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ARTICLE TYPE

A pillared-layer Framework with High Uptake and Selective Sorption of Light Hydrocarbons

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A new pillared-layer Metal-Organic Framework $[Zn_2(NH_2\text{-BTB})(2\text{-nim})]$ **(1)** was successfully synthesized base on mixed ligands, where binuclear $[Zn_2(CO_2)_3]^+$ cluster-based cationic layers $[Zn_2(NH_2\text{-BTB})]^+$ ($NH_2\text{-}H_3BTB$ = 1, 3, 5- (three-benzoic acid) aniline) are connected by 2-nitroimidazoles. Compound **1** shows high uptake and good adsorption selectivities of C_3/C_1 and C_2/C_1. Especially, the C_2H_2 uptake capacity of **1** is up to 152 cm^3 g^{-1} at 273 K and the selectivity of C_3H_8/CH_4 is over 85 at room temperature.

Introduction

In recent years, porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) have attracted much attention not only for their fascinating architectures and intriguing topologies,[1] but also for potential applications in selective gas storage and separation.[2] Light hydrocarbons are very important raw materials for chemical industry and global climate.[3] Methane as the principal component of natural gas, is the priori alternative fuel. C2 hydrocarbons (C2s) play a crucial role in the industrial process. High purity hydrocarbon gas is a prerequisite for these chemical procedures.[4] So it is necessary to explore materials for high-efficient storage and separation of hydrocarbons.

Compared to distillation-based technologies, adsorptive separation is widely considered as a more environment-friendly and cost-efficient alternative.[5] Up to date, a variety of porous adsorbents, such as zeolites, carbon materials, diatomite, have been investigated for hydrocarbon separations.[6] A number of MOFs have been studied for applications in purification and storage of these C1, C2 and C3 light hydrocarbons.[7] However, the application of these promising materials are limited by the separation ratio of C_3/C_1 or C_2/C_1 compared to the commercial materials.[8] More efforts are needed to improve the selectivity of light hydrocarbons and enhance gas uptake capacity.

Here, one pillared-layer MOF $[Zn_2(NH_2\text{-BTB})(2\text{-nim})]$ (**1**, $NH_2\text{-}H_3BTB$ = 1, 3, 5-(three-benzoic acid) aniline, 2-nim = 2-nitroimidazole) was designed and synthesized via the method of charge balance and mixd ligands. The rigid tritopic aromatic polycarboxylate ligands coordinate binuclear zinc ions to form a cationic layer $[Zn_2(NH_2\text{-BTB})]_n$ with special tritopic paddle-wheel zinc clusters, then the layers are further connected to a 3D neutral pillared–layer framework by 2-nitroimidazole pillars. The porous material of **1** exhibit high CO_2 and light hydrocarbon storage capacity as well as good C_3H_8/CH_4, C_2H_6/CH_4, C_2H_4/CH_4 and C_2H_2/CH_4 selective separations. Especially, the selectivity of C_3H_8/CH_4 is over 85 at room temperature and the C_2H_2 uptake capacity of **1** is up to 152 cm^3 g^{-1} at 273 K, is the higher one ever reported.

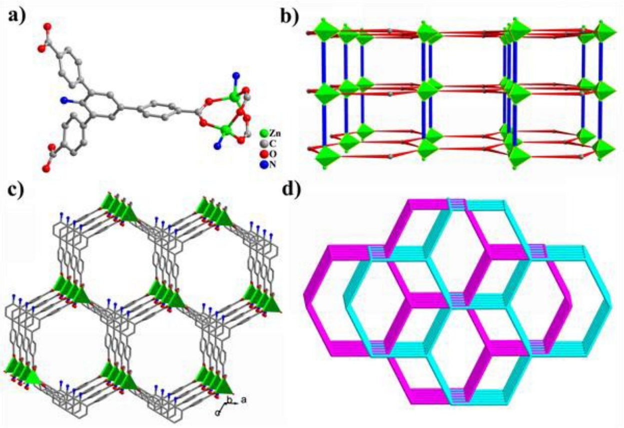

Fig. 1 a) The coordination environment in compound **1**; b) 3D pillared-layer framework of **1** along the a axis (Blue pillar, 2-nitroimidazole; Gree hexahedron, $[Zn_2(CO_2)_3]^+$ cluster); c); 3D framework of **1** along the b axis; d) 2-fold interpenetrated (3,5)-connected **hms** net of **1**.

Experimental section

Material and instrumentation

All reagents and solvents used in this work were commercially available. 1,3,5-(tri-benzoic acid)aniline was synthesized via suzuki reaction.[9] Powder X-ray diffraction (PXRD) patterns were collected on a MiniFlex-II diffractometer using Cu (λ = 1.54178 Å) radiation with a speed of 1 °/min. Thermogravimetric analysis (TGA) was performed in nitrogen by using a Netzsch STA449C equipped with a platinum pan and heated at a rate of 10 °C per minute. Gas sorption experiments were carried out with Accelerated Surface Area and Porosimetry (ASAP) 2020 system has good crystallinity after the removal of solvent molecules. The N_2 sorption isotherms were acquired in the pressure rage of P/P_O from 0.01 to 0.99 at 77 K in a liquid nitrogen bath. The gas sorption experiments of CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and N_2 were conducted at 273 K in a ice-water bath or 297 K. Elemental analyses were performed on a Vario EL III elemental analyzer.

Synthesis of [$Zn_2(NH_2$-BTB)(2-nim)] (1). A mixture of 2-nitroimidazole (2-nim, 0.0156 g, 0.14 mmol), NH_2-H_3BTB (0.0156 g, 0.036 mmol) and $Zn(NO_3)_2·6H_2O$ (0.0416 g, 0.14 mmol), Tetraethylammonium bromide (0.075 mmol, 0.0156 g), which was used to facilitate the crystallization of product, and DMF/H_2O (v:v = 3:0.5, 3.5 mL) was heated in a 20 mL scintillation vials at 100°C for 24 hours, followed by cooling to room temperature. The resulting mixture was washed with DMF and water, and colorless block crystal were collected and dried in air. Calcd for [$Zn_2(NH_2$-BTB)][2-nim]·DMF·$6H_2O$: C, 45.32; H, 4.26; N, 8.04; found: C, 44.97; H, 4.54; N, 8.37.

X-ray diffraction analysis. Single-crystal x-ray structural measurement analysis was performed on a Agilent Super Nava X-ray diffractometer with Cu–Kα radiation ($\lambda_{Cu\text{-}K\alpha} = 1.54178$ Å) at 100 K. The structure was solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package.[10] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Part solvent molecules in the structure were randomly dispersed, and thus their positions were impossible to refine using conventional discrete-atom models. The SQUEEZE option of PLATON was used to eliminate the contribution of disordered guest molecules to the reflection intensities.[11] Crystallographic data for compound **1** is listed in Table S1.

Gas selectivity. The selectivities of C_3, C_2 over CH_4 were calculated by the ideal adsorption solution theory (IAST).[12] IAST is a method for predicting the adsorption equilibria for components in a mixture using only single-component adsorption data at the same temperature and on the same adsorbent.

Results and Discussion

Compound **1** crystallizes in space group $P2_1$/m and features a 3D neutral framework with dinuclear $Zn_2(CO_2)_3$ units. As shown in Figure 1, the asymmetric unit of **1** contains one Zinc atom, a half NH_2-BTB and a half 2-nitroimidazole molecule. Two Zinc cations are eight-coordinated by six carboxylate oxygen atoms from three NH_2-BTB^{3-} ligands and two nitrogen atoms from two 2-nitroimidazoles ligands, forming a similar paddle-wheel building unit $Zn_2(CO_2)_3$. Compound **1** is a typical layered-pillar structure, the axial coordination sites are ligated by μ_2-im groups which acts as a pillar inter-connecting the $Zn_2((NH_2$-BTB)-layers in a axis direction to form a three dimension neutral framework [$Zn_2(NH_2$-BTB)(2-nim)] (Fig. 1b). Due to the large size of NH_2-BTB^{3-} ligand, the pores are large enough for a second net, two such frameworks are mutually interpenetrated (Fig. 1c). From a topological point of view, the $[Zn_2(CO_2)_3]^+$ paddle-wheel-unit can be considered as a 5-connected node, the NH_2-BTB^{3-} anion ligand can be reduced as 3-connected node and the 2- nitroimidazole ligand can be reduced as line. Therefore, framework of **1** can be simplified as a 2-fold interpenetrated hexagon-planar (3,5)-connected **hms** net with Point (Schläfli) symbol of (6^3) $(6^9.8)$ (Fig. 1d).

In order to confirm the crystal structures are truly representative of the crystal materials, the as-synthesized samples of **1** have been characterized by powder X-ray diffraction. As shown in Figure S2, the experimental PXRD pattern is in good agreement with the corresponding simulated one, implying that the synthesized materials and the measured single crystals are the same. The after-activated PXRD patterns also correspond well with the result simulated from the single crystal data (Fig. S2), indicating the structurally stable of **1**.

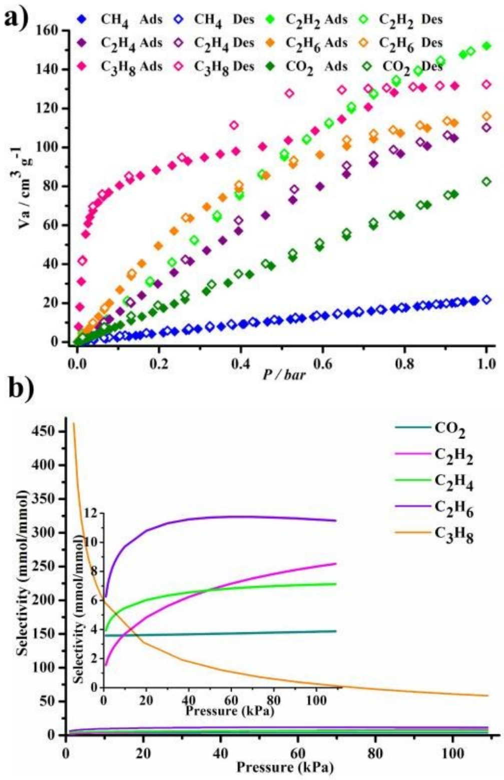

Fig. 2 (a) Small hydrocarbons and CO_2 sorption isotherms of **1** at 273 K; (b) IAST-predicted adsorption selectivity of **1** at 273 K.

Thermogravimetric analysis (TGA) in N_2 atmosphere with a heating rate of 10 °C/min was performed on polycrystalline sample to determine their thermal stability from 25 to 800 °C. The TGA curve of **1** indicated that a weight loss of 20% occurred in the temperature range of 100 - 200 °C, corresponding to the loss of H_2O and DMF guest molecules (expected 20.7%) and it began to decompose from 430 °C (Figure S3). The TGA curve of **1**-activated indicates that the host framework has no weight loss occurred before 410 °C, then the framework decomposed. The results show clearly that there is nothing remained in the framework after the activation.

The rigidity of these porous frameworks as well as the accessibility of guest molecules into the porous framework of **1** was assessed by solid–gas sorption experiments with N_2 and CO_2 as probe molecules. Prior to measurement, as-synthesized crystalline samples were activated as follows: immersing in methanol for three days (solvent was exchanged nine times), following by the thermal/vacuum activation at 303 K, 8 h to generate activated compound **1**. It has a larger pore void comprising ~37% of the cell volume as estimated by PLATON.[11] The N_2 sorption isotherms show type-I behaviors, characterized the typical of crystalline microporous materials

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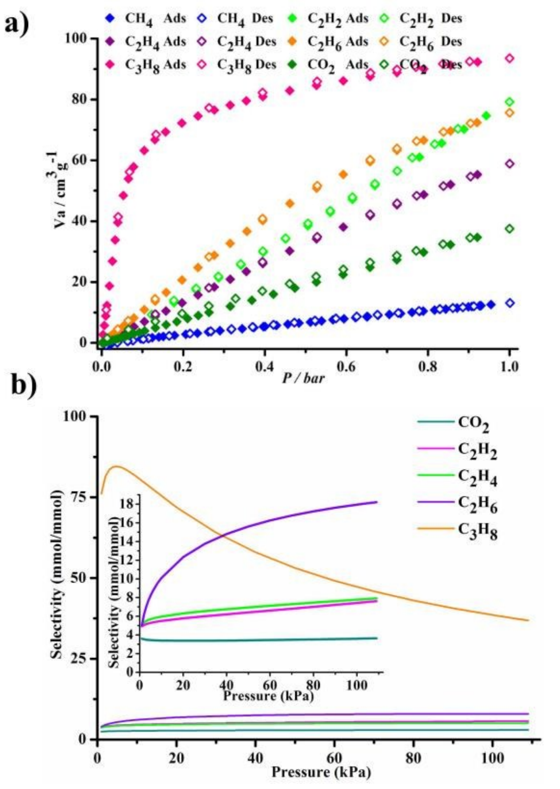

Fig. 3 (a) Small hydrocarbons and CO_2 sorption isotherms of **1** at 297 K; (b) IAST-predicted adsorption selectivity of **1** at 297 K.

(Fig. S4). The BET surface area is 893.83 m^2 g^{-1} and the total pore volume is 0.450 cm^3 g^{-1} (Fig. S4). The CO_2 uptakes for **1** are 82.40 cm^3 g^{-1} at 273 K, and 37.55 cm^3 g^{-1} at 297 K, respectively (Fig. 2a, 3a).

Compound **1** exhibits different adsorption capacities upon response to C_3H_8, C_2H_6, C_2H_4, C_2H_2 and CH_4 at 273 and 297 K (Fig. 2a, 3a). In general, MOFs have an adsorption capacity with the following trend: $C_3 > C_2 > C_1$. Nevertheless, the impressive C_2H_2 uptake of 152 cm^3 g^{-1} at 273 K in compound **1** (Fig. 2a), surpassing those of the previously reported porous adsorbents, such as UMCM-150 (150),[13] NOTT-102 (142),[14] is a higher one ever reported.[1c] More interestingly, a so-called gate-opening effect is observed in the C_3H_8 adsorption isotherm of **1**, which displays a tiny hysteresis phenomenon at 273 K (Fig. 2a), indicating framework has some degree of flexibilty. As shown in Figure 1, 2-nitroimidazole ligand as pillar that plays a important role in the this framework. The pore property can be tuned via rotation of nitro group, thereby inducing gate-opening type adsorption.[7, 15] However, other kinds of hydrocarbons are used as adsorptive probes, the phenomenon can not occur. Take many factors into consideration, the molecular polarizability and molecular size are the dominant effects.[16] First, compared with CH_4, C_2H_2, C_2H_4, C_2H_6, the steep isotherm of C_3H_8 indicates that C_3H_8 has the highest affinity to the framework, consistent with the polarizability of this molecule. Second, the C_3H_8 molecule with the largest molecular size has more opportunities to interact with the 2-nim pillar, which can cause the rotation of 2-nim to generate the open effect. A typically example of the family of pillared-layer frameworks of type $[Zn_2(fu–bdc)_2(dabco)]_n$, which composed of two-dimensional square grids, consisting of paddle-wheel building units, then interconnected to 3D architecture by pillars with dangling different chemical side groups, shows the excellent effect and hysteresis adsorption on the affinity of CO_2 via an combination of functionalized linkers.[17] The isosteric enthalpy of adsorption (Qst) of light hydrocarbons were calculated based on the virial method at zero coverage. The Q_{st} values of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and CO_2 are 16.22, 19.72, 19.81, 21.52, 28.16 and 22.38 kJ/mol for **1** (Note: the hysteresis of C_3H_8 adsorption isotherms is tiny, the adsorption isotherms of C_3H_8 was fitted as type Ι curve).

To estimate the adsorption selectivity of light hydrocarbons, the adsorption selectivities of C_3/C_1, C_2/C_1 and CO_2/CH_4 (equimolar binary mixtures) were calculated by the ideal adsorption solution theory (IAST) at 273 and 297 K (Fig. 2b, 3b). The IAST calculations indicated that the hierarchy of adsorption capacity is commonly $CH_4 < C_2H_4 < C_2H_6 < C_2H_2 < C_3H_8$, making the feasibility of this material for the separation of light hydrocarbons. This framework display of great separation ratio of C_2H_6/CH_4, exceeding 16 at 297 K, the values of **1** is higher than that for ZIF-8(10),[18] Mg-MOF-74(7),[19] while is close to C_2H_6/CH_4 selectivity of Fe-MOF-74(18).[19] Noteworthily, the selectivity of C_3H_8/CH_4 for **1** is over 85 at room temperature, much higher than the very high values of UTSA-35a (80).[20] Such high selectivities further confirm that this material has a great potential in separation application of light hydrocarbons.

Conclusion

In summary, we report a 2-fold interpenetrated pillared-layer compound by paddle-wheel building $[Zn_2(CO_2)_3]$ units and linear 2-nitroimidazole ligands. The adsorption and separation of the carbon dioxide and small hydrocarbons were characterized, the C_2H_2 uptake capacity of **1** is up to 152 cm^3 g^{-1} at 273 K and it also shows good adsorption selectivities of C_3/C_1 and C_2/C_1. Especially, the selectivity of C_3H_8/CH_4 is over 85 at room temperature. These results demonstrate that this compound may be of great value as a promising material for the fuel gas purification and the separation of light hydrocarbons.

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Notes and references

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Electronic Supplementary Information (ESI) available: [addition figures, powder X-ray patterns, adsorption isotherms and cif files (CCDC-1440822)]. See DOI: 10.1039/b000000x/

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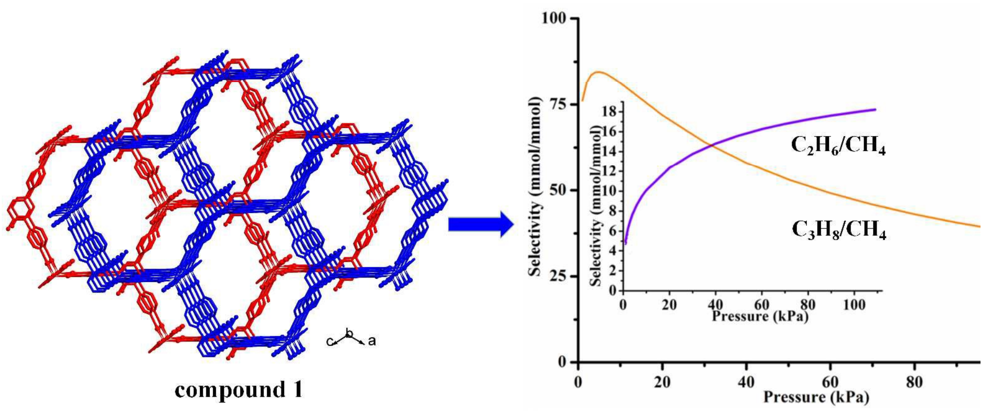
TOC



A pillared-layer Metal-Organic Framework was successfully synthesized, which shows high storage capacity for C_2 light hydrocarbons and good adsorption selectivity of C_3/C_1 and C_2/C_1 at room temperature.