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Structural Stability of *N*-Alkyl-Functionalized Titanium Metal−Organic Frameworks in Aqueous and Humid Environments

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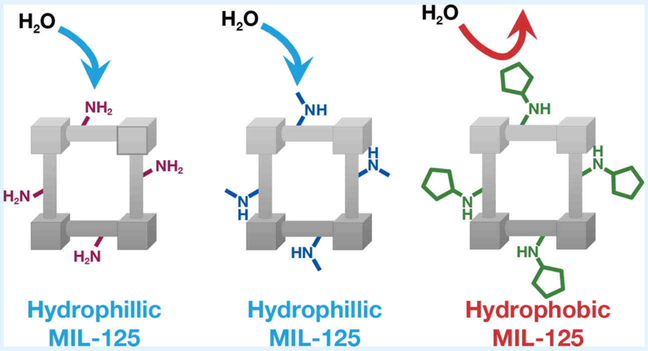
Supporting Information

ABSTRACT: We demonstrate that the highly photoredox active metal−organic framework (MOF) **MIL-125-NHCyp** exhibits crystalline and porosity stability in humid environments for more than 30 days as well as increased hydrophobicity compared to the unfunctionalized framework. This improved stability, in synergy with its high photocatalytic activity, makes this MOF a very promising candidate for large-scale applications in CO_2 photoreduction.



KEYWORDS: *metal−organic frameworks, porous coordination polymers, water adsorption, porous materials, functional materials, photocatalysis*

INTRODUCTION

One of the most common concerns for the widespread realization of metal−organic frameworks (MOFs)[1−3] in real life applications is their perceived instability toward water. Unlike zeolites, which retain crystallinity, porosity, and performance under humid environments, MOFs can be very easily disrupted when exposed to aqueous conditions.[4] Because of the combination of high porosity and the presence of oxygen-rich metal oxide clusters, MOFs tend to be hygroscopic, and often water can induce the collapse of the structure[5−8] or interfere with the adsorption of specific guests.[9−11] Improved structural stability in water has been observed in MOFs built with early transition-metal ions, in particular with zirconium,[12] titanium,[13] and yttrium.[14] Archetypical zirconium-based **UiO-66**-type MOFs can remain untouched for long periods of time when boiled in water and acids, without major loss of structural and porosity properties.[15−17] This superior stability toward water is believed to be an effect of the kinetic stability of the $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster,[18,19] and as a consequence, this framework type has become very popular for water-stable isoreticular MOFs.[20]

Titanium-based MOF **MIL-125** also features a stable $Ti_8O_4(OH)_4(CO_2)_{12}$ cluster that displays water stability; however, a limited number of isoreticular materials have been prepared. These MOFs have gained increased attention because of their exceptional performance as photoredox catalysts.[21−25] In our previous work, we demonstrated that *N*-alkyl functionalization of **MIL-125-NH$_2$** results in improved photophysical and photocatalytic properties, especially for CO_2 photoreduction.[22] Of the series, **MIL-125-NHCyp** (Cyp = cyclopentyl), which bears a cyclopentylamine group at the terephthalate linker, exhibits high photocatalytic efficiency at moderate rates under continuous blue light-emitting diode (LED) irradiation without decomposition. The photocatalytic performance of this MOF inspired us to further study its stability in water-rich environments to understand how the functionalization of the linker plays a role in its structural stability and water exclusion for improved photocatalysis.

RESULTS AND DISCUSSION

We studied the bulk crystallographic stability and water vapor adsorption properties of **MIL-125-NHCyp** compared to **MIL-125-NH$_2$** and **MIL-125-NHMe**. First, we compared the structural stability of the three MOFs by immersing bulk powder samples in water for varied periods of time and measured their powder X-ray diffraction (PXRD) patterns until the anatase phase of TiO_2 started to appear (Figure 1 and Table 1). At 25 °C and pH 7, we observed that both **MIL-125-NH$_2$** and **MIL-125-NHCyp** retain their crystallinity up to 20 d. Although neutral water at room temperature did not produce major differences in the stability between these two MOFs, **MIL-125-NHCyp** exhibited an increased stability after raising the temperature and varying the pH. Upon increasing the temperature to 50 and 70 °C, **MIL-125-NH$_2$** decomposes after 5 and 3 d, respectively, whereas **MIL-125-NHCyp** displays decomposition after 10 and 7 d at the respective temperature.

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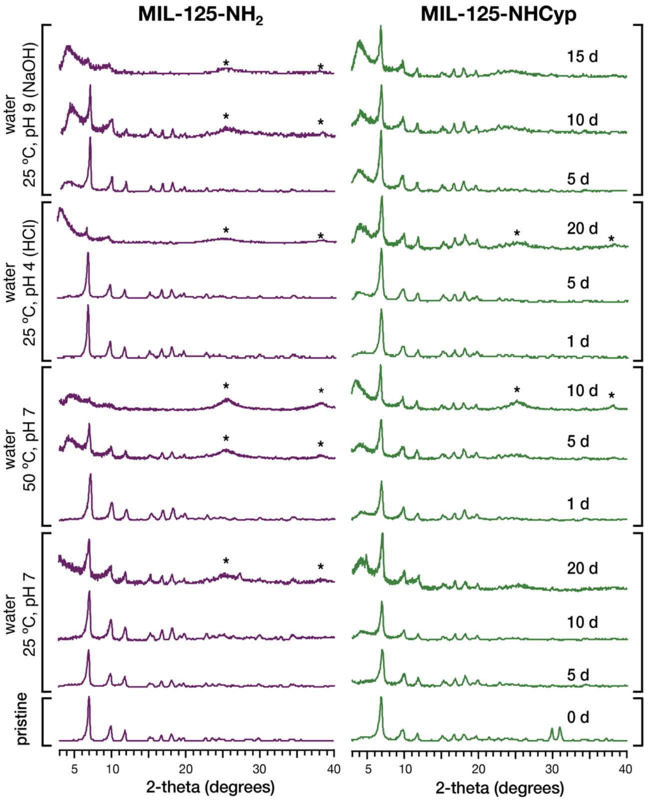


Figure 1. PXRD patterns of **MIL-125-NH$_2$** and **MIL-125-NHCyp** (Cyp = cyclopentyl) after immersion in water at different times, temperatures, and pH. The stars indicate the TiO$_2$ anatase phase.

Table 1. Water Stability Data of MIL-125-NHR MOFs[a]

			time (d)[b]		
solvent	temp (°C)	pH	−NH$_2$	−NHMe	−NHCyp
H$_2$O	25	7	20	10	20
H$_2$O	50	7	5	3	10
H$_2$O	70	7	3	3	7
H$_2$O	25	1	7	3	7
H$_2$O	25	4	15	10	20
H$_2$O	25	9	10	7	15
H$_2$O/MeCN[c]	25	TEOA[d]	>30	>30	>30
MeCN	25	TEOA[d]	>30	>30	>30
MeCN	25	AcOH[d]	>30	>30	>30

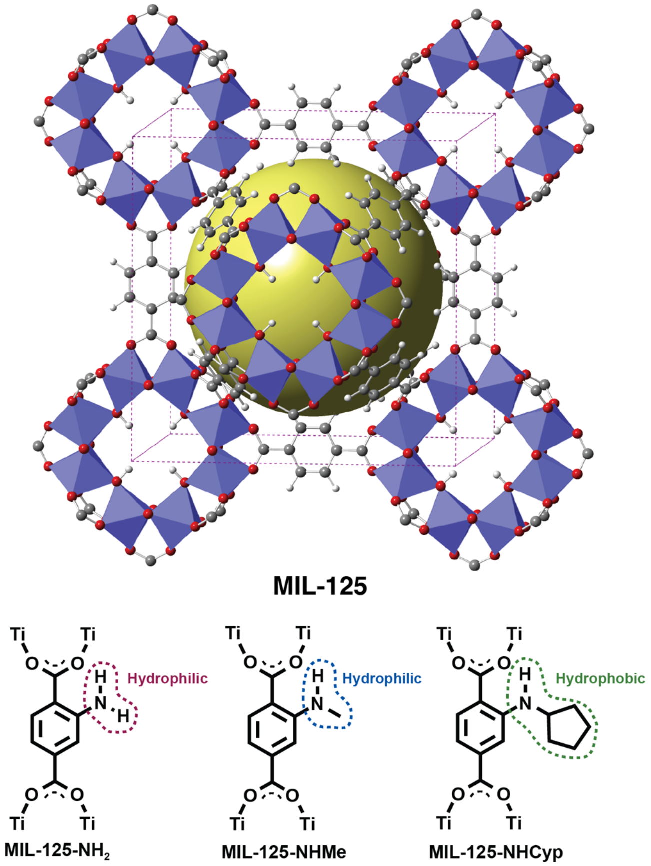
[a] Conditions: 20 mg of MOF in 3.0 mL of solvent at a specified pH and temperature. [b] Time at which TiO$_2$ is observed. [c] 5 v/v % H$_2$O in MeCN. [d] At 0.15 M concentration.

In more acidic environments, upon decreasing the pH to 4, **MIL-125-NHCyp** retains its crystallinity even after being immersed for 20 d and **MIL-125-NH$_2$** retains its crystallinity only up to 15 d. At pH 1, both MOFs remain crystalline, but only up to 7 d. In alkaline media at pH 9, **MIL-125-NHCyp** retains its crystallinity up to 15 d and **MIL-125-NH$_2$** decomposes after 10 d. At a pH higher than 9, we observed almost immediate dissolution of all MOFs. In the case of **MIL-125-NHMe**, we observed that this MOF decomposed at much shorter times under all described conditions (Table 1; see the Supporting Information), evidencing that the nature of the substitution plays a vital role.

Other studies toward water stability in MOFs have been addressed from the point of view of the effect of pK_a of the dicarboxylic acid linker as well as the hydrophobicity of the side chain functionalization. Long et al. proposed that utilizing less acidic organic linkers, that is, increasing their pK_a, should result in stronger metal−linker bonds.[26] In our case, because the only difference between the three linkers is the alkyl functionalization of the aniline in 2-amino-terephthalate (−H, −Me, and −Cyp), we rationalize that the small inductive effects of the substituents result in small increases in the pK_a value. We previously observed that these small inductive effects indeed affect the electronic properties of the MOF, exhibiting decreased band gaps, consistent with the expected trend.[22] We preformed density functional theory (DFT) calculations for each of the three acids and found that the pK_a values are very similar, for **MIL-125-NHMe** and **MIL-125-NHCyp** (see Table S1). Therefore, the inductive effects are too small to influence the Ti−O (carboxylate) bond strength, affecting the stability only marginally.

The second factor affecting the stability is the hydrophobicity of the linker. Cohen[27] and others[28−31] have studied this effect on the water stability of other MOFs (**MOF-5**, **MIL-53**, and **UiO-66** types) and observed that by adding longer alkyl chains, MOFs that are typically hygroscopic can become superhydrophobic. In our case, the N-cyclopentyl group would impart the required hydrophobicity (Chart 1) to exclude water

Chart 1. Top: Crystal Structure of the MIL-125 MOFs (Gray Spheres = Carbon, White Spheres = Hydrogen, Red Spheres = Oxygen, Blue Polyhedra = Titanium; the Yellow Sphere Represents the Pore, and Side Chains Are Not Shown for Clarity) and Bottom: Molecular Structures of the −NHR-Substituted Linkers Indicating the Hydrophilicity/Hydrophobicity of the Side Chains



from potentially attacking the metal oxide cluster (see below). The third factor is the Lewis basicity of the aniline nitrogen, as inductive effects cause increased Lewis basicity of the heteroatom. This basicity should affect the hydrogen bonding ability of the linker. We believe that by substituting the amino group with a methyl, the Lewis basicity increases, causing a better interaction with water (see water adsorption below), making it more attractive toward water. This effect should be accentuated even more in **MIL-125-NHCyp**; however, the steric blocking ability of the cyclopentyl group inhibits hydrogen bonds and renders hydrophobicity.

In our previous study,[22] typical photocatalytic conditions with these MOFs were performed in polar organic solvents, such as acetonitrile (MeCN), under nonanhydrous conditions, and in the presence of sacrificial agents, such as basic triethanolamine (TEOA). Here, we tested their stability under these conditions by exposing all three MOFs to wet acetonitrile and in the presence of either TEOA or acetic acid (AcOH), and no decomposition was observed during the measured times (Table 1). The MOFs also remain stable in wet MeCN/TEOA under constant blue LED irradiation for up to 20 d. All studied MOFs remain crystalline and with optimal photocatalytic operation, even under highly humid environments. This unusual stability prompted us to study how water interacts with the different MOFs, for which we performed water vapor adsorption studies.

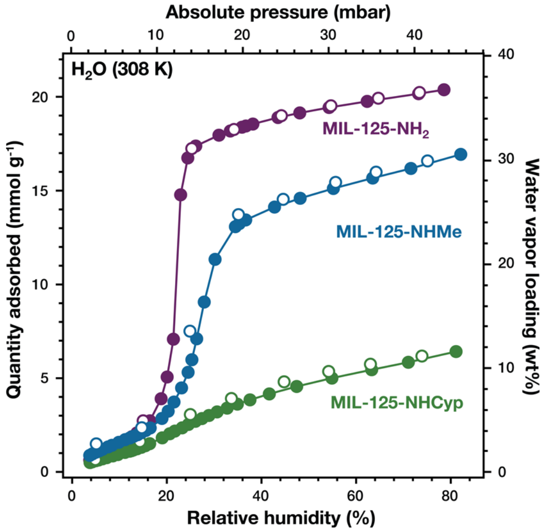


Figure 2. Water vapor adsorption isotherms at 308 K (35 °C) of **MIL-125-NH$_2$** (purple), **MIL-125-NHMe** (blue), and **MIL-125-NHCyp** (green). The closed symbols represent adsorption, and the open symbols represent desorption.

Table 2. Water Adsorption Loadings at 30 and 80% Relative Humidity as Well as Change in BET Surface Area before and after Water Exposure

	loading (wt %)[b]		S_{BET} (m^2 g^{-1})[a]	
MOF	30% RH	80% RH	before	after
$-NH_2$	32	37	1473	1411
−NHMe	20	30	1047	1010
−NHCyp	6	12	510	503[c]

[a] BET surface area, calculated from N_2(g) isotherm at 77 K (see the Supporting Information). [b] Loading measured from water adsorption isotherms at 35 °C. [c] After five water vapor adsorption cycles (Figure S39).

We measured the water vapor isotherms at 35 °C (Figure 2). As previously observed, **MIL-125-NH$_2$** displays an IUPAC isotherm type V, with a characteristic S-shape.[32,33] It has been discussed that the shape of the isotherm is due to either the pressure-induced pore gating or the clustering of water at the surface of the MOF particles at low pressures, followed by "cooperative adsorption" starting at 20% relative humidity (RH), adsorbing between 30 and 40% of its weight in water (at 30−80% RH, Table 2). Following a similar trend, **MIL-125-NHMe** also displays the S-shaped isotherm, but with slightly decreased water uptake, consistent with its high affinity to water and decreased pore volume,[22] adsorbing water between 20 and 30 wt % above 30% RH. **MIL-125-NHCyp**, on the other hand, exhibits a much smaller water uptake, between 6 and 12 wt % at the same RH range as the other MOFs, with a very small inflection point at around 20% RH. The isotherm shape and uptake indicate that this MOF is hydrophobic, excluding water more efficiently than the hydrophilic MOFs. This difference in water adsorption is consistent with the increased hydrophobicity of the cyclopentyl group as discussed above. These differences in water adsorption were studied in **UiO-66** MOFs, where functionalization with $-NH_2$ and −Me groups results in materials with a very similar pore volume, but with more than 20% difference in water uptakes, attributing this difference to be a substitution effect,[30] that is, hydrophobicity. Retention of the porous environment after water vapor adsorption was determined by the comparison of the changes in Brunauer−Emmett−Teller (BET) surface area from their N_2(g) adsorption isotherms before and after water vapor adsorption (Table 2). All three MOFs result in the retention of their BET surface area, decreasing less than 4% of their initial surface area. Moreover, performing five cycles of water vapor adsorption−desorption over **MIL-125-NHCyp** (Figure S39) resulted in a decrease of less than 2% in BET surface area, further demonstrating its stability.

■ CONCLUSIONS

We have demonstrated that *N*-alkyl functionalization of photocatalytically active titanium MOFs results in enhanced water stability. In particular, **MIL-125-NHCyp** is hydrophobic and exhibits superior structural stability toward humid environments, retaining its crystallinity for more than a month under photocatalytic conditions as well as retaining its porosity after multiple water adsorption−desorption cycles. This study demonstrates the importance of the electronic and steric effects that the organic linker can provide for applications of MOFs in real life settings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b15045.

Powder X-ray diffractograms, gas adsorption isotherms, and computational calculations (PDF)

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Notes

The authors declare no competing financial interest.

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