

Metal–Organic Frameworks with Precisely Designed Interior for Carbon Dioxide Capture in the Presence of Water

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Supporting Information

ABSTRACT: The selective capture of carbon dioxide in the presence of water is an outstanding challenge. Here, we show that the interior of IRMOF-74-III can be covalently functionalized with primary amine (IRMOF-74-III-CH₂NH₂) and used for the selective capture of CO₂ in 65% relative humidity. This study encompasses the synthesis, structural characterization, gas adsorption, and CO₂ capture properties of variously functionalized IRMOF-74-III compounds (IRMOF-74-III-CH₃, -NH₂, -CH₂NHBoc, -CH₂NMeBoc, -CH₂NH₂, and -CH₂NHMe). Cross-polarization magic angle spinning ¹³C NMR spectra showed that CO₂ binds chemically to IRMOF-74-III-CH₂NH₂ and -CH₂NHMe to make carbamic species. Carbon dioxide isotherms and breakthrough experiments show that IRMOF-74-III-CH₂NH₂ is especially efficient at taking up CO₂ (3.2 mmol of CO₂ per gram at 800 Torr) and, more significantly, removing CO₂ from wet nitrogen gas streams with breakthrough time of 610 ± 10 s g⁻¹ and full preservation of the IRMOF structure.

Carbon dioxide capture from combustion sources such as flue gas in power plants is an outstanding challenge because CO₂ has to be selectively removed from other gases and, most importantly, water.¹ Porous materials can trap CO₂ in voluminous amounts, but when water is present the efficiency of capture is significantly reduced, as water competes for the binding sites within the pores.² Aqueous monoethanolamine (MEA) solutions are efficient at binding CO₂; however, they present a major energy cost and environmental hazard.³ Thus, a need exists to develop materials capable of addressing this carbon capture challenge.

The preferred method for measuring the efficiency of a given material for capture of CO₂ is to expose a solid form of the material to a mixture of gases containing CO₂ and water, and then to detect the gases and measure the time they take to pass through the material (breakthrough time).⁴ Various porous materials⁵ such as zeolites, mesoporous silica, polymeric resins, porous carbon, and metal–organic frameworks (MOFs) are being studied for their CO₂ capture properties, but a viable

class of materials for this application has yet to emerge. Although carbon capture in mesoporous materials and carbon has been shown under humid conditions,^{4c} MOFs show special promise because of their adjustable chemical functionality, structural diversity, and ease of functionalization.⁶ Capture of CO₂ from dry gas mixtures (nitrogen, methane, and oxygen) has been reported in MOFs incorporating amines bound to either metal sites⁷ or organic linkers.⁸ However, successful demonstrations of MOFs capable of CO₂ capture in the presence of water, and doing so without degradation of performance as a result of competition with water, remain uncommon.^{4b}

In this Communication, we show how the interior of porous MOFs can be designed to overcome the complications presented by the competition of water with CO₂. We chose a MOF constructed from magnesium oxide rods joined by terphenylene organic linkers {IRMOF-74-III, Mg₂(DH3PhDC), where H₄DH3PhDC = 2',5'-dimethyl-3,3'-dihydroxy-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid, Figure 1} to make an extended structure with an *etb* topology supporting one-dimensional channels of 25 Å in their diagonal.⁹ The organic linkers and their corresponding IRMOF-74-III structures were functionalized with -CH₃, -NH₂, -CH₂NHBoc, -CH₂NMeBoc, -CH₂NH₂, and -CH₂NHMe (Boc = *tert*-butyloxycarbonyl), which point toward the center of the channels (Figure 1). Here, we report the synthesis, characterization, porosity, and CO₂ capture properties (in dry and wet nitrogen streams) of IRMOF-74-III with the six different functionalities, *vide supra*. We find that at low pressure IRMOF-74-III-CH₂NH₂ and -CH₂NHMe exhibit strong binding of CO₂ and have the highest uptake, and that in breakthrough experiments the -CH₂NH₂ form shows selectivity toward CO₂ in a wet nitrogen gas stream with 65% relative humidity (RH). Indeed, the behavior of this material under wet conditions remains unchanged from that observed under dry gas stream.

The synthesis of the appropriate linkers for IRMOF-74-III compounds is shown in Figure 1. Starting from the commercially available methyl 2-hydroxy-4-iodobenzoate (1),

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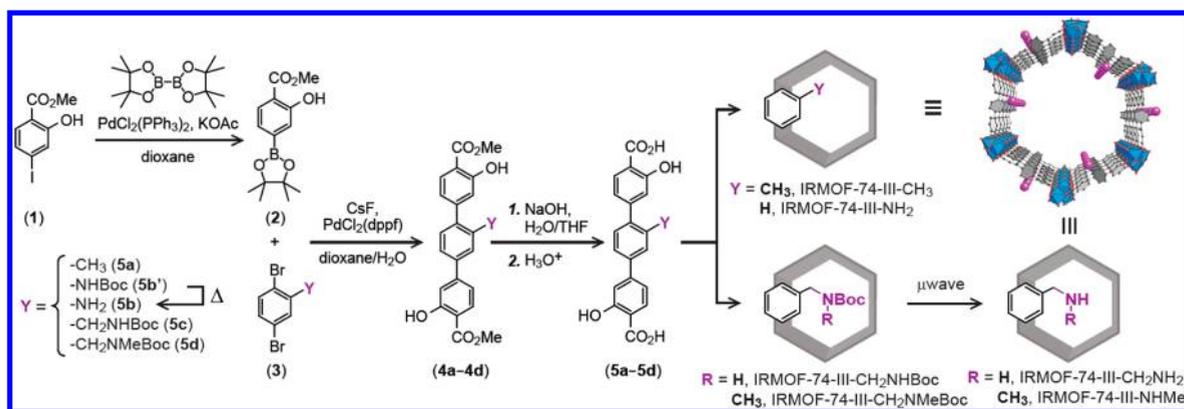


Figure 1. Synthetic pathway for the functionalized organic linkers used in the synthesis of IRMOF-74-III. This methodology allowed us to prepare -CH₃ (5a), -NH₂ (5b), -CH₂NHBoc (5c), and -CH₂NMeBoc (5d) functionalized linkers. On the right is shown a schematic representation of the IRMOF-74-III pore as functionalized with the organic linkers 5a–5d and post-synthetic deprotection of Boc groups. Color code: C in gray, O in red, functional groups in purple, Mg as blue polyhedra.

we synthesized four different organic linkers by using Suzuki–Miyaura coupling of boronic acid pinacol ester (2) and functionalized 1,4-dibromobenzenes (3), followed by saponification reaction of the methyl ester linker derivatives (4a–4d). The synthetic method was designed to achieve versatility in the covalent incorporation of a variety of functional groups within the pores of IRMOF-74-III. The linkers 5a–5d have -CH₃, -NH₂, -CH₂NHBoc, and -CH₂NMeBoc functional groups, respectively. We have employed the Boc protecting group in order to introduce -CH₂NH₂ and -CH₂NHMe into IRMOF-74-III, as the unprotected amines may react with the metal ions used for the MOF structure synthesis. The synthesized linkers were fully characterized by nuclear magnetic resonance (¹H and ¹³C NMR) and electrospray ionization mass spectrometry (ESI-MS), and single-crystal X-ray diffraction (XRD) in the case of -NH₂ and -CH₂NMeBoc linkers [section S1, Supporting Information (SI)].

Four IRMOF-74-III structures incorporating 5a–5d were prepared according to reported conditions.⁹ The synthesis of IRMOF-74-III-CH₂NHBoc is typical: a solvent mixture containing Mg(NO₃)₂·6H₂O (160 mg, 0.62 mmol), linker 5c (90 mg, 0.19 mmol), and 15 mL of *N,N*-dimethylformamide (DMF)/ethanol/water (9:0.5:0.5) was placed in a 20 mL capped vial, which was heated at 120 °C for 20 h. Depending on the functionality incorporated in the interior of the MOF, white (-CH₃), yellow (-NH₂), or pale yellow (-CH₂NHBoc and -CH₂NMeBoc) microcrystalline solids were obtained (Figure S3).

The Boc protecting groups in IRMOF-74-III-CH₂NHBoc and -CH₂NMeBoc were removed using a modification of a reported post-synthetic deprotection procedure.¹⁰ In our case, microwave heating was applied (230 °C) for 10 min in a ternary mixture of solvents [2-ethyl-1-hexanol/ethylene glycol/water (9:1:0.5:0.5)]. This process allowed us to quantitatively obtain the unprotected primary (-CH₂NH₂) and secondary amine (-CH₂NHMe) groups in the interior of those MOFs. The successful deprotection was examined by solution ¹H NMR spectra of the digested samples in 50 mM DCl in a DMSO-*d*₆/D₂O mixture, where the absence of the corresponding Boc group resonance peaks at $\delta = 1.35$ ppm and $\delta = 1.28$ ppm was confirmed for IRMOF-74-III-CH₂NH₂ and -CH₂NHMe, respectively. Similar NMR analysis was carried out for the remaining IRMOF-74-III structures and confirmed the presence of the appropriate functionality (section S4, SI).

To evaluate the porosity and crystallinity of these materials, as-synthesized samples were activated by immersion in 10 mL of DMF for 4 h, the liquid was decanted, and then the process was repeated three times per day for 3 days. This whole protocol was repeated with methanol during 3 additional days to obtain the solid with washed interior. The solvent within the pores of the resulting solids was removed under dynamic vacuum initially at room temperature and then by heating at 120 °C for 12 h. The crystallinity and structure of the evacuated series of IRMOF-74-III compounds were confirmed by the coincidence of the sharp powder X-ray diffraction (PXRD) lines with those of the parent unfunctionalized IRMOF-74-III (section S5, SI). In addition, PXRD analysis of the IRMOF-74-III-CH₂NH₂ and -CH₂NHMe samples further confirmed that the frameworks maintain their structural integrity and porosity after post-synthetic deprotection of the Boc groups. Nitrogen adsorption isotherms were measured at 77 K, and the Brunauer–Emmett–Teller (BET) surface areas were calculated to be 2640, 2720, 2170, 2220, 2310, and 2250 m² g⁻¹ for IRMOF-74-III-CH₃, -NH₂, -CH₂NHBoc, -CH₂NMeBoc, -CH₂NH₂, and -CH₂NHMe, respectively. These values are similar to the BET surface area of the parent IRMOF-74-III (2440 m² g⁻¹),⁹ indicating that porosity is maintained in the functionalized as well as the deprotected forms.

The CO₂ uptake capacity for each of the functionalized IRMOF-74-III compounds was obtained by measuring the corresponding isotherms at 25 °C (Figure 2a). All the compounds showed significant CO₂ uptake, and, as expected, IRMOF-74-III-CH₃, -NH₂, -CH₂NH₂, and -CH₂NHMe exhibit similar capacity at 800 Torr, while the protected compounds IRMOF-74-III-CH₂NHBoc and -CH₂NMeBoc showed lesser uptake because of the sterically bulky Boc groups (Figure 2a). Interestingly, IRMOF-74-III-CH₂NH₂ and -CH₂NHMe showed the highest uptake capacities at low CO₂ pressure range (<1 Torr, Figure 2b) with hysteresis, retaining ca. 20 cm³ g⁻¹ of CO₂ upon desorption down to 10 Torr (Figure 2a). This trend can be attributed to the strong interactions between CO₂ and aliphatic amine functionalities. A second CO₂ isotherm was recorded after evacuation of the sample at room temperature for 2 h (second cycle, Figure 2c). As expected, the initial slope of the CO₂ uptake in the second cycle for IRMOF-74-III-CH₂NH₂ and -CH₂NHMe was 1/3.6 and 1/4.6 compared to the first cycle, and the maximum uptakes at 800 Torr were less than those of the first cycles (by ca. 18 and 15 cm³ g⁻¹ for

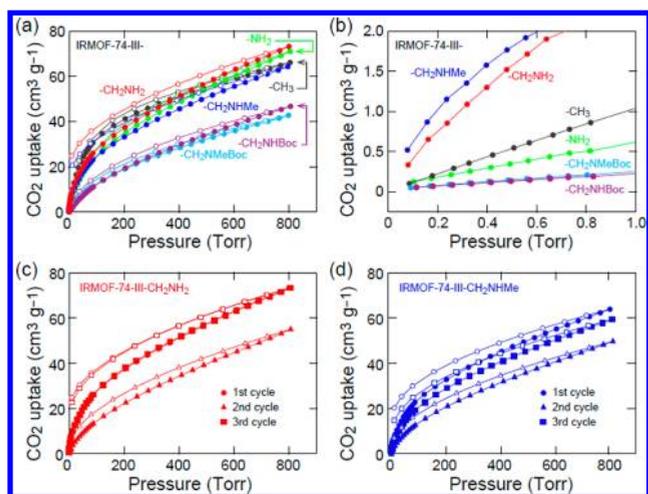


Figure 2. (a) Comparison of CO₂ uptake at 25 °C for IRMOF-74-III-CH₃ (gray), -NH₂ (green), CH₂NH₂ (red), -CH₂NHMe (blue), -CH₂NHBoc (purple), and -CH₂NMeBoc (cyan). (b) Expansion of the low pressure range (>1 Torr). Carbon dioxide isotherms at 25 °C for IRMOF-74-III-CH₂NH₂ (c) and -CH₂NHMe (d). Uptakes for samples after activation (first cycle), after first CO₂ uptake (second cycle), and after 120 °C heating for 1 h for regeneration (third cycle) are shown in circles, triangles, and squares, respectively.

IRMOF-74-III-CH₂NH₂ and -CH₂NHMe, respectively). As this evidence clearly indicated a strongly bound CO₂, the solids were heated to 120 °C under vacuum (10 mTorr) for 1 h, and isotherms for the third cycle of CO₂ uptake were measured. In the case of IRMOF-74-III-CH₂NH₂, the CO₂ was fully desorbed, while partial desorption was observed for IRMOF-74-III-CH₂NHMe (third cycle, Figure 2c,d).

Cross-polarization magic angle spinning ¹³C NMR spectra were collected for each of IRMOF-74-III-NH₂, -CH₂NHBoc, -CH₂NH₂, and -CH₂NHMe to evaluate the possibility of carbamate formation, which would be expected in the reaction of CO₂ with IRMOF-74-III-CH₂NH₂ and -CH₂NHMe and not the others. Activated samples of these MOFs were exposed to ¹³C-labeled CO₂ at room temperature and ca. 760 Torr for 24 h before the samples were transferred into a solid-state NMR rotor. The ¹³C NMR spectra of IRMOF-74-III-CH₂NH₂ and -CH₂NHMe show a broad resonance peak centered at $\delta = 160$ ppm, corresponding to the chemical shift of carbamate species resonance (carbamate ions and carbamic acid) reported in the literature,^{4a,11} while in the case of IRMOF-74-III-NH₂ and

-CH₂NHBoc samples, this peak is absent (Figure S18). This difference in the ¹³C NMR spectra confirms that CO₂ is only chemisorbed by -CH₂NH₂ and -CH₂NHMe amine-functionalized IRMOF-74-III, but not by MOFs with -NH₂ and -CH₂NHBoc functionalities.

Given the fully reversible nature of the CO₂ uptake of IRMOF-74-III-CH₂NH₂ (Figure 2c), we carried out a dynamic separation experiment to evaluate the breakthrough time in the absence and presence of water. Here, a solid sample of IRMOF-74-III-CH₂NH₂ compound (238 mg, 0.56 mmol) was packed in a 10 cm length × 0.6 cm diameter stainless steel column and utilized as an adsorbent bed. A mixed gas containing 16% (v/v) of CO₂ in a nitrogen gas stream was introduced to the column, and the effluent was monitored by a mass spectrometer.⁴ The breakthrough time was determined when the CO₂ concentration in the effluent reached 5% of the influent concentration.

Under dry conditions, the IRMOF-74-III-CH₂NH₂ adsorbent bed held CO₂ up to 670 ± 10 s g⁻¹, which is equivalent to a kinetic CO₂ adsorption capacity of 0.8 mmol g⁻¹. The CO₂ influent was then stopped and, to regenerate the material, we purged the adsorbent bed with dry nitrogen; however, this was not enough to fully remove adsorbed CO₂ (Figure 3a). Therefore, the sample bed was heated at 95 °C under nitrogen flow for 30 min, upon which appearance of CO₂ signal on the mass spectrometer indicated the liberation of chemically bound CO₂. The amount of released CO₂ was calculated by integration of the peak area and found to be 50% of the total uptake capacity of the MOF under these conditions. The regenerated IRMOF-74-III-CH₂NH₂ showed a breakthrough time as long as the one for the first run (Figure S19). This indicates that amine functionalities incorporated into the IRMOF-74-III require moderate regeneration conditions compared to MEA (ca. 120 °C) and other amine-functionalized MOFs.^{7a} As a control experiment, we subjected IRMOF-74-III-CH₃ under the same conditions used for IRMOF-74-III-CH₂NH₂ and found a longer breakthrough time (1380 ± 10 s g⁻¹);¹² however, upon purging the sample with nitrogen, all adsorbed CO₂ was recovered, indicating, as expected, no carbamate formation (Figure S20).

Both IRMOF-74-III-CH₂NH₂ and -CH₃ were examined by similar breakthrough experiments, but now in the presence of water. Prior to the breakthrough measurements, wet nitrogen with 65% RH was introduced to the adsorbent bed until the water concentration of the effluent showed a constant value (>16 h). To estimate the breakthrough time in the presence of water, we introduced a gas mixture containing 16% of dry CO₂

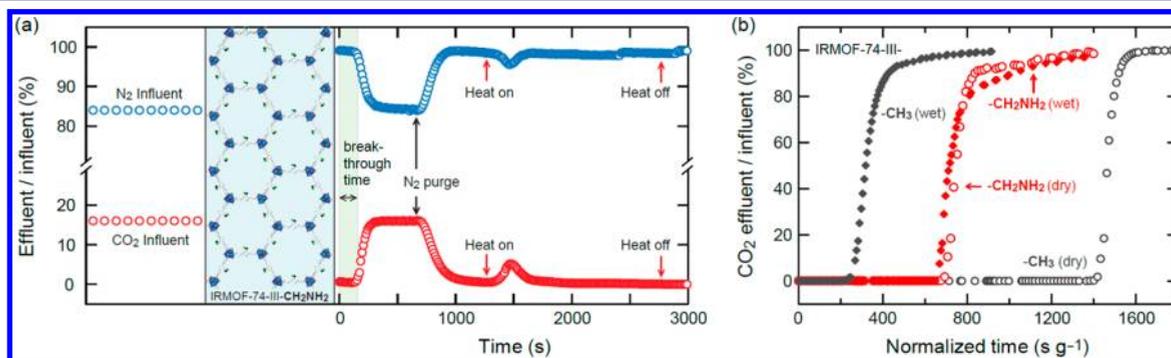


Figure 3. (a) IRMOF-74-III-CH₂NH₂ breakthrough cycle under dry conditions. Breakthrough time is highlighted in light blue. (b) Breakthrough curves for IRMOF-74-III-CH₃ under dry conditions (gray empty markers) and wet conditions (gray filled markers), and for IRMOF-74-III-CH₂NH₂ under dry conditions (red empty markers) and in the presence of water (red filled markers).

and 84% of wet nitrogen (65% RH). IRMOF-74-III-CH₂NH₂ showed a breakthrough time nearly identical to that observed under dry conditions ($610 \pm 10 \text{ s g}^{-1}$) (Figure 3b), while the breakthrough time of IRMOF-74-III-CH₃ under wet conditions showed an 80% decrease compared to that in the absence of moisture. This behavior indicates that the CO₂ uptake in IRMOF-74-III-CH₃ is, as expected, mainly attributable to the open magnesium sites, which are occupied by water molecules under humid conditions.¹² In IRMOF-74-III-CH₂NH₂, the CO₂ uptake takes place at the linker amine sites, while the open magnesium sites are not accessible under dry nor humid conditions (section S7, SI); therefore, the effect of water on the CO₂ uptake should be negligible. This is also supported by the dissimilar desorption behavior compared to IRMOF-74-III-CH₃ (Figures 3a and S20).

IRMOF-74-III-CH₂NH₂ with bound CO₂ was regenerated by purging with dry nitrogen followed by heating at 90 °C to remove the CO₂. A second cycle of humidification and CO₂ uptake was applied as explained above to obtain a nearly identical breakthrough time ($600 \pm 10 \text{ s g}^{-1}$) (section S9, SI). We further note that the PXRD pattern of the sample after these cycles was identical to that of the activated sample, thus indicating full preservation of IRMOF-74-III-CH₂NH₂ structure throughout the CO₂ capture process (Figure S16).

■ ASSOCIATED CONTENT

● Supporting Information

Detailed organic linkers and MOFs synthetic procedures, including characterization by NMR spectra, PXRD, nitrogen adsorption, breakthrough experiments, and complete refs 4b, 5g, and 9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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