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ARTICLE

A Metal-Organic Framework Based on Cyclotriphosphazene Functionalized Hexacarboxylate for Selective Adsorption of CO$_2$ and C$_2$H$_6$ from CH$_4$ at Room Temperature

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By using a flexible cyclotriphosphazene functionalized hexacarboxylate, a novel metal-organic framework **ZJNU-60** has been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction. **ZJNU-60** consists of dicopper paddlewheel secondary building units interconnected by the organic linkers to form a bilayer with a rectangular channel running along the *b* axis. Upon desolvation, the framework underwent severe distortion and pore contraction, but the permanent porosity has been established as shown in C$_2$H$_6$, CO$_2$ and CH$_4$ gas isotherms. Furthermore, the activated **ZJNU-60a** displayed impressive adsorption selectivities toward C$_2$H$_6$ and CO$_2$ over CH$_4$, indicating the potential for the separation of CO$_2$ and C$_2$H$_6$ from CH$_4$. This is the first example of MOF constructed from a flexible cyclotriphosphazene-functionalized hexcarboxylate for selective gas separation.

1. Introduction

Metal-organic frameworks (MOFs), or porous coordination polymers (PCPs), have been emerging as a relatively new class of porous materials consisting of metal ions or clusters interconnected by polytopic organic linkers to create a networked structure with well-defined pores. Compared to traditional porous materials such as active carbons, and zeolites, one of the intriguing features of MOFs is the availability of a huge combination of metal ions and organic linkers allowing the construction of a large variety of MOFs bearing different pore structures. Also, the pore surface of MOFs can be modified pre-synthetically and post-synthetically by grafting various functional groups to the organic linkers or metal nodes to direct the recognition of the target molecules. Such favourable characteristics of MOFs make them extremely versatile for applications involving host-guest interactions such as gas storage and separation, heterogeneous catalysis, sensing and recognition, drug delivery and others.[1]

The selection of organic ligands is very crucial to target MOFs with desired properties. In terms of MOFs for gas adsorption, typically, it is necessary to have rigid organic linkers to stabili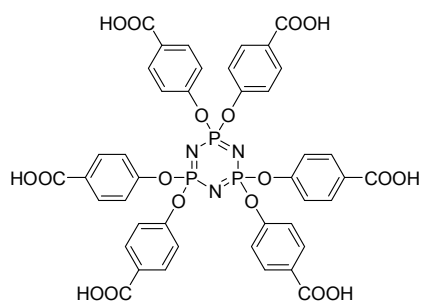ze the frameworks and thus establish their permanent porosities for their gas adsorption. Virtually, some research groups pursued elegant synthetic methodologies that produced a variety of rigid organic linkers which have been successfully incorporated into a series of robust MOFs.[2] In contrast, utilization of flexible ligands to construct porous MOFs is very challenging due to their conformational freedom and flexibility making the framework very difficult to stabilize. If the flexible organic ligands can be used to construct robust MOFs, it will give a new insight for MOFs adsorbent design. In this regard, extensive efforts have been pursued and some progress has been made, but the examples of MOFs constructed from flexible ligands exhibiting gas adsorption are still very limited.[3] For example, Xue *et al.* reported a robust microporous MOF constructed from a flexible organic linker, tetrakis[(3,5-dicarboxyphenoxy)methyl] methane, for acetylene storage at room temperature.[3a] Guo *et al.* reported a porous MOF based on a flexible ligand, tetrakis[4-(carboxyphenyl)oxamethyl]methane acid, exhibiting multifunctional properties including methane adsorption.[3c] We thus become interested in utilizing a flexible multicarboxylate as a ligand for the fabrication of MOFs for gas adsorption studies.

Cyclotriphosphazene (CTP), composed of alternating nitrogen and phosphorus atoms, is an important class of inorganic backbones. Some related derivatives have been widely used in supramolecular and polymer chemistry. However, there are very limited reports of MOFs utilizing cyclotriphosphazene based ligands.[4] With the above background in mind, a hexacarboxylic acid based on the fully substituted cyclotriphosphazene inorganic scaffold, hexakis(4-carboxylatephenoxy)cyclotriphosphazene (H$_6$L, Scheme 1), was selected specifically as a flexible organic ligand in this work. Herein, we wish to report on the synthesis, characterization,

Scheme 1 The organic linker H₆L used to construct MOF **ZJNU-60**.

crystal structure, and gas sorption properties of a new MOF solvothermally constructed from this newly designed ligand and copper ions. To the best of our knowledge, this is the first example of MOF constructed from a flexible cyclotriphosphazene-functionalized hexacarboxylate for selective gas separation.

2. Experimental

2.1 Material and general methods

All the starting materials were of reagent grade and used as received from the commercial suppliers. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruke AV 600 or 400 spectrometer. Chemical shifts (δ) are reported relative to trace amounts of CHCl₃ (δ_H = 7.26 ppm, δ_C = 77.0 ppm), or DMSO (δ_H = 2.50 ppm, δ_C = 39.5 ppm) in the corresponding deuterated solvents. Elemental analyses for CHN were carried out using a Perkin–Elmer 240 CHN analyzer. Fourier transform infrared (FTIR) spectra were recorded in the region of 400-4000 cm⁻¹ with a Nicolet 5DX FT-IR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was performed with a Netzsch STA 449C thermal analyzer over a temperature range of 30-800 °C under a nitrogen atmosphere at a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were recorded using a Philips PW3040/60 automated powder diffractometer using Cu-K_a radiation (λ = 1.5406 Å) in the 2θ range from 5 to 50°. Gas adsorption-desorption isotherms up to 1 bar were measured using an ASAP 2020 HD88 gas sorption analyzer. Prior to sorption experiments, the samples were degassed at room temperature under a dynamic vacuum until the degassed rate reached 3 μmHg min⁻¹. The gases used had the following specifications (volume percentage): N₂ 99.9999%, CH₄ 99.99%; C₂H₆ 99.5%; CO₂ 99.999%.

2.2 X-ray crystallographic study

Single-crystal X-ray diffraction data for **ZJNU-60** were collected using a Bruke SMART APEX II with graphite monochromated Cu K_a radiation at a low temperature of 100 K. The structure was solved by direct methods and refined using full matrix least square techniques on F^2 with the program SHELXL-97.[5] There are large solvent-accessible void volumes in the crystals. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities.[6] Structures were then refined again using the data generated. All nonhydrogen atomic

positions were located in difference Fourier maps and refined anisotropically. Crystal and structural refinement data for **ZJNU-60** are displayed in Table S2. CCDC-1060803 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3 Synthesis and characterization of the organic linker H₆L

In a round-bottom flask equipped with a condenser for refluxing and a magnetic stirring bar, methyl 4-hydroxybenzoate (5.78 g, 37.99 mmol), phosphonitrilic chloride trimer (2.00 g, 5.75 mmol), potassium carbonate (5.25 g, 37.99 mmol) and dry acetone (100 mL) were added. The mixture was stirred under reflux under a nitrogen atmosphere for 24 h, and then cooled to room temperature. After the solvent was removed by rato-evaporation, water (100 mL) and dichloromethane (200 mL) were added. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The organic phase was combined, washed with brine, dried over anhydrous MgSO₄, and filtered. After removal of the volatile solvent, the residue was purified by silica gel column chromatography (Qingdao Haiyang Chemical, 100-200 mesh) using petroleum ether and ethyl acetate (1:1, v/v) as eluent to afford the hexamethyl intermediate as a pure white solid in 92% yield (5.50 g, 5.28 mmol). ^{1}H NMR (CDCl₃, 400.1 MHz) δ (ppm): 7.858 (d, J = 8.8 Hz, 12H), 6.998 (d, J = 8.8 Hz, 12H), 3.930 (s, 18H); ^{13}C NMR (CDCl₃, 150.9 MHz) δ (ppm): 165.978, 153.618, 131.350, 127.359, 120.573, 52.303.

To the hexamethyl intermediate (5.50 g, 5.28 mmol) in methanol (25 mL) and THF (25 mL) was added NaOH aqueous solution (4 M, 25 mL). The mixture was stirred at a nitrogen atmosphere at room temperature for 48 h. After the solvent was rato-evaporated, the residue was dissolved in water, and acidified with concentrated HCl under ice-water bath. The resulting precipitation was collected by suction, washed with water twice, and dried at 70 °C under vacuum, affording the target compound as an off-white solid in 97% yield (4.89 g, 5.11 mmol). ^{1}H NMR (DMSO-d_6, 400.1 MHz) δ (ppm): 13.03 (s, br, 6H), 7.841 (d, J = 8.8 Hz, 12H), 7.005 (d, J = 8.8 Hz, 12H); ^{13}C NMR (DMSO-d_6, 100.6 MHz) δ (ppm): 166.746, 153.240-153.172, 131.742, 128.711, 121.014; Selected FTIR (KBr, cm⁻¹): 1704, 1604, 1504, 1425, 1280, 1209, 1180, 1161, 1016, 949, 889, 860, 775, 737, 692, 617, 553, 503.

2.4 Synthesis and characterization of ZJNU-60

A mixture of H₆L (5.0 mg, 5.2 μmol) and Cu(NO₃)₂·3H₂O (5.0 mg, 20.7 μmol) was dissolved in a mixed solvent of *N,N*-dimethylacetamide (DMA, 1.0 mL), ethanol (0.5 mL) and H₂O (0.5 mL) in a 20-mL vial. After 20 μL of 6 M HCl was added, the vial was capped and heated at 80 °C for 24 h. After spontaneous cooling to room temperature, the blue block-shaped crystals were collected by filtration, washed with DMA. The yield was 5.1 mg based on the ligand. Selected FTIR (KBr, cm⁻¹): 1664, 1603, 1558, 1502, 1412, 1269, 1203, 1182, 1157, 1099, 1014, 955, 889, 864, 787, 742, 700, 642, 490; anal. for C₇₀H₁₀₃N₈O₃₂P₃Cu₃, calcd: C, 45.39%, H, 5.61%, N, 6.05%; found: C, 45.23%, H, 5.69%, N, 6.12%.
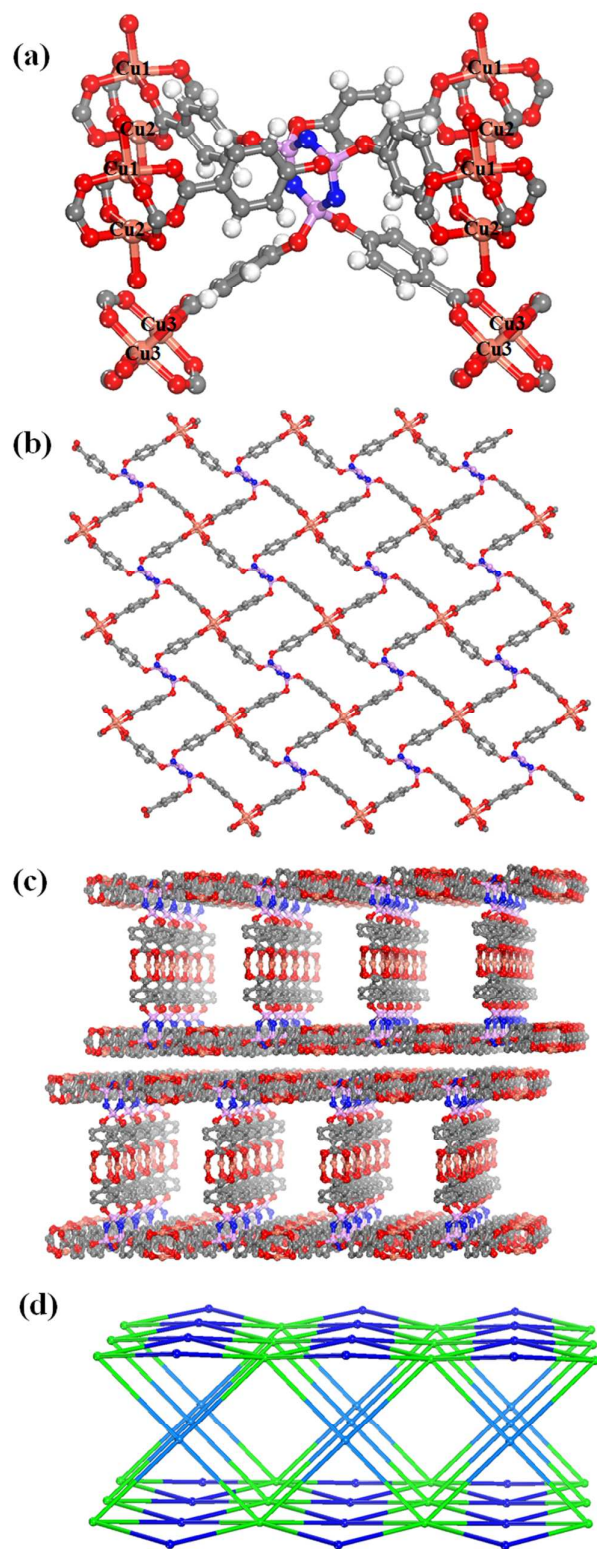
Fig. 1 (a) The coordination environment of the organic linker; (b) 2D layer formed by dicopper paddlewheel Cu1Cu2(COO)$_4$ that was linked by four arms of the linkers; (c) 2D layers were connected together by Cu3 ions ligated by the remaining two arms of the linkers; (d) the topological structure with Schläfli symbol of $\{4^4 \cdot 6^2\}_3\{4^9 \cdot 6^6\}_2$.

3. Results and discussion

The ligand, hexakis(4-carboxylatephenoxy) cyclotriphosphazene (H$_6$L), was readily synthesized by a nucleophilic substitution reaction of phosphonitrilic chloride trimer and methyl 4-hydroxybenzoate in the presence of K$_2$CO$_3$ as base followed by hydrolysis and acidification in good yield and gram scale. The chemical structure was fully characterized by standard spectroscopic techniques (Fig. S5). The solvothermal reaction of the ligand with Cu(NO$_3$)$_2$·3H$_2$O in DMA/EtOH/H$_2$O under acidic conditions at 80 ^{o}C for 24 h afforded small blue crystals of **ZJNU-60**. Based on single-crystal X-ray structure determination, thermogravimetric analysis (TGA, Fig. S1) and microanalysis, **ZJNU-60** can be best formulated as [Cu$_3$L(H$_2$O)$_3$]·5DMA·4EtOH·2H$_2$O.

Single-crystal X-ray diffraction analysis reveals that **ZJNU-60** crystallizes in triclinic system and space group *P*-1. Besides the guest solvent molecules, the asymmetric unit contains three crystallographically independent copper ions (Cu1, Cu2 and Cu3), two deprotonated ligands and three terminal water molecules. Regarding the organic linker, three of the six carboxylatephenoxy arms around the central cyclotriphosphazene ring of the ligand are situated above the central scaffold, and the other three below (Fig. 1a). The average P-N distance is 1.576 Å, and the average N-P-N and P-N-P angles are 117.03 and 122.94^o, respectively, which are very similar to the ones previously reported for cyclotriphosphazene derivatives.[4] The cyclotriphosphazene ring nitrogen atoms do not take part in coordination with Cu^{2+} ions, whilst all six carboxylate groups of the organic linker are deprotonated and involved in metal coordination adopting the same *syn-syn* bis-monodentate bridging coordination mode (μ_2-η^1:η^1). All Cu atoms show a similar coordination mode and are five-coordinated by four carboxylate oxygen atoms from four different ligands and one oxygen atom from one terminal water molecule. The Cu-O$_{carboxylate}$ bond lengths range from 1.900 to 2.000 Å, which is comparable to other Cu-O$_{carboxylate}$ bond distances reported in the literature.[7] Two adjacent Cu1 and Cu2 ions are bridged by four carboxylate groups to form dicopper paddlewheel Cu1Cu2(COO)$_4$ secondary building units (SBUs), which are connected with each other through four arms of the ligands generating a (4,4)-connected 2D layer in ab plane (Fig. 1b). Two such layers are further combined together by Cu3 ions ligated by the remaining two arms of the ligand, resulting in a bilayer (Fig. 1c). There exists a 1D rectangular channel with the size of ca. 9×13 Å^2 along the crystallographic *b* axis, taking into account of van der Waals radii of atoms. These bilayers are packed by C-H¨N and O$_{water}$-H¨O interactions to form a 3D supramolecular architecture (Fig. 1c). The void space accounts for approximately 53.3% of the whole crystal volume (2101.1 Å^3 out of 3937.73 Å^3 *per* unit cell volume) as estimated by PLATON analysis after removal of free solvent and terminal water molecules. Topologically, if the dicopper paddlewheel and the organic linker are regarded as 4-connected and 6-connected nodes, respectively, the overall framework has a novel (4,4,6)-coordinated net with Schläfli topological symbol of $\{4^4 \cdot 6^2\}_3\{4^9 \cdot 6^6\}_2$.
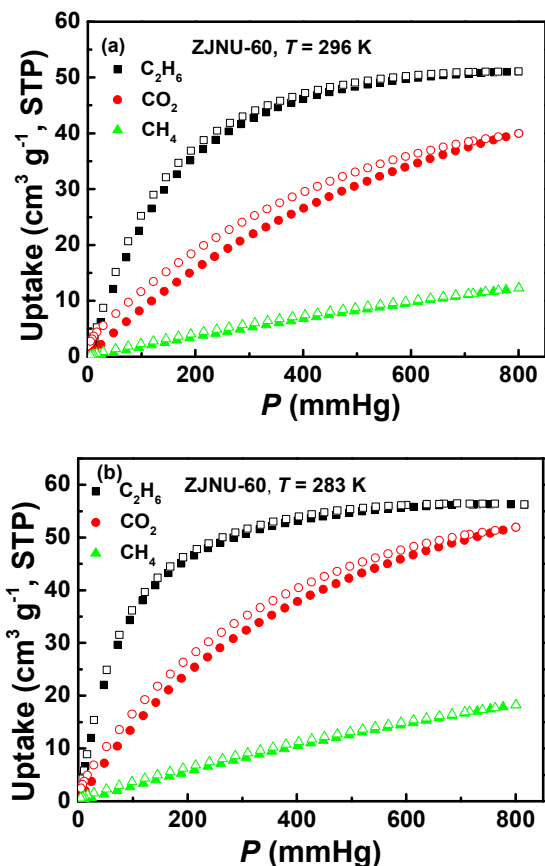
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Fig. 2 C_2H_6, CO_2 and CH_4 sorption isotherms of **ZJNU-60a** at 296 K (a) and 283 K (b). Solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.

Natural gas purification is one of the important objectives in the petrochemical industries. Natural gas consists predominantly of methane and also contains varying amount of other components including CO_2 and heavier hydrocarbons such as ethane. The presence of CO_2 reduces the combustion power efficiency, contributes to climate change and often leads to pipeline corrosion. Also, recovery of ethane from natural gas provides an alternative chemical source of ethane for further processing. To meet natural gas standards and increase the commercial value of natural gas, it is critical to remove these components from natural gas. The use of an adsorbent to achieve this aim may offer cost advantages over the usual method of cryogenic distillation and furthermore conserve energy. The key lies in development of suitable adsorbents that are selective towards ethane and CO_2 over methane at ambient temperature.[1o, 1v, 2a, 2b, 7b, 8]

To investigate the potential of **ZJNU-60** for natural gas purification, single-component gas adsorption measurements were carried out at two different temperatures of 283 K and 296 K for CO_2, CH_4 and C_2H_6. Prior to gas sorption measurements, the as-synthesized sample was washed with DMA, and guest-exchanged with dry acetone followed by evacuation under dynamic vacuum at room temperature until

the degassed rate reached 3 μmHg min^{-1}, generating the activated sample **ZJNU-60a** (thereafter, the letter "a" indicates the activated MOF materials). The activated **ZJNU-60a** took up a very small amount of N_2 at 77 K (Fig. S2). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas are calculated to be 27 and 42 m^2 g^{-1}, which are significantly lower than the theoretical values calculated by PLATON analysis, indicating the framework underwent severe distortion and pore contraction upon desolvation, which is supported by the powder X-ray diffraction studies of the activated sample showing that some diffraction peaks disappeared and shifted compared to those observed in as-synthesized sample (Fig. S3). Such phenomena were also observed in some MOFs constructed from the rigid organic linkers.[9] The big change of PXRD pattern of the compound before and after activation is understandable considering the fact the compound is composed of bilayers stacked together by C-H¨N and O_{water}-H¨O weak hydrogen bond interactions, and the organic linker is flexible. The mild activation method such as supercritical CO_2 drying is needed to retain the framework.[10] To rule out the possibility that the solvent molecules trapped in the interior pores might not have been evacuated properly, the activation temperatures were optimized to establish higher porosities. The acetone-exchanged samples were evacuated using three different activation temperatures, namely, room temperature (22 °C), 60 °C and 100 °C, until the degassed rates reached 3 μmHg min^{-1}. It was found that when the activation temperature is increased from RT to 100 °C, no further sample mass loss was observed, indicating that the guest molecules are fully removed. In fact, different activation temperatures gave basically the same CO_2 isotherms (Fig. S4). TGA of the sample activated at RT (Fig. S1) showed an initial little weight loss, which may be attributed to the water molecules adsorbed during the transfer of the activated sample to the TGA sample pan. Therefore we chose the RT-activated sample to collect all gas adsorption isotherms. Fig. 3 shows the adsorption isotherms of CH_4, CO_2, and C_2H_6 carried out at two different temperatures of 296 K and 283 K on **ZJNU-60a**. It can be observed that **ZJNU-60a** shows different adsorption capacities to C_2H_6, CO_2 and CH_4. The C_2H_6 isotherm reached a plateau within the pressure range measured. The most remarkable and significant feature is that **ZJNU-60a** adsorbs much more C_2H_6 and CO_2 than CH_4. At 296 K, for example, **ZJNU-60a** can take up a significant amount of C_2H_6 (51.1 cm^3 (STP) g^{-1}, 68.5 mg g^{-1}), and CO_2 (40.0 cm^3 (STP) g^{-1}, 78.5 mg g^{-1}), but a negligible amount of CH_4 (12.3 cm^3 (STP) g^{-1}, 8.8 mg g^{-1}) at 1 atm, highlighting that **ZJNU-60a** is a promising material for selective adsorption of CO_2 and C_2H_6 from CH_4 at room temperature. The C_2H_6 adsorption amount is comparable to those in **UTSA-30a** (46.2 cm^3 g^{-1})[2b], **ZIF-8** (53.2 cm^3 g^{-1})[11], **UTSA-35a** (54.3 cm^3 g^{-1})[12], but greatly larger than that of **UTSA-32a** (21.3 cm^3 g^{-1})[13], and **SBA-15** (11.2 cm^3 g^{-1})[14] under the same conditions.

To understand the interaction between gases and the framework, the Q_{st} values were determined using the Clausius–Clapeyron equation by fitting the adsorption isotherms taken at 283 and 296 K to the dual-site Langmuir-Freundlich expression. As shown in Fig. 3, **ZJNU-60a** exhibits
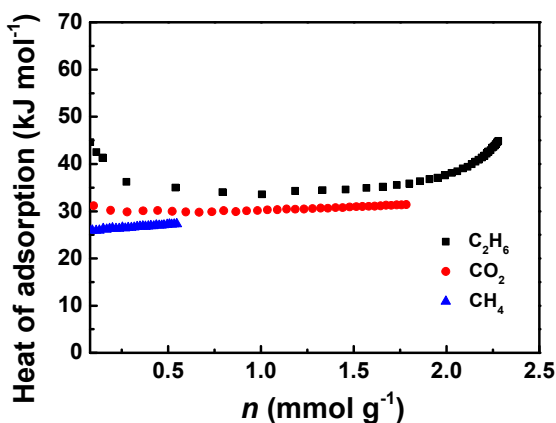
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Fig. 3 The adsorption heat of C_2H_6, CO_2 and CH_4 in **ZJNU-60a** as a function of gas loading.

higher C_2H_6 and CO_2 binding affinity than CH_4 throughout the adsorption process. The higher heat of adsorption of C_2H_6 and CO_2 relative to CH_4 suggests that C_2H_6 and CO_2 is adsorbed more strongly in **ZJNU-60a** compared with CH_4, which are also reflected by the adsorption isotherms of CO_2 and C_2H_6 being much steeper than that for CH_4. This might be attributed to the increasing polarizabilities and critical temperatures of these gases following in the order: CH_4 (25.93×10^{-25} cm^3, 190.56 K) < CO_2 (29.11×10^{-25} cm^3, 304.12 K) < C_2H_6 (44.3–44.7×10^{-25} cm^3, 305.32 K). The higher the critical temperature, the more condensable the gas. The larger the polarizability, the stronger the gas-framework interaction. Besides, the slight positive charge that rests on the carbon of CO_2 is susceptible to attack by Lewis basic nitrogen donors. The exposed copper sites can interact with the oxygen atoms of the CO_2.

4.   Conclusion

In conclusion, we have used a flexible cyclotriphosphazene-functionalized hexacarboxylate to synthesize a novel copper-organic framework whose permanent porosity was established by various gas adsorption studies. This guest-free phase exhibited impressive preferable adsorption towards C_2H_6 and CO_2 over CH_4, making it a very promising adsorbent material for natural gas separation and purification. Selective adsorption of C_2H_6 and CO_2 from CH_4 is attributed to their diverse interactions with the host framework. This is the first example of MOF constructed from a flexible cyclotriphosphazene-functionalized hexacarboxylate ligand for selective gas separation. Combination of the ligand, or the related ones, and other metal clusters into MOFs and their applications in diverse gas separations are ongoing and these results will be presented in the near future.

Acknowledgements

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TOC

A new metal-organic framework constructed from a flexible cyclotriphosphazene functionalized hexacarboxylate exhibits selective adsorption of CO_2 and C_2H_6 from CH_4 at room temperature.

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