3D Porous Metal-Organic Frameworks with High Performance for Gas Adsorption and Separation

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Two porous MOFs, [NO\textsubscript{3}]\{In\textsubscript{3}OL\}_3\cdot4\text{DMF}\cdot3\text{H}_2\text{O} (JLU-Liu\textsubscript{18}), [CdL]·0.5\text{DMF} (JLU-Liu\textsubscript{19}) \ H_2L = \text{pyridine-3,5-bis(phenyl-4-carboxylic acid)}, have been solvothermally synthesized and structurally characterized. Both of the two compounds possess saturated coordination metal centre without open metal sites (OMSs) leading to the remarkable thermal and water vapour stability. JLU-Liu\textsubscript{18} displays a rare occurrence of 9-connected trinuclear \{In\textsubscript{3}O(CO\textsubscript{3})\textsubscript{6}N\}_3 secondary building units (SBUs) in a porous crystal with high adsorption for small molecule gases, especially for CO\textsubscript{2} (129 and 400 cm\textsuperscript{-1} at 273 K and 195 K under 1 bar). It also performs commendable selectivity for O\textsubscript{2} over N\textsubscript{2} and CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{2} over CH\textsubscript{4}. JLU-Liu\textsubscript{19} possesses outstanding performance for sieving small gases owing to its ultramicropores of 3.5 Å. Both of the two MOFs are promising materials for gas adsorption and purification.

Introduction

Environment and energy problems are hot issues concerned by the global world all this time. In recent years, the dramatic increasing level of atmospheric CO\textsubscript{2} resulting from anthropogenic emissions is one of the greatest environmental concerns facing our civilization.\textsuperscript{1-3} Furthermore, regardless of the greenhouse effect, CO\textsubscript{2} is also an impurity in natural gas, biogas, post-combustion flue gases generated from coal-fired power stations and many other gas streams which will reduce energy conversion efficiency.\textsuperscript{4,6} Methane as the primary component of natural gas and biogas is considerable cleaner energy source for our daily life.\textsuperscript{7} However, a quantity of hydrocarbon impurities will reduce the utilization efficiency of methane. Therefore, exploring new materials that not only efficiently capture and sequestrate CO\textsubscript{2} but also purify methane from natural gas and biogas in order to improve the conversion rate is an issue that needed to be addressed as a matter of urgency.

Porous metal-organic frameworks (MOFs), which offer large surface areas, high void volumes, tunable pore size and chemical tenability, have been actively pursued in the past decades on account of their potential applications in gas storage and separation technologies towards small molecules.\textsuperscript{8, 9} The promising performance is owing to the micropores within MOFs can be tuned by selecting kinds of ligands with different functional groups and diverse metal cores to construct a variety of metal-containing secondary building units (SBUs). The metal-containing SBUs can be mononuclear, bi-nuclear, tri-}

nuclear, tetra-nuclear, hexa-nuclear, and even more.\textsuperscript{10} Particularly, the MOFs materials based on multi-nuclear SBUs exhibit high stability and permanent porosity after desolvation. Herein, we choose the heterofunctional ligand pyridine-3,5-bis(phenyl-4-carboxylic acid) (H\textsubscript{2}L) which containing carboxylate and pyridyl groups to construct new MOFs materials based on the following aspect: 1) the diverse coordinate mode of -COOH and N donor with metal centre is coordination without open metal sites (OMSs), which remarkably increasing the thermal and water vapour stability.\textsuperscript{11} In the two compounds, the terminal of metal ions is coordinated by pyridine groups leading to the metal centre saturated coordination without open metal sites (OMSs), which remarkably increasing the thermal and water vapour stability. To the best of our knowledge, most of the In-MOFs based on trinuclear \{In\textsubscript{3}O(C\textsubscript{2}H\textsubscript{3}CR\textsubscript{2})\textsubscript{6} \text{SBUs is usually 6-connected and possesses OMSs. However, JLU-Liu18 is a rare occurrence of 9-connected \{In\textsubscript{3}O(CO\textsubscript{3})\textsubscript{6}N\}_3 \text{SBUs. Compared with the nonporous MOF constructed by a shorter ligand, JLU-Liu19 with ultramicropores exhibits extraordinary and specific carbon capture and separation (CCS). It is worth noting that two compounds with air and water vapour stability exhibit high-}
capacity adsorption and high-efficiency separation of small gases. The selectivity for CO₂/CH₄, C₂H₆/CH₄ and C₃H₆/CH₄ were appraised by the ideal adsorbed solution theory (IAST).

**Experimental**

**Materials and Methods**

All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Elemental analyses (C, H, and N) were achieved by vario MICRO (Elementar, Germany). The thermal gravimetric analyses (TGA) were performed on TGA Q500 thermogravimetric analyzer used in air with a heating rate of 10 °C min⁻¹.

**Synthesis of JLU-Liu18**

Single crystals of compound JLU-Liu18 were obtained by solvothermal reaction of In(NO₃)₃·4H₂O (12 mg 0.03 mmol) and H₂L (5 mg, 0.015 mmol) in N,N-dimethylformamide (DMF) (2 mL)/1,4-dioxane (DOA) (0.6 mL) with HNO₃ (0.225 mL) (2.2 mL HNO₃ in 10 mL DMF) at 105 °C for 24 hours. The mixture was then cooled to room temperature. Colorless cubic crystals were obtained and air-dried (yield 40%, based on H₂L). Elemental analysis calcd (%) for JLU-Liu18: [NO₃][In₄O(C₂H₁₁N(NO₃)₂)·4DMF·3H₂O: C, 48.13; H, 3.98; N, 7.03. The experimental PXRD pattern is in good agreement with the simulated one based on the single-crystal X-ray data, indicating the purity of the as-synthesized product (Fig. S1†).

**Synthesis of JLU-Liu19**

Colorless block crystals of JLU-Liu19 were obtained by solvothermal reaction of Cd(NO₃)₂·4H₂O (5 mg, 0.016 mmol) and H₂L (5 mg, 0.015 mmol) in DMF (1 mL) with HNO₃ (0.2 mL) (2.2 mL HNO₃ in 10 mL DMF) at 105 °C for 24 hours. The mixture was then cooled to room temperature. The crystals were collected and washed with DMF, then dried in air (yield 45% based on H₂L). Elemental analysis calcd (%) for JLU-Liu19: [Cd(C₂H₁₁N(NO₃)₂)]·0.5DMF·3H₂O: C, 52.79; H, 3.11; N, 4.5%; Found: C, 52.01; H, 3.05; N, 4.28. The experimental PXRD pattern agrees well with the simulated one based on the single-crystal X-ray data, indicating the purity of the as-synthesized product (Fig. S2†).

**X-ray Crystallography**

Crystallographic data for two compounds were collected on a Bruker Apex II CCD diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F² using version 5.1. All the metal atoms were located first, and then the oxygen and carbon atoms of the compound were subsequently found in difference Fourier maps. The hydrogen atoms of the ligand were placed geometrically. All non-hydrogen atoms were refined anisotropically. The final formula was derived from crystallographic data combined with elemental and thermogravimetric analysis data. The detailed crystallographic data and selected bond lengths and angles for two compounds are listed in Table S1-3†, respectively. Crystallographic data for JLU-Liu18 (1403645) and JLU-Liu19 (1402651) have been deposited with Cambridge Crystallographic Data Centre. Data can be obtained free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif. Topology information for the two compounds were calculated by TOPOS 4.0.¹⁸

**Gas adsorption measurements**

The N₂, H₂, O₂, Ar, CO₂, CH₄, C₂H₆ and C₃H₆ gas adsorption measurements were performed on a Micromeritics ASAP 2420 and a Micromeritics ASAP 2020 instrument. Before gas adsorption measurements, the samples were exchanged with fresh methanol 10 times for 2 days to completely remove the non-volatile solvent molecules, which can be proved by TGA analysis (Fig. S3-4†). The sample was activated by drying under a dynamic vacuum at room temperature for 1 hour. Before the measurement, the sample was dried again by using the ‘outgas’ function of the surface area analyzer for 10 h at 100 °C.

**Results and discussion**

Single-crystal X-ray diffraction analysis shows that JLU-Liu18 crystallizes in the R-3c space group. As shown in Figure 1a, JLU-Liu18 adopt the [In₃(µ₁-O)(CO₂)₃N₃] SBU with the bridging-O residing at the centre of the three indium atoms with In-O bonds of 2.0289(3)Å, while the three indium atoms are chelated by six carboxylate groups and three pyridyl groups. Although there are many similar SBUs composed of other metals have been reported in the literature,¹⁹,²⁴ the 9-connected [In₃(µ₁-O)(CO₂)₃N₃] trimer is really rare in reported InMOFs. From a topological point of view, the trinuclear indium cluster can be simplified to be a 9-connected node with tetrakaidecahedron geometry, and the ligand can be regarded as 3-connected node with triangular geometry. Consequently, the structure of JLU-Liu18 can be described as a (3, 9)-connected network, which belongs to xmx⁴⁻²⁵ topology with a Schläfli symbol of (4²6)₆(4⁶6⁵²⁵)₈. Furthermore, regarding the trinuclear indium cluster as a node and linked by the tridentate ligand, distorted cubic cages with a diameter of about 8.3 Å regardless of the Van der Waals radius can be clearly seen in the Figure 1c. As shown in Figure 1c, there are two types of tile of [4.6]² and [6]⁶. The PLATON calculation reveals a total solvent-accessible volume equal of 9488.4 Å³ per unit cell, which counts for approximately 62.0% of the cell volume, exhibiting high porosity and offering possibilities for gas adsorption.

The X-ray crystallographic analysis revealed that JLU-Liu19 crystallizes in the C2/c space group. As depicted in Figure 2a, each cadmium ion is five coordinated to four oxygen atoms and one nitrogen atom from five ligands and then forming
Fig. 1 Single-crystal structure for JLU-Liu18: (a) topology simplification of ligand and metal core. (b) polyhedron view of the \( \text{xzm} \) net. (c) pores in the framework shown as yellow spheres. (e) topological features of the compound displayed by tiling. Colour scheme: carbon = gray, nitrogen = blue, oxygen = red, indium = green. Guest molecules and H atoms have been omitted for clarity.

Fig. 2 Single-crystal structure for JLU-Liu19: (a) topology simplification of ligand and metal core. (b) polyhedron view of the \( \text{bnn} \) net. (c) topological features of the compound displayed by tiling. (d) the formation of 3D framework from 1D metal chain and 2D layer. Colour scheme: carbon = gray, nitrogen = blue, oxygen = red, cadmiums = green. Guest molecules and H atoms have been omitted for clarity.

Thermal gravimetric analyses (TGA) under an atmospheric environment were then carried out to assess the thermal stability of the two compounds and the pore volume that occupy by guest molecules. The results show that JLU-Liu18 framework can be stable up to about 350 °C with approximately 22% weight loss observed before 200 °C because of the removal of guest molecules (Fig. S3†). While JLU-Liu19 is stable until 450 °C and it is approximately 10% weight loss observed before 200 °C for the removal of guest molecules (Fig. S4†). Both of the two compounds exhibit higher thermal stability than JLU-Liu1 with octa-nuclear SBU.27 It can be also observed that JLU-Liu18 has more solvent occupied volume than JLU-Liu19, which indicates that JLU-Liu18 is supposed to possess more open pore volume after desolvation. It should be to note that both of the two compounds exhibit good air and water vapour stability. When exposed to air for several months or treated by water vapour for 1, 3, 6 and 12 hours, respectively, the frameworks of the two compounds still retain stability which can be proved by the crystallinity of PXRD (Fig. 3). The excellent stable behaviour of the two compounds is of extremely importance for their practical applications.

Fig. 3 PXRD patterns for JLU-Liu18 (a) and JLU-Liu19 (b) after exposed to water vapor for 1, 3, 6 and 12 hours, respectively.

The permanent porosity and surface areas of desolvated JLU-Liu18 were probed by reversible \( \text{N}_2 \) sorption experiments at 77 K. The \( \text{N}_2 \) adsorption of activated JLU-Liu18 reveals a reversible type-I isotherm characteristic of microporous material (Fig. 4). The BET surface areas and Langmuir surface areas for JLU-Liu18 were calculated to be 1300 m\(^2\) g\(^{-1}\) and 1800 m\(^2\) g\(^{-1}\), respectively, which is about triple to the Mg analogues11 and close to Ni and Fe analogues.12 It is among the highest of all known InMOFs.28,29 The micropore volume is 0.65 cm\(^3\) g\(^{-1}\) which is close to the theoretical value of 0.72 cm\(^3\)

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g\(^{-1}\). N\(_2\) gas sorption isotherm of JLU-Liu19 was also measured at 77 K under 1 bar, there is almost no N\(_2\) adsorption (Fig. 4).

On account of the high BET and adsorption performance of CO\(_2\) for JLU-Liu18, we investigate its adsorption performance for some other small gases. As shown in Figure S6\(^\dagger\), the low-pressure uptake for H\(_2\) is completely reversible and the adsorption amount is 1.81 wt\% (203 cm\(^3\) g\(^{-1}\)) and 1.34 wt\% (150 cm\(^3\) g\(^{-1}\)) at 77 and 87 K under 1 bar, which are quite comparable with the highly porous MOFs under the same conditions.\(^{43, 44}\) Furthermore, the maximum adsorption amount of O\(_2\) is 529 cm\(^3\) g\(^{-1}\) at 77 K (Fig. S7\(^\dagger\)), which is comparable to those of highly porous MOFs.\(^{45, 46}\) Comparing with N\(_2\) gas sorption isotherms measured at the same condition, O\(_2\) is more favourably adsorbed over N\(_2\) with a O\(_2\)/N\(_2\) selectivity of 1.24 at 0.2 P/P\(_{0}\), such sorption behaviour is commensurate with Fe/Cu-BTC and Co/Cu-BTC with OMSs.\(^{47}\) However, as far as saturated coordination MOFs to be concerned, the O\(_2\)/N\(_2\) selectivity of JLU-Liu18 is relatively high. With the temperature increasing, O\(_2\) loadings decrease to be 9 and 5 cm\(^3\) g\(^{-1}\) (Fig. S8\(^\dagger\)). The \(Q_\text{st}\) at the highest loadings is observed to be 16 kJ mol\(^{-1}\) (Fig. S9\(^\dagger\)), which exceed the highest \(Q_\text{st}\) in metal-substituted Cu-BTC.\(^{47}\) deducing the stronger interactions between O\(_2\) and host framework.

Both of the two MOFs explored the CO\(_2\) adsorption performance. As shown in Figure 5a, the amount of CO\(_2\) uptake for JLU-Liu18 is 129 and 63 cm\(^3\) g\(^{-1}\) at 273 and 298 K under 1 bar, respectively. Although large numbers of MOF with good CO\(_2\) capture performance have been reported, it is still scarce for MOFs that forereach 100 cm\(^3\) g\(^{-1}\) at 273 K and 1 bar. It is worthly mentioned that such high CO\(_2\) uptake can be even compared to the MOFs with OMSs or uncoordinated N-donor sites.\(^{34, 35}\) To acquire further insight into CO\(_2\) sorption, the behaviour of the isosteric heat was calculated. The adsorption enthalpy of JLU-Liu18 is 24.9 kJ mol\(^{-1}\) (Fig. 5b), indicating the strong interactions between the CO\(_2\) molecules and host framework.

Although there is no N\(_2\) adsorption for JLU-Liu19, the CO\(_2\) adsorption was observed to be 56 and 42 cm\(^3\) g\(^{-1}\) at 273 and 298 K under 1 bar (Fig. 5c). Albeit these values are lower than JLU-Liu18, it is considerably higher than many well-known MOFs without OMSs or uncoordinated N-donor sites.\(^{36, 37}\) It is also far beyond the Zn analogues.\(^{14-16}\) JLU-Liu18 shows a near-zero coverage \(Q_\text{st}\) value of 34.2 kJ mol\(^{-1}\) (Fig. 5d) which surpass JLU-Liu18 and compare to MOFs materials with OMSs,\(^{38, 39}\) indicating the strong host-guest C-H···O interaction between the CO\(_2\) molecules and phenyl rings in the host framework, and the quadrupole-quadrupole interactions between the CO\(_2\) molecules.\(^{40}\) Considerable uptake of CO\(_2\) with N\(_2\) not adsorbed is known for ultramicroporous MOFs. It is commendable for ultramicroporous MOFs with considerable uptake of CO\(_2\) but no N\(_2\) adsorption. JLU-Liu19 fortunately possess the uncommon performance, which can be ascribed to the small internal channel size of 3.5 Å lying intermediate among that of N\(_2\) (3.64 Å), CH\(_4\) (3.87 Å) and CO\(_2\) (3.3 Å). The unusual cavity diameter can be regarded as ultramicroporous,\(^{13, 41, 42}\) which leading to excellent sieving and selective adsorption performance.

With stable and permanent porosity, JLU-Liu18 is evaluated its potential storage and selective separation application for CO\(_2\) and small hydrocarbons, which are the prim composition of flue gas, natural gas and biogas. The adsorption isotherms of CH\(_4\), C\(_2\)H\(_6\) and C\(_3\)H\(_8\) are measured at 273 and 298 K under 1 bar, respectively. The maximum adsorption for CH\(_4\) is 23 and 12 cm\(^3\) g\(^{-1}\), C\(_2\)H\(_6\) is 128 and 92 cm\(^3\) g\(^{-1}\) and C\(_3\)H\(_8\) is 138 and 116 cm\(^3\) g\(^{-1}\), respectively (Fig. S10 to S12\(^\dagger\)). At zero loading, \(Q_\text{st}\) of CH\(_4\), C\(_2\)H\(_6\) and C\(_3\)H\(_8\) adsorption is 18, 25 and 44 kJ mol\(^{-1}\), respectively, as estimated from the sorption isotherms at 273 and 298 K (Fig. S13 to S15\(^\dagger\)). It indicated that the unique cage structures of JLU-Liu18 with medium pore size induce stronger interaction with larger hydrocarbons than the smaller ones.\(^{49}\) The types of interaction are presumably the combined
effects of the van der Waals host-guest interactions and the electrostatic host-guest interactions in the system.\textsuperscript{50}

In order to estimate the practical separate ability for CO\textsubscript{2}, theoretical gas mixtures of CO\textsubscript{2}/CH\textsubscript{4} (5 \%, 95\%, 50\% and 50\%) are conducted by the IAST model which is a common method to predict binary mixture adsorption from experimental single-component isotherms. We successfully use the dual-site Langmuir-Freundlich equation to fit the data.\textsuperscript{51-53} As shown in Figure 6a, the model fits the isotherms at 298 K very well ($R^2=0.9999$). The fitting parameters were then used to predict multi-component adsorption with IAST (listed in Table S5). At 298 K and 1 bar, the selectivity of CO\textsubscript{2} over CH\textsubscript{4} for JLU-Liu\textsubscript{18} according to the experimental data is 5.4 and 4.5 (Fig. 5b), which surpass the values of MIL-53(Al), MOF-5 and some carbon materials under the same measurement conditions.\textsuperscript{54-56}

The potential application for the industrially important small hydrocarbon separation is also explored for JLU-Liu\textsubscript{18} by IAST. As shown in Figure 5d, the obtained values of the resulting selectivity of C\textsubscript{2}H\textsubscript{6} over CH\textsubscript{4}, C\textsubscript{3}H\textsubscript{8} over CH\textsubscript{4} for equimolar is 13.1, 108.2 at 298 K and 1 bar, respectively. It is noteworthy that the selectivity of C\textsubscript{2}H\textsubscript{6} over CH\textsubscript{4} is much higher than the very high value for UTSA-35a\textsuperscript{57} and JLU-Liu5.\textsuperscript{58}

Conclusions

In summary, we have successfully synthesized two novel microporous MOFs based on a tridentate heterofunctional ligand with indium nitrate and cadmium nitrate. Both of the two compounds exhibit high thermal and water vapour stability as well as highlighted adsorption performance for small gases. Meanwhile, JLU-Liu\textsubscript{18} also displays outstanding selectivity for O\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}/CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}/CH\textsubscript{4}. JLU-Liu\textsubscript{19} with unique ultramicropores possesses uncommon sieving effect for the gases with different kinetic diameter. It is promising to apply these emerging porous materials to the field of industrially important gas storage and separation of in the near future.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21373095, 21371067 and 21171064).

Notes and references

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† Electronic Supplementary Information (ESI) available: [materials and methods, crystal data and structure refinement, structure information, XRD, TGA, gases adsorption and adsorptive selectivity. CCDC 1403645, 1402651]. See DOI: 10.1039/b000000x/
