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Improvement of Methane—Framework Interaction by Controlling Pore Size and Functionality of Pillared MOFs

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Supporting Information



ABSTRACT: The rational design of functionalized porous metal—organic frameworks (MOFs) for gas adsorption applications has been applied using three spacer ligands H₂DPT (3,6-di(pyridin-4-yl)-1,4-dihydro-1,2,4,5-tetrazine), DPT (3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine), and BPDH (2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) to synthesize TMU-34, $[Zn(OBA)(H_2DPT)_{0.5}]_n$. DMF, TMU-34(-2H), $[Zn(OBA)(DPT)_{0.5}]_n$. DMF, and TMU-5, $[Zn(OBA)(BPDH)_{0.5}]_n$.1.5DMF, respectively. By controlling the pore size and chemical functionality of these three MOFs, we can improve the interactions between CO₂ and especially CH₄ with the frameworks. Calculated $Q_{st}(CH_4)$ for TMU-5, TMU-34, and TMU-34(-2H) are 27, 23, and 22 kJ mol⁻¹, respectively. These Q_{st} values are among the highest for CH₄-framework interactions. For systematic comparison, two reported frameworks, TMU-4 and TMU-5, have been compared with TMU-34 and TMU-34(-2H) in CO₂ adsorption.

1. INTRODUCTION

Metal–organic frameworks (MOFs), a class of porous materials, show great promise for applications in gas storage and separation, because of their crystalline structure, high permanent porosity, high surface area, high pore volume, and adjustable pore size and shape.^{1–5} MOFs consist of metal ions or clusters as inorganic nodes which are connected by organic linkers through coordination bonds.^{6,7} Combination of a large variety of components, for example, metal ions and functionalized organic ligands, can afford a broad range of framework motifs with a large variety of pores.^{8,9} Hybrid materials like MOFs that combine the rigidity of inorganic clusters with the flexibility and tunability of organic molecules are promising candidates for a large variety of applications, especially gas storage and separation.^{10–12}

Mixed ligand MOFs are a subclass of MOFs which are tunable for targeted applications like gas adsorption. In mixed-linker MOF structures, usually two-dimensional metal carbox-ylate layers are pillared by linear linkers for increasing dimensionality to generate three-dimensional porous frame-works.^{13–15} Bispyridyl ligands have been employed often as spacers in order to tune the interlayer distance and chemical functionality.^{16–19} This approach provides a simple, rational,

and effective way to prepare desired porous frameworks for gas separation and storage.

Natural gas, which mainly consists of methane, after hydrogen, is a promising candidate as a clean energy source. Methane has the minimum number of carbons possible for a hydrocarbon, so it releases the minimum amount of CO_2 into the atmosphere.^{20–24} Mitigating the level of carbon dioxide in the atmosphere, with CO_2 being the major contributor to the greenhouse gas effect, is one of the most important present-day environmental concerns.^{25,26} On the other hand, methane has the maximum ratio of hydrogen to carbon, so it has the maximum theoretical octane number.^{20,27} Hence, the design of promising and efficient metal–organic frameworks for CH_4 storage and CO_2 capture is considered to be an effective way to reduce CO_2 emissions.

To date, a great deal of research has been devoted to the design of solid sorbents for methane storage by controlling a variety of parameters like surface area and pore volume and pore size and shape and introducing coordinately unsaturated metal sites (open metal sites, OMSs) or functional groups in

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Scheme 1. Representation of Oxygen and Nitrogen Donor Ligands



the structure.²³ There are two challenges to consider when introducing OMSs: (i) the difficulty of introducing and activating OMSs and (ii) the decrease in deliverable capacity of CH₄ in MOFs with OMSs.^{20,27} As deliverable methane capacity is more important in some cases than total methane storage capacity,²⁷ it is necessary to improve the other parameters such as pore size and functionality rather than introducing OMSs. Thus, mixed-ligand MOFs which are highly tunable in pore size and functionality are good candidates for improving methane—framework interactions.

In this work, our strategy is based on the design of mixedlinker MOFs with OBA (4,4'-oxybis(benzoic acid)) as the dicarboxylate linker coupled with functionalized pillared spacers for optimization of CO2 and CH4 adsorption by controlling pore size and functionality of the frameworks. OBA is a flexible, V-shaped oxygen donor ligand (Scheme 1) that we used previously to generate stable mixed-ligand MOFs.²⁸⁻³⁰ The azine-functionalized TMU-4 and TMU-5 frameworks have been reported. TMU-5 contains narrow pores that have stronger interactions with CO₂ in comparison with TMU-4.³¹ Herein, tetrazine-functionalized pillar spacers have been chosen for a systematic comparison with azine functional groups as Lewis bases. Tetrazine ligands also are nitrogen rich and hence Lewis basic, suggesting that (similar to azine groups) they can polarize CO₂ and to some extent also CH₄ molecules (Scheme 1).^{32,33} These two properties make tetrazine groups good candidates for gas adsorption. As a consequence, TMU-34 and TMU-34(-2H) were synthesized which contain tetrazinefunctionalized pores for systematic comparison with TMU-4 and TMU-5. TMU-4 along with TMU-34 and TMU-5 along with TMU-34(-2H) are isostructures. Furthermore, these frameworks have been investigated for their interaction with methane because of their appropriate pore size and functionality. For all MOFs, similarities (structure and pore shape) and differences (functionality and pore size) let us compare the influence of structure, functional groups, and pore size on CH₄-framework binding energy.

2. EXPERIMENTAL SECTION

2.1. Material and Characterization. All required chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted.

Melting points were measured on an Electrothermal 9100 apparatus. Infrared spectra were recorded using Thermo Nicolet IR 100 FT-IR. Ultrasonication was carried out in an ultrasonic bath SONICA-2200 EP (frequency of 40 kHz). The thermal behavior was measured with a PL-STA 1500 apparatus with a rate of 10 °C min⁻¹ in a static atmosphere of argon. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu K α radiation. Elemental analyses (carbon, hydrogen, and nitrogen) were carried out using a high-resolution Costech ECS 4010 CHNS-O Elemental Analyzer.

2.2. Gas Sorption Measurement. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms, and noncryogenic temperatures were controlled with a water circulator. N_2 isotherm measurements were collected at 77 and 298 K, CO_2 isotherm measurements were carried out at 273, 283, and 298 K, also CH_4 isotherm measurements were collected at 273 and 298 K.

2.3. X-ray Collection and Structure Determination. Intensity data were collected at 100 K on an ADSC Quantum 210r diffractometer device with a silicon double-crystal diffraction monochromator by synchrotron radiation type. The structure was solved by Phi Scan methods. Reflections were merged by SHELXL according to the crystal class for calculation of statistics and refinement. The solvent of DMF could not be located. Thus, PLATON/SQUEEZE has been used to calculate the diffraction contribution of the solvent molecule, thereby producing a set of solvent-free diffraction intensities. CCDC-1499123 contains the supplementary crystallographic data for TMU-34. The data can be obtained free of charge from the Cambridge Crystallographic Date Center via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Synthesis of Frameworks. Here, solvothermal methods for synthesizing appropriate crystals of TMU-34 and the sonochemical method for synthesizing a powder of all three frameworks are described. For all gas adsorption measurements, the powder of all three frameworks have been used which are synthesized by sonochemical methods.

Synthesis of $[Zn(OBA)(H_2DPT)_{0.5}]_n$ ·DMF (TMU-34). Solvothermal Method. Single crystals of TMU-34 suitable for X-ray diffraction were obtained by mixing $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 g, 0.2 mmol), H_2OBA (0.05 g, 0.2 mmol), and H_2DPT (0.048 g, 0.2 mmol) in 12 mL of DMF. This mixture was sonicated until all solids were uniformly dispersed (~5 min), and it was then heated at 120 °C in a glass vial. After 72 h, brown-orange crystals of TMU-34 were collected. Yield: 0.06 g (70% based on OBA). IR data (KBr pellet, ν/cm^{-1}) selected bands: 660(m), 777(m), 871(m), 1162(s), 1241(vs), 1391(vs), 1606(vs), 1679(s), 2926(m), 3271(m). Anal. Calcd for [Zn-(C₁₄O₅H₈)(C₁₂N₆H₁₀)_{0.5}]·(C₃ONH₇): C, 53.8; N, 10.9; H, 3.9. Found: C, 54.1; N, 11.4; H, 4.1.

Sonochemical Method. For synthesis of TMU-34 as a powder, $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.22 g, 1 mmol), H_2OBA (0.26 g, 1 mmol), and H_2DPT (0.24 g, 1 mmol) in 30 mL of DMF were mixed together. The mixture was sonicated for 160 min at ambient temperature and atmospheric pressure. Then the mixture was centrifuged, and the resulting powder was washed with DMF and dried at room temperature. Yield: 0.34 g (78% based on OBA). IR data (KBr pellet, ν/cm^{-1}) selected bands: 661(m), 778(m), 872(m), 1162(s), 1241(vs), 1407(vs), 1607(vs), 1674(s), 2928(m), 3273(m). Anal. Found for $[Zn(C_{14}O_5H_8)(C_{12}N_6H_{10})_{0.5}]$, (C_3ONH_7) : C, 54.0; N, 10.8; H, 4.2. Synthesis of $[Zn(OBA)(DPT)_{0.5}]$, DMF (TMU-34(–2H)). Sonochem-

Synthesis of $[Zn(OBA)(DPT)_{0.5}]_n$ DMF (TMU-34(-2H)). Sonochemical Method. A powdered sample of TMU-34(-2H) was synthesized by mixing Zn(CH₃COO)₂·2H₂O (0.22 g, 1 mmol), H₂OBA (0.26 g, 1 mmol), and DPT (0.24 g, 1 mmol) in 30 mL of DMF/acetonitrile (1:1) and sonicating for 60 min at ambient temperature and atmospheric pressure. The mixture was then centrifuged, and the resulting powder was washed with DMF and dried at 80 °C for 48 h. Yield: 0.37 g (85% based on OBA). IR data (KBr pellet, ν/cm^{-1}) selected bands: 656(w), 780(w), 874(w), 1091(w), 1160(m), 1231(m), 1399(vs), 1500(s), 1629(s), 1672(s), 3429(m). Anal.



Figure 1. (a) Binuclear Zn_2 cluster in TMU-34 (O, red; N, blue; C, gray; Zn, pink). (b) 3D Connolly surface representation of porous TMU-34 along the [1 0 1] direction. (c) Representation showing the pore channels and that the network is 2-fold interpenetrated (in brown and blue). (d) Representation of the pores highlighting the azine groups (blue balls) pointing toward the pores of TMU-34. In the Connolly surface representations, gray represents outside the surface and blue inside the surface. Hydrogen atoms and DMF molecules are omitted for clarity.

Found for $[Zn(C_{14}O_5H_8)(C_{12}N_6H_8)_{0.5}] \cdot (C_3ONH_7)$: C, 54.0; N, 10.9; H, 3.9.

Synthesis of $[Zn(OBA)(BPDH)_{0.5}] \cdot 1.5DMF$ (TMU-5). Sonochemical Method. TMU-5 was synthesized according to a reported procedure.²⁹ A powdered sample of TMU-5 was synthesized by mixing $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.22 g, 1 mmol), H_2OBA (0.26 g, 1 mmol), and BPDH (0.17 g, 0.7 mmol) in 30 mL of DMF and sonicating for 60 min at room temperature and pressure. The mixture was then centrifuged, and the resulting powder was washed with DMF and dried at 80 °C for 48 h. Yield: 0.35 g (80% based on OBA). IR data (KBr pellet, ν/cm^{-1}) selected bands: 652(s), 779(m), 873(m), 1021(m), 1092(m), 1162(s), 1233(vs), 1397(vs), 1499(m), 1631(vs), 1671(vs), 3414(w-br). Anal. Found for $[Zn(C_{14}O_5H_8)(C_{14}N_4H_{14})_{0.5}] \cdot (C_3ONH_7)_{1.5}$: C, 54.8; H, 4.2; N, 8.8.

2.5. Activation Method. For activating TMU-34 and TMU-34(-2H) frameworks before gas adsorption measurements, both samples were soaked in acetonitrile for 2 days to exchange the DMF. Then all samples were outgassed under high dynamic vacuum at 120 °C (Figures S1–S6). TMU-5 was activated as previously reported.²⁹

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The MOFs, TMU-5, TMU-34, and TMU-34(-2H), were synthesized via sonochemical reaction as detailed in the Experimental Section using zinc acetate, H₂OBA, and a pillared spacer ligand. PXRD patterns of all synthesized MOFs show that the sonochemical syntheses gave rise to TMU-5, TMU-34, and TMU-34(-2H), which are structurally identical to those prepared via solvothermal methods (Figure S5 and S6). Here, we used sonochemical methods for synthesizing all three frameworks instead of solvothermal methods, because the former is easy, fast, and scalable.

A new MOF, TMU-34, was synthesized via solvothermal method and characterized by X-ray crystallography. TMU-34 crystallizes in the monoclinic crystal system and $P2_1/c$ space group. TMU-34 is based on a binuclear Zn₂ unit (Zn1 and Zn2). Zn1 is tetrahedrally coordinated to three carboxylate O atoms (O2, O4, and O6) from three OBA ligands and one N atom (N1) from the H₂DPT ligand. Zn2 is tetrahedrally coordinated to three carboxylate O atoms (O1, O7, and O10)

from three OBA ligands and one N atom (N6) from the H₂DPT ligand (Figure 1a). The distance between Zn1 and Zn2 is 3.432 Å. Each binuclear Zn₂ unit is further linked to four equivalent neighbors through four OBA ligands to give 2D sheets. The 2D sheets are connected through the linear H₂DPT, extending the structure in three dimensions (Figures 1b). TMU-34 is doubly interpenetrated as shown in Figure 1c and shows one-dimensional 5.4×6.2 Å pores including the van der Waals radius. The internal surface of these pores is functionalized with the tetrazine groups of the H₂DPT ligands, which are highlighted in Figure 1d. For calculation of solventaccessible volume and porosity in the rigid framework of TMU-34, void space and pore volume have been calculated by PLATON to give 25% (nitrogen probe) and 0.27 cm³·g⁻¹, respectively.³⁴ Thermogravimetric analysis (TGA) of TMU-34 revealed a first weight loss in the range of 50-300 °C (calcd 14.4%, found 15.7%), which is attributed to the removal of DMF molecules inside the framework. Then a second weight loss was observed in the range of 315-500 °C, corresponding to the decomposition of the framework. The final residual weight for TMU-34 corresponds to that of ZnO (Figure S2).

By applying BPDB, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, instead of H₂DPT, TMU-4 is generated, which has been reported before.³¹ Similar to TMU-34, TMU-4 contains one-dimensional pores (6.8 \times 7.8 Å, including van der Waals radii) which are functionalized with azine groups along with a 2-fold interpenetrated framework (Figure 2).

TMU-5 is constructed from paddlewheel $Zn_2(COO)_4$ clusters that are pillared by BPDH spacer ligands. TMU-5 is shown in Figure 3a and functionalized with azine groups (Figure 3b). By using a DPT spacer ligand instead of BPDH, TMU-34(-2H) is generated and isostructural to TMU-5 (Figure S9, Table S3).^{31,35} Both structures contain 3-dimensional and interconnected pores (4.4 × 8.1 Å for TMU-34(-2H) and 3.8 × 5.6 Å TMU-5, including van der Waals radius) which have identical pore shape but different pore size and functionality. The TMU-34(-2H) framework is shown in Figure 3c and is functionalized with tetrazine groups (Figure



Figure 2. Comparison of TMU-4 and TMU-34 structure. (a) Twofold interpenetrated framework of TMU-4. (b) Azine-functionalized pore of TMU-4. (c) Two-fold interpenetrated framework of TMU-34. (d) Tetrazine-functionalized pore of TMU-34.



Figure 3. (a) Connolly representation of TMU-5. (b) Azinefunctionalized pore of TMU-5. (c) Connolly representation of TMU-34(-2H). (d) Tetrazine-functionalized pore of TMU-34(-2H).

3d). For TMU-5 void space and pore volume (PLATON) are calculated to be 24.1% (nitrogen probe) and 0.24 cm³·g⁻¹, respectively, while for TMU-34(-2H) these data are 24.6% (nitrogen probe) and 0.25 cm³·g⁻¹, respectively.³⁴

3.2. Gas Adsorption Measurements. 3.2.1. N_2 Adsorption at 77 K. The permanent porosity of TMU-5, TMU-34, and TMU-34(-2H) synthesized by sonochemical methods was verified by N_2 adsorption at 77 K, Figure 4. For all frameworks, isotherms reveal a type-I behavior which is a characteristic of a microporous material, but TMU-34(-2H) and TMU-5 show a



Figure 4. N₂ adsorption properties of TMU-5, TMU-34, and TMU-34(-2H) at 77 K.

hysteresis type H4 which is often associated with narrow pores in microporous materials.³⁶ TMU-5, TMU-34, and TMU-34(-2H) have BET surface areas of 580, 540, and 670 m² g⁻¹, respectively. The results show that the calculated pore volumes from N₂ adsorption, 0.30, 0.28, and 0.31 cm³ g⁻¹ at 77 K and p/ $p^{\circ} = 0.98$, are higher than the static pore volumes of 0.24, 0.27, and 0.25 cm³ g⁻¹ for TMU-5, TMU-34, and TMU-34(-2H), respectively. TMU-4 is nonporous toward N₂ molecules.³¹

3.2.2. CO_2 Adsorption and Separation. The sorption behavior of TMU-34 and TMU-34(-2H) toward CO₂ revealed that they can adsorb 29.6 (3.7% wt) and 43.5 $\rm cm^3 \cdot g^{-1}$ (5.44% wt), respectively, at 298 K and 1 bar (Figures 5a, S12, and S13). The isosteric heat of adsorption (Q_{st}) for CO₂ as a function of relative pressure was calculated for evaluating the affinity of tetrazine-functionalized frameworks, TMU-34 and TMU-34-(-2H), toward CO₂. CO₂ adsorption single-component isotherms at 273, 283, and 298 K have been fitted by the virial method. The calculated magnitudes of Qst at zero coverage for TMU-34 and TMU-34(-2H) are 23 and 30 kJ mol^{-1} , respectively (Figure 5b). In all pressure ranges, the magnitude of Q_{st} for TMU-34(-2H) is higher than TMU-34. These data reveal that TMU-34(-2H) has a higher affinity toward CO_2 in comparison with TMU-34 (Table S4). To evaluate the sorption performance of these two MOFs toward CO_2 in a binary mixture of CO_2/N_2 (15%/85%), we calculated the CO_2/N_2 selectivity factor. The selectivity factor was calculated at 298 K based on the IAST method and singlecomponent isotherm of CO₂ and N₂ proposed by Myers and Prausnitz (Figure 5c).³⁷ The selectivity factors for TMU-34 and TMU-34(-2H) initially were calculated to be 15.5 and 29.5, which increase up to 18.1 and 33.1 at higher pressure respectively (Table S9).

 CO_2 adsorption of TMU-4 and TMU-5 has been reported previously where TMU-5 has higher CO_2 adsorption and Q_{st} rather than TMU-4.³¹ Similar to TMU-4 and TMU-5 behavior in CO_2 adsorption, TMU-34(-2H), which is an isostructure with TMU-5, has a higher amount of adsorption and affinity toward CO_2 rather than TMU-34, which is an isostructure with TMU-4. This observation demonstrates that azine and tetrazine groups in 3D interconnected pores of TMU-5 and TMU-34(-2H) frameworks are more accessible rather than these Lewis basic groups in one-dimensional pores of TMU-4 and TMU-34 frameworks.

In two isostructural frameworks TMU-5 and TMU-34(-2H) the $Q_{st}(CO_2)$ are 43 and 30 kJ mol⁻¹, respectively.³¹ This noticeable difference is related to the different pore size and functionality of these two frameworks. The pores of TMU-5



Figure 5. CO_2 adsorption properties of TMU-34 and TMU-34(-2H): (a) CO_2 at 298 K, (b) isosteric heat of CO_2 adsorption, and (c) CO_2/N_2 selectivity.



Figure 6. CH₄ adsorption of TMU-5, TMU-34, and TMU-34(-2H): (a) CH₄ at 298 K and (b) isosteric heat of CH₄ adsorption.

contain methyl groups, and the presence of this group leads to a narrower pore size in TMU-5 rather than TMU-34(-2H). Also, methyl groups simply can increase the polarizability of the framework. Hence, narrower pore size and improved polarizability of the framework lead to higher affinity of CO₂ molecules toward TMU-5 framework.

On the other hand, in comparison of another two isostructure frameworks, TMU-4 and TMU-34, with onedimensional pores, calculated $Q_{\rm st}(\rm CO_2)$ are 25 and 23 kJ mol⁻¹. In contrast to TMU-5 and TMU-34(-2H), there is no significant difference in affinity of TMU-4 and TMU-34 toward CO₂ molecules. This phenomenon may be attributed to the one-dimensional pores of these two structures, which leads to limited accessibility of CO₂ molecules toward Lewis basic sites of these two structures.

3.2.3. CH₄ Adsorption. For CH₄ storage, it is necessary to optimize capacity and CH₄-framework interactions simultaneously.²⁷ Here, we focused on CH₄-framework interactions by combining the optimization of pore size and chemical functionality.

CH₄ adsorption was performed for TMU-5, TMU-34, and TMU-34(-2H) at 298 K and 1 bar (Figure 6a). The data show that TMU-5, TMU-34, and TMU-34(-2H) can adsorb 20.3 (2.54 wt %), 7.4 (0.93 wt %), and 15.5 cm³ g⁻¹ (1.96 wt %) of CH₄, respectively. TMU-4 did not adsorb CH₄ at all. By comparing the two isostructural frameworks, TMU-5 and TMU-34(-2H), the latter has higher pore size and BET surface area, but the former adsorbs more CH₄ at low pressure and room temperature. This may due to a stronger framework– CH₄ in TMU-5 compared to TMU-34(-2H). This behavior of TMU-5 and TMU-34(-2H) toward CH₄ is completely identical to the behavior of these two frameworks toward CO₂ molecules. For evaluating the binding energy of CH_4 -framework interactions, we calculated the Q_{st} for CH_4 adsorption in TMU-5, TMU-34, and TMU-34(-2H) at 273 and 298 K based on the virial method (Supporting Information). The Q_{st} for CH_4 adsorption was calculated at 1 bar, because errors in highpressure isotherm measurements are more significant than at low pressure.²⁷ Calculated Q_{st} for TMU-5, TMU-34, and TMU-34(-2H) are 28, 24, and 23 kJ mol⁻¹ at zero coverage, respectively (Figure 6b), which are among highest reported values for Q_{st} of CH_4 adsorption (Table 1).

Table 1. Comparison for Q_{st} Values of Methane Uptake

compound	Q _{st} (kJ mol ⁻¹) zero coverage	functionality	ref
PCN-14	30	anthracene	40
PCN-14	18.7	anthracene	27
NENU-520	29	tetrazole	41
TMU-5	27	azine, methyl	this work
MIL-120	27	Al-centered octahedral	42
SNU-50	26.8	iimide, OMSs	43
TMU-34	23	dihydrotetrazine	this work
TMU-34(-2H)	22	tetrazine	this work
Ni ₂ (dhtp)	22	OMSs	44

Optimal pore sizes for CH₄ uptake are in very good agreement with the kinetic diameter of one (4 Å) and two (8 Å) methane molecules.²⁰ In this case, the pore sizes of TMU-5 and TMU-34(-2H) are well matched with the kinetic diameter of one and two methane molecules, respectively. Hence, by controlling the pore size and functionality in these three MOFs,

Table 2. Comparison of BET Surface Area and CH4 Uptake with Some of the Other MOFs

		condition					
compound	BET (m^2/g)	pore volume (cm ³ /g)	T (K)	P (bar)	CH ₄ uptake (wt %)	ref	
SNU-25	795	0.368	298	1.01	0.7	45	
CUK-1	630	0.26	298	1.01	0.6	46	
Cu(tip)	810	0.34	298	1.01	1.6	47	
$Co_3(ndc)(HCOO)_3(\mu_3-OH)$	1386	0.58	298	1.0	1.1	48	
TMU-5	582	0.24	298	1.06	2.54	this work	
TMU-34(-2H)	667	0.25	298	1.06	1.94	this work	
TMU-34	536	0.27	298	1.06	0.93	this work	

we succeeded to improve the interaction between CH_4 and the framework.

Despite the moderate BET surface area and pore volume, the high $Q_{\rm st}$ values and improved methane uptake capacity (wt %) at room temperature and pressure (Table 2) can be attributed to the azine- and tetrazine-functionalized narrow pores in the MOFs discussed. This is especially the case for TMU-5, which is well matched with the kinetic diameter of CH₄. Also, the pores of TMU-5 consist of methyl groups which simply add to the polarizability of the framework and thereby increase London dispersion interactions with CH₄ molecules. Such behavior has been reported in which a methyl group can increase the interaction between a framework and CH₄.³⁸

On the other hand, in comparison of two tetrazinefunctionalized frameworks, TMU-34(-2H) has higher CH₄ adsorption in the entire range of pressure. Again, this higher adsorption may be attributed to differences in the structure of two frameworks whose 3D interconnected pores of TMU-34(-2H) cause to effectively interact with the framework with CH₄ molecules compared with limited accessibility of tetrazine groups to gas molecules in TMU-34. However, a slightly higher $Q_{\rm st}$ (CH₄) for TMU-34 in low pressures and zero coverage may be related to the more basic N(sp²) of H₂DPT pillar spacers.³⁹

These results reveal that controlling the pore size and chemical functionality in two tetrazine-functionalized frameworks, TMU-34 and TMU-34(-2H), and azine-functionalized MOF, TMU-5, can enhance the affinity of MOF toward CH₄ gas.

4. CONCLUSIONS

Three pillar-containing MOFs, TMU-5, TMU-34, and TMU-34(-2H), have been synthesized and investigated for CO₂ and CH₄ storage. We demonstrated that Lewis basic functionalized pores with appropriate size can enhance Q_{st} values and lead to higher methane uptake capacities. This may be attributed to the optimal azine- and tetrazine-functionalized pores in these three MOFs. TMU-5 is especially promising for methane uptake at ambient temperature and pressure because the pores are well matched with the kinetic diameter of CH₄ and the presence of methyl groups can increase the London dispersion interaction between the framework and CH₄.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02758.

Synthesis of pillar spacers, FTIR and TGA analysis, PXRD patterns, single-crystal X-ray diffraction data, N₂,

 $\rm CO_2$, and $\rm CH_4$ isotherms, $\rm Q_{st}$ and selectivity calculations (PDF)

(CIF)

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Notes

The authors declare no competing financial interest.

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