

Enhancement of Gas Sorption and Separation Performance via Ligand Functionalization within Highly Stable Zirconium-Based Metal–Organic Frameworks

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Supporting Information

ABSTRACT: By using a modulated synthetic strategy, three isostructural Zr-based metal organic frameworks $[Zr_6O_4(OH)_4(EDDC)_6]$ (JLU-Liu34), $[Zr_6O_4(OH)_4(EDDC-NO_2)_6]$ (JLU-Liu35), and $[Zr_6O_4(OH)_4(EDDC-NH_2)_6]$ (JLU-Liu36) (H₂EDDC = (E)-4,4'-(ethene-1,2-diyl)dibenzoic acid, H₂EDDC-NO₂ = (E)-2,2'-dinitro-4,4'-(ethene-1,2-diyl)dibenzoic acid, H₂EDDC-NH₂ = (E)-2,2'-diamino-4,4'-(ethene-1,2-diyl)dibenzoic acid) which possess different substituent groups have been successfully synthesized. Significantly, the framework and crystallinity of the functionalized Zr-metal-organic frameworks (Zr-MOFs) are wellretained even though the nature of the functional group is different (NO₂ is electron-withdrawing, whereas NH₂ is



electron-releasing). All of the three analogues display 12-connected fcu topology, and the classical Zr_6 clusters in the porous crystal make the whole framework approach high chemical and thermal stability. As a result of the functionalization effect, the three analogues show different sorption and separation abilities to small gases, especially for JLU-Liu34 which exhibits a significant C_3H_8 uptake capacity of 303 cm³ g⁻¹ at 273 K under 1 bar. Although JLU-Liu36 shows lower Brunauer–Emmett–Teller surface area than JLU-Liu34, it possesses enhanced CO₂ adsorption enthalpy and selectivity for CO₂ over CH₄ influenced by the additional amino groups. Ligand modification provides an efficient strategy to design and synthesize porous MOFs materials for small gases sorption and separation.

INTRODUCTION

Metal–organic frameworks (MOFs), as a class of porous architectures composed of diverse organic and inorganic building blocks, have developed rapidly in the fields of chemistry and material science.^{1–3} Because of their high porosity, well-defined open channels, structural diversity, and rich functionalities, MOFs play significant roles in many different applications such as gas storage and separation, catalysis, drug delivery, and sensing.^{4–7} However, because of their relatively low chemical and thermal stabilities, the potential applications of these materials are limited. To overcome this limitation, diverse MOFs materials with reinforced secondary building units (SBUs), such as Zn_4O -(CO_2)₆, $Cu_2(CO_2)_4$, $Cr_3O(CO_2)_6$, $Al_8(OH)_8(CO_2)_{16}$, and $Ti_8O_8(OH)_4(CO_2)_6$, have been constructed by rationally

choosing metal sources and ligands.^{8–13} Recent reports indicate that Zr-based MOFs, in particular those with $Zr_6O_4(OH)_4$ clusters, exhibit dramatically improved chemical and mechanical stabilities.¹⁴ Most UiO-66-type zirconium MOFs possess highly porous frameworks and comprise large octahedral cages and smaller tetrahedral cages. Therefore, the porous frameworks and high chemical stabilities of Zr-based MOFs make them promising candidates for gas sorption and separation.¹⁵

Recently, a large number of porous MOFs with enhanced gas uptake have been designed and synthesized through predesigning the organic ligands.^{16,17} Among them, utilizing linkers with

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similar length but distinct functionalities in the construction of isostructural MOFs is a succinct method to construct functionalized MOF materials for adjusting gas adsorption and separation performance. $^{18-21}$ One of the representative examples is the successful synthesis of multivariate MOFs (MTV-MOFs) presented by Yaghi and co-workers.²² These isoreticular $Zn_4O(CO_2)_6$ SBUs-based MOF materials exhibit different gas adsorption performances for their different grafted substituent groups. Owing to diverse fascinating features, functionalized MOFs have been shown to exhibit great potential over the conventional adsorbents for mixture separation. For instance, Fe-MIL-101-NH₂ exhibits an exciting CO₂ adsorption capacity,²³ and UiO-66(Zr)-COOH presents high selectivity of \hat{CO}_2 from a CO_2/CH_4 gas mixture.²⁴ Among them, UiO-66-type modified MOF materials possess not only pore tunability and structural diversity, but also high thermal and chemical stabilities. The remarkable stability makes modified Zr-based MOFs an ideal platform for further investigations of the functionalization effect on the small molecular gases capture.

Herein, we employ a series of linear dicarboxylic acids ligands with different substituent groups (H₂EDDC = (E)-4, 4'-(ethene-1,2-diyl)dibenzoic acid, $H_2EDDC-NO_2 = (E)-2,2'$ dinitro-4,4'-(ethene-1,2-diyl)dibenzoic acid, H₂EDDC-NH₂ = (E)-2,2' diamino-4,4'-(ethene-1,2-diyl)dibenzoic acid) to fabricate MOFs materials with different functional groups and explore the effect of the functional groups in the gas sorption and separation. By using modulated synthetic strategy, different functionalized linear linkers have been introduced to form a class of porous isostructural Zr-MOFs with fcu topologies, JLU-Liu34 (Zr-H₂EDDC), JLU-Liu35 (Zr-H₂EDDC-NO₂), and JLU-Liu36 (Zr-H2EDDC-NH2), respectively. All the materials contain a highly stable $Zr_6O_4(OH)_4$ cluster, which leads to a strong resistance toward water or even hydrochloric acid solution. Unfortunately, only compounds JLU-Liu34 and JLU-Liu36 exhibit a high BET surface area after the removal of guest molecules. Compound JLU-Liu34 exhibits high C3H8 adsorption behavior, and compound JLU-Liu36 possesses high adsorption enthalpy of CO₂ as well as selectivity of CO₂ over CH₄. Guest molecules in compound JLU-Liu35 cannot be removed absolutely by solvent exchange or heat treatment.

EXPERIMENTAL SECTION

Materials and Physical Characterizations. Apart from two functionalized ligands, H₂EDDC-NO₂ and H₂EDDC-NH₂, all the other reagents 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 working with Cu–K α radiation ($\lambda = 1.5418$ Å) at room temperature. Thermogravimetric analyses (TGA) were carried out with the TA Q500 thermogravimetric analyzer under a heating rate of 10 °C min⁻¹ to 800 °C in air. The infrared spectra were recorded within a Bruker IFS-66v/S FTIR spectrometer in the range of 400–4000 cm⁻¹ using a KBr pellet. The N₂ sorption experiments were measured by a Micrometrics ASAP 2040 instrument at 77 K. The CO₂, CH₄, C₂H₆, and C₃H₈ adsorption isotherms were measured at 273 and 298 K with a Micrometrics 3-Flex instrument.

Synthesis and Characterization of Organic Ligands (Scheme 1). Synthesis of (E)-2,2'-Dinitro-4,4'-(ethene-1,2-diyl)dibenzoic Acid and (E)-2,2'-Diamino-4,4'-(ethene-1,2-diyl)dibenzoic Acid. There are three steps in the sythesis process, which were described in detail, respectively.

Synthesis of 3-Nitro-(4-chloromethyl) Benzoic Acid (Step 1). 230 mL of 96% sulfuric acid are poured into a 500 mL flask, and 130 mL of fuming nitric acid are slowly added under stirring. The above solution

Scheme 1. Synthesis Route of Modified Linear Ligands, H₂EDDC-NO₂ and H₂EDDC-NH₂



is cooled through a water and ice bath to a temperature of 0 °C. At this point, 10 g (0.0580 mol) of reagent are added, small portions at each time. The reaction continues for about 90 min, in which it is important that the reagent is completely dissolved inside the acid mixture. Then the mixture was poured into about 700 mL of water and ice. Solid white substance precipitates were formed, which are filtered off and subsequently washed in a beaker in order to remove the acid residues. The crystallization occurs in toluene.

Synthesis of (E)-2,2'-Dinitro-4,4'-(ethene-1,2-diyl)dibenzoic Acid (H_2 EDDC-NO₂) (Step 2). 45 mL of absolute ethanol are poured into a 250 mL beaker and 5.47 g (0.0970 mol) of KOH are slowly dissolved therein. At this point, 5.00 g (0.023 mol) of 3-nitro-(4-chloromethyl) benzoic acid are added. The precipitation of a brownish powder in the system immediately starts, being the potassium salt of dinitro-stilbenedicarboxylic acid. The system is left to react at room temperature for a time of about 45 min. The salt is filtered off under a vacuum and is dissolved in about 70 mL of water; it is necessary to increase the temperature until complete dissolution occurs. At this point, the acid ligand is precipitated with dilute hydrochloric acid, until pH = 1 is reached. The solid product is recovered, then dried in the stove. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C) δ (ppm): 12.97 (s, 2H), 8.62 (d, J = 3.0 Hz, 2H), 8.27 (d, J = 1.5 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.69 (s, 2H).

Synthesis of (E)-2,2'-Diamino-4,4'-(ethene-1,2-diyl)dibenzoic Acid ($H_2EDDC-NH_2$) (Step 3). 100 mL of distilled water are poured into a 250 mL beaker and 6.90 g (0.0288 mol) of sodium sulfide are dissolved therein. Once the salt is dissolved, 5.00 g (0.0138 mol) of dinitro-stilbenedicarboxylic acid are added. The system is kept boiling for a time of 15 min. At this point, under stirring, dilute hydrochloric acid is added up to a pH = 4–5. (E)-2,2'-diamino-4,4'-(ethene-1,2diyl)dibenzoic acid is precipitated, which is redissolved and reprecipitated in aqueous solution so to remove possible residues containing sulfur. The product is dried in an oven at 120 °C. ¹H NMR (300 MHz, DMSO- d_6 , 25 °C) δ (ppm): 12.97 (s, 2H), 8.62 (d, J = 1.8 Hz, 2H), 8.49 (d, J = 1.2 Hz, 4H), 8.3 (d, J = 1.2 Hz, 4H), 8.2 (d, J = 1.2 Hz, 4H), 7.69 (s, 2H).

Synthesis of Isostructural Zr-MOFs on the Basis of Modulated Synthetic Strategy. Synthesis of $[Zr_6O_4(OH)_4[EDDC)_6]$ (JLU-Liu34, Zr-H₂EDDC). A mixture of H₂EDDC (0.009 g, 0.034 mmol), ZrCl₄:4H₂O (0.007 g, 0.034 mmol), acetic acid (175 μ L), and DMF (2 mL) was sealed in a 20 mL vial and heated to 115 °C for 50 h, and then cooled to room temperature. The colorless octahedral crystals were collected and air-dried. The agreement between the experimental and simulated PXRD patterns indicated the phase-purity of as-synthesized product (Supporting Information, Figure S2).

Synthesis of $[Zr_6O_4(OH)_4(EDDC-NO_2)_6]$ (JLU-Liu35, Zr-H₂EDDC-NO₂). A mixture of H₂EDDC-NO₂ (0.012 g, 0.034 mmol), ZrCl₄. 4H₂O (0.007 g, 0.034 mmol), benzoic acid (0.240 g, 0.002 mol), and DMF (2 mL) were sealed in a 20 mL vial and heated to 115 °C for 50 h, and then cooled to room temperature. The yellow octahedral crystals were collected and soaked in DMF solution. The agreement between the experimental and simulated PXRD patterns indicated the phase-purity of as-synthesized product (Supporting Information, Figure S2).

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Synthesis of $[Zr_6O_4(OH)_4(EDDC-NH_2)_6]$ (JLU-Liu36, Zr-H₂EDDC-NH₂). A mixture of H₂EDDC-NH₂ (0.010 g, 0.034 mmol), ZrCl₄· 4H₂O (0.007 g, 0.034 mmol), benzoic acid (0.180 g, 0.0015 mol), and DMF (2 mL) was sealed in a 20 mL vial and heated to 115 °C for 50 h, and then cooled to room temperature. The orange octahedral crystals were collected and soaked in DMF solution. The agreement between the experimental and simulated PXRD patterns indicated the phase-purity of as-synthesized product (Supporting Information, Figure S2).

X-ray Structure Determination. Single-crystal X-ray diffraction data for suitable crystalline JLU-Liu 34 were recorded on a Bruker Apex II CCD diffractometer. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares analyses on F^2 (SHELXTL-97).²⁵ Unfortunately, because of the small crystal size and atom vibration, only a general structure can be determined by single-crystal X-ray diffraction data. Therefore, powder XRD patterns for JLU-Liu 34 were recorded in 2θ degree ranging from 4 to 140° with a 0.016 step size. To obtain accurate crystalline information, the General Structure Analysis System (GSAS)-EXPGUI was used to refine the XRD patterns.²⁶ For these isostructural compounds, carbon-carbon double bonds in the ligand cause a strong vibration in the framework, so we use both powder X-ray diffraction data and crystallographic data to complete the final structure simulation. All the XRD patterns of assynthesized samples match well with the simulation model as we expected.

RESULTS AND DISCUSSION

Introducing functional groups into pores of MOFs through ligand modification provides an efficacious strategy for tuning gas adsorption and separation performances without altering the original topologies.^{27–29} Therefore, we design and synthesize two functionalized ligands, H₂EDDC-NO₂ and H₂EDDC-NH₂, which have the same linear molecular geometry as H₂EDDC. On the basis of the modulated synthetic strategy,³⁰ two kind monocarboxylic acids (acetic acid or benzoic acid) were added to the Zr-MOFs synthetic system as modulators, and three isostructural crystalline Zr-MOFs with or without functional groups were successfully synthesized. All the resulting crystalline compounds exhibit the same crystal structure with **fcu** topologies and contain different substituent groups in the pores. The structures of these isostructural compounds have been described in detail, together with their chemical stabilities and gas sorption properties.

Structure Descriptions. Crystal Structure of JLU-Liu 34– 36. Selective single-crystal X-ray diffraction data for crystalline JLU-Liu 34 were recorded and analyzed. Because of the low diffraction intensity and carbon-carbon double bond atom vibrations, only a general structure can be determined. To further confirm and construct the simulated structure proposed by single-crystal X-ray diffraction data, the PXRD patterns of JLU-Liu34 are measured and refined by the GASA program.³¹ All the $R_{\rm w}$ and $R_{\rm wp}$ of the data are under 10% and 12%, respectively. Rietveld refinement of PXRD patterns for desolvated JLU-Liu34 could be obtained with satisfactory R factors using simulated models that predict biased Zr-O and Zr-Zr distances. On the basis of the results of XRD refinement and crystallographic data, we successfully calculated and constructed the structural models for these isostructural compounds. The experimental PXRD patterns (Figure S2, Supporting Information) obtained from the as-synthesized samples reveal that all the compounds are isostructural, although the modified functional groups of the ligand are different. The crystal structure of JLU-Liu34 was representatively illustrated in detail. JLU-Liu34 crystallizes in the cubic

 $Fm\overline{3}m$ space group with the cell of 29.99 Å. Each Zr atom is eight-coordinated by oxygen atoms in the as-synthesized materials and six Zr atoms form a 12-connected $Zr_6O_4(OH)_4$ metal center. Similar to the recently reported ZrMOF materials, the triangular faces of the Zr_6 octahedron are alternatively capped by μ_3 -O and μ_3 -OH groups.^{29,32} As shown in Figure 1,



Figure 1. Illustration for the construction of MOF-fcu.

all the polyhedron edges are bridged by the linear carboxylates (μ_2 -COO) originating from the dicarboxylic acids to form a $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster. There are also two types of polyhedral cages in these analogous UiO-66 type frameworks.^{33–35} Every six hexanuclear Zr cluster is linked to each other by ligands to form an octahedral cage with a distance of 24.6 Å between the opposite Zr_6 clusters, and another tetrahedral cages were consisted of five Zr_6 clusters with the side length of polyhedron is 17.4 Å (Figure 2). Different from other previous works which are focused on the moducation of ethynyl and ethenyl,^{36,37} two substituents were grafted to benzene rings to achieve isostructural functionalized compounds **JLU-Liu35** and **JLU-Liu36**.

FT-IR Spectroscopy Characterizations of JLU-Liu34-36. The presence of the introduced functional groups on the linear ligands and tagged Zr-MOFs was further evidenced by IR spectroscopy. The presence of the nitro group on the linkers is confirmed by the presence of typical spectroscopic features arising from aromatic nitro compounds. In particular, the nitro group shows absorption because of asymmetric and symmetric N–O stretching modes.³⁸ Asymmetric modes typically result in a strong band in the 1550-1500 cm⁻¹ region, symmetric modes absorption peaks in 1360-1290 cm⁻¹ region. JLU-Liu35 shows the presence of two additional bands in the abovementioned regions. The first is centered at 1340 cm⁻¹ and the second appears as a shoulder peaks at 1420 and 1525 cm^{-1} , which can be reasonably ascribed to the -NO₂ group.³⁹ As shown in Figure S3, the IR spectra of the JLU-Liu36 have two medium absorptions which is different from the spectra of JLU-Liu34; one is centered at 3355 cm⁻¹ and the other one is centered at 3450 cm⁻¹. These peaks stand for the asymmetric and symmetric N-H stretching modes, respectively.

Thermal Stability and Chemical Stability of JLU-Liu 34– 36. Thermogravimetric analysis (TGA) was performed on crystalline samples under atmosphere from 30 to 800 °C (Figure S4) which indicates that all of isostructural Zr-MOFs display high thermal stability due to their stable Zr₆ clusters.⁴¹ It is worth mentioning that even the electrons of the functional groups are different; the NH₂-modified JLU-Liu36 is electron rich and NO₂-modified JLU-Liu35 is electron poor, and there is not any loss for the thermal stabilities. JLU-Liu34 is selected



Figure 2. Two types of cages in isostructural Zr-MOFs with different sizes.



Figure 3. (a) The different functional groups in the section and PXRD patterns of as-synthesized tagged Zr-MOFs, showing the framework stability of upon treatments in water, pH = 1, and pH = 12 aqueous solutions for 3 days, (b) JLU-Liu34; (c) JLU-Liu35; (d) JLU-Liu36, respectively.

as an example to discuss the thermal stability of the three compounds. The TG curve shows a mass loss of 35.7% below 500 °C due to the release of nomadic DMF molecules, unbonded acetic acid, and the coordinated DMF molecules. The sharp weight loss of 41.4% from 500 to 700 °C corresponds to the decomposition of the ligand. Thus, JLU-Liu34 could undergo decomposition at a rather high temperature at ~500 °C. As for the other two modified MOFs, JLU-Liu35 and JLU-Liu36 also maintain their frameworks above 450 °C. Moreover, the release rate of nomadic solvent molecules slow down at a lower temperature which is caused by the steric hindrance in the functionalized materials. This phenomenon also attests to the existence of

functional groups and their strong intermolecular interaction with solvents. In spite of these variations, it is worth mentioning that all of these isostructural Zr-MOFs with or without functional groups exhibit better thermal stability than UiO-66 and other MOFs materials.^{33,42}

The stabilities of these compounds toward water, acid (HCl aqueous solution, pH = 1), and base (NaOH aqueous solution, pH = 12) were also tested and analyzed. A series of Zr-H₂EDDC samples were immersed in the corresponding solvent for 3 days at room temperature. As it is shown in Figure 3, all of these materials revealed quite high resistance toward these chemical treatments, and the chemical stabilities of modified Zr-H₂EDDC materials were similar to the untagged JLU-Liu34.



Figure 4. (a) The N_2 adsorption and desorption isotherms of JLU-Liu34 and JLU-Liu36 at 77 K; (b) pore size distribution of JLU-Liu34 and JLU-Liu36 calculated using the DFT method.



Figure 5. (a) CO₂₁ (b) CH₄₁ (c) C₂H₆₁ (d) C₃H₈ gas sorption isotherms for JLU-Liu34 and JLU-Liu36 at 273 and 298 K under 1 bar.

In addition, even in water and HCl solution, all of them maintain their good crystallinity. However, **JLU-Liu35** showed the best structure stability in high concentrations of NaOH aqueous solution which is better than **JLU-Liu34** and -NH₂ grafted **JLU-Liu36**. The high water stability of **JLU-Liu35** can be ascribed to the low hydration number of the nitro group.^{15,43} The results demonstrate that thermal and chemical stability of Zr₆-based MOFs are completely retained even after function-alization. These high stable materials show potential applications in different fields, such as postsynthesis, catalysis, and biochemistry.^{44–47}

Gas Adsorption Behaviors. Inspired by the large void volume of the frameworks, gas adsorption properties of these isostructural materials were studied. The as-synthesized samples of **JLU-Liu34**, **JLU-Liu35**, and **JLU-Liu36** were respectively solvent exchanged with CH₃CN, EtOH, and CH₂Cl₂ several times, and all of them were activated for 10 h under 150 °C

before gas adsorption measurement (Figures S5-S7). In order to evaluate the permanent porosity of these isostructural MOFs, N₂ adsorption experiments were detected at 77 K. As shown in Figure 4, JLU-Liu34 and JLU-Liu36 exhibit similar Type I nitrogen gas adsorption isotherms, and Brunauer-Emmett-Teller (BET) surface area were calculated to be ca. 2496 and 2619 m² g⁻¹, respectively. The pore size distributions of JLU-Liu34 and JLU-Liu36 calculated by using a nonlocal density functional theory (NLDFT) method show a microporous feature with a pore size of about 1.2 nm, which is homologous to the crystalline data (Figure 4b). As shown in Figure S12, JLU-Liu35 exhibits less BET surface area which was calculated to be ca. 1103 $m^2 g^{-1}$. This is because the guest molecules cannot be removed absolutely by solvent exchange or evacuation, which could be confirmed by PXRD and TGA (Figures S10 and S11). Recently, similar structural material UBMOF-9 with high hydrogen storage capacity has been

Article



Figure 6. (a) Adsorption enthalpies of CO_2 for JLU-Liu34 (red) and JLU-Liu36 (blue), (b) CO_2/CH_4 mixture adsorption selectivity is predicted by IAST at 298 K and 100 kPa for JLU-Liu36.



Figure 7. CO_2 , CH_4 , C_2H_6 , and C_3H_8 adsorption isotherms at 298 K along with the dual-site Langmuir Freundich (DSLF) fits (a, c); gas mixture adsorption selectivity are predicted by IAST at 298 K and 100 kPa for JLU-Liu34 (b, d).

reported, but a systematic study of the other small molecular gas storage performance has not been carried out.¹⁵ Therefore, the CO₂ and small hydrocarbon gas adsorption isotherms of **JLU-Liu34** and **JLU-Liu36** were measured to investigate the roles of amino group in gas sorption and separation properties. At 273 K and atmospheric pressure, the amount of CO₂ uptake of **JLU-Liu34** and **JLU-Liu36** was close and reaches 58.9 and 54.7 cm³ g⁻¹ (ca. 2.63 and 2.46 mmol g⁻¹), respectively. To compare the affinity of **JLU-Liu34** and functionalized **JLU-Liu36** to CO₂, the isosteric heat (Q_{st}) was also calculated (Figure 6). At zero-coverage, the Q_{st} value of CO₂ for **JLU-Liu34** and **JLU-Liu36** is ca. 22.2 and 26.8 kJ mol⁻¹, respectively. The increased Q_{st} of -NH₂ modified **JLU-Liu36** could be due to favorable interactions between adsorbed CO₂ molecules and the Lewis basic sites in amine groups decorated in the pores.^{48,49} The adsorption isotherms of CH₄, C₂H₆ and C₃H₈ are also measured at 273 and 298 K under 1 bar, respectively. The maximum adsorption of **JLU-Liu34** for CH₄ is 16.0 and 9.1 cm³ g⁻¹, C₂H₆ is 118.8 and 59.4 cm³ g⁻¹, and C₃H₈ is 303.2 and 240.0 cm³ g⁻¹, respectively (Figure 5). It is worth mentioning that the maximum adsorption of **JLU-Liu34** for C₃H₈ is higher than many reported MOF materials.^{50,51} At zero loading, Q_{st} of CH₄, C₂H₆, and C₃H₈ adsorption of **JLU-Liu34** is 23.0, 22.2, and 30.2 kJ mol⁻¹, respectively (Figure 7). For comparison, the maximum adsorption of **JLU-Liu36** for CH₄ is 14.7 and 8.6 cm³ g⁻¹, C₂H₆ is 109.5 and 55.6 cm³ g⁻¹, and C₃H₈ is 291.1 and 223.2 cm³ g⁻¹, respectively. The Q_{st} of CH₄, C₂H₆, and C₃H₈ adsorption of **JLU-Liu36** was calculated to be 15.3, 22.0, and 29.6 kJ mol⁻¹, respectively. These results demonstrate that **JLU-Liu36** can inherit most small hydrocarbon gas adsorption capacities of **JLU-Liu34**, due to their similar BET surface area and pore sizes.

The CO_2/CH_4 (50% and 50%, 5% and 95%) adsorption selectivity was also calculated by ideal adsorption solution theory (IAST).^{52,53} All of results were obtained by fitting the experimental single-component isotherms through the dual site Langmuir Freundlich (DSLF) model at 298 K and 1 atm.⁵⁴ The selectivity of CO₂ over CH₄ for JLU-Liu34 according to the experimental data is 5.2 and 5.9 (Figure 7). In comparison, the selectivity of CO₂/CH₄ is 5.8 and 6.2 for JLU-Liu36 (Figure 6). It is highlighted that the selectivity of CO_2/CH_4 for JLU-Liu36 is comparable to the higher values for many reported MOFs, such as JLU-Liu15,⁵⁵ JLU-Liu18,⁵⁶ BUT-10,⁵⁷ and MOF-508b (Table S2).⁵⁸ The selectivity of CO_2/CH_4 for JLU-Liu36 is much higher than isostructural JLU-Liu34, demonstrating that functionalized amino groups of the ligands are able to efficaciously enhance the CO_2 adsorption capacities. Furthermore, the selectivity of equimolar mixtures C_2H_6/CH_4 and C3H8/CH4 for JLU-Liu34 is 8.7 and 45.9, respectively (Figure 6). The C_2H_6/CH_4 and C_3H_8/CH_4 adsorption selectivity for JLU-Liu36 were also calculated and fitted (Figure S13). Because of their similar structures and pore sizes, the results for separation of C₂H₆/CH₄ and C₃H₈/CH₄ were close to that of JLU-Liu34. Therefore, these results show that introducing the amino groups in the pores is indeed useful in decorating MOFs for CO₂ capture and selectivity.

CONCLUSION

In summary, with the aim of investigating the role of the functional groups in gas sorption and separation, three isostructural functionalized Zr6-based MOFs materials with fcu topologies have been assembled and analyzed by using a modulated synthetic strategy. In terms of highly stable 12connected $Zr_6O_4(OH)_4(CO_2)_{12}$ SBUs in the framework, functionalized MOFs with different substituent groups retain high thermal and chemical stabilities. Furthermore, JLU-Liu34 and JLU-Liu36 exhibit high BET surface area and significant gas adsorption behaviors. In spite of the decreased pore sizes and surface areas compared with the parent JLU-Liu34, JLU-Liu36 exhibits a relatively high CO₂ adsorption selectivity which demonstrates that incorporating amino groups onto the Zr₆-based MOF structure can effectively enhance the affinity toward CO_2 molecules. In addition, the CO_2/CH_4 adsorption selectivity and adsorption enthalpy for the amino modified JLU-Liu36 were also significantly increased. On the basis of ligand functionalization, the affinity of JLU-Liu34 to CO_2 has been enhanced successfully. Hence, this work not only illustrates a successful case of designing functionalized Zr-MOFs with high thermal and chemical stabilities, but also provides a convenient strategy to obtain efficient CO₂ capture materials.

ASSOCIATED CONTENT

S Supporting Information

These materials are available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00090.

Optical images, PXRD patterns, the FT-IR spectra, and thermogravimetric analysis for JLU-Liu34–36, N₂, CO₂, CH₄, C_2H_6 , and C_3H_8 gas adsorption isotherm and pore

size distribution for JLU-Liu35, CO₂, CH₄, C₂H₆, and C₃H₈ adsorption isotherms at 298 K along with the dualsite Langmuir Freundich (DSLF) fits and gas mixture adsorption selectivity for JLU-Liu36, and isosteric heat of CH₄ and C₂H₆ for JLU-Liu34 and JLU-Liu36 (PDF)

Accession Codes

CCDC 1533694 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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