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Enhancing Gas Adsorption and Separation Capacity through Ligand Functionalization of Microporous Metal–Organic Framework Structures

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Abstract: Hydroxyland aminofunctionalized [Zn(BDC)- $(TED)_{0.5}$]•2DMF•0.2H₂O leads to two new structures, [Zn(BDC-OH)- $(TED)_{0.5}$]-1.5DMF-0.3H₂O and [Zn-(BDC-NH₂)(TED)_{0.5}]-xDMF-yH₂O (BDC=terephthalic acid, TED=triethylenediamine, BDC-OH=2-hydroxvlterephthalic acid, BDC-NH₂=2-aminoterephthalic acid). Single-crystal Xray diffraction and powder X-ray diffraction studies confirmed that the structures of both functionalized compounds are very similar to that of their parent structure. Compound [Zn- $(BDC)(TED)_{0.5}]$ ·2DMF·0.2H₂O can be considered a 3D porous structure with interlacing 1D channels, three [Zn(BDC-OH)whereas both

$\label{eq:cted_constraint} \begin{array}{ll} (TED)_{0.5}] \cdot 1.5DMF \cdot 0.3H_2O & and & [Zn-(BDC-NH_2)(TED)_{0.5}] \cdot xDMF \cdot yH_2O \end{array}$

contain only 1D open channels as a result of functionalization of the BDC ligand by the OH and NH₂ groups. A notable decrease in surface area and pore size is thus observed in both compounds. Consequently, $[Zn(BDC)-(TED)_{0.5}]\cdot 2DMF \cdot 0.2H_2O$ takes up the highest amount of H₂ at low temperatures. Interestingly, however, both $[Zn(BDC-OH)(TED)_{0.5}]\cdot 1.5DMF \cdot 0.3H_2O$ and $[Zn(BDC-NH_2)(TED)_{0.5}]$ •xDMF·yH₂O show significant enhance-

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Introduction

Rapid CO₂ accumulation, predominantly arising from the sharp increase of anthropogenic activities, for example, com-

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ment in CO2 uptake at room temperature, suggesting that the strong interactions between CO₂ and the functionalized ligands, indicating that surface chemistry, rather than porosity, plays a more important role in CO2 adsorption. A comparison of single-component CO₂, CH₄, CO, N₂, and O₂ adsorption isotherms demonstrates that the adsorption selectivity of CO₂ over other small gases is considerably enhanced through functionalization of the frameworks. Infrared absorption spectroscopic measurements and theoretical calculations are also carried out to assess the effect of functional groups on CO₂ and H₂ adsorption potentials.

bustion of fossil fuels, forest clearing, and other biomass burning, has been recognized as the driving force of climate change and global warming.^[1] To prevent the situation from getting worse, considerable effort has been made to develop effective methods and materials capable of capturing and sequestering CO₂.^[2] Current techniques proposed to capture CO₂ include adsorption, membrane separation, and chemical absorption.^[3] Among them, adsorption using porous materials may be energetically efficient and economically competitive.^[4] Recent work on microporous metal-organic frameworks (MMOFs) has demonstrated their potential for storing and/or separating CO2.^[5] However, despite numerous interesting results and findings,^[6] a great challenge remains in the design of porous materials with exceptionally high capacity and selectivity toward CO₂ adsorption. This is because most of the materials that strongly adsorb CO₂ also exhibit high adsorption of other small gases, such as CH₄, CO, N₂, and O₂. One of the ongoing endeavors to effectively enhance the performance of these materials is to functionalize organic linkers.^[7] Through this process, the pore properties (e.g., pore size and shape, pore volume and surface area) of the MMOF materials and the host-guest interactions (surface chemistry) can be systematically tuned to enhance their uptake capacity and selectivity toward a



targeted gas. Modification of the ligands with functional groups prior to the formation of MOFs (pre-synthesis functionalization) is one of the two main approaches for such functionalization. Studies have shown that the introduction of functional groups into MMOFs could generate extraordinary advantages over their parent frameworks. These include, but are not limited to, control of pore size and shape without changing the structure topology, manipulation of the level of interpenetration to tune the porosity, addition of reactive sites to improve affinity and selectivity towards certain gas species, and introduction of a targeted environment to adjust hydrophilicity/hydrophobicity and/or acidity/basicity.^[8] Another way to chemically functionalize a framework is by post-synthesis modification, in which functional groups, for example, an amine or aldehyde, are brought to the surface of the pores after the MOF synthesis.^[9]

Among numerous organic ligands, terephthalate ligands are a highly studied family and can be easily functionalized with chemical groups of various polarities, hydrophilicities, and acidities.^[10] Examples include a series of isoreticular MOF (IRMOF) structures possessing large pores and high surface areas,^[11] MIL-53 and related compounds,^[12] and many others.^[13]

To better understand how selected functional groups may affect the adsorption properties of a given structure type, we targeted three microporous MOFs, have [Zn [Zn(BDC-OH)- $(BDC)(TED)_{0.5}]$ · 2DMF · 0.2H₂O (1), $(TED)_{0.5}]$ · 1.5DMF · 0.3H₂O and [Zn(BDC-NH₂)-(2), $(TED)_{0.5}]$ ·xDMF·yH₂O (3) in this study (BDC = terephthalic acid, TED=triethylenediamine, BDC-OH=2-hydroxylterephthalic acid, $BDC-NH_2=2$ -aminoterephthalic acid). The three structures are closely related in such a way that 1) they are isostructural and 2) they differ only in the functional group (-R) of the terephthalate, BDC-R (Scheme 1). We report the pre-synthesis functionalization of ligands, the



Scheme 1. Modified terephthalate ligands and schematic representation of the modification on the MOF pore surface.

solvothermal synthesis and structure characterization of three MOFs, their gas adsorption and separation properties, and the effect of functional groups on these properties.

Results and Discussion

Structure characterization: Compounds 1–3 were all prepared by solvothermal synthesis. Single-crystal X-ray diffraction analysis of compound 2 revealed its jungle-gym-type 3D framework, as shown in Figure 1. Compounds 1 and 3



Figure 1. View of the crystal structure of compound **2**. Zn (black), O (dark grey), N (grey), and C (light grey). For clarity, solvent molecules and hydrogen atoms are omitted.

are very similar to 2. All three structures contain paddlewheel dinuclear Zn clusters $[Zn_2(COO)_4]$ (or secondary building unit, SBU) that are bridged by BDC-R ligands $(R=H, OH, and NH_2 \text{ for } 1, 2, and 3, respectively)$, to form a two-dimensional (2D) 4⁴ grid. The BDC-R ligands in the 2D nets bend significantly, making the grid highly nonsymmetric. The neighboring 2D grids are pillared by TED molecules and extended to a three-dimensional (3D) framework. Upon the removal of solvent molecules, the BDC-R ligand in all three guest-free frameworks 1', 2', and 3' becomes linear and the 4⁴ grid becomes symmetric. Intercrossing channels of two different sizes are found in compound 1:^[13a] the cross section of 7.5×7.5 Å (measured between the C–C atoms in the two lateral BDC ligands excluding the van der Waals radius of carbon) along the c axis; and of 4.8×3.2 Å along the a and b axes (measured between C-C and H-H atoms, excluding van der Waals radius of carbon or hydrogen atoms). In such an interconnected porous structure, a very large void (61.3%) is accessible for solvent and guest molecules. Differing from 1, the two small windows along the *a* and *b* axes in compound **2** (4.8×2.6 Å measured from the single-crystal structure) become inaccessible for most

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small gas molecules due to the grafting of the OH group onto the benzene ring. Hydroxyl groups were found almost parallel to the benzene ring without protruding into the channel along the c axis, thus compound **2** features a 1D channel structure along the c axis. As calculated by PLATON, 53.6% of the unit cell becomes accessible to guest molecules upon the removal of the solvent from **2**. Despite the unsuccessful attempt to produce a single crystal suitable for structure analysis, the phase and purity of compound **3** were identified by powder X-ray diffraction analysis. Both compounds **2** and **3** have very similar PXRD patterns to that of compound **1** (Figure 2), confirming that the



Figure 2. Powder X-ray diffraction (PXRD) patterns of compound **1** (bottom), **2** (middle), and **3** (top).

pillared 3D structure is retained upon ligand functionalization. Considering the size of the amino group in 3, a similar 1D channel structure to compound 2 is expected for 3.

The thermal stability measurements by thermogravimetric analysis (TGA) indicate that all solvent molecules trapped in compound 1 (32.2%) can be removed at about 150°C. The resulting framework was stable to 260°C, followed by a decomposition at about 300 °C. For compound 2, 29.5% of weight loss was observed upon heating to 180°C, which corresponds well to the amount of solvent molecules. The guest-free structure was stable up to 250 °C. TGA data show all guest molecules of compound 3 (30.3%) can be removed at about 200°C, and the decomposition of the guest-free framework occurred at about 230 °C. The experimental mass losses are in good agreement with the solvent weight calculated from single-crystal data: 34.4% for 1 and 27.6% for 2. The PXRD analysis indicates that upon removal of solvent molecules, all three compounds (1', 2', and 3') remain highly crystalline.

Pore characterization: To determine the surface areas and porosity of the three compounds, argon and nitrogen adsorption-desorption experiments were carried out. The evacuated compound 1' shows much higher N₂ adsorption capacity than 2' and 3', confirming a larger pore size and

surface area in **1**'. The Brunauer–Emett–Teller (BET) and Langmuir surface areas are estimated to be 1937/2057, 1023/1111 and 1081/1183 m^2g^{-1} for compounds **1**', **2**', and **3**', respectively (Table 1). The pore volumes calculated by the

Table 1. Summary of surface area, pore volume, $H_2,$ and CO_2 adsorption data for 1', 2', and 3'.

	Surface area [m ² g ⁻¹] Langmuir (BET)	Pore volume [cm ³ g ⁻¹]	Uptake [wt %] 77 K, 1 atm	$\begin{array}{c} {\rm H}_2 \\ Q_{\rm st} \\ [\rm kJmol^{-1}] \\ (0.01- \\ 0.7{\rm wt}\%) \end{array}$	C Uptake [wt %] 298 K, 1 atm	O_2 Q_{st} $[kJ mol^{-1}]$ $(1-$ $6 wt \%)$
1' 2' 3'	2057 (1937) 1111 (1023) 1183 (1081)	0.75 0.56 0.46	2.1 1.8 1.5	≈ 5.0 5.5-4.9 4.4-3.9	7.4 13.1 9.5	19.8–20.3 24.2–26.9 22.8–22.9

Horvath–Kawazoe (HK) method are 0.75, 0.56, and 0.46 cm³g⁻¹ for **1'**, **2'**, and **3'**, respectively.^[14] Apparently, the significantly lower surface areas and the pore volumes found in the functionalized compounds **2'** and **3'** are a direct result of occupation by the functional groups (OH and NH₂) in the voids.

Hydrogen adsorption: As shown in Figure 3, the hydrogen adsorption–desorption isotherms were measured at 77 and 87 K as a function of pressure ranging from 10^{-4} to 1 atm.



Figure 3. H_2 adsorption-desorption isotherms at 77 K for 1' (square), 2' (circle), and 3' (triangle); adsorption branch: open symbols, desorption branch: filled symbols.

At 77 K, the uptake of hydrogen corresponds to 2.1, 1.8, and 1.5 wt% at 1 atm for $\mathbf{1'}$, $\mathbf{2'}$, and $\mathbf{3'}$, respectively. Compound $\mathbf{1'}$ shows the highest H₂ adsorption capacity at 77 K, which is consistent with its large surface area and pore volume. The isosteric heats of H₂ adsorption (Q_{st}), derived from the modified Clausius–Clapeyron equation were used to estimate the extent of interactions between H₂ and the frameworks (Figure 4).^[15] The higher uptake amount of H₂ in $\mathbf{1'}$ over $\mathbf{2'}$ suggests that the pore size (and thus pore volume and surface area) of framework rules, since the isosteric



Figure 4. Isosteric heats of H₂ adsorption (Q_{st}) for 1' (square), 2' (circle), and 3' (triangle) calculated by Virial method.

heats of adsorption (Q_{st}) are generally comparable for the two compounds but with higher values for **2'** at low loadings: for **2'** they range from 4.9 to 5.5 kJ mol⁻¹ between 0.01 and 0.7 wt% and are about 5.0 kJ mol⁻¹ for **1'** in the same loading range. Compared with those of **3'** (3.9 to 4.4 kJ mol⁻¹ in the same loading range), the Q_{st} values indicate stronger H₂-MOF interactions in **2'** than in **3'**. This is also consistent with the observation that **2'** takes up more H₂ although it has a comparable surface area to **3'**.

Carbon dioxide adsorption and separation: The CO₂ adsorption isotherms for evacuated compounds **1'**, **2'**, and **3'** were collected at 278, 288, and 298 K, and the results are plotted in Figure 5. In contrast to the adsorbed amount of H₂, an opposite trend is obtained for the CO₂ uptake in **1'** and **2'**, which is clearly not coincident with the order of surface area and pore size. As seen from the isotherm data, compound **2'** has a maximum CO₂ uptake of 23.7 and 13.0 wt % at 278 and 298 K (1 atm), respectively, corresponding to about 16 and 10 CO₂ molecules per unit cell. For **1'**, the CO₂ uptake decreased to 18.4 and 7.4 wt % at 278 and 298 K



Figure 5. CO_2 adsorption–desorption isotherms at 298 K for 1', 2', and 3'; adsorption branch: open symbols, desorption branch: filled symbols.

(1 atm), respectively. Note the adsorbed amount of CO_2 is nearly doubled in 2' with respect to that by its parent structure 1' at room temperature.

The isosteric heats of CO_2 adsorption were calculated based on the adsorption raw data collected at 278, 288, and 298 K without fitting (Figure 6). The highest Q_{st} values for



Figure 6. Isosteric heats of CO₂ adsorption (Q_{st}) values for 1' (square), 2' (circle), and 3' (triangle).

compound 2' are $24.2-26.9 \text{ kJ mol}^{-1}$ at low loadings (1-6 wt %), in comparison with those of $\mathbf{1}'$ (19.8–20.3 kJ mol⁻¹) and **3'** (22.8–22.9 kJ mol⁻¹), respectively. The trend in the Q_{st} values is clearly in accordance with the uptake amount. Both follow the order: 2' > 3' > 1' and override the trend in surface area values $(1' \gg 3' \approx 2')$. The higher adsorption enthalpies of CO_2 in 2' and 3' that have functionalized BDC ligands compared with those of 1' suggest stronger interactions between the functionalized frameworks and CO₂. For compound 2', the primary interaction between CO_2 and the framework is considered to be the electron donor-acceptor reaction, in which the oxygen atom of the hydroxyl group serves as the electron-donor center, whereas the C atom of CO₂ as the electron-acceptor center. In addition, the dipolar or quadrupolar interactions between the hydroxyl group and CO₂ molecule also contribute to the observed trend. Accordingly, a similar but weaker electron donor-accepter interaction may be expected in the CO₂ adsorption by amino group functionalized compound 3', due to the lower electron-donating ability of NH₂ compared with the OH group. Consequently, the enhanced CO₂ adsorption can be achieved by functionalizing MOF structures to increase gasframework interactions.

The enhancement of CO_2 uptake found in functionalized MOF structures prompted us to further investigate their CO_2 selectivity over other important gases, including CH_4 , CO, N_2 , and O_2 . The adsorption isotherms of CO_2 , CH_4 , CO, N_2 , and O_2 on compounds **1'** and **2'** were performed under the same conditions (298 K, up to 1 atm), and are shown in Figure 7. Experimental data reveals that both compounds possess significantly higher affinity to CO_2 than to CH_4 , CO, N_2 , and O_2 . Compared with compound **1'**, slight decreases in

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Figure 7. Comparison of CO_2 (square) and selected gases (CH₄, circle; CO, triangle; N₂, rhombus; O₂, hexagon) adsorption–desorption isotherms of compound **1'** (top) and **2'** (bottom) at 298 K; adsorption branch: open symbols, desorption branch: filled symbols.

the uptake capacity for other small gases, including CH₄, CO, N_2 , and O_2 are found in compound 2'. These changes coincide with the reduction of void size and surface area due to the space occupation by functional groups. Moreover, in virtue of the significant enhancement of CO₂ uptake in compound 2', its selectivity of CO_2 to CH_4 , CO, N_2 , and O_2 will therefore be further improved. The single-component separation ratios of CO₂/CH₄, CO₂/CO, CO₂/N₂, and CO₂/O₂ at 298 K and 1 atm are calculated to be 4:1(v/v), 10:1(v/v), 15:1(v/v), and 14:1(v/v) for compound 1', 7:1(v/v), 16:1(v/v), 23:1(v/v), and 15:1(v/v) for compound 2', respectively. And the selectivity will be further increased at higher pressure. In addition to the stronger electron donor-acceptor interactions between the CO₂ molecule and hydroxyl group, another two factors should also be taken into account for the high CO_2 selectivity in 2'. First, since the higher molecular polarity can lead to stronger interactions and faster sorption rates, it is expected that the introduction of polar OH groups will be in favor of the attraction of CO₂, which has the largest quadrupole moment (13.4 Cm^2) and polarizability (2.93)among all small gases investigated (the quadrupole moments of CO, N₂, and O₂ are 8.3, 4.7, and 1.3 Cm², respectively, and CH₄ is nonpolar).^[16] Second, the confinement by the

pore and channel may also help the enhancement of selectivity.^[17] The selectivity found in compound **2'** is comparable to those reported for zeolite and carbon adsorbents (e.g., zeolite 13X: CO_2/CH_4 , 2–24; CO_2/N_2 , 18), as well as some other MOFs (e.g., Cu-BTC: CO_2/CH_4 , 6; CO_2/N_2 , 20) under similar conditions.^[18] The relatively high CO_2 uptake capacity and selectivity of **2'** place it in the category of qualified candidates for further development of CO_2 capture and sequestration.

IR study: To characterize and understand interactions of H_2 and CO_2 within the pores of **1'**, **2'**, and **3'**, we performed IR absorption spectroscopy measurements. Figure 8 shows the



Figure 8. IR absorption spectra of H_2 at 55 bar in 2' (top) and 3' (bottom) at room temperature (gas-phase subtracted).

IR absorption spectra of H₂ at 55 bar in 2' and 3' referenced to the MOFs in vacuum, after subtracting the contribution from high pressure H₂ gas, as described earlier.^[19] An IR red shift of about -38 cm^{-1} from the unperturbed *ortho*-H₂ at 4155 cm⁻¹ is observed for $\tilde{\nu}(H_2)$ in 2' as shown in the left panel of Figure 8. This shift is similar to shifts that were observed for $\tilde{\nu}$ (H₂) in 1'.^[19–20] A slightly larger red shift of about -41 cm^{-1} is observed for $\tilde{\nu}$ (H₂) in 3' as shown in the right panel of Figure 8. This slightly larger shift in 3' indicates that the incorporation of amine groups in the pores leads to a relatively small perturbation of the adsorption po-

tential. Moreover the integrated area of the H₂ band for both **2'** and **3'** is similar. This indicates a similar amount of adsorbed H₂ for both MOFs, which is again consistent with the low loading regime (<0.012 wt%), shown in Figure 3. The measured IR shifts are not inconsistent with the measured $Q_{\rm st}$ values, since previous IR work has clearly shown that IR shifts do not correlate with binding energies.^[19] For example, the binding energy of H₂ in the [Ni₃(COOH)₆] MOF is 8.3 kJ mol⁻¹ with an IR shift of -30 cm⁻¹, whereas the corresponding results for H₂ in **1'** are a binding energy of about 5 kJ mol⁻¹ with an IR shift of -38 cm⁻¹.

The IR absorption spectroscopy measurements of CO_2 adsorption were also carried out on all three compounds. Plotted in Figures 9 and 10 are the IR absorption spectra of CO_2



Figure 9. Room temperature IR absorption spectra of CO_2 in 3' (top) and 1' (bottom).

trapped in the pores of the MOFs upon loading at 4 torr and subsequent evacuation. A shift of about -13 cm^{-1} in $\tilde{\nu}_{as}$ -(O=C=O) was observed for amine modified **3'**, as shown in Figure 9 (left), which is similar to that observed for $\tilde{\nu}_{as}$ -(O=C=O) in unmodified **1'** (Figure 9, right). A slightly smaller shift (\approx -11 cm⁻¹) was found for $\tilde{\nu}_{as}$ (O=C=O) in **2'** as shown in Figure 10. The red-shifted absorption for $\tilde{\nu}_{as}$ -(CO₂) from the unperturbed gas-phase value (2349 cm⁻¹) further supports the finding that CO₂ acts as an electron acceptor^[21] and that the interaction is involving the carbon of the CO₂.



Figure 10. IR absorption spectrum of CO_2 trapped in the pores of 2' at room temperature.

The similarities in the magnitude of the IR shifts indicate that the adsorption environment of CO_2 is not greatly affected by the incorporation of hydroxyl or amine in [Zn(BDC)-(TED)_{0.5}]. More specifically, the shapes of the potential are similar in the three cases. These results support the conclusions of earlier studies with H₂ that IR shifts of molecules incorporated in MOFs do not to have a direct correlation with binding energies. First principles calculations are necessary to determine whether the variation in isosteric heats of adsorption shown in Figure 6 are due to variations in binding energies or variations in kinetic barriers for CO_2 removal.

Theoretical calculations: To have a better understanding of H_2 -MOF interactions, we performed first-principles calculations for H_2 in **1'** and **2'**. As shown in reference [20], there are two types of H_2 adsorption channel in **1'**. The first type is labeled *a* and is near the $[Zn_2(COO)_4]$ cluster and runs along the *c* axis. The other one is near the face center of the BDC–TED plane, labeled as *b* in Figure 11. The two channels have similar binding energies of around 10–11 kJ mol⁻¹ before zero-point energy corrections and each channel can accommodate 2 hydrogen molecules so a total of 12 sites



Figure 11. Two types of H_2 adsorption site in **1'** (light-grey dumbbells) and **2'** (dark-grey dumbbells). The H_2 bond at the *b* site is perpendicular to the plane and the hydrogen atom in the back is not shown.

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per primitive cell (each unit cell contains four primitive cells in the simplified structure) are predicted. These calculated results are consistent with the experimental H_2 isotherms at 77 and 87 K. Each of the two isotherms can be fitted to a single Langmuir isotherm and the number of adsorption sites extracted from the fit is around 13. The calculated frequency shift is also consistent with IR measurements confirming the location of the adsorption sites.

When **1'** is functionalized by replacing one hydrogen atom in the benzene ring with a OH group, the binding energies of the sites near $[Zn_2(COO)_4]$ change only slightly. The face center sites, however, are significantly affected and the binding energy decreases from about 11 to around 8 kJ mol⁻¹, as shown in Table 2. The reduction can be attributed to the re-

Table 2. Calculated H_2 stretch frequency shift and binding energy in 1^\prime and $2^{\prime,[a]}$

	Site <i>a</i>		Site b	
	$\Delta ilde{ u} \ [ext{cm}^{-1}]$	Binding energy [kJ mol ⁻¹]	$\Delta ilde{ u} \ [ext{cm}^{-1}]$	Binding energy [kJ mol ⁻¹]
[Zn(BDC)(TED) _{0.5}] 1' [Zn(BDC-OH)(TED) _{0.5}] 2'	-32 -29	10.4 10.6	-25 -14	10.9 8.0

[a] The zero-point energies, which are not included, are typically $\approx 2.5 \text{ kJ mol}^{-1}$ for H₂ in MOFs,^[22] but have not been explicitly calculated in these cases. The sites are illustrated in Figure 11.

pulsion from the OH group since the b site moves upwards and away from OH in 2' compared with that in 1', as can be seen in Figure 11. The equilibrium position for site a also changes slightly. However, the binding energies remain almost constant, which is consistent with the fact that the measured $Q_{\rm st}$ values are comparable for 1' and 2'. The change in binding energies also shows that the potential well along the moving direction is very flat for the *a* site, but is very deep for the b site. Now the number of adsorption sites in 2' at low pressure arises mainly from the $[Zn_2(COO)_4]$ sites and a total of 8 is predicted. These are consistent with the surface area and pore volume reduction discussed above. Furthermore, the fitting of the isotherms of 2' with Langmuir isotherms gives 9.4 adsorption sites per cell for 77 K and 10.5 for 87 K, whereas the fit of the isotherm of 1' implies around 13. Both the total number of sites and the decrease are consistent with the calculations.

The change in frequency shift upon OH functionalization is similar to that in binding energy, as shown in Table 2. The shift at site *b* is much smaller for **2'**. Unfortunately, this site has a high symmetry so that the H₂ stretch vibration is almost inactive to IR compared with the corner sites a.^[19] For site *a* in Figure 11, the frequency shift is comparable for **1'** and **2'**, consistent with the small change in binding energies and also with IR measurements. We should point out here that the four corners around $[Zn_2(COO)_4]$ are not completely equivalent due to the 3-fold symmetry in the TED unit. The range of the variation in binding energy and frequency shift are about 1 kJ mol⁻¹ and 5 cm⁻¹, respectively.^[19]

Conclusion

We have carried out a systematic study to investigate and understand the effect of (pre-synthesis) ligand functionalization in the gas adsorption and separation processes on three isostructural microporous metal-organic framework compounds. Hydroxyl and amino groups were used for such functionalization. The amount of H₂ uptake correlates to both pore properties of the MOF structures and the extent of sorbate-sorbent interactions. The introduction of hydroxyl and amino groups in compounds 2 and 3 leads to a significant decrease in the pore size and surface area of the framework structure, and consequently lower H₂ adsorption capacity than that of compound 1. In contrast to the H_2 adsorption, our study demonstrates that the CO₂ adsorption is primarily affected by the chemical properties of the framework. Upon functionalization of the frameworks by hydroxyl and amino groups, the modified compounds 2 and 3 show greatly enhanced CO_2 uptake than that of **1** at room temperature, in the order of 2 > 3 > 1. Such a significant enhancement can be attributed primarily to the strong electron donor-acceptor interaction between the framework and CO₂ molecule, in which the O and N atoms containing lone pairs of electrons from hydroxyl and amino groups serve as the electron donor centers. Due to the high CO_2 affinity through functionalization, considerable improvement of CO₂ selectivity to CH₄, CO, N₂, and O₂ is also observed in both 2 and 3. This study helps to better understand and explain the functionalization effect of MOFs, and will provide useful information toward future design and synthesis of new MOFs with improved gas adsorption and separation capacity through functionalization.

Furthermore, the IR data show that the adsorption environment for both H_2 and CO_2 changes little upon functionalization of the pores. For H_2 the incorporation of NH_2 and OH groups modifies the H_2 potential very little (there is a slightly larger shift with NH_2). For CO_2 , the situation is similar with a very slightly smaller shift with OH. The IR shifts for H_2 in 2' are consistent with the theoretical calculations of the IR shifts for site *a*, which is least affected by the functionalization. These results also confirm earlier findings that IR shifts do not correlate with binding energies, as evidenced by the measured isosteric heats of adsorption.

The results from vdW–DF calculations for H_2 adsorption in **1'** and **2'** indicate that both the binding energy and the vibrational frequency for the $[Zn_2(COO)_4]$ sites are only slightly changed by the OH functionalization. The BDC-TED face center sites, however, are significantly affected and the binding energy decreased by about 3 kJ mol⁻¹ reducing the predicted adsorption sites from around 12 to 8 at low pressures. These results are consistent with the measured H₂ uptake, Q_{st} , and IR frequency as well.

Experimental Section

Materials: All chemicals were purchased from commercial sources (Alfa Aesar, Acros, Aldrich, or TCI America) and used as received. The 2-hydroxyterephthalic acid was prepared according to the literature.^[23]

2-Hydroxyterephthalic acid: 2-Bromoterephthalic acid (2.45 g, 10 mmol) and NaOH (1.20 g, 30 mmol) were mixed in water (40 mL). NaOAc (2.05 g, 25 mmol) and Cu powder (0.02 g) were then added while stirring. The solution was heated to reflux for 3 d. Aqueous NaOH (1 M) solution was added occasionally during the reaction to keep the solution alkaline and a few drops of phenolphthalein were used here as an indicator. After cooling to room temperature, the solution was filtered and the filtrate was acidified to pH 1 using HCl (1 M). The light gray product was collected by filtration and used without further purification (1.80 g, 99% yield). **Compound 1:** [Zn(BDC)(TED)_{0.5}]-2DMF-0.2H₂O (1) was synthesized fol-

lowing the same procedure reported previously.^[13a]

Compound 2: $[Zn(BDC-OH)(TED)_{0.5}]$ -1.5DMF-0.3H₂O (2) was prepared by a solvothermal reaction of $[Zn(NO_3)]$ -6H₂O (0.089 g, 0.3 mmol), BDC-OH (0.055 g, 0.3 mmol), and TED (0.022 g, 0.2 mmol) in DMF (10 mL). The mixture was sealed in a Parr reaction vessel and heated at 373 K for 2 d. After naturally cooling to room temperature, the colorless rod-like single crystals of 2 (0.080 g, 64 % yield based on metal) were isolated by filtration and washed with DMF.

Compound 3: $[Zn(BDC-NH_2)(TED)_{0.5}]\cdot xDMF \cdot yH_2O$ (**3**) was synthesized from $[Zn(NO_3)] \cdot 6H_2O$, BDC-NH₂, and TED by using the same procedure described above for **2**. The reaction yielded 0.075 g of **3** as grey needle crystals.

Crystal structure analysis: Single-crystal X-ray diffraction analysis was performed at 100 K on a Bruker-AXS smart APEX CCD system with graphite-monochromatized Mo K α radiation (λ =0.71073 Å). For compound **2**, a total number of 22338 reflections were collected (2764 unique, R(int)=0.0228) between a θ angle of 1.72 to 28.28°. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL package. Crystal data for **2**: C_{15.50}H_{21.12}ZnN_{2.50}O_{6.81}; FW=416.84 gmol⁻¹; tetragonal; I4m (No. 87); *a*= 15.0208(8), *b*=15.0208(8), *c*=19.217(2) Å; *V*=4335.9 Å³; *Z*=8; ρ_{caled} = 1.277 gcm⁻³; R1=0.0380 (2764 data with $I > 2\sigma(I)$); wR2=0.1001 (all data). CCDC-792747 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

PXRD analysis: Powder X-ray diffraction experiments were conducted using a D/M-2200T automated system (Ultima⁺, Rigaku) with Cu K α radiation (λ =1.5406 Å). The PXRD patterns were collected between 2 θ angles of 3 to 50° at a scan rate of 5 deg min⁻¹. A graphite monochromator was used and the generator power settings were at 40 kV and 40 mA. The PXRD patterns of the simulated, as-made, and outgassing samples of 1–3 are shown in Figures S1–S3, respectively.

Thermogravemetric analysis: The thermal properties of the compound were evaluated using a TA Instruments Q50 TG unit. The samples (≈ 10 mg) were loaded onto a sample pan and heated from room temperature to 600 °C at a rate of 10 °C min⁻¹ under N₂ (flow and purge rate at 40 mL min⁻¹ and 60 mL min⁻¹, respectively). The TG profiles for all three compounds are given in Figure S4.

Gas adsorption experiments: All gas sorption experiments were performed on a volumetric gas sorption analyzer (Autosorb-1-MP, Quantachrome Instruments). Liquid nitrogen and liquid argon were used as coolant to achieve cryogenic temperatures (77 and 87 K). Ultra high purity Ar (99.995%) and H₂, N₂, CO, CO₂, and CH₄ (99.999%) were used. The Ar and N₂ sorption isotherms were collected in a relative pressure range of 10^{-6} to 1 atm at 87 and 77 K, respectively. The initial outgassing process for each sample was carried out at 373 K for compounds 1 and 3, and 448 K for 2, under vacuum overnight. Outgassing samples in the amount of around 85–90 mg were used for gas sorption measurements and the weight of each sample was recorded before and after outgassing to confirm the removal of guest molecules and to ensure the framework integrity. The outgassing procedure was repeated on the same sample between experiments for about 0.5–1 h. Pore properties (e.g., pore volume, pore size, and surface area) were analyzed using Autosorb v1.50 software. The N₂ adsorption–desorption isotherms for **1'–3'** are plotted in Figure S5. The hydrogen adsorption–desorption isotherms were collected in the pressure range from 10^{-4} to 1 atm at 87 and 77 K, respectively. Results for **1'–3'** are plotted in Figure S6. Temperature-dependent adsorption–desorption isotherms of CO₂ (278, 288, and 298 K) on **1'–3'** were collected from 10^{-3} to 1 atm and are depicted in Figure S7. Plots in Figures S8 and S9 are isotherms of CO₂ in **1'** and **2'** compared with those of other selected small gases (298 K and up to 1 atm).

IR experiment: Infrared absorption spectroscopy measurements were performed using a Thermo 6700 FTIR spectrometer equipped with a high pressure cell and a liquid-N₂-cooled InSb detector. The MOF powders were gently pressed onto a KBr support and measurements were performed in transmission. Hydrogen uptake measurements were carried out at room temperature at a pressure of 55 bar. CO_2 measurements were performed by sequential loading to a pressure of 4 torr into the activated MOFs and subsequent evacuation to remove the gas phase CO_2 , thereby providing information on the CO_2 molecules that are most strongly bound within the pores and their stability.

Theoretical calculations: Calculations were performed within the planewave implementation of the density functional theory in the ABINIT package,^[24] which we have adapted to incorporate the van der Waals interaction.^[25] The basic structure was taken from single-crystal data. For 1', we used the simplified structure eliminating the disorder of C in TED and O in BDC.^[13c] For 2', we started from 1' and replaced one hydrogen atom in the benzene by a OH group which was relaxed for optimal orientations while keeping all the other MOF atoms fixed. The H₂ adsorption sites in $\mathbf{1}'$ were established in a previous paper. $^{[20]}$ We used these sites as our initial estimate for H_2 binding positions in 2' and then relaxed it for final positions. After these equilibrium positions and orientations were obtained, we preformed a series of total energy calculations with different H₂ bond lengths while keeping the center of H₂ and the MOF atoms fixed. The resulting total energies were used in the Schrodinger equation to obtain the vibrational frequencies. An energy cutoff of 50 Ry and $2\times$ 2×2 Monkhorst–Pack grids were used throughout the calculations.

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- [1] E. Kintisch, Science 2007, 317, 184-186.
- [2] IEA Greenhouse Gas R&D Programme 2006, CO₂ Capture and Storage.
- [3] a) J. T. Yeh, H. W. Pennline, *Energy Fuels* 2001, 15, 274–278; b) J. C. Hicks, J. H. Drese, D. J. Fauth, M. L. Gray, G. G. Qi, C. W. Jones, J. Am. Chem. Soc. 2008, 130, 2902–2903; c) J. C. Abanades, E. S. Rubin, E. J. Anthony, *Ind. Eng. Chem. Res.* 2004, 43, 3462–3466; d) K. B. Lee, M. G. Beaver, H. S. Caram, S. Sircar, *Ind. Eng. Chem. Res.* 2008, 47, 8048–8062; e) R. S. Franchi, P. J. E. Harlick, A. Sayari, *Ind. Eng. Chem. Res.* 2005, 44, 8007–8013; f) D. Luebke, C. Myers, H. Pennline, *Energy Fuels* 2006, 20, 1906–1913; g) S. R. Venna, M. A. Carreon, J. Am. Chem. Soc. 2010, 132, 76–78; h) L. H. Bao, M. C. Trachtenberg, J. Membr. Sci. 2006, 280, 330–334.
- [4] A. Duffy, G. M. Walker, S. J. Allen, Chem. Eng. J. 2006, 117, 239– 244.
- [5] a) D. Britt, H. Furukawa, B. Wang, T. G. Glover, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* 2009, *106*, 20637–20640; b) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* 2010, *43*, 58–67; c) J. R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* 2009, *38*, 1477–1504.
- [6] a) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939–943; b) A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998–17999; c) B.

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Chem. Eur. J. 2011, 17, 5101-5109

Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, O. M. Yaghi, Nature 2008, 453, 207-211; d) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc. 2009, 131, 3875-3877; e) H. Furukawa, O. M. Yaghi, J. Am. Chem. Soc. 2009, 131, 8875-8883; f) A. Ö. Yazaydin, R. Q. Snurr, T. H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, R. R. Willis, J. Am. Chem. Soc. 2009, 131, 18198-18199; g) J. P. Zhang, X. M. Chen, J. Am. Chem. Soc. 2009, 131, 5516-5521; h) A. Demessence, D. M. D'Alessandro, M. L. Foo, J. R. Long, J. Am. Chem. Soc. 2009, 131, 8784-8786; i) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim, K. Kim, J. Am. Chem. Soc. 2004, 126, 32-33; j) Y. S. Bae, O. K. Farha, J. T. Hupp, R. Q. Snurr, J. Mater. Chem. 2009, 19, 2131-2134; k) K. Nakagawa, D. Tanaka, S. Horike, S. Shimomura, M. Higuchi, S. Kitagawa, Chem. Commun. 2010, 46, 4258-4260; I) S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, J. Am. Chem. Soc. 2008, 130, 10870-10871; m) H. J. Park, M. P. Suh, Chem. Eur. J. 2008, 14, 8812-8821; n) P.K. Thallapally, J. Tian, M.R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, J. L. Atwood, J. Am. Chem. Soc. 2008, 130, 16842-16843; o) J. An, S. J. Geib, N. L. Rosi, J. Am. Chem. Soc. 2010, 132, 38-39.

- [7] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* 2002, 295, 469–472; b) H. X. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* 2010, 327, 846–850.
- [8] a) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc. 2008, 130, 11650-11661; b) T. Yamada, H. Kitagawa, J. Am. Chem. Soc. 2009, 131, 6312-6313; c) C. Yang, X. P. Wang, M. A. Omary, J. Am. Chem. Soc. 2007, 129, 15454-15455; d) T. Gadzikwa, B. S. Zeng, J. T. Hupp, S. T. Nguyen, Chem. Commun. 2008, 3672-3674; e) J. L. C. Rowsell, O. M. Yaghi, J. Am. Chem. Soc. 2006, 128, 1304-1315.
- [9] a) Z. Q. Wang, S. M. Cohen, J. Am. Chem. Soc. 2009, 131, 16675– 16677; b) W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee, O. M. Yaghi, J. Am. Chem. Soc. 2008, 130, 12626–12627.
- [10] a) M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen, O. M. Yaghi, *Chem. Commun.* 2001, 2532–2533; b) A. L. Grzesiak, F. J. Uribe, N. W. Ockwig, O. M. Yaghi, A. J. Matzger, *Angew. Chem.* 2006, *118*, 2615–2618; *Angew. Chem. Int. Ed.* 2006, *45*, 2553–2556; c) S. Horike, S. Bureekaew, S. Kitagawa, *Chem. Commun.* 2008, 471–473.
- [11] H. L. Li, C. E. Davis, T. L. Groy, D. G. Kelley, O. M. Yaghi, J. Am. Chem. Soc. 1998, 120, 2186–2187.
- [12] a) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, J. Am. Chem. Soc. 2002, 124, 13519–13526; b) L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. van Beek, E. Jolimaître, A. Vimont, M. Daturi, G. Férey, J. Am. Chem. Soc. 2009, 131, 17490–17499; c) S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, F. Kapteijn, J. Am. Chem. Soc. 2009, 131, 6326–6327; d) D. Himsl, D. Wallacher, M. Hartmann, Angew. Chem. 2009,

121, 4710-4714; Angew. Chem. Int. Ed. 2009, 48, 4639-4642; e) C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, Adv. Mater. 2007, 19, 2246-2251; f) P. L. Llewellyn, S. Bourrelly, C. Serre, Y. Filinchuk, G. Férey, Angew. Chem. 2006, 118, 7915-7918; Angew. Chem. Int. Ed. 2006, 45, 7751-7754.

- [13] a) J. Y. Lee, D. H. Olson, L. Pan, T. J. Emge, J. Li, Adv. Funct. Mater. 2007, 17, 1255–1262; b) K. Seki, W. Mori, J. Phys. Chem. B 2002, 106, 1380–1385; c) D. N. Dybtsev, H. Chun, K. Kim, Angew. Chem. 2004, 116, 5143–5146; Angew. Chem. Int. Ed. 2004, 43, 5033– 5036; d) Z. Q. Wang, K. K. Tanabe, S. M. Cohen, Inorg. Chem. 2009, 48, 296–306; e) K. Uemura, F. Onishi, Y. Yamasaki, H. Kita, J. Solid State Chem. 2009, 182, 2852–2857.
- [14] G. Horváth, K. Kawazoe, J. Chem. Eng. Jpn. 1983, 16, 470-475.
- [15] A. Clark, *Theory of Adsorption and Catalysis*, Academic Press, New York 1970
- [16] Y. S. Bae, C. H. Lee, Carbon 2005, 43, 95-107.
- [17] B. Liu, Q. Yang, C. Xue, C. Zhong, B. Chen, B. Smit, J. Phys. Chem. C 2008, 112, 9854–9860.
- [18] a) S. Cavenati, C. A. Grande, A. E. Rodrigues, *J. Chem. Eng. Data* 2004, 49, 1095–1101; b) A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, R. Q. Snurr, *Chem. Mater.* 2009, 21, 1425–1430; c) R. V. Siriwardane, M. S. Shen, E. P. Fisher, J. A. Poston, *Energy Fuels* 2001, 15, 279–284.
- [19] N. Nijem, J. F. Veyan, L. Z. Kong, K. H. Li, S. Pramanik, Y. G. Zhao, J. Li, D. Langreth, Y. J. Chabal, J. Am. Chem. Soc. 2010, 132, 1654– 1664.
- [20] L. Z. Kong, V. R. Cooper, N. Nijem, K. H. Li, J. Li, Y. J. Chabal, D. C. Langreth, *Phys. Rev. B* 2009, 79, 081407(R).
- [21] A. Vimont, A. Travert, P. Bazin, J. C. Lavalley, M. Daturi, C. Serre, G. Férey, S. Bourrelly, P. L. Llewellyn, *Chem. Commun.* 2007, 3291– 3293.
- [22] L. Z. Kong, G. Román-Pérez, J. M. Soler, D. C. Langreth, *Phys. Rev. Lett.* 2009, 103, 096103.
- [23] Y. Miura, E. Torres, C. A. Panetta, R. M. Metzger, J. Org. Chem. 1988, 53, 439–440.
- [24] X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, D. C. Allan, *Comput. Mater. Sci.* 2002, 25, 478–492.
- [25] a) M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, *Phys. Rev. Lett.* 2004, *92*, 246401; b) T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, D. C. Langreth, *Phys. Rev. B* 2007, *76*, 125112; c) G. Román-Pérez, J. M. Soler, *Phys. Rev. Lett.* 2009, *103*, 096102.

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