

Tuning Hydrogen Sorption Properties of Metal–Organic Frameworks by Postsynthetic Covalent Modification

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Abstract: Postsynthetic modification is presented as a means to tune the hydrogen adsorption properties of a series of metal–organic frameworks (MOFs). IRMOF-3 (isoreticular metal–organic framework), UMCM-1-NH₂ (University of Michigan crystalline material), and DMOF-1-NH₂ (DABCO metal–organic framework) have been covalently modified with a series of anhydrides or isocyanates and the hydrogen sorption properties have been studied. Both the storage capacities and isosteric heats of adsorption clearly

show that covalent postsynthetic modification can significantly enhance the sorption affinity of MOFs with hydrogen and in some cases increase both gravimetric and volumetric uptake of the gas as much as 40%. The significance of the present study is illustrated by: 1) the nature of the substituents introduced by postsynthetic modification

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result in different effects on the binding of hydrogen; 2) the covalent postsynthetic modification approach allows for systematic modulation of hydrogen sorption properties; and 3) the ease of postsynthetic modification of MOFs allows a direct evaluation of the interplay between MOF structure, hydrogen uptake, and heat of adsorption. The findings presented herein show that postsynthetic modification is a powerful method to manipulate and better understand the gas sorption properties of MOFs.

Introduction

Metal–organic frameworks (MOFs), comprising metal ions or metal ion clusters and bridging organic ligands, have recently emerged as an important family of porous materials due to their high porosity and tunable, crystalline structure.^[1] In particular, MOFs have been extensively studied for their capability to store hydrogen, which is viewed as a future energy carrier, particularly for on-board vehicle applications.^[2–6] However, the weak interaction of H₂ with most materials, including MOFs, often leads to isosteric heats of adsorption far below the optimal value;^[7] as a result, cryogenic temperatures and/or high pressures are required to achieve significant hydrogen uptake. A number of strategies aimed at improving the performance of MOFs for

H₂ storage have been recently demonstrated. These can be classified into two major categories: 1) presynthetic approaches, including catenation^[8–10] and ligand functionalization,^[10–12] and 2) postsynthetic *noncovalent* approaches, such as generation of unsaturated metal centers,^[6] ion exchange,^[13–15] framework reduction,^[16,17] and doping with metallic nanoparticles or hydrogen spillover.^[18–21] Herein, we report a new strategy that is based on postsynthetic *covalent* modification.^[22] We show that by modifying the pore structure of MOFs, both hydrogen uptake and heat of adsorption can be significantly increased. More importantly, this covalent approach provides a means to perform systematic studies that will lead to a better understanding of how changes to the MOF cavities affect H₂ sorption behavior. This may afford unique opportunities to improve the design of future hydrogen storage materials.

It has been demonstrated that, by targeting their organic components, MOFs can be readily modified in a postsynthetic manner with a wide array of covalent transformations under mild conditions.^[22] A number of recent reports have described this approach to modifying MOFs.^[23–31] We recently showed that three distinct, porous MOFs, IRMOF-3 (isoreticular metal–organic framework), UMCM-1-NH₂ (University of Michigan crystalline material), and DMOF-1-NH₂ (DABCO metal–organic framework), which are all based on

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Zn^{II} and 2-amino-1,4-benzenedicarboxylate ($\text{NH}_2\text{-BDC}$), can be modified at the free amino groups with alkyl anhydrides or isocyanates, forming amide and urea products, respectively.^[32–35] Postsynthetic covalent modification allows gradual modulation of the MOF structure^[32,36] by controlling the number and types of functional groups within the MOF. This makes systematic evaluation and optimization of gas sorption properties possible in a way that is hard to achieve by most other functionalization strategies for MOFs. In this study, we present the first extensive investigation on the effects of postsynthetic covalent modification on the hydrogen sorption properties of several MOFs.

Results and Discussion

Aromatic anhydrides and isocyanates, such as benzoic anhydride and phenylisocyanate, can modify these three MOFs in a similarly straightforward manner. Following reported synthetic protocols,^[32–36] a number of new MOFs, including IRMOF-3-AMPh, IRMOF-3-URPh,^[35] UMCM-1-AMPh, and DMOF-1-AMPh (Figure 1), were obtained starting from IRMOF-3, UMCM-1- NH_2 , or DMOF-1- NH_2 in good quality (typically as single crystals) and modest to good conversion (ranging from 32 % to 76 %; Table 1). Conversion could also be controlled by changing the reaction time (or reactant concentration), as shown by the ^1H NMR spectra of several IRMOF-3-AMPh samples (Figure 2). These materials were characterized by powder X-ray diffraction (PXRD, Figure 3), which confirm modification of the MOFs and the structural integrity of the products (see Figure S1–S4 in the Supporting Information). N_2 sorption data (77 K) indicate that the modified MOFs retain microporosity with reasonable Brunauer–Emmett–Teller (BET) surface areas relative to their respective parent MOFs (Table 1).

The H_2 sorption isotherms of IRMOF-3-AMPh and IRMOF-3-URPh samples were measured by using a volumetric gas sorption apparatus. Both MOFs show higher gravimetric uptake than unmodified IRMOF-3 at 77 K and 1 atm, with a noticeable increase from 1.51 wt % (IRMOF-

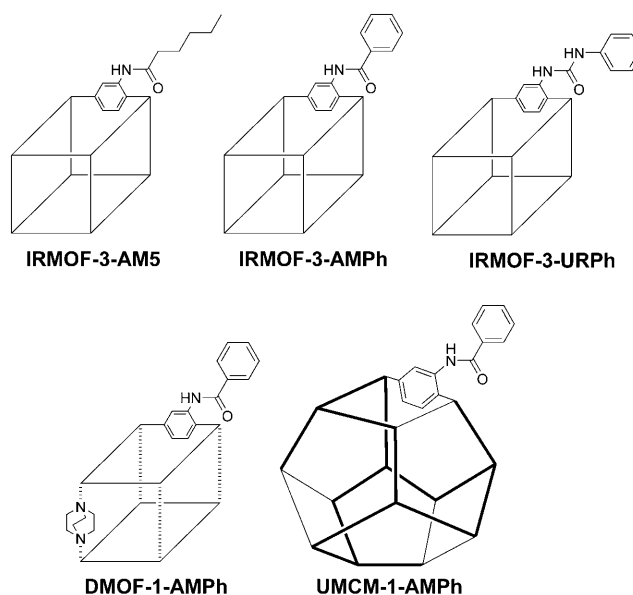


Figure 1. Schematic representation of the five modified MOFs utilized in this study.

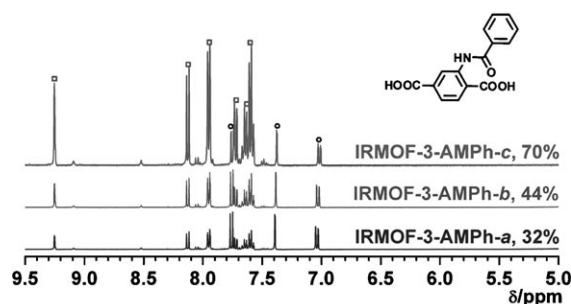


Figure 2. ^1H NMR spectra of digested IRMOF-3-AMPh samples with different degrees of postsynthetic modification. Unmodified $\text{NH}_2\text{-BDC}$ and modified $\text{NH}_2\text{-BDC}$ are indicated by circles and squares, respectively.

3) to as high as 1.73 wt % (IRMOF-3-AMPh) and 1.54 wt % (IRMOF-3-URPh). This increase is highly reproducible (see

Table 1. A summary of hydrogen sorption properties of three distinct MOFs upon postsynthetic modification.

Material	Conversion	SA_{BET} [m^2g^{-1}] ^[a]	H_2 [wt %] ^[a]	H_2 [per f.u.] ^[b,c]	$+\text{H}_2/\text{L}'$ ^[d]	H_2 [g L^{-1}] ^[e]	ΔH_{ads} [kJ mol^{-1}] ^[f]
IRMOF-3 ^[g]	N.A.	2639 ± 61	1.51 ± 0.02	6.07 ± 0.03	N.A.	9.59 ± 0.10	5.3 ± 0.3
AMPh-a	32 %	2267	1.73	7.84	1.86	12.30	5.3
AMPh-b	44 %	2052	1.73	8.16	1.60	12.80	5.7
AMPh-c	70 %	1657	1.68	8.60	1.21	13.49	6.0
URPh	41 ± 5 %	1940 ± 52	1.54 ± 0.06	7.33 ± 0.33	1.02 ± 0.23	11.50 ± 0.51	5.7 ± 0.3
AM5	86 ± 3 %	1239 ± 46	1.21 ± 0.02	6.40 ± 0.14	0.13 ± 0.06	10.05 ± 0.22	5.7 ± 0.3
UMCM-1- NH_2 ^[h]	N.A.	3917 ± 137	1.35 ± 0.05	6.91 ± 0.25	N.A.	5.39 ± 0.21	4.6 ± 0.4
AMPh	76 ± 1 %	3770 ± 93	1.54 ± 0.04	8.49 ± 0.18	1.84 ± 0.27	6.61 ± 0.16	5.2 ± 0.2
DMOF-1- NH_2 ^[h]	N.A.	1369 ± 14	2.08 ± 0.01	6.21 ± 0.02	N.A.	18.24 ± 0.08	5.6 ± 0.0
AMPh	63 ± 1 %	913 ± 37	1.69 ± 0.05	6.13 ± 0.22	-0.09 ± 0.17	18.00 ± 0.63	7.0 ± 0.1

[a] Gravimetric uptake at 77 K and 1 atm. [b] f.u. (IRMOF-3 s): $\text{Zn}_4\text{O}(\text{L})_{3(1-x)}(\text{L}')_x$, x is the conversion, L is $\text{NH}_2\text{-BDC}$, and L' is the modified BDC ligand; f.u. (UMCMs): $\text{Zn}_4\text{O}(\text{BTB})_{4/3}(\text{L})_{1-x}(\text{L}')_x$; f.u. (DMOFs): $\text{Zn}_2(\text{L})_{2(1-x)}(\text{L}')_{2x}$ (DABCO). [c] Molar uptake at 77 K and 1 atm. [d] $+\text{H}_2/\text{L}'$ represents the number of additional H_2 molecules per modified BDC ligand. [e] Volumetric uptake at 77 K and 1 atm, estimated from calculated crystal density. It is assumed that the cell volume, and thus macroscopic volume of the MOF crystals do not change noticeably upon postsynthetic modification (ref 32). [f] Heat of adsorption at zero coverage calculated from the virial-type equation. [g] Average values and errors based off of three independent experiments. [h] Average values and errors based off of two independent experiments.

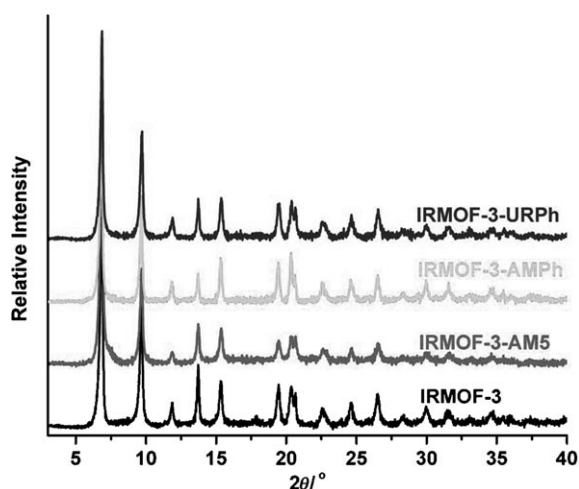


Figure 3. PXRD spectra of IRMOF-3, IRMOF-3-AM5, IRMOF-3-AMPh, and IRMOF-3-URPh. All samples were soaked in CHCl_3 and briefly air-dried prior to analysis.

Figure S5–S11 and Table S1 in the Supporting Information) and strongly suggests that the newly-incorporated aromatic moieties impart favorable H_2 -binding capacity to IRMOF-3.

This effect is perhaps even more compelling when the N_2 sorption data are also taken into account. The lower overall N_2 uptake at 77 K for both IRMOF-3-AMPh and IRMOF-3-URPh when compared to the parent IRMOF-3 is not unexpected as covalent modification necessarily reduces free volume of the MOF.^[32] Therefore, the enhancement of H_2 uptake by these modified MOFs is likely due to specific interaction of H_2 molecules with the added phenyl groups. To corroborate this hypothesis, an H_2 sorption isotherm of IRMOF-3-AM5,^[32] which contains a straight-chain alkane modification (Figure 1), was also examined. Interestingly, while the gravimetric uptake of IRMOF-3-AM5 is somewhat enhanced at low pressure (below 250 mmHg), it drops notably below that of IRMOF-3 at higher pressure (Figure 4a). These results together suggest that the aromatic substituents indeed contribute favorably to the enhancement of H_2 sorption on a gravimetric basis. Intriguingly, all three modified MOFs, including IRMOF-3-AM5, show higher uptake when the data are interpreted on either a per molar basis or volumetric basis (see Figure S13 in the Supporting Information and Table 1). This suggests that the decrease in H_2 gravimetric uptake under higher pressure for IRMOF-3-AM5 is largely due to an increase in sample mass as a result of postsynthetic modification. Nevertheless, the enhance-

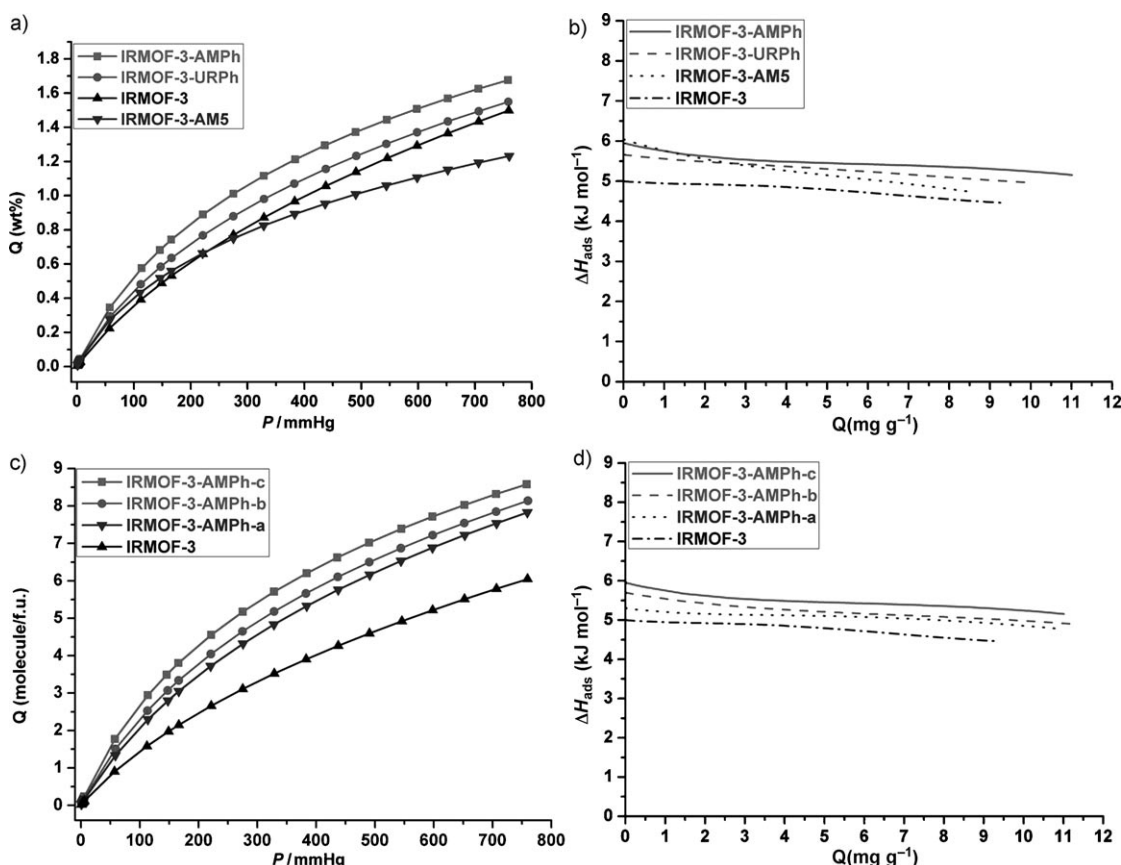


Figure 4. H_2 gravimetric uptake (a) and isosteric heat of adsorption (b) for IRMOF-3, IRMOF-3-AMPh, -URPh, and -AM5 at 77 K. H_2 molar uptake (c) and isosteric heat of adsorption (d) for IRMOF-3 and IRMOF-3-AMPh-a, -b, -c at 77 K. The isosteric heats of adsorption are calculated from the H_2 isotherms at both 77 K and 87 K, based on the virial equation.

ment appears to be much more pronounced for phenyl than alkyl substitutes, as indicated by the *number of additional H₂ per modified ligand* (ca. 1–2 additional H₂ molecules for the former and <0.2 for the latter; Table 1). We hypothesize that this drastic difference is attributed to the formation of well-defined, extra binding sites for H₂ molecules as a result of the newly-introduced phenyl groups, although it is also plausible that the aromatic systems are capable of reinforcing the binding affinity at the metal sites more strongly than their alkyl counterparts. In either scenario, the results highlighted here suggest that the organic components of MOFs may play a more critical role in binding H₂ molecules than previously recognized.^[37]

The coverage-dependent heat of adsorption for these three modified MOFs was also examined along with that of the starting IRMOF-3 using H₂ isotherms at both 77 K and 87 K. Both the virial-type^[38] and Langmuir–Freundlich^[39] equations are commonly used for this purpose. We note that while these two models agree reasonably well with each other at higher loadings, there exists a large discrepancy at near-zero coverage (see Figure S16–S23 in the Supporting Information), presumably because the Langmuir–Freundlich model is not suitable for calculating the zero-coverage value,^[39] which is often the value used to compare different systems. In addition, sample variation of MOFs can influence the zero-coverage value quite significantly (see Figure S16–S23 in the Supporting Information). Therefore, caution should be taken when reporting and comparing these values. Nevertheless, we were able to obtain reproducible results using either model (see Figure S16–S23 in the Supporting Information), although the virial-type equation will be used for the following discussion.

Similar to the H₂ molar uptake, all three modified IRMOF-3 samples show higher heat of adsorption values for the entire coverage range (Figure 2b), with a margin of increase close to 1 kJ mol^{−1} (i.e., 6.0 kJ mol^{−1} vs. 5.3 kJ mol^{−1}; Table 1). This further corroborates that the increase in H₂ uptake indeed originates from stronger binding of H₂ molecules within the MOF pores modulated by the organic functional groups introduced by covalent postsynthetic modification.

An important aspect of these postsynthetically modified MOFs is that their degree of modification can be conveniently controlled by the reaction conditions.^[36] To address the correlation of percent conversion of the MOF with its H₂ sorption property, the IRMOF-3-AMPh system was used as a model system. A series of three different MOFs, designated as IRMOF-3-AMPh-*a*, -*b*, and -*c*, with percent conversions of 32 %, 44 %, and 70 %, respectively, were isolated by combining IRMOF-3 with benzoic anhydride for different reaction times (Figure 2). Interestingly, while all three IRMOF-3-AMPh samples achieve a significant improvement over the parent IRMOF-3, the H₂ gravimetric uptake among them show little difference at 77 K and below 1 atm (see Figure S12 in the Supporting Information). This was somewhat unexpected but can nevertheless be accounted for by considering the two counteracting effects: increase of H₂

uptake and increase of sample mass. Indeed, when analyzed on a per molar basis, these H₂ sorption isotherms manifest the expected positive correlation between the uptake and percent conversion (Figure 4c). A similar trend is also apparent for the heat of adsorption (Figure 4d). It should be noted that the IRMOF-3-AMPh-*c* sample accomplishes a rather remarkable enhancement for its molar and volumetric uptake, with an increase of more than 40 %, as compared to that of the starting IRMOF-3 (Table 1).

Finally, the influence of the MOF topology on the extent of H₂ storage enhancement by covalent postsynthetic modification was also investigated. This was achieved by evaluating the H₂ sorption isotherms of UMCM-1-AMPh and DMOF-1-AMPh along with those of their parent systems. In the UMCM system,^[34,40] the uptake of H₂ by UMCM-1-AMPh also appears to be improved over the starting UMCM-1-NH₂ on both a gravimetric and volumetric basis, although the margin of increase is not as significant as in the IRMOF-3 system (Figure 5, Figure S24, Table 1).^[41] DMOF-1-AMPh, on the other hand, sees an initial increase of H₂ uptake (in both gravimetric and volumetric terms) under lower pressure but drops at higher pressures as compared to DMOF-1-NH₂ (Figure 5 and Figure S24 in the Supporting Information).

The difference in H₂ sorption behaviors in IRMOF-3-AMPh, UMCM-1-AMPh, and DMOF-1-AMPh can be explained by the difference in the overall porosity of their

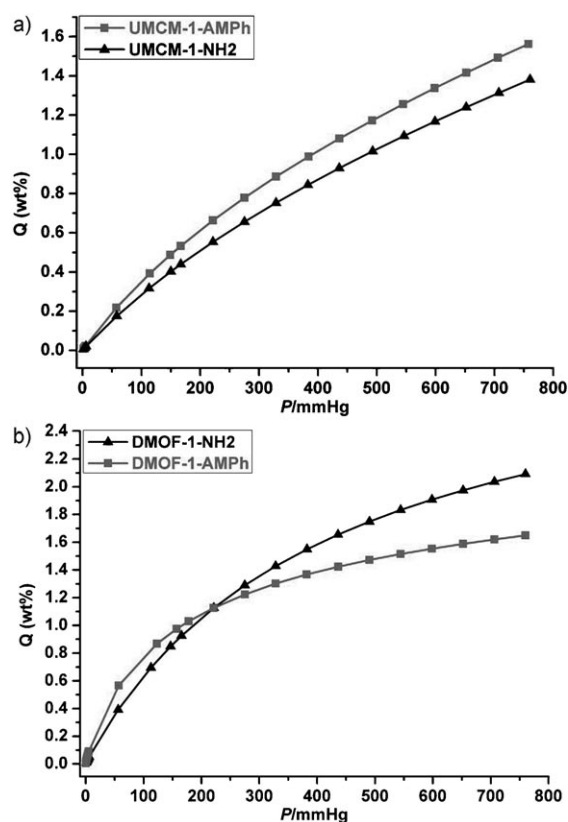


Figure 5. H₂ gravimetric uptake of H₂ for UMCM-1-NH₂ and UMCM-1-AMPh (top) and DMOF-1-NH₂ and DMOF-1-AMPh (bottom) at 77 K.

parent MOFs. Both IRMOF-3 and UCMC-1-NH₂, which have BET surface areas of about 2500 m²g⁻¹ and about 4000 m²g⁻¹, respectively, contain cavities presumably large enough to accommodate the phenyl groups without sacrificing any effective free volume that is being utilized by H₂ molecules at 77 K and 1 atm. In contrast, the hydrogen sorption capacity of DMOF-1-NH₂, which has a surface area of about 1400 m²g⁻¹, may be compromised by covalent modification due to its relatively lower surface area and narrower pore dimensions. Interestingly, the trend for the heat of adsorption is reversed for these three MOF systems: DMOF-1-AMPh achieves an enhancement comparable to, if not more pronounced than, IRMOF-3-AMPh in binding energy, whereas UCMC-1-AMPh shows a much smaller increase (see Figure S25 and S26 in the Supporting Information). This is again in accordance with their relative pore dimensions as smaller pores are likely to induce higher binding affinity. In fact, the significant enhancement of adsorption energy in DMOF-1-AMPh can satisfactorily explain the initial increase of H₂ uptake at low pressure (Figure 5 and Figure S24 in the Supporting Information), as a recent simulation study reveals a positive, linear correlation between these two parameters.^[42]

Conclusions

In summary, we have demonstrated an unprecedented post-synthetic covalent modification strategy that can significantly increase both H₂ uptake capacity and heat of adsorption of MOFs. This new approach allows precise modulation over MOF structures and facilitates identification of optimal conditions for the hydrogen storage. By initiating a systematic evaluation, we have established a route toward better understanding on the interplay of pore dimensions, H₂ uptake, and heat of adsorption for MOF materials. We believe these findings will play a guiding role in designing the future generation of storage and separation materials for a variety of gases including hydrogen, methane, carbon monoxide, and others.

Experimental Section

General: Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). IRMOF-3, DMOF-1-NH₂, and UCMC-1-NH₂ were synthesized and activated as described previously.^[32–34]

Modification of MOFs: For IRMOF-3: IRMOF-3-AM5 and IRMOF-3-URPh were synthesized on a double scale (ca. 120 mg of IRMOF-3, 0.4 mmol equiv of -NH₂) following literature procedures.^[32] IRMOF-3-AMPh-*a,b,c* were prepared by combining IRMOF-3 crystals (ca. 120 mg, 0.4 mmol equiv of -NH₂) with benzoic anhydride dissolved in CHCl₃ (36 mg mL⁻¹, 10 mL). The mixtures were allowed to stand at room temperature for a duration of 1 day, 2 days, and 8 days, respectively. For the latter two cases, approximately every 24 h, the solution was decanted and the crystals were washed with CHCl₃ (3 × 6 mL) before a fresh solution of benzoic anhydride (36 mg mL⁻¹, 10 mL) was added. At the end of the re-

action, the CHCl₃ solution was decanted and the crystals were washed with CHCl₃ (3 × 6 mL) before soaking in pure CHCl₃ (10 mL) for three days, with fresh CHCl₃ added every 24 h. After three days of soaking the crystals were stored in the last CHCl₃ solution until needed. For UCMC-1-AMPh: UCMC-1-NH₂ (ca. 112 mg, ca. 0.10 mmol equiv of -NH₂) was combined with benzoic anhydride (8 equiv; 0.80 mmol) in CHCl₃ (4 mL). The sample was placed in an oven at 55 °C for 24 h. After removing the sample from the oven, the solution was decanted and the crystals were washed with CHCl₃ (3 × 10 mL) before soaking in CHCl₃ (10 mL) for 24 h. After repeating the washes and soaks for 3 days, the crystals were stored in the last CHCl₃ solution until analyzed. For DMOF-1-AMPh: DMOF-1-NH₂ (ca. 120 mg, ca. 0.40 mmol equiv of -NH₂) was combined with benzoic anhydride (4 equiv, 1.60 mmol) in CHCl₃ (4 mL). The sample was placed in an oven at 55 °C for 24 h. After removing the sample from the oven, the solution was decanted and the crystals were washed with CHCl₃ (3 × 6 mL) before soaking in CHCl₃ (10 mL) for 24 h. After repeating the washes and soaks for 3 days, the crystals were stored in the last CHCl₃ solution until analyzed.

Digestion and analysis by ¹H NMR spectroscopy: ¹H NMR spectra were recorded on a Jeol FT-NMR (500 MHz) or a Varian FT-NMR spectrometer (400 MHz). Approximately 5 mg of modified MOF (DMOF-1-NH₂, UCMC-1-NH₂, or IRMOF-3) from gas sorption experiments (i.e., thoroughly dried and evacuated; vide infra) was digested with sonication in [D₆]DMSO (500 μL) and dilute DCl (100 μL; 35% DCl (23 μL) in D₂O diluted with [D₆]DMSO (1.0 mL)).

PXRD analysis: Approximately 15 mg of modified IRMOF-3, DMOF-1-NH₂, or UCMC-1-NH₂ (typically soaked in CHCl₃) was air dried before PXRD analysis. Powder X-ray diffraction (PXRD) data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Kα (λ = 1.5418 Å), with a scan speed of 5 s/step or 10 s/step, a step size of 0.02° in 2θ, and a 2θ range of 3–40°. The experimental backgrounds were corrected using the Jade 5.0 software package.

H₂ sorption analysis: Approximately 100–140 mg of modified IRMOF-3, DMOF-1-NH₂, or UCMC-1-NH₂ was evacuated on a vacuum line for 5–18 h. The sample was then transferred to a preweighed sample tube and degassed at 105 °C for approximately 24 h on an ASAP 2020 or until the outgas rate was <5 μmHg min⁻¹. The sample tube was re-weighed to obtain a consistent mass for the degassed modified IRMOF-3, DMOF-1-NH₂ or UCMC-1-NH₂. For each sample, BET surface area (m²g⁻¹) measurements were collected at 77 K by dinitrogen and at 87 K by argon on an ASAP 2020 using volumetric technique. The sample was then manually degassed on the analysis port overnight at 105 °C for approximately 12 h. H₂ sorption isotherms were collected at 77 K. The sample was manually degassed for an additional 1–2 h at 105 °C prior to collecting H₂ sorption isotherms at 87 K.

Calculation of isosteric heat of adsorption: Two different curve-fitting methods were used in determining the coverage-dependent isosteric heat of adsorption. Hydrogen adsorption isotherms were collected at 77 K and 87 K for each sample. Both the 77 K and 87 K data sets were fitted using the virial-type equation and the Langmuir-Freundlich equation.

Method 1: Virial-type equation [Eq. (1) and (2)]: *P* = Pressure (kPa); *Q* = Amount adsorbed (mg g⁻¹); *R* = 8.314 J mol⁻¹ K⁻¹; *m* and *n* = Number of coefficients.

$$\ln P = \ln Q + \frac{1}{T} \sum_{i=0}^m a_i Q^i + \sum_{i=0}^n b_i Q^i \quad (1)$$

$$\Delta H_{ads} = -R \sum_{i=0}^m a_i Q^i \quad (2)$$

Method 2: Langmuir-Freundlich equation [Eq. (3)]: *Q* = Amount adsorbed (mg g⁻¹); *Q_m* = Amount adsorbed at saturation (mg g⁻¹); *P* = Pressure (kPa); *B* and *t* = Constants.

$$\frac{Q}{Q_m} = \frac{BP^{(1/t)}}{1 + BP^{(1/t)}} \quad (3)$$

The Langmuir-Freundlich equation can be rearranged in terms of solving

for P and substituted into a modified version of the Clausius–Clapeyron equation to solve for the isosteric heat of adsorption [Eq. (4)–(6)]:

$$P = \left(\frac{Q/Q_m}{B - BQ/Q_m} \right) \quad (4)$$

$$\ln \left(\frac{P_1}{P_2} \right) = \Delta H_{ads} \frac{T_2 - T_1}{RT_1 T_2} \quad (5)$$

$$\Delta H_{ads} = \frac{RT_1 T_2}{T_2 - T_1} \ln \left(\frac{Q/Q_{m1}}{B_1 - B_1 Q/Q_{m1}} \frac{Q/Q_{m2}}{B_2 - B_2 Q/Q_{m2}} \right) \quad (6)$$

The curve-fitting of H_2 sorption isotherms (77 K and 87 K) using these two equations is exemplified by one of the three independent IRMOF-3 samples (see Figure S14 and S15 in the Supporting Information). Calculations based on the virial and Langmuir–Freundlich equations both reveal good reproducibility for the independent trials of each MOF. While there typically exists a large discrepancy between these two models at low loadings, they agree reasonably well with each other at high loadings.

Acknowledgements

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