

Enhanced Carbon Dioxide Adsorption on Post-Synthetically Modified Metal-Organic Frameworks

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Four MOFs functionalized with **1**-Me, **1**-Pr, **1**-Ph, and **1**-PhCF₃ were prepared through post-synthetic modifications of a metal-organic framework (MOF), UMCM-1-NH₂ (**1**) with acetic, butyric, benzoic, and 4-(trifluoromethyl)benzoic anhydrides, respectively. Methane adsorption measurements between 253 and 298 K at pressures up to 1 bar indicated that both **1**-Ph and **1**-PhCF₃ adsorbed more CH₄ than the parent MOF, **1**. All the functionalized MOFs adsorbed more CO₂ than **1** under conditions similar to the CH₄ test. The introduction of functional groups promoted adsorption of both CH₄ and CO₂ despite significantly reducing Brunauer-Emmet-Teller (BET) surface area: 4170 (**1**), 3550 (**1**-Me), 2900 (**1**-Pr), 3680 (**1**-Ph), and 3520 m²/g (**1**-PhCF₃). Electron-withdrawing aromatic groups (**1**-Ph, **1**-PhCF₃) more effectively enhanced CO₂ adsorption than electron-donating alkyl groups (**1**-Me, **1**-Pr). In particular, **1**-Ph adsorbed 23% more CO₂ at 298 K and 50% more at 253 K than **1**.

Key Words : Metal-organic framework, Post-synthetic modification, Adsorption, Methane, Carbon dioxide

Introduction

Metal-organic frameworks (MOFs) – structures of metal ions connected to organic linkers through coordination bonds – can achieve very large Brunauer-Emmet-Teller (BET) surface areas of over 4000 m²/g.¹⁻⁶ Large surface areas generally aid MOFs to act as gas adsorbents and catalysis. To enhance the effectiveness of very porous MOFs for recognizing target adsorbents or substrates, their framework surfaces can be optimized or functionalized.⁷ For this, post-synthetic modification of MOFs can easily introduce various functional groups, allowing tuning of pore properties.^{8,9} Various post-synthetic modifications have been recently reported.¹⁰ For example, post-synthetic modification of microporous IRMOF-3 and DMOF-1 could control or improve the pore properties of the parent MOFs.¹¹⁻¹⁵ Both MOFs have 2-aminoterephthalate (BDC-NH₂) linkers, the amino groups of which can react with extrinsic modifiers such as organic anhydrides. A similar approach has also been applied to mesoporous UMCM-1-NH₂ using benzoic anhydride, producing UMCM-1-AMPh with increased hydrogen storage capacity at 77 K and 1 bar compared with the original UMCM-1-NH₂.¹⁵

UMCM-1-NH₂ (**1**), formulated as Zn₄O(BTB)_{4/3}(BDC-NH₂), has a similar structure to UMCM-1 (Zn₄O(BTB)_{4/3}(BDC)), though the BDC in UMCM-1 is replaced by BDC-NH₂ in **1**.^{3,15} These MOFs show unique N₂ isotherms at 77 K, exhibiting a clear step starting at P/P₀ = 0.2, attributable to the filling of the pores of the hexagonal channels that have 2.4 nm × 2.9 nm openings. Therefore, gas adsorption at pressures lower than P/P₀ = 0.2 is largely due to the fused microporous cages (1.4 nm × 1.7 nm) that form the wall of the large channel (Fig. 1). As the BDC-NH₂ linkers are located at the junctions of the microporous cages (Fig. 1),

the introduction of small functional groups to the linkers through post-synthetic modification would mainly affect the pore environment of the cages, without affecting the porosity of the large channel.

The capture and short-term storage of CO₂ are potentially important processes for mitigating climate change or purifying

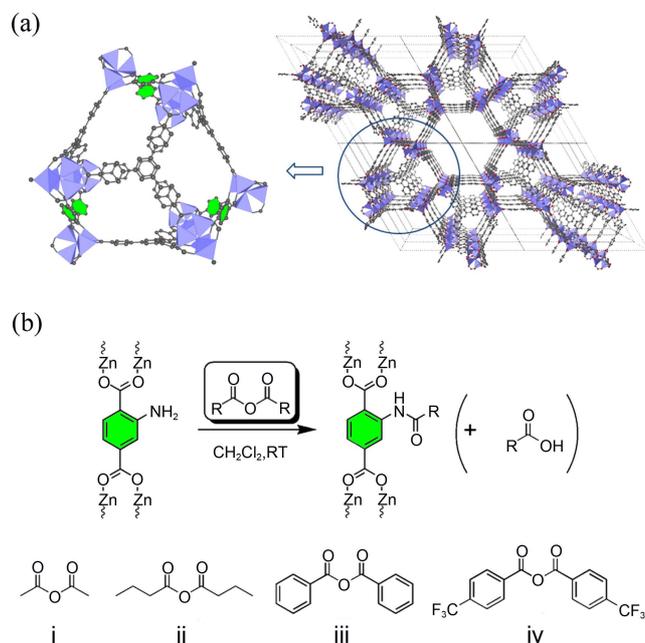


Figure 1. (a) Structure of UMCM-1-NH₂ (**1**) and its cage; Zn₄O units are shown as blue tetrahedra, and six BDC-NH₂ linkers are shown as green hexagons. The disordered -NH₂ groups are not shown; crystal coordinates are from ref. 13. (b) The post-synthetic modification of **1** with anhydrides to prepare functionalized MOFs, **1**-R, and the anhydrides used: i) acetic anhydride for **1**-Me, ii) butyric anhydride for **1**-Pr, iii) benzoic anhydride for **1**-Ph, and iv) 4-(trifluoromethyl)benzoic anhydride for **1**-PhCF₃.

natural gas. Therefore, many approaches have been investigated to increase CO₂ adsorption by MOFs, for example open-metal sites, framework interpenetration, flexible frameworks, interactions with amines, and polar framework surfaces.¹⁶ This work reports the tuning of CO₂ adsorption properties through functionalizing pores using functional groups with different inductive effects: electron-donating alkyl groups and electron-withdrawing aryl groups. Four MOFs (**1-R**, where R is Me, Pr, Ph, or PhCF₃) were prepared through the post-synthesis modification of **1** with acetic, butyric, benzoic, and 4-trifluoromethyl phenyl anhydrides, respectively (Fig. 1). Pr is a better electron-donating group than Me, and PhCF₃ is a better electron-withdrawing group than Ph. CO₂ adsorption isotherms of the MOFs were measured at 253, 273, and 298 K and at pressures up to 1 bar. Methane adsorption measurements were also conducted for comparison as both gases have similar polarizabilities but very different quadrupole moments.¹⁶ **1-Ph** and **1-PhCF₃**, functionalized by electron-withdrawing aromatic groups, were more effective CO₂ adsorbents than **1-Me** and **1-Pr**, modified by electron-donating alkyl groups.

Experimental

Chemicals. Acetic anhydride, butyric anhydride, 2-aminoterephthalic acid (H₂BDC-NH₂), dichloromethane, *N,N*-dimethylformamide (DMF), and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) were purchased from Sigma-Aldrich. Benzoic anhydride and 4-(trifluoromethyl)benzoic anhydride were purchased from TCI. All starting materials were used without further purifications. H₃BTB (4,4',4''-benzene-1,3,5-triyl-tribenzoic acid) was prepared according to a published procedure.

Physical Measurements. Elemental analyses were carried out on an EA 1110, CE instrument. IR spectra were recorded on a JASCO FT/IR-4000 spectrophotometer with samples prepared as KBr pellets. ¹H-NMR spectra of digested MOF crystals in DCI/DMSO were obtained on a Bruker 400 MHz NMR spectrometer. X-ray powder diffraction (XRPD) data were collected on a Rigaku MiniFlex diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Gas Adsorption Measurements. Adsorption isotherms of N₂, CO₂ and CH₄ at pressures up to 1 bar were measured by standard volumetric procedures on BELSORP-mini (BEL-Japan, INC.) equipment. Each sample was dried and fully outgassed at 160 °C under vacuum ($< 1.0 \times 10^{-3}$ torr) for 6 hr immediately before measurement. The dead volume of the sample cell was automatically measured using helium gas. Pressure equilibrium points were also collected automatically by the equipment. Each sample's weight was measured without exposing it to air. Using nitrogen isotherm points below $P/P_0 = 0.20$, BET surface areas were determined by the equation provided by the manufacturer. During CH₄ and CO₂ adsorption measurements, sample cells were maintained at 253 K in a dry ice/acetone bath, at 273 K in an ice/water bath, or at 298 K in a water bath. Plots of isosteric heats of adsorption were calculated using a virial equation; zero-coverage values were regarded as each MOF's heat of

adsorption.

Syntheses.

UMCM-1-NH₂ (1**):** H₃BTB (0.127 g, 0.29 mmol), H₂NH₂BDC (0.147 g, 0.811 mmol), and Zn(NO₃)₂·6H₂O (0.850 g, 2.86 mmol) were dissolved in DMF (30 mL). The reaction mixture was heated at 95 °C in a capped vial for 48 hr to give brown needle-shaped crystals (**1**). These were filtered and washed with neat DMF (5 \times 30 mL) and dichloromethane (5 \times 30 mL). The crystals were stored in dichloromethane for further use. Anal. Calcd (%) for the evacuated sample, Zn₄O(C₂₇H₁₅O₆)_{4/3}(C₈H₅NO₄): C, 48.99; H, 2.77; N, 1.30. Found: C, 49.00; H, 2.91; N, 1.31. FT-IR (KBr pellet, 4000-400 cm⁻¹): 3353 (br, w), 1585 (vs), 1541 (vs), 1406 (vs), 1253 (w), 1184 (w), 1109 (w), 1016 (m), 854 (m), 811 (w), 780 (s), 705 (m), 672 (w), 584 (w), 484 (w). ¹H-NMR spectrum (400 MHz, DCI/DMSO-*d*₆, δ): 8.10 (s, 4H), 8.07 (s, 16H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.45 (s, 1H), 7.11 (d, $J = 8.4$ Hz, 1H).

1-Me: Before its post-synthesis modification, **1** was washed again with dichloromethane and evacuated under reduced pressure ($< 1.0 \times 10^{-3}$ Torr) for 6 hr at 160 °C. Each batch reaction used *ca.* 30 mg sample in 1.0 mL stock solution prepared by dissolving acetic anhydride (f.w. 102.09, 2.0 mL) in 100 mL dichloromethane. After one day, the crystals were filtered and washed with neat dichloromethane (3 \times 5 mL) to remove the produced acetic acid. They were then placed in 1.0 mL fresh stock solution for one more day. This procedure was conducted a third time to complete the modification of **1** with acetic anhydride. Finally, the crystals were washed with neat dichloromethane (3 \times 5 mL) and left in neat dichloromethane for 48 hr to remove un-reacted species. Anal. Calcd (%) for the evacuated sample, Zn₄O(C₂₇H₁₅O₆)_{4/3}(C₁₀H₇NO₅): C, 49.33; H, 3.08; N, 1.25. Found: C, 49.31; H, 3.16; N, 1.41. FT-IR (KBr pellet, 4000-400 cm⁻¹): 3266 (br, w), 1585 (vs), 1544 (vs), 1407 (vs), 1304 (w), 1250 (w), 1184 (w), 1016 (m), 855 (m), 811 (w), 779 (s), 704 (m), 672 (w), 484 (w). ¹H-NMR (400 MHz, DCI/DMSO-*d*₆, δ): 9.03 (s, 1H), 8.10 (s, 4H), 8.07 (s, 16H), 7.68 (d, $J = 8.4$ Hz, 1H), 2.16 (s, 3H).

1-Pr: The post-synthetic modification was similar to that for **1-Me**. A stock solution was prepared by dissolving butyric anhydride (f.w. 158.19, 2.0 mL) in 100 mL dichloromethane. Three modification steps were conducted and the complete conversion of **1** to **1-Pr** took six days. Anal. Calcd (%) for the evacuated sample, Zn₄O(C₂₇H₁₅O₆)_{4/3}(C₁₂H₁₁NO₅): C, 50.46; H, 3.08; N, 1.23. Found: C, 50.47; H, 3.05; N, 1.22. FT-IR (KBr pellet, 4000-400 cm⁻¹): 3265 (br, w), 1585 (vs), 1543 (vs), 1408 (vs), 1184 (w), 1108 (w), 1016 (m), 960 (w), 854 (m), 811 (w), 779 (s), 705 (m), 672 (w), 562 (w), 507 (w). ¹H-NMR (400 MHz, DCI/DMSO-*d*₆, δ): 9.03 (s, 1H), 8.10 (s, 4H), 8.07 (s, 16H), 7.67 (d, $J = 8.4$ Hz, 1H), 2.38 (t, $J = 7.2$ Hz, 2H), 1.65 (q, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H).

1-Ph: The post-synthetic modification was similar to that for **1-Me**. Instead of making a stock solution, anhydride solution was prepared for each reaction step by dissolving benzoic anhydride (f.w. 226.23, 47.5 mg) in 1.0 mL dichloro-

methane. The complete conversion of **1** to **1-Ph** required three post-synthetic modification steps and took nine days. Anal. Calcd (%) for the evacuated sample, $\text{Zn}_4\text{O}(\text{C}_{27}\text{H}_{15}\text{O}_6)_{4/3}(\text{C}_{15}\text{H}_9\text{NO}_5)$: C, 50.63; H, 3.05; N, 1.16. Found: C, 50.63; H, 3.10; N, 1.13. FT-IR (KBr pellet, $4000\text{--}400\text{ cm}^{-1}$): 3247 (br, w), 1584 (vs), 1542 (vs), 1407(vs), 1305 (w), 1252 (w), 1184 (w), 1016 (m), 963 (w), 854 (m), 811 (w), 779 (s), 705 (m), 562 (w), 486 (w). $^1\text{H-NMR}$ (400 MHz, $\text{DCI}/\text{DMSO-}d_6$, δ): 9.27 (s, 1H), 8.13 (d, $J = 6.8\text{ Hz}$, 1H), 8.10 (s, 4H), 8.07 (s, 16H), 7.97 (d, $J = 7.2\text{ Hz}$, 2H), 7.75 (d, $J = 6.8\text{ Hz}$, 1H), 7.67 (t, $J = 4.8\text{ Hz}$, 1H), 7.62 (t, $J = 7.2\text{ Hz}$, 2H).

1-PhCF₃: The post-synthetic modification was similar to for **1-Ph**. Anhydride solution was prepared for each reaction step by dissolving 4-(trifluoromethyl)benzoic anhydride (f.w. 362.22, 76.1 mg) in 1.0 mL dichloromethane. The complete conversion of **1** to **1-Ph** required three post-synthetic modification steps and took six days. Anal. Calcd (%) for $\text{Zn}_4\text{O}(\text{C}_{27}\text{H}_{15}\text{O}_6)_{4/3}(\text{C}_{16}\text{H}_8\text{NO}_5\text{F}_3)$: C, 50.42; H, 2.54; N, 1.13. Found: C, 50.41; H, 2.50; N, 1.11. FT-IR (KBr pellet, $4000\text{--}400\text{ cm}^{-1}$): 3264 (br, w), 1584 (vs), 1543 (vs), 1409 (vs), 1326 (m), 1252 (w), 1171 (m), 1128 (m), 1065 (m), 1015 (m), 899 (w), 855 (m), 811 (w), 779 (s), 706 (m), 509 (w). $^1\text{H-NMR}$ (400 MHz, $\text{DCI}/\text{DMSO-}d_6$, δ): 9.18 (s, 1H), 8.15 (d, $J = 8.0\text{ Hz}$, 2H), 8.14 (d, $J = 8.0\text{ Hz}$, 1H), 8.09 (s, 4H), 8.06 (s, 16H), 7.99 (d, $J = 8.0\text{ Hz}$, 2H), 7.77 (d, $J = 8.0\text{ Hz}$, 1H).

Results and Discussion

Syntheses and Characterization. **1-Me**, **1-Pr**, and **1-Ph** have been previously reported as UCMC-1-AM1, UCMC-1-AM3, and UCMC-1-AMPh, respectively by Cohen *et al.*^{14,15} In this work, these materials were prepared by modified procedures and dichloromethane solvent. **1-Ph** was produced with a higher conversion yield. During the reactions, crystals in the reaction batch were collected and analyzed by $^1\text{H-NMR}$ to monitor the degree of conversion. Conversions were generally 85-90% after the first reaction step, ~95% after the second, and >99% after the third. All the functionalized MOFs could be quantitatively obtained, though with markedly different reaction times: **1-Me**, 3 days; **1-Pr**, 6 days; **1-Ph**, 9 days; **1-PhCF₃**, 6 days. While it took 3 days to obtain both **1-Me** and UCMC-1-AM1, the reaction time for **1-Pr** was much longer than that for UCMC-1-AM3. The preparation of **1-Ph** had reaction conditions very different from those for UCMC-1-AMPh, which had a conversion yield of ~76%. **1-Ph** was obtained quantitatively over 9 days at room temperature in dichloromethane, whereas UCMC-1-AMPh was prepared by heating the reaction mixture for one day at 55 °C in chloroform.

PXRD patterns of all the samples were consistent throughout the course of the reaction, indicating that their periodic structures were not affected during the reactions (Fig. 2). The $^1\text{H-NMR}$ spectra showed evidence of successful modifications. The signals attributed to the $\text{H}_2\text{BDC-NH-R}$ linkers shifted significantly down-field compared with those of $\text{H}_2\text{BDC-NH}_2$ (Fig. 3). Elemental analysis showed good

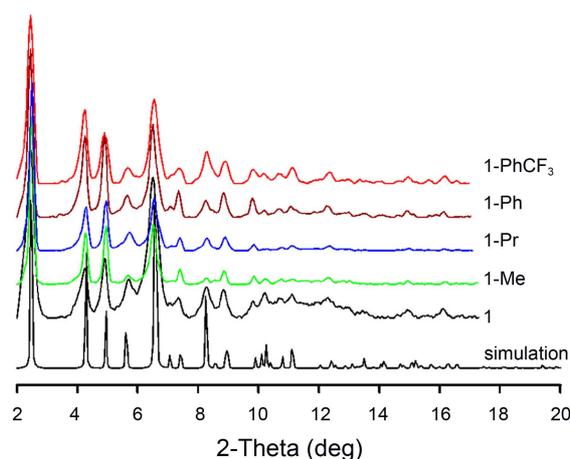


Figure 2. PXRD patterns of the functionalized and original MOFs.

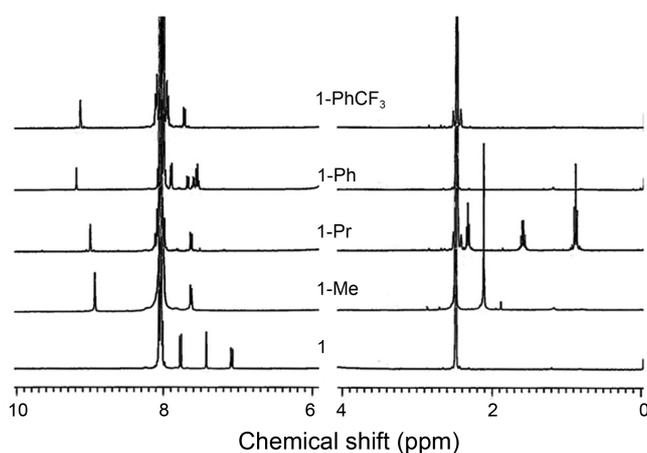


Figure 3. $^1\text{H-NMR}$ spectra of the original and functionalized MOFs measured in $\text{DCI}/\text{DMSO-}d_6$. The large signals commonly observed at 8.1 ppm are attributable to H_3BTB . Broad water signals were observed between 4 and 6 ppm; for clarity, they are not shown.

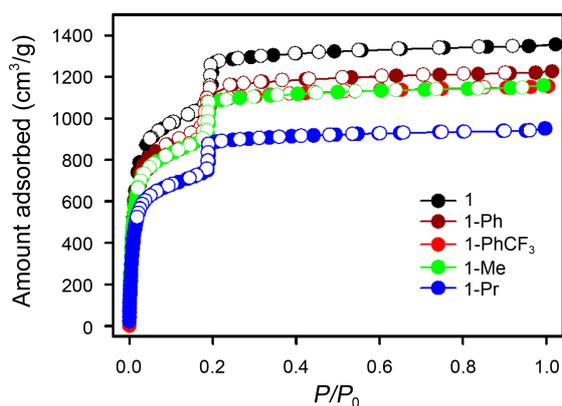
agreement with the formulae of all the modified MOFs, within allowable errors, supporting the quantitative modification of the parent MOF, **1**.

N₂ Adsorption Measurements. The nitrogen sorption isotherm of the four functionalized MOFs showed clear second steps at $P/P_0 = 0.2$, similar to **1** (Fig. 4). However, each functionalized MOF showed different heights of the first step, suggesting that the modifications had produced micropores different from **1**. The amounts of N_2 adsorbed by each MOF were similar in the second step. This suggests that the introduction of functional groups to **1** did not perturb the mesoporous channels, only the microporous cages. An independent structural study suggested that the large channel of **1** could be altered only by the modification with alkyl chains longer than dodecane. Therefore, it is not strange that the N_2 adsorption isotherms of the functionalized MOFs showed large decreases in N_2 uptake only at lower pressures.

The BET surface areas of the MOFs in this work were predicted to correlate with the mass of the frameworks: **1** > **1-Me** > **1-Pr** > **1-Ph** > **1-PhCF₃**. However, the surface areas

Table 1. Formula weights and measured surface areas of the MOFs in this work. Parentheses show changes (%) in f.w. and BET surface areas relative to **1**

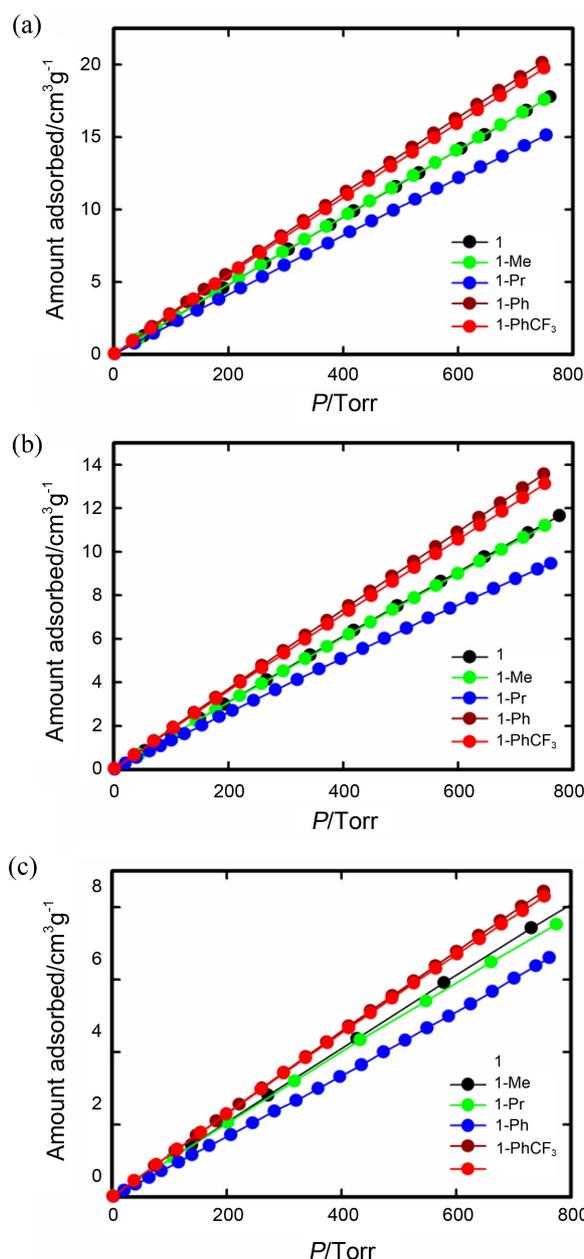
MOF		Surface area (m ² /g)	
Name	f.w. (g/mol)	BET	Langmuir
1	1037	4170	6020
1-Me	1079 (+4.1)	3550 (-14.9)	5100
1-Pr	1107 (+6.8)	2900 (-30.5)	4180
1-Ph	1141 (+10.0)	3680 (-11.8)	5300
1-PhCF₃	1209 (+16.6)	3520 (-15.6)	5100

**Figure 4.** N₂ adsorption isotherms of the original and functionalized MOFs at 77 K. The filled and open circles respectively correspond to adsorption and desorption.

of the modified samples were reduced by *ca.* 12-31% compared with that of **1**, in decreasing order: **1** > **1-Ph** > **1-Me** ~ **1-PhCF₃** > **1-Pr**, i.e.: 4170 (**1**), 3550 (**1-Me**), 2900 (**1-Pr**), 3680 m²/g (**1-Ph**), and 3520 m²/g (**1-PhCF₃**) (Table 1). Increases of framework weight did not directly correlate with the reduction of surface area; therefore, changes of framework volume or pore size are not considered here to avoid possible ambiguities. The aromatic groups of **1-Ph** and **1-PhCF₃** appear to have provided more adsorptive sites for nitrogen molecules than the alkyl groups of **1-Me** and **1-Pr**. Similar was observed for UCM-1-AMPh, which could adsorb more hydrogen than UCM-1-NH₂.

CH₄ Adsorption Measurements. CH₄ and CO₂ adsorption isotherms of **1** and the four modified MOFs were measured at 253, 273, and 298 K at pressures up to 1 bar. These measurements were expected to reveal the temperature-dependence of the MOFs' gas adsorption behaviors, and show which functional groups would be preferable for CO₂ adsorption. The CH₄ adsorption results can aid the understanding of how the introduced functional groups affect the MOFs. Because CH₄ has similar polarizability to CO₂ but lacks a quadrupole moment, it shows different adsorption behavior from CO₂ that has a large quadrupole moment. The results can be used to elucidate the roles of the introduced functional groups in improving CO₂ adsorption.

At every tested temperature, the uptake of CH₄ at P/P₀ = 1 by the functionalized MOFs was correlated with their BET surface area. CH₄ uptake amounts: **1-Ph** > **1-PhCF₃** > **1-Me** >

**Figure 5.** CH₄ sorption isotherms for **1**, **1-Me**, **1-Pr**, **1-Ph**, and **1-PhCF₃** measured at (a) 253 K, (b) 273 K, and (c) 298 K. For clarity, only the adsorption branch points are shown; all the isotherms were reversible.**Table 2.** CH₄ uptakes of the original and functionalized MOFs at different temperatures. Parentheses indicate changes (%) relative **1**. The isosteric enthalpies of adsorption extrapolated to zero coverage were calculated using virial-type equations

MOF	CH ₄ uptake amounts (mg/g)			ΔH_{ads} (kJ/mol)
	253 K	273 K	298 K	
1	12.7	8.3	5.5	11.4
1-Me	12.6 (-1.2)	8.0 (-3.8)	5.4 (-2.1)	12.2
1-Pr	10.8 (-14.9)	6.8 (-18.8)	4.7 (-14.1)	11.5
1-Ph	14.4 (+13.3)	9.7 (+16.5)	6.0 (+9.7)	12.7
1-PhCF₃	14.1 (+11.1)	9.4 (+12.6)	5.9 (+7.9)	12.3

1-Pr vs. BET surface areas, 1-Ph > 1-Me ~ 1-PhCF₃ > 1-Pr (Fig. 5, Table 2). This is in accordance with what was expected from the nitrogen adsorption experiments. That is, that the aromatic groups of **1-Ph** and **1-PhCF₃** aided CH₄ adsorption more than the alkyl groups of **1-Me** and **1-Pr**. **1-PhCF₃**, with a surface area similar to that of **1-Me**, adsorbed significantly more CH₄ than **1-Me**. This simple correlation does not apply when **1** is considered in the series with the functionalized MOFs. Adsorbed amounts of CH₄: **1-Ph** > **1-PhCF₃** > **1** > **1-Me** > **1-Pr**. This does not match the surface area trend because **1** had the largest surface area of the MOFs in this work.

The modification of **1** with aromatic functional groups was more effective at lower temperature. **1-Ph** could adsorb 13.4% more CH₄ than **1** at 253 K, and only 9.1% more at 298 K. As temperature increased, bulkier groups appeared to experience more thermal motion than smaller groups. This reduced the strength of interaction with CH₄, although the effect was small. The relative changes in CH₄ uptake as temperature increased from 253 K to 298 K were -56.7% (**1**), -57.1% (**1-Me**), -56.5% (**1-Pr**), -58.3% (**1-Ph**), and -58.2% (**1-PhCF₃**). UMCM-1 was reported to have an isosteric enthalpy of adsorption of 6.5 kJ/mol. Therefore, the increased adsorption enthalpy of UMCM-1-NH₂ (**1**), 11.4 kJ/mol, is attributable to the presence of NH₂ groups in the framework. Similarly, the increased enthalpies of the functionalized MOFs (11.5-12.7 kJ/mol) were due to the introduction of the functional groups. These increases were achieved despite the decreased surface areas of the functionalized MOFs.

CO₂ Adsorption Measurements. Similar to CH₄ adsorption, aromatic groups better aided CO₂ adsorption than alkyl groups. However, all the functionalized MOFs showed greater CO₂ uptakes than **1** at every tested temperature: **1-Ph** > **1-PhCF₃** > **1-Me** > **1-Pr** > **1** (Fig. 6, Table 3). The CO₂ adsorption capacity of the functionalized MOFs increased significantly compared with the increases of CH₄ adsorption. For example, **1-Ph** adsorbed 50% more CO₂ than **1** at 253 K, and 23% more at 298 K, whereas its increases in CH₄ adsorption relative to **1** at the same temperatures were only 13.4% and 9.1%, respectively. The trend in the change of the CO₂ adsorption capacity with temperature was similar to that of CH₄ adsorption. The relative changes of CO₂ uptake by the MOFs as temperature increased from 253 K to 298 K were -66.0% (**1**), -68.9% (**1-Me**), -70.5% (**1-Pr**), -72.3% (**1-Ph**), and -71.1% (**1-PhCF₃**).

Although the average change of the MOFs' CO₂ adsorption (-69.8%) was much greater than that (-57.4%) for CH₄ in this work, the average isosteric enthalpy for CO₂ (17.9 kJ/mol) is significantly larger than that of CH₄ (12.0 kJ/mol). This is presumed to be due the quadrupole moment of CO₂, which introduces an adsorption interaction that is dependent on the relative orientation of the adsorptive sites and CO₂. This interaction may be diminished as the temperature increased due to increased thermal motion of the organic linkers.

CO₂ adsorption enthalpies are usually greater than those of CH₄ for most sorbents such as zeolites, activated carbons,

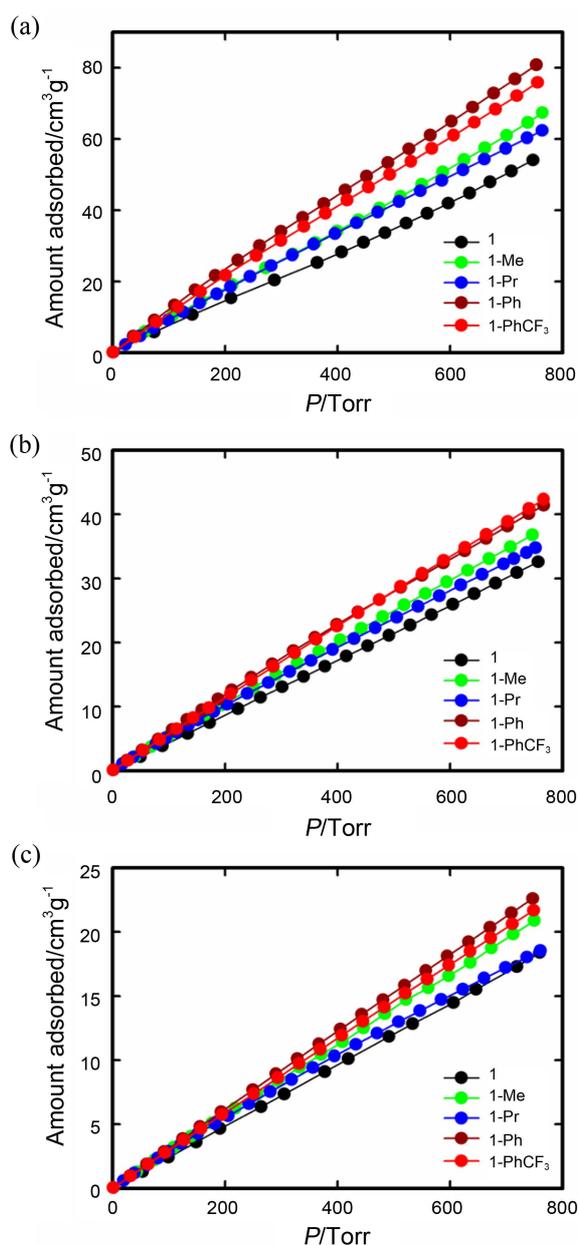


Figure 6. CO₂ adsorption isotherms for **1**, **1-Me**, **1-Pr**, **1-Ph**, and **1-PhCF₃** measured at (a) 253 K, (b) 273 K, and (c) 298 K. For clarity, only adsorption branch points are shown; all the isotherms were reversible.

Table 3. CO₂ uptake of the original and functionalized MOFs at different temperatures. Parentheses indicate changes (%) relative to **1**. Isosteric enthalpies of adsorption extrapolated to zero coverage were calculated using virial-type equations

MOF	CO ₂ uptake amounts (mg/g)			ΔH_{ads} (kJ/mol)
	253 K	273 K	298 K	
1	106	64	36	16.3
1-Me	132 (+29)	72 (+13)	41 (+14)	17.3
1-Pr	122 (+15)	68 (+7)	36 (+0)	17.7
1-Ph	159 (+50)	81 (+27)	44 (+23)	19.6
1-PhCF₃	149 (+40)	83 (+30)	43 (+18)	18.8

and MOFs.¹⁸ These results follow this trend. The isosteric heat of CO₂ adsorption for **1-Ph** was 19.6 kJ/mol, much smaller than those of MOFs with open metal sites, for example, MIL-100 (63 kJ/mol), COP-27-Ni (ca. 42 kJ/mol),¹⁹ and Mg-MOF-74 (39 kJ/mol),²⁰ but was larger than that of UMCM-1 (11.9 kJ/mol).¹⁸ When compared with UMCM-1, the increased CO₂ adsorption enthalpies of the MOFs in this work can be largely attributed to the presence of amino or amide groups, as demonstrated by aminoMIL-53(Al) (38.4 kJ/mol) and MIL-53(Al) (20.1 kJ/mol).²¹ The differences between the MOFs must be due to the introduced functional groups.

As mentioned above, MOFs' structural factors can increase interactions with CO₂, for example open-metal sites, framework interpenetration, flexible frameworks, amines in the frameworks, and polar framework surfaces.¹⁶ Among these, the last two are related to the MOFs in this work. This is because of the amine (-NH₂) groups in **1** and the amide groups (-NHCOR) in the functionalized MOFs that have different functional groups, which exert varying local polarity. However, common amide functionality alone cannot explain the differences in the MOFs' adsorption enthalpies of CH₄ (12.0 kJ/mol) and CO₂ (17.9 kJ/mol). All the functionalized MOFs were better adsorbents for CO₂ than **1**, whereas only **1-Ph** and **1-PhCF₃** were better adsorbents of CH₄. Therefore, considering that CO₂ is more sensitive than CH₄ towards polar surfaces, it was shown that the modification of **1** with anhydrides increased the local polarity of the MOF framework surfaces. Aromatic groups were better modifiers than alkyl groups to improve the CO₂ affinity of **1** because in addition to producing favorable adsorptive sites, aromatic, electron-withdrawing, groups can provide more polar framework surfaces than alkyl, electron-donating, groups.

Conclusions

Four MOFs (**1-Me**, **1-Pr**, **1-Ph**, and **1-PhCF₃**) were prepared by post-synthesis reactions of a very porous MOF, UMCM-1-NH₂ (**1**), and corresponding anhydrides. The MOFs' BET surface areas were not correlated with the mass increases in their frameworks. Predicted BET surface areas: **1** > **1-Me** > **1-Pr** > **1-Ph** > **1-PhCF₃**; observed BET surface areas: **1** > **1-Ph** > **1-Me** ~ **1-PhCF₃** > **1-Pr**. This indicates that the aromatic groups provided more adsorptive sites for nitrogen molecules.

CH₄ and CO₂ adsorption measurements were conducted at 253, 273, and 298 K at pressures up to 1 bar to investigate the effects of the modifications. At every tested temperature, adsorbed amounts of CH₄ were ranked: **1-Ph** > **1-PhCF₃** > **1** > **1-Me** > **1-Pr**. In contrast, CO₂ uptake was ranked: **1-Ph** > **1-PhCF₃** > **1-Me** > **1-Pr** > **1**. These observations show that

post-synthetic modification could enhance affinity for both CH₄ and CO₂. Also, both alkyl and aromatic groups increased local polarity, enhancing CO₂ adsorption. The aromatic electron-withdrawing groups enhanced CO₂ uptake more than the electron-donating alkyl groups.

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