

# Gas Adsorption in R<sub>2</sub>-MOF-5 Difunctionalized with Alkyl Groups

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Zinc terephthalate metal—organic framework (MOF) **MOF-5** and some of its dialkylated derivatives ( $R_2$ -**MOF-5**; R = Me, Et, Pr, Bu) were obtained from a solvothermal synthesis using 2,5-dialkyl-1,4-benzenedicarboxylic acids with zinc nitrite. The effect of the solvent on the solvothermal synthesis of  $R_2$ -**MOF-5** was investigated. For R = H and Me, interpenetrating or non-interpenetrating MOFs obtained depending on the choice of reaction solvent, while for R = Et, Pr, and Bu, no such solvent effect was observed, and only jungle-gym-type MOFs were generated. All compounds were fully characterized using

## Introduction

Metal-organic frameworks (MOFs) are porous and crystalline materials with infinite network structures constructed from metal ions and organic ligands.<sup>[1-6]</sup> Their efficient adsorption of small molecules has led to applications in e.g. gas adsorption,<sup>[7-9]</sup> catalysis,<sup>[10-14]</sup> as well as energy storage and conversion.[15-18] The interest in porous MOFs stems from their desirable physical and chemical properties, such as high surface area, tuneable pore size, modularity, as well as high micro- and mesoporous volume. The zinc terephthalate MOF MOF-5 currently represents the area of highest interest within the field of MOFs. MOF-5 has a zeolite-like framework in which inorganic [Zn<sub>4</sub>O] clusters are joined in an octahedral array of 1,4benzenedicarboxylate (BDC) groups to form a robust and highly porous cubic framework.<sup>[19]</sup> MOF-5, which has a large surface area, high thermal and chemical stability, as well as very high pore volume, exhibits excellent gas-adsorption properties. Functionalization and modification of the organic ligands to construct new MOFs is a fascinating and significant area in crystal engineering owing to the potential applications of the resulting materials. Consequently, the number of functionalized MOFs that has been synthesized and reported is steadily increasing.<sup>[20-27]</sup> Functionalizing the organic ligands of MOFs is an effective method to adjust the performance of MOFs, as the attachment of functional groups can lead to considerable enhancement in their adsorption properties. Likewise, enhancement of the frameworks and tuning of the sorption

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100466 powder X-ray diffraction analysis (PXRD), Fourier-transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA). After activation, all these compounds exhibit significant porosity, as confirmed by N<sub>2</sub>-, H<sub>2</sub>-, and CO<sub>2</sub>-sorption experiments. The N<sub>2</sub>-adsorption capacity of these compounds depends on the size of the attached alkyl groups, while the H<sub>2</sub>- uptake values tend to increase for the alkyl-functionalized MOFs relative to the unfunctionalized parent MOFs and exhibit a maximum value for **Pr<sub>2</sub>-MOF-5**.

properties can be attained through functionalization of the well-known MOF-5 with alkyl-ether groups.[27] Recently, we have reported the controlled synthesis of non-interpenetrated and interpenetrated methyl-modified MOF-5 derivatives, which exhibit different pore structures.[28] These compounds were prepared via a hydrothermal synthesis using 2,5-dimethyl-1,4benzenedicarboxylic acid and  $Zn(NO_3)_2 \cdot 6H_2O$ , in which the choice of solvent (N,N-dimethylformamide or N,N-diethylformamide) is of critical importance. Our results suggest that the suppression of framework interpenetration and control over the pore architecture is not only the result of simple steric criteria regarding the ligand but may be governed by other mechanisms such as solvent templating. In the present study, we further investigated this system by varying the chemical substituents at the 2- and 5-positions of the phenylene unit in the MOF-5 framework (R2-MOF-5; R=Me, Et, Pr, or Bu). The total N<sub>2</sub> uptake of the obtained jungle-gym-type MOFs decreased with the increasing length of the incorporated alkyl chain. The highest H<sub>2</sub> adsorption was observed for jungle-gymtype Pr<sub>2</sub>-MOF-5 rather than the jungle-gym-type H-substituted MOF (MOF-5), demonstrating that the H<sub>2</sub> adsorption showed a different trend than the N<sub>2</sub> adsorption. We have also reported the CO<sub>2</sub>/N<sub>2</sub> selectivity of these MOFs, which can be related to the increasing chain length of the alkyl substituents.

Using reported procedures,<sup>[29,30]</sup> 2,5-dialkyl-1,4-benzenedicarboxylic acids (R<sub>2</sub>BDC; R=Et, Pr, Bu) were synthesized in three steps from commercially available 1,4-dialkylbenzene as shown in Scheme 1. High yields of the 2,5-dialkyl-1,4-benzenedicarboxylic acids were obtained, and their purity was confirmed by <sup>1</sup>H NMR spectroscopy (Figures S1–S3). **MOF-5** and **Me<sub>2</sub>-MOF-5** were synthesized via a previously reported solvothermal reaction between Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and terephthalic acid in *N*,*N*dimethylformamide (DMF) or *N*,*N*-diethylformamide (DEF).<sup>[28]</sup> The chosen synthetic route to the difunctionalized **R<sub>2</sub>-MOF-5** (R=Et, Pr, or Bu) is similar to that of **MOF-5**. Colorless microcrystalline powders were obtained following slow cooling

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Scheme 1. Synthetic route to R<sub>2</sub>-MOF-5 (R = Me, Et, Pr, or Bu).

of the reaction mixtures to room temperature, and their structures were subsequently analyzed using powder X-ray diffraction (PXRD) analysis, Fourier-transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (Figure S4), and gas-adsorption analysis.

#### **Results and Discussion**

The PXRD spectra of **MOF-5** and **R**<sub>2</sub>-**MOF-5** (R = Me, Et, Pr, or Bu) are shown in Figure 1a, Figure 1b, and Figures S5–S14). In our previous report, we investigated the effect of the solvent (DMF of DEF) on the solvothermal synthesis of **Me**<sub>2</sub>-**MOF-5**. Under otherwise identical reaction conditions, non-interpenetrated or interpenetrated **Me**<sub>2</sub>-**MOF-5** were obtained using DEF or DMF, respectively. As shown in Figure 1a, **MOF-5** and **Me**<sub>2</sub>-**MOF-5** are considered to be interpenetrated MOFs due to a splitting of the diffraction peak near 10° and the ratio of the intensity of the peak at 13.8° relative to that at 6.8°, while **Et**<sub>2</sub>-**MOF-5**, **Pr**<sub>2</sub>-**MOF-5**, and **Bu**<sub>2</sub>-**MOF-5** exhibit jungle-gym-type patterns (Fig-

ure S5).<sup>[31]</sup> When DEF was used as the reaction solvent (Figure 1b), the main peak positions of all resulting  $R_2$ -MOF-5 patterns (R=Me, Et, Pr, or Bu; diffraction peaks at 6.8° and 13.8°) were consistent with those of MOF-5. These results suggest that the ligand functionalization does not affect the crystallinity of the MOFs. In the cases of Et<sub>2</sub>-MOF-5, Pr<sub>2</sub>-MOF-5, and Bu<sub>2</sub>-MOF-5, interpenetrating MOFs were not observed, suggesting that the solvent-dependent structural change during synthesis is probably due to steric hindrance. In other words, the PXRD analysis revealed that the same jungle-gymtype MOFs are generated for Et<sub>2</sub>-MOF-5, Pr<sub>2</sub>-MOF-5, and Bu<sub>2</sub>-MOF-5 regardless of whether DMF or DEF is used in the solventhermal synthesis.

FT-IR analysis was employed to confirm the formation of covalent bonds in  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu). As shown in Figure 2, all spectra include the characteristic bands of MOF-5, which confirms the successful formation of the framework for all samples. The sharp peaks at approximately 1360, 1410, and 1580 cm<sup>-1</sup> are related to the CO–O group of the dicarboxylate linker, while the band near 750 cm<sup>-1</sup> corresponds to the CH vibrations of the aromatic ring, and the characteristic band at 520 cm<sup>-1</sup> to the Zn–O bonds in the MOF-5 structure. The IR bands related to the alkyl groups are observable near 2900 cm<sup>-1</sup> in  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu), thus corroborating the successful functionalization of the aromatic ring with alkyl groups.

Bulk samples of **MOF-5** and **R**<sub>2</sub>-**MOF-5** (R=Me, Et, Pr, or Bu) were used for this study, and any changes to their structures were tracked using PXRD and thermogravimetric analyses (TGA). The TGA measurements were conducted from room temperature to 500 °C after the MOFs had been completely dried under reduced pressure at 150 °C. All MOFs were thermally stable up to 400 °C (Figure S4). To investigate the porosity of the structures of **MOF-5** and **R**<sub>2</sub>-**MOF-5** (R=Me, Et, Pr, or Bu), their N<sub>2</sub>-adsorption/desorption isotherms were



Figure 1. Experimental PXRD patterns of R<sub>2</sub>-MOF-5 (R = Me, Et, Pr, or Bu) synthesized in DMF (a) and in DEF (b).





Figure 2. FTIR spectra of MOF-5 and R<sub>2</sub>-MOF-5 (R = Me, Et, Pr, or Bu).

measured at 77 K after degassing for 6 h at 135 °C (Figure 3a). Each isotherm showed Type-I isotherm features, indicating a microporous nature of MOF-5 and R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, or Bu). The  $S_{BET}$  values determined by N<sub>2</sub> adsorption for the interpenetrated MOF-5 (985 m<sup>2</sup>g<sup>-1</sup>) and Me<sub>2</sub>-MOF-5 (663 m<sup>2</sup>g<sup>-1</sup>) are much lower than those of the non-interpenetrated MOFs. The  $S_{BET}$  values (m<sup>2</sup> g<sup>-1</sup>) of the jungle-gymtype  $R_2$ -MOF-5 structures decrease in the order MOF-5 (3,483) >  $Me_2$ -MOF-5 (2,340) >  $Et_2$ -MOF-5 (1,931) >  $Pr_2$ -MOF-5 (1,723) > Bu<sub>2</sub>-MOF-5 (1,339), which corresponds to the increasing size of the attached alkyl groups. The H2-adsorption measurements were carried out with the activated  $R_2$ -MOF-5 (R = Me, Et, Pr, or Bu) samples at 77 K and pressures of up to 1 bar. As shown in Figure 3b, the H<sub>2</sub> adsorption isotherms of all the samples follow type-I behavior in the pressure range from 0 to 1 bar. The H<sub>2</sub>uptake values (wt%) of R2-MOF-5 decrease in the order Pr2-MOF-5 (1.50) >  $Et_2$ -MOF-5 (1.49) >  $Me_2$ -MOF-5 (1.42) > MOF-5(1.27) > Bu<sub>2</sub>-MOF-5 (1.26) (cf. Table 1). Based on the reduced surface area of the R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, or Bu) with increasing alkyl-group length, it is certain that the introduced functional groups contribute to the enhanced H<sub>2</sub> uptake. The CO<sub>2-</sub>adsorption isotherms for activated R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, or Bu) samples were collected at 258, 273, and 298 K, and the results are plotted in Figure 3c, Figures S16, and S17. Compared to the N<sub>2</sub>-adsorption measurements, an almost opposite trend is obtained for the CO<sub>2</sub> uptake in the  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu) structures, which clearly does not coincide with the surface area trend. Pr<sub>2</sub>-MOF-5 has a maximum CO<sub>2</sub> uptake of 3.84, 2.37, and 1.12 mmolg<sup>-1</sup> at 258, 273, and 298 K (1 bar), respectively. This is a moderate amount of CO<sub>2</sub> adsorption, comparable to that of MIL-101(Cr) (1.17 mmol g<sup>-1</sup> at 1 bar and 298 K) and UiO-66 (2.20 mmolg<sup>-1</sup> at 1 bar and 273 K).<sup>[32-34]</sup> It should be noted here that the amount of CO<sub>2</sub> adsorbed by Pr<sub>2</sub>-MOF-5 is nearly double that of its parent structure MOF-5 at 258 K. The isosteric heat of adsorption  $(Q_{t})$  is the heat generated during the adsorption of CO<sub>2</sub> and represents the force between CO<sub>2</sub> and the adsorbent surface. MOFs with higher  $Q_{st}$  for CO<sub>2</sub> tend to exhibit better capture performance. The  $Q_{st}$  values of  $R_2$ -MOF-5 were calculated based on the raw adsorption data collected at 273, and 298 K with virial fitting (Figure 3d, Figures S18–S22).<sup>[35]</sup> The modest adsorption enthalpy of R2-MOF-5 highlights the absence of strong binding centers in R<sub>2</sub>-MOF-5, with open metal sites and active amines reported to increase the  $Q_{st}$  to 35–45 and 50–100 kJ·mol<sup>-1</sup>, respectively.  $\ensuremath{^{[32]}}$  The slightly higher adsorption enthalpies of  $\ensuremath{\mathrm{CO}_2}$ in the R2-MOF-5 (R=Me, Et, Pr, or Bu) structures with functionalized BDC ligands compared to those of the parent structure MOF-5 suggest weak interactions between the functionalized frameworks and CO<sub>2</sub>. At zero CO<sub>2</sub> loading, a reduction in pore size of the MOFs was observed to increase the CO<sub>2</sub> uptake through an increase in the enthalpy of adsorption at low pressure.<sup>[36]</sup> CO<sub>2</sub> bound preferentially to the strong sites until saturation, and then adsorbed on the weak sites, resulting in a decrease in  $Q_{st}$ . The enthalpy of  $R_2$ -MOF-5 (R = Me, Et, Pr, or Bu) did not decrease more than that of MOF-5 because the introduced functional groups act as adsorption sites. Similarly, the smaller pores of the MOFs were found to be effective for CO<sub>2</sub> capture.<sup>[37]</sup> Therefore, the enhancement of the  $CO_2$  uptake found in the R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, or Bu) structures prompted us to further investigate their selectivity toward CO<sub>2</sub> over N<sub>2</sub>. The adsorption isotherms of CO<sub>2</sub> and N<sub>2</sub> on activated R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, or Bu) samples were performed under the same conditions (298 K, up to 1 bar). To predict their selectivity towards a CO<sub>2</sub>/N<sub>2</sub> binary mixture, ideal adsorbed solution theory (IAST) calculations with Henry's law simulation were employed based on the single-component  $R_2$ -MOF-5 (R = Me, Et, Pr, or Bu) isotherms (Figures S23 and S24).<sup>[38]</sup> Table 1 and Figure S25 show the predicated CO<sub>2</sub>/N<sub>2</sub> selectivity as a function of the pressure when the gas-phase mole fraction

<b>Table 1.</b> Temperature-dependent N <sub>2</sub> -, H <sub>2</sub> -, and CO <sub>2</sub> -uptake capacity of <b>MOF-5</b> and <b>R<sub>2</sub>-MOF-5</b> (R = Me, Et, Pr, or Bu) and the corresponding isosteric heat of adsorption ( $Q_{st}$ ) of CO <sub>2</sub> .								
R	N <sub>2</sub> at 1 bar [cm <sup>3</sup> g <sup>-1</sup> ] 77 K	BET surface area [m <sup>2</sup> g <sup>-1</sup> ]	H <sub>2</sub> at 1 bar [wt%] 77 K	CO <sub>2</sub> at 1 bar [cm <sup>3</sup> g <sup>-1</sup> (mmol g 258 K	<sup>[-1</sup> )] 273 K	298 K	Q <sub>st</sub> [kJ mol <sup>-1</sup> ]	Selectivity CO <sub>2</sub> /N <sub>2</sub> [298 K]
н	860	3483	1.27	45.2 (2.02)	30.5 (1.36)	16.3 (0.738)	17.3	4.7
Me	606	2340	1.43	63.7 (2.84)	41.5 (1.85)	21.0 (0.938)	18.3	6.1
Et	511	1931	1.49	69.2 (3.09)	44.0 (1.96)	21.3 (0.951)	19.1	7.2
Pr	457	1723	1.50	86.0 (3.84)	53.0 (2.37)	25.1 (1.12)	19.1	8.8

50.0 (2.23)

24.3 (1.08)

19.3

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1339

1.26

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Bu

80.2 (3.58)

9.8





Figure 3. a)  $N_2$ -sorption isotherms at 77 K, b)  $H_2$ -adsorption isotherms at 77 K, c)  $CO_2$ -adsorption isotherms at 273 K, and d) heat of adsorption for  $CO_2$  for MOF-5 and  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu).

is 15/85, which is a typical feed composition for flue gas. The IAST selectivities of  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu) toward CO<sub>2</sub> in the presence of N<sub>2</sub> are 4.7, 6.1, 7.2, 8.8, and 9.8 for MOF-5, Me<sub>2</sub>-MOF-5, Et<sub>2</sub>-MOF-5, Pr<sub>2</sub>-MOF-5, and Bu<sub>2</sub>-MOF-5 at 298 K and 1 bar, respectively (Figure S25). The most remarkable point of the CO<sub>2</sub>/N<sub>2</sub> selectivity of R<sub>2</sub>-MOF-5 (R=Me, Et, Pr, Bu) is enhanced according to the size of the alkyl group. For this condition, the selectivities of R<sub>2</sub>- MOF-5 (R=Me, Et, Pr, Bu) are not particularly high, but comparable to those of ZIF-8 (5–7) and MOF-508b (4–6).<sup>[39,40]</sup>

## Conclusion

In conclusion, we have demonstrated the synthesis and gasadsorption properties of functionalized  $R_2$ -MOF-5 (R=Me, Et, Pr, or Bu) materials. These compounds, along with the previously reported **MOF-5**, were prepared via a solvothermal synthesis using 2,5-dialkyl-1,4-benzenedicarboxylic acids (R<sub>2</sub>BDC) and zinc nitrite in *N*,*N*-dimethylformamide (DMF) or *N*,*N*-diethylformamide (DEF). When 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC) or Me<sub>2</sub>BDC were used, specific solvent effects were observed in the interpenetrated or non-interpenetrated structures of **MOF-5** and **Me<sub>2</sub>-MOF-5**, while Et<sub>2</sub>, Pr<sub>2</sub>, and Bu<sub>2</sub>BDC produced only non-interpenetrated **R**<sub>2</sub>-**MOF-5** (R=Et, Pr, or Bu). All the non-interpenetrated MOFs exhibit significant porosity, as revealed by the N<sub>2</sub>- (*S*<sub>BET</sub>: 1339–3483 m<sup>2</sup>/g) and H<sub>2</sub>- (uptake: 1.26–1.50 wt%) adsorption analyses. The N<sub>2</sub>-adsorption capacity of these MOFs depends on the size of the attached alkyl groups. Moreover, their CO<sub>2</sub>/N<sub>2</sub> selectivity at 1 bar is higher than those of the parent structure **MOF-5**, indicating that **R<sub>2</sub>-MOF-5** (R=



Me, Et, Pr, or Bu) adsorb  $CO_2$  more selectively upon introduction of the alkyl groups.

# **Experimental Section**

General considerations: <sup>1</sup>H NMR (400 MHz) spectra were measured in CDCl<sub>3</sub> and dimethylsulfoxide- $d_6$  using a JEOL JNM ECS-400SS spectrometer. The signals arising from the residual CHCl<sub>3</sub> (7.26 ppm) in CDCl<sub>3</sub> and C<sub>2</sub>D<sub>5</sub>HSO (2.50 ppm) in DMSO- $d_6$  were used as the internal standard. High-resolution mass spectra (HRMS) were recorded using a JEOL JMS–T100LP (ESI and DART) mass spectrometer. All melting points were measured on a SMP-300CT capillary melting point apparatus and are uncorrected. 2,5-Dialkyl-1,4benzenedicarboxylic acids were synthesized in three steps from the commercially available 1,4-dialkylbenzenes.

1,4-Dialkyl-2,5-dibromobenzenes ( $2_R$ ); general procedure: Bromine (6.39 g, 40.0 mmol) was added to a mixture of 1,4-diethylbenzene (2.68 g, 20.0 mmol) and iodine (0.51 g, 2.00 mmol) in CHCl<sub>3</sub> at 0 °C, and the reaction mixture was then allowed to warm to room temperature. After stirring the mixture overnight, 20% NaOH aq. and a small amount of potassium iodide were added before the reaction mixture was extracted with CHCl<sub>3</sub>. The organic layer was dried over MgSO<sub>4</sub>, filtered, and all volatiles were removed *in vacuo* to give 1,4-diethyl-2,5-dibromobenzene ( $2_{Et}$ ) (5.78 g, 19.8 mmol, 99%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.38 (s, 2H), 2.68 (q, J=7.5 Hz, 4H), 1.21 (t, J=7.5 Hz, 6H); 1,4-dipropyl-2,5-dibromobenzene ( $2_{Pr}$ ): 96%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (s, 2H), 2.63 (t, J=7.9 Hz, 4H), 1.62 (m, 4H), 0.97 (t, J=7.9 Hz, 6H); 1,4-dibutyl-2,5-dibromobenzene ( $2_{Bu}$ ): 86%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 (s, 2H), 2.65 (t, J=7.9 Hz, 4H), 1.62 (m, 4H), 1.40 (m, 4H), 0.95 (t, J=7.9 Hz, 6H).

2,5-Dicyano-1,4-dialkylbenzenes ( $\mathbf{3}_{R}$ ); general procedure:  $2_{Et}$  (1.00 g, 3.42 mmol) and CuCN (0.92 g, 10.3 mmol) were stirred in refluxing DMF for 1 day, before the reaction mixture was poured into NH<sub>4</sub>OH aq. The thus obtained precipitate was washed with H<sub>2</sub>O and dissolved in CHCl<sub>3</sub>. The resulting solution was washed with brine and the organic layer was dried over MgSO<sub>4</sub>, filtered, and all volatiles were removed *in vacuo* to give 1,4-dicyano-2,5-diethylbenezene ( $\mathbf{3}_{Et'}$  0.56 g, 3.06 mmol, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.58 (s, 2H), 2.88 (q, *J*=7.5 Hz, 4H), 1.32 (t, *J*=7.5 Hz, 6H); 1,4-dicyano-2,5-dipropylbenzene ( $\mathbf{3}_{Ft}$ ): 75%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (s, 2H), 2.82 (t, *J*=7.5 Hz, 4H), 1.69 (m, 4H), 1.0 (t, *J*=7.1 Hz, 6H); 1,4-dicyano-2,5-dibutylbenzene ( $\mathbf{3}_{Bu}$ ): 95%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35 (s, 2H), 2.65 (t, *J*=7.5 Hz, 4H), 1.56 (m, 4H), 1.37 (m, 4H), 0.95 (t, *J*=7.5 Hz, 6H).

2,5-Dialkyl-1,4-benzenedicarboxylic acids ( $4_{R}$ ); general procedure: A mixture of  $3_{Et}$  (1.10 g, 6.00 mmol) and 10 M NaOH aq. (7.5 mL, 75.0 mmol) was stirred for 1 day in refluxing ethylene glycol (100 mL). After cooling to room temperature, the reaction mixture was poured into HCl aq. The resulting precipitate was filtered, washed with H<sub>2</sub>O, and dried *in vacuo* to give 2,5-diethyl-1,4-benzenedicarboxylic acid ( $4_{Et}$ ; 1.25 g, 5.63 mmol, 94%): <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.61 (s, 2H), 2.85 (q, J=7.5 Hz, 4H), 1.11 (t, J=7.5 Hz, 6H); 2,5-dipropyl-1,4-benzenedicarboxylic acid ( $4_{Pr}$ ): 89%, <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.62 (s, 2H), 2.85 (t, J=7.5 Hz, 4H), 1.53 (m, 4H), 0.88 (t, J=7.5 Hz, 6H); 2,5-dibutyl-1,4-benzenedicarboxylic acid ( $4_{Bu}$ ): 94%, <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  7.61 (s, 2H), 2,87 (t, J=7.5 Hz, 4H), 1.49 (m, 4H), 1.31 (m, 4H), 0.88 (t, J=7.1 Hz, 6H).

Samples of **MOF-5** and **R**<sub>2</sub>-**MOF-5** (R=Me, Et, Pr, or Bu) were synthesized via a solvothermal method:  $Zn(NO_3)_2 \cdot 6H_2O$ (0.80 mmol), the appropriate 2,5-dialkyl-1,4-benzenedicarboxylic acid (0.40 mmol), and DMF or DEF (8 mL) were added to a screwcapped vial and maintained at 120 °C for 24 h. After cooling the reaction mixture to room temperature, the colorless precipitate was separated by centrifugation and washed with DMF. The solid was further washed with CHCl<sub>3</sub> to remove any remaining DMF and subsequently immersed in CHCl<sub>3</sub> overnight. The precipitate was separated by centrifugation and treated at 150 °C for 6 h under high vacuum to afford **MOF-5** and **R**<sub>2</sub>-**MOF-5** (R=Me, Et, Pr, or Bu) in the form of colorless crystals.

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# **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Functionalization · Gas adsorption · Hydrogen storage · Metal-organic frameworks · Microporous materials

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