Inorganic Chemistry

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Modulation of Topological Structures and Adsorption Properties of Copper-Tricarboxylate Frameworks Enabled by the Effect of the **Functional Group and Its Position**

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analyses revealed that the variation of functionalities and their positions furnished three different types of topological structures, which we ascribed to the steric effect exerted by the methyl group and the chelating effect involving the pyridinic-N atom. Furthermore, gas adsorption studies showed that three of them are potential candidates as solid separation media for acetylene (C_2H_2) purification, with the separation potential tailorable by altering functionalities and their locations. At 106.7 kPa and 298 K, the C_2H_2 uptake capacity varies from 64.1 to 132.4 cm³ (STP) g⁻¹, while the adsorption selectivities of C_2H_2 over its coexisting components of CO_2 and CH_4 fall in the ranges of 3.28–4.60 and 14.1–21.9, respectively.

Copper

1. INTRODUCTION

Metal-organic frameworks (MOFs), as a subclass of coordination polymers, are a new class of porous crystalline materials made up of a wide range of inorganic (metallic ions/ clusters) and organic (multidentate organic ligands) building blocks that link via dative bonds to generate ordered periodic networks featuring modular design and fabrication as well as mild synthetic conditions, in conjunction with a large surface area, exceptional porosity, tunable pore size, and designable framework functionality that are unattainable in the conventional porous solids. By virtue of such a structural superiority, MOFs have been developing fleetly as a research arena for myriad applications including but not limited to molecular capture/separation,^{1,2} recognition/sensing,³ chemical transformation,⁴ and drug delivery.⁵ Specifically, for the separation of environment/energy-relevant gases, molecular-sieving separation,⁶⁻⁹ selectivity-reversing adsorption,¹⁰⁻¹⁷ and singlecolumn multicomponent purification¹⁸ of mixed gases with very similar properties have been realized by using porous MOF solids as physisorbents, which have the potential to significantly simplify the separation scheme and process design.

Cu(II)-based MOFs were solvothermally constructed. Diffraction

The structural modulation of MOFs is of great theoretical and practical significance because the physicochemical properties and applications of MOF materials are intimately related to their structures. The previous topology design was achieved by using the geometrically matched molecular building blocks to replace the network nodes, but this method is restricted by a limited number of network prototypes.^{19,20} A turning point is the evolution of reticular chemistry wherein the single-metal ions are replaced with the polynuclear clusters, providing access to a multitude of MOFs with diversified topologies. Nonetheless, to fully explore the potential utility and push forward the structural development, it is still highly desirable to expand the topological diversity and enhance the structural complexity of MOFs. In general, the ligand design and selection are very critical factors in MOF construction. By employing the ligand elongation/contraction/truncation/desymmetry/angle variation strategies, the organic ligands can be engineered in terms of size, rigidity/flexibility, geometry, shape, symmetry/unsymmetry, and connectivity. Such a high level of

ZJNU-113

Received: March 11, 2021 Published: May 21, 2021



Article







^aFor H₃L1, partial atomic labels are shown.

ligand designability delivers flexibility, diversity, complexity, and tunability to topological structures of the MOF materials, which have been successfully demonstrated by some famous research groups of Zhou, Li, Maspoch, Trikalitis, Eddaoudi, Matzger, and so on.²²⁻³⁰ For example, by disrupting the ligand collinearity, Maspoch et al. used zigzag-shaped dicarboxylate linkers to construct a family of isoreticular Zr-based MOFs adopting a 8-connected bcu topology instead of a 12connected fcu topology typically observed for the linear dicarboxylate linkers.²⁶ Zhou and Li et al. very recently prepared a series of rare-earth MOFs derived from tetracarboxylate ligands with different sizes, rigidities, and symmetries and disclosed that the topological structure is heavily dependent on the ligand backbone geometry.²⁴ In particular, two unprecedented (4, 8)-c net topologies of lxl and jun were also obtained in their systematic exploration. Although remarkable progress has been made in MOF structural development by judicious ligand design, structural modulation in a synthetically controllable and predictable manner remains a significant challenge. Furthermore, to facilitate the future rational design of MOFs, it is necessary to understand which structural parameter of the ligands plays a key role in dictating the finial network architectures of the resultant MOFs.

As we know, ligand functionalization has been frequently applied to engineer the pore surface, thus endowing the MOFs with varied properties including selective adsorption, framework flexibility,³¹ and stability against water³¹ and desolvation.^{32,33} In principle, the incorporation of accessible polarized functional groups can strengthen the framework affinity toward some specific gas molecules with large quadrupole moments such as C_2H_2 and carbon dioxide (CO₂) and thus improve their adsorption properties.³⁴⁻³⁷ Besides, ligand functionalization also has a complicated influence on the formation and structure of MOFs. Upon coordination of the installed functionality with the metal ions, the isoreticulation and even the formation of MOFs might be prohibited. Even though the functional group remains uncoordinated, it is also capable in some cases of altering the conformation of an organic ligand, which further offers an opportunity for the design and discovery of unusual structures deviating from the default topology.³⁸ Zhou³⁹ and Farha⁴⁰ et al. respectively reported the structural tuning of Zr-tetracarboxylate frameworks toward diverse topologies by ligand functionalization controlling linker conformation. Recently, by introducing the methyl group into ligand skeleton to fix the ligand conformation, we successfully targeted the fabrication of a Cu(II)-triisophthalate framework with a novel topology instead of the usually observed rht type.⁴¹ Considering that UMCM-150,⁴² a well-known MOF based on a biphenyl tricarboxylate ligand featuring symmetrically unequivalent carboxylate groups, displays excellent

performance in gas-phase and liquid-phase adsorption,⁴³ we in this work aimed to enrich structural diversities and tune the gas adsorption properties of the UMCM-150-based system by employing a ligand functionalization strategy. By introducing the methyl group and pyridinic-N atom at the different positions of the biphenyl scaffold, we designed and synthesized two pairs of tricarboxylate linkers (Scheme 1) and constructed their corresponding Cu(II)-based MOFs under suitable solvothermal conditions. Their structural elucidations via Xray diffraction studies and performance evaluations via singlecomponent isotherm measurements and IAST selectivity predictions were systematically conducted. The results showed that engineering the substituents and their positions provides access to three different kinds of topological structures and enables facile modulation of selective gas adsorption properties related to C₂H₂ separation and purification.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization Details. Dimethyl 5-(pinacolboryl) isophthalate was prepared by following our own published protocol. ⁴⁴ All of the other starting materials are commercially available and used as received without further depuration. All of the solvents used are analytical grade. Deionized water (H_2O) was used throughout this research. Silica gel (100–200 mesh) purchased from Qingdao Haiyang Chemical Lt. Co. was used for column chromatography purification. Solution-state ¹H/¹³C NMR (nuclear magnetic resonance) spectra were recorded on a Bruker AV400/600 NMR instrument, with the samples dissolved in CDCl₃ (for trimethyl ester intermediates) or DMS \hat{O} - d_6 (for target ligands). The proton and carbon chemical shifts (δ) were referenced to the residual solvent peaks. The δ values were reported in parts per million (ppm), and coupling constants (J), in Hertz (Hz). FTIR (Fourier transform infrared) spectral data were gathered in transmission mode on a Nicolet 5DX FTIR spectrometer in the wavenumber range of 4000-400 cm⁻¹ with the sample dispersed in a KBr pellet (sample/ KBr = 1:100 by mass). The CHN contents were assayed on a PerkinElmer 240 CHN elemental analyzer. Thermal behaviors were characterized by thermogravimetric analyses (TGA), which were conducted on a Netzsch STA 449C thermal analyzer in a flow of dinitrogen (N_2) at a heating rate controlled to 5 K min⁻¹. PXRD (powder X-ray diffraction) investigations were accomplished on a Bruker D8 Advance diffractometer with Cu K α radiation (λ = 1.5418 Å) over an angular range of 5–45° (2 θ). Predicted powder patterns were generated from single-crystal structures using Mercury software. Gas adsorption isotherm data were collected on a Micrometrics ASAP (accelerated surface area and porosimetry) 2020 HD88 instrument. The dead space estimation is based on helium (He, 99.999% purity). The gases used for adsorption measurements have the following purities (C₂H₂, 99.9%; CO₂, 99.99%; methane (CH₄), 99.999%; and N_2 , 99.9999%). Before the isotherm data collection, the sample activation was carried out according to the protocol below. The guest species in as-made ZJNU-111 and ZJNU-114 were exchanged with anhydrous acetone, and then the exchanged samples were heated at a rate of 1 K min⁻¹ to a temperature of 373 K under a dynamic vacuum.

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For ZJNU-112 and ZJNU-113, the as-synthesized solids were subsequently guest-exchanged with acetone, dichloromethane, and *n*-hexane and heated at a rate of 1 K min⁻¹ to a temperature of 333 K under a dynamic vacuum. The samples were considered to be activated when the degassed rate of 2 μ m Hg min⁻¹ was approached. The PXRD measurements revealed that their framework structures were retained after the above activation treatments (Figure S1). During the gas adsorption measurement, the samples were refrigerated at 77 K by immersing the sample tube in a liquid-N₂ bath and maintained at the other temperatures by using a circulating H₂O bath.

2.2. Single-Crystal X-ray Diffraction. Diffraction intensity data for ZJNU-111-114 were collected with a Bruker D8 Venture Photon II diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å). A Cryostream 800 system (Oxford Cryosystems) and a SADABS program were used for temperature regulation and absorption correction, respectively. The direct method and full-matrix least-squares method on F^2 were used to solve and refine all of the structures, with anisotropic thermal parameters for all non-hydrogen (H) atoms. The H atoms were placed in calculated positions with fixed isotropic thermal parameters. The lattice guest molecules were treated as the diffuse contribution to the overall scattering by SQUEEZE/PLATON.⁴⁵ The details on crystallographic data and refinement parameters were listed in Table S1 in the Supporting Information.

2.3. Synthesis and Characterization of the Organic Ligands. *2.3.1. 3'-Methylbiphenyl-3,4',5-tricarboxylic Acid (H₃L1).* Into a 500 mL Schlenk flask were placed dimethyl 5-(pinacolboryl)isophthalate (2.31 g, 7.22 mmol), methyl 4-bromo-2-methylbenzoate (1.50 g, 6.55 mmol), anhydrous Cs₂CO₃ (3.20 g, 9.82 mmol), Pd(PPh₃)₄ (0.19 g, 0.164 mmol), and dry 1,4-dixoane (150 mL), and the resultant mixture was stirred gently under reflux and a N₂ atmosphere for 48 h. After the usual workup, chromatography purification on a silica gel column with the eluent consisting of petroleum ether/ethyl acetate (4/1 v/v) afforded the trimethyl ester precursor as an off-white solid with a yield of 24% (0.54 g, 1.58 mmol). ¹H NMR (CDCl₃, 600.1 MHz) δ (ppm): 8.710 (t, *J* = 1.8 Hz, 1H), 8.500 (d, *J* = 1.8 Hz, 2H), 8.056 (d, *J* = 9.0 Hz, 1H), 7.551–7.564 (m, 2H), 4.013 (s, 6H), 3.952 (s, 3H), 2.722 (s, 3H).

Target ligand H₃L1 was quantitatively obtained by 6 mol L⁻¹ NaOH-mediated saponification of the trimethyl ester precursor and subsequent acidification with concentrated HCl. ¹H NMR (DMSO $d_{6^{\prime}}$ 600.1 MHz) δ (ppm): 13.280 (br, 3H), 8.485 (s, 1H), 8.414 (s, 2H), 7.958 (d, *J* = 7.8 Hz, 1H), 7.690 (s, 1H), 7.654 (d, *J* = 7.8 Hz, 1H), 2.510 (s, 3H). ¹³C NMR (DMSO- $d_{6^{\prime}}$ 150.9 MHz) δ (ppm): 168.794, 166.891, 141.743, 140.711, 140.478, 132.623, 131.916, 131.739, 130.509, 130.399, 129.825, 124.789, 21.779. Selected FTIR data (KBr, cm⁻¹): 1736, 1695, 1610, 1460, 1423, 1308, 1284, 1261, 1209, 1186, 1147, 1074, 768, 719, 673, 652, 447.

2.3.2. 2'-Methylbiphenyl-3,4',5-tricarboxylic Acid (H₃L2). The synthesis procedure of H₃L2 is similar to that of H₃L1, except that methyl 4-bromo-3-methylbenzoate was used in place of methyl 4bromo-2-methylbenzoate. The trimethyl ester precursor was purified by silica gel column chromatography with the petroleum ether/ethyl acetate (10/1 v/v) as an eluent. The overall yield is approximately 36%. For the precursor of trimethyl ester, ¹H NMR (CDCl₃, 600.1 MHz) δ (ppm): 8.725 (t, J = 1.2 Hz, 1H), 8.221 (d, J = 1.2 Hz, 2H), 8.008 (s, 1H), 7.953 (d, J = 7.8 Hz, 1H), 7.326 (d, J = 7.8 Hz, 1H), 3.992 (s, 6H), 3.972 (s, 3H), 2.325 (s, 3H). For the target ligand H₃L2, ¹H NMR (DMSO-*d*₆, 600.1 MHz) δ (ppm): 13.290 (br, 3H), 8.507 (s, 1H), 8.102 (s, 2H), 7.926 (s, 1H), 7.861 (d, J = 7.8 Hz, 1H), 7.407 (d, J = 7.8 Hz, 1H), 2.509 (s, 3H); ¹³C NMR (DMSO- d_{6} , 150.9 MHz) δ (ppm): 167.572, 166.851, 144.106, 141.544, 135.793, 133.869, 132.058, 131.883, 130.821, 130.356, 129.446, 127.619, 20.393; selected FTIR (KBr, cm⁻¹): 1740, 1689, 1458, 1429, 1323, 1296, 1273, 1196, 1138, 1111, 1051, 924, 899, 881, 849, 762, 719, 673, 656, 650, 467.

2.3.3. 5-(6-Carboxypyridin-3-yl)isophthalic Acid (H_3L3). H_3L3 was synthesized according to the protocol for H_3L1 except that methyl 5-bromopicolinate was used instead of methyl 4-bromo-2-

methylbenzoate. The ester precursor was purified by recrystallization in toluene. The overall yield is approximately 25%. For the precursor of trimethyl ester, ¹H NMR (CDCl₃, 400.1 MHz) δ (ppm): 9.037 (d, J = 2.4 Hz, 1H), 8.781 (t, J = 1.6 Hz, 1H), 8.507 (d, J = 1.6 Hz, 2H), 8.285 (d, J = 8.0 Hz, 1H), 8.133 (dd, J = 8.0 Hz, 2.4 Hz, 1H), 4.078 (s, 3H), 4.023 (s, 6H); for the target ligand H₃L3, ¹H NMR (DMSO d_{60} 600.1 MHz) δ (ppm): 13.537 (br, 3H), 9.087 (s, 1H), 8.523 (s, 1H), 8.476 (s, 2H), 8.365 (d, J = 7.2 Hz, 1H), 8.149 (d, J = 7.8 Hz, 1H); ¹³C NMR (DMSO- d_{61} , 150.9 MHz) δ (ppm): 166.764, 166.425, 148.260, 148.202, 137.657, 137.233, 136.274, 132.864, 132.293, 130.421, 125.409; selected FTIR (KBr, cm⁻¹): 1728, 1593, 1454, 1387, 1240, 1151, 1080, 1034, 906, 872, 800, 758, 723, 681, 536, 438.

2.3.4. 5-(5-Carboxypyridin-2-yl)isophthalic Acid (H_3L4). The synthesis protocol of H_3L1 was adopted to prepare target ligand H_3L4 except that methyl 4-bromo-2-methylbenzoate was substituted with methyl 6-bromonicotinate. The overall yield is approximately 43%. For the precursor of trimethyl ester, ¹H NMR (CDCl₃, 400.1 MHz) δ (ppm): 9.345 (dd, J = 2.0 Hz, 0.8 Hz, 1H), 8.957 (d, J = 1.6 Hz, 2H), 8.801 (t, J = 1.6 Hz, 1H), 8.434 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.967 (dd, J = 8.0 Hz, 0.8 Hz, 1H), 4.021 (s, 6H), 4.017 (s, 3H). For target ligand H₃L4, ¹H NMR (DMSO- d_6 , 600.1 MHz) δ (ppm): 13.510 (br, 3H), 9.182 (s, 1H), 8.882 (s, 2H), 8.544 (s, 1H), 8.362 (d, J = 8.4 Hz, 1H), 8.249 (d, J = 8.4 Hz, 1H); ¹³C NMR (DMSO- d_6 , 150.9 MHz) δ (ppm): 166.804, 166.505, 157.721, 150.992, 138.971, 138.899, 132.562, 131.957, 131.473, 126.274, 120.925; selected FTIR (KBr, cm⁻¹): 1911, 1720, 1605, 1450, 1414, 1375, 1240, 1134, 1082, 1036, 930, 903, 864, 804, 787, 756, 725, 677.

2.4. Synthesis and Characterization of the MOFs. 2.4.1. ZJNU-111. To a 20 mL glass vial preloaded with CuCl₂· 2H₂O (10.0 mg, 58.7 μ mol) and H₃L1 (5.0 mg, 16.7 μ mol) were added 1.5 mL of DMF (*N*,*N*-dimethylformamide), 0.2 mL of deionized H₂O, and 20 μ L of 6 mol·L⁻¹ HCl aqueous solution. The vial was screw-capped tightly and placed in a preheated oven at the temperature of 353 K for 48 h. During this period, the green, thin, plate-shaped crystals of ZJNU-111 were generated, which were isolated by decanting off the mother liquor and washing with fresh DMF several times. The yield is about 67% based on H₃L1. Selected FTIR (KBr, cm⁻¹): 3433, 1657, 1439, 1389, 1365, 1254, 1099, 775, 729, 663; elemental analysis for C₁₆₅H₂₂₉Cu₉N₂₃O₆₆, calcd: C, 47.61%, H, 5.55%, N, 7.74%; found: C, 47.69%, H, 5.58%, N, 7.66%.

2.4.2. ZJNU-112. To a 20 mL glass vial containing CuCl₂·2H₂O (15.0 mg, 88.0 μ mol) and H₃L2 (5.0 mg, 16.7 μ mol) were added N-methylformamide/tetrafluoroboric acid (NMF/HBF₄, 1.5 mL/0.1 mL). The vial was screw-capped tightly and placed in an isothermal oven at 353 K. After the vial was held at this temperature for 72 h under autogenous pressure, it was removed from the oven. The blue, thin, plate-shaped crystals of ZJNU-112 formed from the solution were isolated by decanting off the mother liquor and washed thoroughly with fresh DMF several times. The yield is about 54% based on H₃L2. Selected FTIR (KBr, cm⁻¹): 3433, 1664, 1585, 1541, 1439, 1414, 1369, 1095, 918, 777, 758, 737, 723, 661, 492. Elemental analysis for C₆₄H₇₄Cu₄N₆O₂₆. Calcd: C, 48.12%, H, 4.67%, N, 5.26%; found: C, 48.27%, H, 4.69%, N, 5.33%.

2.4.3. ZJNU-113. A mixture of $Cu(NO_3)_2$ · $3H_2O$ (5.0 mg, 20.7 μ mol) and H₃L3 (5.0 mg, 17.4 μ mol) was dispersed in 1.0 mL of DMA (*N*,*N*-dimethylacetamide), 50 μ L of deionized H₂O, and 50 μ L of 3 mol·L⁻¹ HCl, which was added to a 20 mL glass vial. The vial was screw-capped tightly and placed in a preheated oven at 363 K. After an incubation period of 96 h under autogenous pressure, the blue crystals of ZJNU-113 thus formed were isolated by decanting off the mother liquor and washed with fresh DMA several times. The yield is about 49% based on H₃L3. Selected FTIR (KBr, cm⁻¹): 3446, 3082, 2794, 2482, 1653, 1605, 1574, 1360, 1265, 1043, 769, 685; elemental analysis for C₃₂H₃₆CuN₄O₁₅. Calcd: C, 49.26%, H, 4.65%, N, 7.18%; found: C, 49.49%, H, 4.68%, N, 7.22%.

2.4.4. ZJNU-114. DMF (1.5 mL) and deionized H₂O (0.2 mL) were added to a 20 mL glass vial containing CuCl₂·2H₂O (10.0 mg, 58.7 μ mol) and H₃L4 (5.0 mg, 17.4 μ mol). The vial was screw-capped tightly and placed in a preheated oven at 358 K. After 48 h under autogenous pressure, the blue, thin, plate-shaped crystals of



Figure 1. SCXRD structure of **ZJNU-111**. Views of three different types of (a-c) Cu(II)-carboxylate clusters, (d-f) tricarboxylate anions featuring varied torsional angles, and (g-i) Cu(II)-organic polyhedral cages. Spheres of different colors highlight the cage voids. (j) A view of the 3D network along the crystallographical *c* direction. Color codes of the atoms: C, gray; O, red; N, blue; Cu, pink. For clarity, hydrogen atoms were deleted.

ZJNU-114 thus acquired were harvested by decanting off the mother liquor and washing with fresh DMF several times. The yield is about 44% based on H₃L4. Selected FTIR (KBr, cm⁻¹): 3421, 1655, 1439, 1387, 1296, 1279, 1254, 1103, 771, 727. Elemental analysis for $C_{46}H_{62}Cu_3N_8O_{22}$. Calcd: C, 43.51%, H, 4.92%, N, 8.83%; found: C, 43.59%, H, 4.89%, N, 8.94%.

3. RESULTS AND DISCUSSION

The unsymmetrical tritopic biaryl tricarboxylate linkers investigated in this work were facilely obtained in a two-step organic synthesis with decent to good isolated yields. Briefly, starting with dimethyl 5-(pinacolboryl)isophthalate and the corresponding brominated methyl esters as starting materials, a palladium-catalyzed cross-coupling reaction produced the respective trimethyl ester precursors, which underwent deesterification under basic conditions and acidification with HCl to furnish the target tricarboxylate ligands. ¹H and ¹³C NMR measurements (Figure S19) and FTIR spectroscopic characterizations (Figure S3) unequivocally verified their chemical structures. Subsequently, the targeted ligands were solvothermally coassembled with the Cu(II) cation, affording crystalline solids whose structures can be established by single-crystal Xray diffraction. For the convenience of the following description, the resulting compounds were termed ZJNU-111, ZJNU-112, ZJNU-113, and ZJNU-114 corresponding to linkers H₃L1, H₃L2, H₃L3, and H₃L4, respectively. The final chemical formulas of ZJNU-111, ZJNU-112, ZJNU-113, and ZJNU-114 were best established to be $[Cu_9(L1)_6(H_2O)_7(DMF)_2] \cdot 21DMF, [Cu_4(L2)_3(H_2O)] \cdot$ MeNH₃·5DMF·2H₂O, $[Cu(HL3)_2]$ ·2Me₂NH₂·3H₂O, and $[Cu_3(L4)_2(H_2O)_3]$ ·6DMF·H₂O according to single-crystal structural analyses, the SQUEEZE results, TGA (Figure S2), and microanalyses. As shown in Figure S1, the experimental and predicted PXRD patterns were coincident, affirming the homogeneity of the as-synthesized bulk materials.

Single-crystal X-ray diffraction characterization shows that compounds ZJNU-111 and ZJNU-114 are isostructural but crystallize in different space groups: Ama2 for ZJNU-111 and P6₃/mmc for ZJNU-114. The structural details are illustrated below by taking ZJNU-111 as a representative. The asymmetrical unit consists of three fully deprotonated ligands connecting to six crystallographically unique divalent Cu(II) ions axially coordinated by five H₂O molecules and one DMF molecule. The occupancy is 0.5 for half of the Cu(II) ions (Cu4, Cu5, and Cu6) and H_2O molecules ($H_2O(1-5)$, $H_2O(1-6)$, and $H_2O(1-7)$) and 1.0 for the remaining species. All of the Cu(II) centers are pentacoordinated by four oxygen atoms coming from four carboxylate groups and one oxygen atom provided by the terminal species, displaying squarepyramidal geometry. The Cu–O_{COO} bond lengths range from 1.879 to 2.007 Å. As commonly observed in Cu(II)carboxylate frameworks, bridging a pair of adjacent Cu(II) ions by four carboxylate groups from isophthate units yields the ubiquitous $[Cu_2(COO)_4]$ paddlewheel-shaped diCu(II) cluster acting as a secondary building unit (SBU). It is worth noting that there exist two crystallographically distinct paddlewheel units dubbed SBU-I (Cu2-Cu3, Figure 1a) and SBU-II (Cu1–Cu1, Figure 1b), with intrapaddlewheel Cu…Cu distances of 2.664 and 2.673 Å, respectively. The H₂O and DMF molecules serving as terminal ligands are binding to the axial locations of SBU-I and SBU-II, respectively. The diCu(II) paddlewheel unit is connected to four tricarboxylate ligands and thus can be taken as a square-planar 4-connected node. SBU-III consists of three neighboring Cu(II) ions bridged by six carboxylate groups from methylbenzoate units, providing a trigonal-prism-shaped 6-connected node by linking to six L1³⁻ anions (Figure 1c). As shown in Figure 1d-f, three crystallographically unique ligands assume different conformations, with the torsional angles between the two central benzene rings of 29.1, 30.5, and 29.3° for λ -L1, τ -L1, and ω -L1,

Figure 2. SCXRD structure of **ZJNU-112**. Views of (a, b) two different kinds of metallic SBUs and (c) the organic ligand with a torsional angle of 86.7° between the two central benzene rings. Views of (d, e) two different kinds of Cu(II)-organic polyhedral cages and (f) the 3D network structure along the *c* axis. The color codes of the atoms are the same as those in Figure 1. The hydrogen atoms are omitted for clarity.



Figure 3. SCXRD structure of ZJNU-113. Views of (a) the coordination modes and environments of Cu(II) ions and (b, c) the ligands with the different backbone torsional angles. (d) A side view of a metal-organic square flanked with two ligands. Views of (e) the 2D layer along the *bc* plane and (f) the 3D supramolecular network along the *b* axis, with hydrogen bonds indicated by blue broken lines. The color code of the H atom is white, while those of the other atoms are the same as those in Figure 1.

respectively. All of the ligands connect to two diCu(II) clusters and one triCu(II) cluster, serving as a 3-connected node. By means of the assembling fashion above-mentioned, a threeperiodic (3,4,6)-connected three-nodal network was generated with the agw topological type and the $\{6^3\}_6\{6^4\cdot 8^2\}_3\{6^6\cdot 8^3\cdot 10^6\}$ point symbol, as calculated with Topos software. A careful inspection of the entire structure revealed three different types of polyhedral cages denoted as A, B, and C in a 1:1:1 ratio, whose voids were highlighted with different colors in Figure 1g–i. Cage A consists of 6 ligands $(2 \lambda - L1 + 2 \tau - L1 + 2 \omega - L1)$ connected to 6 diCu(II) clusters (4 SBU-I + 2 SBU-II) and 3 triCu(II) clusters. Cage B is formed by 6 diCu(II) clusters (4 SBU-I + 2 SBU-II) and 2 triCu(II) clusters bridged by 6 ligands (2 λ -L1 + 2 τ -L1 + 2 ω -L1). Cage C is encircled by 6 diCu(II) clusters (4 SBU-I + 2 SBU-II), 3 triCu(II) clusters, 12 ligands (4 λ -L1 + 4 τ -L1 + 4 ω -L1), and 6 isophthalate units. The maximum diameters of the spheres embedded in cages A-C are estimated to be 11.3, 9.8, and 12.2 Å, respectively, taking the van der Waals radii into account. As estimated by PLATON calculations, the potential solventaccessible pore volume is as high as 16643 Å³ after removal of all of the guest species and coordinated solvent molecules, which is equivalent to 70.5% of the unit cell volume, highlighting its significant structural porosity.

When the methyl substituent is shifted from the 3'-position to the 2'-position, the resulting compound, ZJNU-112,

exhibits a network structure distinctly different with that of its corresponding counterpart, ZJNU-111 (Figure 2f). ZJNU-112 crystallizes in the trigonal space group of R32:H, with lattice parameters of a = b = 18.3673(19) Å and c = 36.460(6)Å. In addition to the disordered guest species, the content of the asymmetrical unit includes two independent Cu(II) cations (Cu1 and Cu2) with occupancies of 1 and 1/3 for Cu1 and Cu2, one fully deprotonated ligand anion, and one H₂O molecule coordinated to a Cu2 ion, thus leading to a negatively charged framework with a chemical formula moiety of $Cu_4(L2)_3(H_2O)$, which is balanced by the disordered methanaminium in situ generated by NMF decomposition during solvothermal transformation. The Cu1 ion is surrounded by five carboxylate oxygen atoms originating from five different ligands, adopting square-pyrimidal coordination geometry, while the Cu2 ion displays an octahedral coordination geometry completed by three carboxylate oxygen atoms from three separate linkers and three terminal water molecules. The adjacent Cu1 ions are bridged by four carboxylate groups from isophthalate units to create a diCu(II) paddlewheel-shaped cluster with the axial positions occupied by carboxylate oxygen atoms from methylbenzoate units (Figure 2b, SBU-IV), which is distinct with the diCu(II) cluster in its counterpart ZJNU-111, wherein the axial position is accompanied by a H₂O or DMF molecule. Besides a diCu(II) cluster, a mononuclear {CuO₄} SBU is formed

around a Cu2 ion (Figure 2a, SBU-V), which is rarely observed in the literature MOFs. The diCu(II) cluster is linked to six organic ligands, thus serving as a 6-connected node, while the mononuclear SBU is connected to three organic ligands, which can be treated as a 3-connected node. Different from ZINU-111, the tricarboxylate ligand incorporated in ZJNU-112 adopts only one conformation with a torsional angle of 86.7° between the two central phenyl rings (Figure 2c) and connects to six Cu(II) ions through its three carboxylate groups. The carboxylate groups at the 3,5-position and 4'-position assume *cis-cis* and *trans-cis* $\mu_2:\eta^1\eta^1$ bridging coordination modes, respectively. The organic ligand is connected to three diCu(II) clusters and one mononuclear ion and therefore can be regarded as a 4-connected node. In such an assembly fashion, a (3,4,6)-connected 3-nodal network is generated with a new topology type and the $\{4^2 \cdot 6^4\}_6 \{4^4 \cdot 6^8 \cdot 8^3\}_3 \{6^3\}_2$ point symbol, as revealed by the Topos calculation. Two different types of Cu(II)-organic polyhedral cages are also observed in the entire network, which are illustrated in Figure 2d,e. If the metallic SBUs are taken as the polyhedral vertices, then cage D is a hexagonal bipyramidal cage composed of two mononuclear SBUs, six diCu(II) SBUs, and six organic ligands (Figure 2d), while cage E can be described as a bicapped triangular antiprism consisting of six diCu(II) SBUs and two mononuclear SBUs connected to six ligands (Figure 2e). The two kinds of cages are packed alternatively along the crystallographic c axis. The sizes of cages D and E were about 8.8 and 5.3 Å, respectively. The potential solvent-accessible pore volume equals 50.0% of the unit cell volume, as estimated by PLATON software.

Upon shifting the pyridinic N atom from the 2'-position to the 3'-position, the obtained compound ZJNU-113 exhibits a network structure distinctly different with that of its corresponding counterpart, ZJNU-114. ZJNU-113 is a discrete binuclear complex that crystallizes in the $P\overline{1}$ space group. The asymmetric unit is composed of one Cu(II) ion and two partially deprotonated HL3 ligands, two Me₂NH₂⁺ cations generated by in situ DMF decomposition, and one lattice water molecule. The Cu(II) center displays square-pyramidal geometry, with the coordinating donors provided by two trans pyridinic N atoms and two trans carboxylate oxygen atoms from two chelating pyrdine carboxylate units located in the equatorial plane and one carboxylate oxygen atom occupying at the axial position (Figure 3a). Because of the Jahn-Teller effect, the separation of 2.587 Å between the Cu(II) cation and the carboxylate oxygen atom at the apical position is larger than the corresponding values between the Cu(II) ion and the carboxylate oxygen atoms in the equatorial plane falling in the range of 1.931-1.938 Å. The Cu-N_{pvrdine} distance varies from 1.967 to 1.979 Å. As shown in Figure 3b,c, the two independent organic ligands are almost coplanar with slightly different torsional angles, which are 2.7 and 9.8° for α -L3 and β -L3, respectively. Besides different conformations, they also exhibit different coordination modes toward Cu(II) ions. The α -L3 ligand is connected to one Cu(II) ion through the pyridine carboxylate group adopting a bidentate chelating mode, while the β -L3 ligand is linked to two Cu(II) ions through its pyridine carboxylate group and isophthalate carboxylate group, which respectively assume bidentate chelating and monodentate coordination modes. Two Cu(II) ions with a separation of 9.787 Å are bridged by two oppositely aligned ligands to form a molecular square flanked by the two ligands (Figure 3d). The molecular squares are interlinked via

hydrogen bonding and $\pi-\pi$ interactions to form a 2D layer (Figure 3e), which are further packed together by hydrogen bonding (H4–1…O1–2 distance = 1.690 Å) to generate a 3D supramolecular network with the void filled by Me₂NH₂⁺ and H₂O forming hydrogen bonds with the framework carboxylate oxygen atoms (Figure 3f).

From the structural description above, it can be seen that the functionality and its position in the ligand backbone have a very important influence on the finial network architecture. To uncover the underlying reason responsible for the structural discrepancy, we first compare the structures of each pair of MOFs produced by using the same functional group grafted at different positions. When MOFs ZJNU-111 and ZJNU-112, with the ligand modified by the methyl group at different positions, are considered, it can be observed that the methyl group, as a noncoordinated group, is capable of sterically regulating the torsional angle of the ligand skeleton, depending on the position at which it is grafted. As expected, because of the steric hindrance effect of the methyl group adjacent to the isophthalate unit, the 2'-methyl-decorated ligand backbone displays a larger torsional angle than the 3'-methyl-modified counterpart. Accordingly, different torsional angles correspond to different ligand conformations. As such, the ligands with different conformations can function as organic nodes with different connectivities and connecting modes. Furthermore, to meet the specific requirement of ligand conformation and asymmetry, diversified inorganic SBUs might be formed in the coassembly process. Indeed, apart from the typical diCu(II) cluster, uncommon kinds of inorganic SBUs of trinuclear $Cu_3(COO)_6$ and mononuclear $Cu(COO)_3(H_2O)_3$, which are extremely rare for Cu(II) ions, are observed in the structures of ZJNU-111 and ZJNU-112, respectively. As a result, ZJNU-111 and ZJNU-112 display distinctly different network architectures. From the above analyses, it can be concluded that the structural difference between ZJNU-111 and ZJNU-112 mainly originates from the steric effect of methyl functionality regulating ligand conformations. Looking at another pair of MOFs with the ligands decorated with the pyridinic N atom, namely, ZJNU-113 and ZJNU-114, we notice that compared to the methyl group, the pyridinic N atom possesses one pair of lone electrons and therefore in principle can serve as a coordinating site. In ZJNU-113, the pyridinic N atom and carboxylate group are situated in adjacent locations and thus are capable of simultaneously binding to the same metallic ion. As a consequence, the thermodynamically favored chelating effect is yielded, significantly limiting the formation of the 3D coordination network. When the pyridinic N atom is far away from the carboxylate group, it remains free and the corresponding chelating effect does not occur. Obviously, whether a pyridinic N atom is involved in the chelating effect is the main reason for the structural discrepancy between ZJNU-113 and ZJNU-114. Next, we analyzed the structures of MOFs with the ligands decorated with different functional groups but at the same position. It can be observed that although the methyl group and the pyridinic N atom are introduced at the same location, the resulting MOFs possess distinctly different network architectures, indicating that the positional effect of the functional group varies from functionality to functionality. The above results demonstrate that engineering the functionality and its position is a potential synthesis strategy employed to modulate the MOF structures.

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Table 1. Summary	of the Text	ural Parameters	and Gas	Adsorption	Properties	of ZJNU-111,	ZJNU-112,	ZJNU-114, and	d
UMCM-150 ^a									

			gas uptake (cm ³ g ⁻¹ , STP) ^b		IAST adsorption selectivity ^b		
MOFs	$S_{\rm BET}/S_{\rm Langmuir}~({ m m}^2~{ m g}^{-1})$	$V_{\rm p}~({\rm cm^3~g^{-1}})$	C_2H_2	CO ₂	CH_4	C_2H_2/CH_4	C_2H_2/CO_2
ZJNU-111	2900/3109	1.1089	123.6	65.9	16.1	18.8	4.02
ZJNU-112	728/823	0.2990	64.1	43.1	15.6	14.1	3.28
ZJNU-114	3042/3375	1.2111	132.4	66.6	15.6	21.9	4.60
UMCM-150	3020/3375	1.2140	123.0	63.1	15.3	19.5	4.31

 ${}^{a}S_{\text{BET}}/S_{\text{Langmuir}}$: SSAs calculated according to BET and Langmuir equations. V_{p} : Total pore volume. ${}^{b}At$ a temperature of 298 K and a pressure of 106.7 kPa.



Figure 4. Gas adsorption properties of ZJNU-111, ZJNU-112, and ZJNU-114. (a) 77 K N₂ isotherms. (b) DFT-based pore size distributions. C_2H_2 , CO_2 , and CH_4 isotherms at (c) 298, (d) 288, and (e) 278 K. (f) Isosteric heat of C_2H_2 , CO_2 , and CH_4 adsorption as a function of gas loadings. The filled and unfilled symbols represent adsorption and desorption data. The vertical line in (f) indicated the error bar. STP stands for standard temperature and pressure.

It has been reported that a given coordinating group can be obliged to tilt away from its preferred orientation through the deliberate incorporation of steric hindrance in its ortho position, leading to a twisted ligand that in turn provides access to topologies that are generally not easily accessible.⁴⁰ However, in ZJNU-111, the steric hindrance of the methyl group does not induce a significant torsional angle between the carboxylate group and the benzene ring to which it is attached. Furthermore, the biphenyl backbone is almost coplanar, thus allowing the L1 ligand to display a comparable conformation to that of the undecorated tricarboxylate ligand used to construct its parent compound UMCM-150.42 As a consequence, ZJNU-111 is isostructural with UMCM-150. Similarly, the introduction of the pyridinic N atom in the 2'-position does not induce a significant distortion of the ligand skeleton, and thus ZJNU-114 is also isostructural with its parent compound, UMCM-150. Future work will focus on the introduction of substituents much bulkier than the methyl group in the ortho position of the 4'-carboxylate group to develop uncommon topological structures of Cu(II)-tricarboxylate frameworks.

An evaluation of their pore textural properties was conducted by volumetric measurements of N_2 sorption isotherms at 77 K. Their textural parameters, together with gas adsorption properties as discussed below, are summarized

in Table 1. As depicted in Figure 4a, ZJNU-113 displayed a negligible amount of N₂ adsorption, which is reasonable due to its nonporous supramolecular structure as revealed above by single-crystal X-ray diffraction. The nonporous nature of ZJNU-113 was also confirmed by the negligible uptakes of C_2H_2 , CO_2 , and CH_4 at 298 K (Figure S8). In contrast, the other three compounds instead adsorbed significant amounts of N₂, and according to their IUPAC classification, they exhibited typical type-I adsorption isotherms with a sharp uptake increase in the relatively low pressure region, indicative of their microporous structures. Employing BET (Brunauer-Emmet-Teller)/Langmuir equations with N₂ adsorption data gave the corresponding specific surface areas (SSAs) of 2900/ 3109 m² g⁻¹ for ZJNU-111, 728/823 m² g⁻¹ for ZJNU-112, and 3042/3375 m² g⁻¹ for ZJNU-114, respectively (Figures S4-S7). The relative pressure range used for BET SSA calculations was based on three consistency criteria defined by Rouquerol et al.⁴⁷ An estimation of the total pore volumes from the saturated amounts of N₂ adsorbed furnished the respective results of 1.1089 cm³ g⁻¹ for ZJNU-111, 0.2990 cm³ g⁻¹ for ZJNU-112, and 1.2111 cm³ g⁻¹ for ZJNU-114. As shown in Figure 4b, the DFT (density functional theory)based pore size distribution analyses showed that the pore diameter was mainly centered at 11.8 Å for ZJNU-111 and ZJNU-114 and was in the range of 5.0–8.0 Å for ZJNU-112,

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Figure 5. IAST adsorption selectivities of ZJNU-111, ZJNU-112, and ZJNU-114. Equimolar component (a) C_2H_2/CH_4 and (b) C_2H_2/CO_2 adsorption selectivities as a function of the bulk gas-phase pressures at 298 K. Influence of the measurement temperature on the equimolar-component (c) C_2H_2/CH_4 and (d) C_2H_2/CO_2 adsorption selectivities at a pressure of 106.7 kPa. Influence of the mixture composition on (e) C_2H_2/CH_4 and (f) C_2H_2/CO_2 adsorption selectivities at 298 K and 106.7 kPa. The connected lines were used as guides for the eyes.

which is consistent with the structural analyses above. Compared to their isostructural parent compound UMCM-150, ZJNU-114 has a comparable surface area and pore size, while ZJNU-111 exhibits much less data due to the methyl substituent occupying the partial pore volume and the terminal DMF molecules residing in a section of diCu(II) clusters. Compared to ZJNU-111 and ZJNU-114, ZJNU-112 displays a smaller surface area and pore size mainly as a result of different topological structures.

 C_2H_2 is regarded as a strategic resource used as not only an energy carrier but also a versatile organic building block for synthesizing various valuable chemicals. Despite wide applications in daily life and the chemical industry, one issue to be solved is associated with C2H2 separation and purification involving the recovery of C2H2 from unconverted CH₄ and CO₂ impurities because CO₂ is inevitably formed in the manufacturing process of C2H2 by oxidative coupling of CH₄. Because of the simple operational process as well as the environmentally friendly, cost-efficient, and energy-saving nature, a promising alternative to the traditional separation methods of solvent extraction and cryogenic distillation is based on the physisorption technology, which heavily relies on the development of porous materials. Burgeoning MOF materials have been recognized to be promising candidates as efficient separation adsorbents. The establishment of permanent porosity stimulated us to evaluate their utility as solid adsorbents for C₂H₂ separation and purification. As a starting point, measurements of the equilibrium adsorption data with respect to C₂H₂, CO₂, and CH₄ were undertaken under a pressure of up to 106.7 kPa and at three different temperatures of 278, 288, and 298 K. As shown in Figure 4ce, the adsorption-desorption process is fully reversible for each of the isotherms, as indicated by the overlapping of the adsorption and desorption branches. They displayed good cyclic stability, as revealed by consecutive isotherm measurements showing no apparent loss of uptake capacity (Figure

S9). Interestingly, the three compounds exhibited distinctly different adsorption behavior toward C2H2, CO2, and CH4 enabled by the effect of functionality and its position. For example, at 106.7 kPa and 298 K, the C2H2, CO2, and CH4 uptake capacities were recorded as 123.6, 65.9, and 16.1 cm³ (STP) g^{-1} for ZJNU-111, 64.1, 43.1, and 15.6 cm³ (STP) g^{-1} for ZJNU-112, and 132.4, 66.6, and 15.6 cm³ (STP) g⁻¹ for ZJNU-114. Not surprisingly, as a result of exothermic physical adsorption, the uptake values increased with the decrease in temperature. Of the three compounds, ZJNU-112 exhibited the lowest adsorption amounts of C₂H₂ and CO₂, presumably as a result of its lowest specific surface area. Compared to its isostructural compound ZJNU-114, ZJNU-111 exhibited comparable CO₂ and CH₄ uptake capacities despite a lower specific surface area. However, ZJNU-114 adsorbed a 7.1% larger amount than ZJNU-111 with respect to C₂H₂, which is mainly attributed to the larger specific surface area as well as the Lewis base pyridinic-N atom capable of yielding a hydrogen-binding interaction with the C_2H_2 molecule adsorbed. More intriguingly, each of the three compounds exhibited a higher adsorption capacity toward C₂H₂ than CO₂ and CH₄ in the temperature range investigated. The uptake ratios of C₂H₂ vs CO₂ and CH₄ at 298 K and 106.7 kPa are 1.88 and 7.68 for ZJNU-111, 1.49 and 4.11 for ZJNU-112, and 1.99 and 8.49 for ZJNU-114. The C_2H_2/CO_2 uptake ratio of ZJNU-114 is comparable to and even higher than that of some literature MOFs published for C_2H_2/CO_2 separation such as DICRO-4-Ni-I (1.87),⁴⁸ MFM-160 (1.86),⁴⁹ SIFSIX-Cu-TPA (1.73),⁵⁰ FeNi-M'MOF (1.58),⁵¹ UTSA-74 (1.53),⁵² NbU-10 (1.46),⁵³ ZJNU-13 (1.35),⁵⁴ ZJU-74 (1.29),⁵⁵ and NKMOF-1-Ni (1.19).⁵⁶ Apart from a higher C_2H_2 uptake capacity, each of them also displayed a larger isotherm profile slope with respect to C_2H_2 than CO_2 and CH_4 in the low-pressure region, indicating a much stronger binding strength toward C₂H₂ than toward CO₂ and CH₄. To quantity the gas-framework interaction, the isosteric heat of adsorption (Q_{st}) was

calculated from the isotherm data measured at 278, 288, and 298 K by the implementation of the Clausius–Clapeyron method, and the loading dependences of Q_{st} for C_2H_2 , CO_2 , and CH_4 are presented in Figure 4f. Indeed, each compound displayed higher Q_{st} values for C_2H_2 than for CO_2 and CH_4 during the whole adsorption process. In particular, the near-zero-coverage Q_{st} values for C_2H_2 are less than 35 kJ mol⁻¹ for all three compounds, implying relatively low energy consumption required for adsorbent regeneration. Taken together, the higher uptake capacity and adsorption affinity toward C_2H_2 than toward CO_2 and CH_4 indicated that they can be considered to be prospective adsorption agents employed for C_2H_2/CO_2 and C_2H_2/CH_4 separations.

To evaluate the adsorptive separation efficiency, we predicted the adsorption selectivity from unary isotherm data by employing widely used IAST (ideal adsorbed solution theory) methodology.⁵⁷ Before the IAST calculations were started, we correlated the isotherms data at three different temperatures simultaneously with the single-site Langmuir-Fredunlich equation, $q = q_{sat}bp^{\nu}/(1 + bp^{\nu})$, with *T*-dependent parameter $b, b = b_0 \exp(E/RT)$, yielding the corresponding fitting parameters listed in Tables S3-S5, which were used as input data in selectivity computations (Figures S10-S12). Figure 5a,b showed the calculated equimolar-component C_2H_2/CH_4 and C_2H_2/CO_2 adsorption selectivities as a function of the bulk gas-phase pressures at a temperature of 298 K. It can be seen that the adsorption selectivity of C_2H_2 over CH₄ and CO₂ exhibited a declining trend in the pressure range of 1-109 kPa. Specifically, at the atmospheric pressure, the C_2H_2/CH_4 and C_2H_2/CO_2 adsorption selectivities reached 18.8 and 4.02 for ZJNU-111, 14.1 and 3.28 for ZJNU-112, and 21.9 and 4.60 for ZJNU-114. Both C_2H_2/CH_4 and C_2H_2/CO_2 adsorption selectivities followed the hierarchy of ZJNU-114 > ZJNU-111 > ZJNU-112, which is also consistent with the priority order of C₂H₂ uptake capacity described above. The maximum values of uptake capacity and adsorption selectivity correspond to ZJNU-114 featuring the maximum specific area and uncoordinated pyridinic-N-functionalized site, meaning that ZJNU-114 performed the best among the three compounds for the recovery of C₂H₂ from CO₂ and CH₄. The C₂H₂/CO₂ adsorption selectivity of ZJNU-114 parallels and even transcends those of some reported MOFs such as TCuI (5.3),⁵⁸ JXNU-5 (5.0),⁵⁹ ZJU-195 (4.7),⁶⁰ SNNU-45 (4.5),⁶¹ UTSA-220 (4.4),⁶² ZJNU-15 (4.4),⁶³ FJU-90 (4.3),⁶⁴ JNU-1 (4.0),⁶⁵ BSF-1 (3.3),⁶⁶ and Co(btzip)(H₂btzip) (2.5),⁶⁷ and UPC-200(Al)-F-BIM (3.15)⁶⁸ but is surpassed by those of several top-performing MOFs (Table S8). Also, the C_2H_2/CH_4 selectivity value of ZJNU-114 rivals those of some literature MOFs, such as pyridine-decorated Zr-MOF Py-UiO-66 (21),⁶⁹ BUT-70B (23.3),⁷⁰ and UTSA-10 (6.2).⁷¹ Compared to undecorated compound UMCM-150, methylfunctionalized MOFs ZJNU-111 and ZJNU-112 exhibited a lower adsorption selectivity of C₂H₂ over CO₂ and CH₄, while the N-decorated MOF ZJNU-114 displayed higher selectivity values at 298 K and 106.7 kPa (Figures S16-S18). As shown in Figure 5c-f, when the analysis temperature and mixture composition are varied, the selectivity sequence is basically preserved. With decreasing temperatures, the adsorption selectivity of C₂H₂ in preference to CH₄ increased (Figure 5c), while that of C_2H_2 over CO_2 displayed different trends for all three compounds (Figure 5d and Figures S13-S15). Decreasing C₂H₂ content in mixed gases leads to increasing adsorption selectivity of C₂H₂ over its competing components

(Figure 5e,f). Collectively, the above results indicated that similar to the uptake capacity, the adsorption selectivity can also be tuned by the effect of functional groups and their locations.

4. CONCLUSIONS

We elaborately designed and synthesized two pairs of unsymmetrical biaryl tricarboxylate ligands that were modified with the methyl and pyridinic N atom aligned at different positions and used them to solvothermally fabricate the corresponding Cu(II)-based MOFs. Structural determinations showed that each couple of MOFs displayed different topological structures, depending on the functionality location. Also, when the functional group is changed from a methyl to a pyridinic N atom even at the same position, the resulting topological structure is not identical, revealing that the positional effect of the functional group varies from functionality to functionality. Besides topological structures, the gas adsorption properties can also be modulated by changing the functionality and its disposition, as revealed by systematic single-component isotherm measurements and comprehensive IAST adsorption selectivity analyses. This work not only reported a family of Cu(II)-tricarboxylate frameworks with diverse topologies and the promising potential for C₂H₂ separation and purification but more importantly revealed that engineering the functionality and its position is an effective strategy employed for regulation on the MOF structures and properties. The availability of various substituents not only facilitates structural design for the discovery of various and even unique topological structures but also enables access to tailored properties by pore surface modification. The application of such a design strategy to the other MOF systems is undergoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00753.

Additional figures displaying PXRD patterns, TGA curves, FTIR and NMR spectra, isotherm fitting, and SSA and IAST selectivity calculations; additional tables presenting the parameters with respect to structure refinement and isotherm fitting; and a summary of adsorption data (PDF)

Accession Codes

CCDC 2068417–2068420 contain 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.

ACKNOWLEDGMENTS

We acknowledge financial support from the Natural Science Foundation of China (no. 21771162) and the Natural Science Foundation of Zhejiang Province, China (LR16B010001).

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