Amides Do Not Always Work: Observation of Guest Binding in an Amide-Functionalized Porous Metal–Organic Framework

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Supporting Information

ABSTRACT: An amide-functionalized metal organic framework (MOF) material, MFM-136, shows a high CO2 uptake of 12.6 mmol g−1 at 20 bar and 298 K. MFM-136 is the first example of an acylamide pyrimidyl isophthalate MOF without open metal sites and, thus, provides a unique platform to study guest binding, particularly the role of free amides. Neutron diffraction reveals that, surprisingly, there is no direct binding between the adsorbed CO2/CH4 molecules and the pendant amide group in the pore. This observation has been confirmed unambiguously by inelastic neutron spectroscopy. This suggests that introduction of functional groups solely may not necessarily induce specific guest-host binding in porous materials, but it is a combination of pore size, geometry, and functional group that leads to enhanced gas adsorption properties.

Recent developments in materials chemistry and crystal engineering have shown that metal–organic frameworks (MOFs) have promising properties that complement or outperform zeolites and activated carbons in various applications.1 MOFs are crystalline porous coordination polymers consisting of polyatomic organic ligands linked to metal ions/clusters by covalent bonds.2 MOFs have shown great promise for gas adsorption and storage owing to their high porosity and internal surface area, and tunable functionality on the pore surface for selective gas binding. Generation of open metal sites3 and incorporation of pendant functional groups4 at the pore surface are two dominant methods of functionalizing MOF cavities. For example, MOFs with open Cu(II) sites can show strong adsorption affinity to molecular H2.5 Recently, the detailed binding mechanisms to saturated and unsaturated light hydrocarbons have been rationalized in a hydroxyl-functionalized MOF.6 Within the field of carbon capture, materials functionalized with amines (−NH2), imines (−NH), and amides (−CONH) dominate, largely because of their potential to form specific interactions with CO2, leading to highly selective CO2 uptakes. Although high CO2 adsorption has been observed in a number of amine-, imine- and amide-functionalized MOFs,7 molecular insight into the direct binding between adsorbed CO2 molecules and porous host (especially toward these functional groups) is largely lacking. Recently, direct H2N(δ−)···(δ+)CO2 binding has been observed in a Zn(II) MOF incorporating amine groups that protrude into the pore, providing structural insight into the observed high CO2 adsorption in this material.4

The incorporation of pendant amide (−CONH−) and/or amine groups into MOFs is thus regarded generally as a promising approach to enhance CO2 uptake due to the formation of hydrogen bonds with amides serving as both hydrogen bond acceptors (via C==O) and donors (via N−H). A series of amide-functionalized MOFs have been synthesized and shown to exhibit high CO2 uptakes and selectivities.7,8 Likewise, computational studies attribute this to the specific binding and formation of hydrogen bonds between adsorbed CO2 molecules and free amide or amine groups thus enhancing adsorption affinity and selectivity for CO2.7,9 However, to date there are few physical investigations on the precise role of amides in CO2 binding in MOFs. The challenge of such investigations is further increased in MOF systems containing open metal sites owing to the inevitable competition for guest binding between the open metal sites and the organic functional group(s) in the pore. Here, we report the synthesis, structure, and gas adsorption properties of an amide-functionalized pyrimidyl Cu(II)-isophthalate MOF, MFM-136, which shows a high CO2 adsorption capacity (12.6 mmol g−1) at 20 bar and 298 K). In MFM-136, all Cu(II) sites are fully coordinated and shown to exhibit high CO2 uptakes. Although

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in guest binding in the pore. Combined neutron diffraction and inelastic neutron spectroscopy have revealed the preferred binding sites for CO\(_2\) in the pore and the corresponding host–guest binding dynamics. Surprisingly, there is no direct binding between adsorbed CO\(_2\)/CD\(_4\) and free amides in this case. This is supported by grand canonical Monte Carlo (GCMC) simulations.

Solvothermal reaction of 5-[4-(pyrimidin-5-yl)benzamido]-isophthalic acid (H\(_4\)L, Figure 1a) with Cu(NO\(_3\))\(_2\)-3H\(_2\)O in DMF at 80 °C for 16 h yields MFM-136 as green single crystals. MFM-136 crystallizes in space group P2\(_1\)2\(_1\)2\(_1\) and shows a 3D binodal (3,6)-connected network with a rare eca-topology\(^{8,10}\). In MFM-136, the binuclear [Cu\(_2\)(O\(_2\)CR)\(_3\)] paddlewheels coordinate to two pyrimidyl nitrogen atoms from two different ligands at both axial positions, resulting in the absence of open Cu(II) sites in the entire structure (Figure 1). The metal–ligand connectivity in MFM-136 affords two types of cages (A and B). Cage A is surrounded by 12 [Cu\(_2\)(O\(_2\)CR)\(_3\)] paddlewheel units and six linkers and has a prolate-ellipsoid shape (length 24.9 Å, width 10.6 Å). Cage B is enclosed by six [Cu\(_2\)(O\(_2\)CR)\(_3\)] paddlewheel units and six linkers and has a more spherical shape (length 16.2 Å, width 12.5 Å). The overall structure is an alternate packing of these two types of cages to give a highly porous and robust framework material with a void fraction of 54% and BET surface area of 1634 m\(^2\) g\(^{-1}\) (Figure S6).

At 273 K, the CO\(_2\) sorption isotherms of desolvated MFM-136 show an uptake of 7.3 mmol g\(^{-1}\) at 1 bar and 14.3 mmol g\(^{-1}\) at 20 bar, representing the highest CO\(_2\) uptake in monoamide-functionalized MOFs reported to date (Table S2). Methane adsorption in MFM-136 gives a lower uptake of 2.9 mmol g\(^{-1}\) at 1 bar and 8.3 mmol g\(^{-1}\) at 20 bar at 273 K. The experimental CO\(_2\) adsorption isotherms show good agreement with grand canonical Monte Carlo (GCMC) simulations (Figure 2). In contrast, MFM-136 shows negligible N\(_2\) uptake under the same conditions, leading to selectivities for CO\(_2\)/N\(_2\) of 27:1 and 6.3:1, respectively, at 273 K. The isosteric heats of adsorption for CO\(_2\) and CH\(_4\) in MFM-136 are calculated using the Virial method as 25.6 and 16.0 kJ mol\(^{-1}\), respectively, at low surface coverage. The selective CO\(_2\) uptake in MFM-136 is lower than the leading ultramicroporous MOFs\(^{11}\), however, the high capacity indicates MFM-136 remains a promising candidate in the separation of CO\(_2\) over CH\(_4\) and N\(_2\).\(^{12}\) The lack of open Cu(II) sites in the pores of MFM-136 prevents strong binding to water molecules, which often triggers framework collapse or hydrolysis in MOFs containing open metal sites.\(^{13}\) Previously reported MOFs containing amides in the absence of open metals sites have exhibited high CO\(_2\) capacities,\(^{14}\) however, the role of the amides in CO\(_2\) binding was not defined structurally.

It is reported that the excellent uptake of CO\(_2\) in amide-functionalized MOFs is a consequence of specific CO\(_2\)-amide interactions based upon hydrogen bond formation between the amide –NH(\(\delta^+\)) and the O(\(\delta^-\)) of CO\(_2\).\(^{7c,8a}\) To gain experimental insight, preferred binding sites in MFM-136 have been determined by in situ neutron powder diffraction (NPD) as a function of gas loading (CO\(_2\) and CD\(_2\)). NPD patterns were recorded at 7 K for the desolvated material and at loadings of 1.8 and 2.3 CO\(_2\)/Cu and 1.1 CD\(_2\)/Cu. Fourier difference map analysis of the NPD patterns revealed positions of the adsorbed CO\(_2\) and CD\(_2\) molecules, which were further developed by Rietveld refinement. All binding sites were checked carefully for their unambiguous presence in the final structural model; i.e., a parallel refinement without each of the binding sites was carried out to confirm the presence of each site by comparing the R factors and the residual peaks.

The NPD data at a loading of 1.8 CO\(_2\)/Cu reveals eight binding sites A–H distributed between cages A and B (Figure 3). The CO\(_2\) molecules are constrained to be linear with equal C–O bond lengths, while their crystallographic occupancies and positions (including orientations) have been refined. At low CO\(_2\) loading, adsorbate–adsorbate interactions will be negligible meaning that the site occupancies directly reflect the binding strength between CO\(_2\) and the framework. Three CO\(_2\) sites A–C have significantly higher occupancies (0.65, 0.44, and 0.40, respectively) than the remaining five sites D–H (ranging within 0.26–0.11); surprisingly none of the sites makes an apparent hydrogen bonding interaction with the amide moiety. Site A resides on a 3-fold symmetry axis in the center of a triangular pocket formed by a [Cu\(_2\)(isophthalate)]\(^3+\) unit, where the CO\(_2\) makes three identical long contacts to the phenyl rings.
than that of remaining sites B–H (range 0.50–0.18). In the structure of MFM-136 loaded with 1.1 CD$_4$/Cu(II), an equivalent site to site A in the center of the triangular pocket (C1A$_{CD_4}$···ring centroid = 4.33(2) Å) is observed to have the highest occupancy of 0.36. Additional CD$_4$ binding sites with lower occupancies were observed without notable interaction to the MOF host (Figure S19). To date, crystallographic characterizations of adsorbed gas molecules in MOFs have been mostly limited to one or two binding sites for materials with narrow pores. Simultaneous refinement of a large number of sites as reported in this work is made possible by the neutron diffraction data which give equal prominence to the light guests (particularly for CD$_4$) and heavy framework.

The absence of adsorbed CO$_2$ molecules at the pendant amide group could be due to the transition between “dynamic” and “kinetic” products in which the adsorbed CO$_2$ has great mobility to translate/diffuse along the pore and form interactions with amide groups in a “come and go” fashion. The static crystallographic experiment can only paint a picture averaged over an extended time scale. Hence, only more stable environments of CO$_2$ can be seen from the diffraction study. Thus, to gain direct insight into the binding dynamics of adsorbed CO$_2$ molecules and the free amide groups, inelastic neutron spectroscopy (INS) was measured for MFM-136 as a function of CO$_2$ loading (Figure 4). INS spectra for the bare MOF show multiple features which have been identified via DFT calculations (Figure S20). Specifically, the peak at 69 meV corresponds to the out-of-plane wagging modes of the N−H group, and peaks around 110–160 meV originate from the motion of aromatic C−H groups and deformational modes of adsorbed CO$_2$ molecules.

Figure 3. Binding sites of guests in MFM-136 at loadings of 1.8 CO$_2$/Cu(II) and 1.1 CD$_4$/Cu(II) elucidated from Rietveld refinement of NPD data. Colors: carbon, black; hydrogen, white; oxygen, red; nitrogen, blue; copper, teal; CO$_2$/CD$_4$ guests, purple/dark blue/green for sites A/B/C, respectively. Refined chemical occupancies of guest molecules inset.

Figure 4. (a) Overlay of the INS spectra for bare and CO$_2$-loaded MFM-136; (b) difference INS spectrum for the bare and CO$_2$-loaded MFM-136.
the phenyl rings. Comparison of the INS spectra for bare and CO$_2$-loaded MFM-136 shows very small changes to the overall vibrational peaks except for a guest–host stiffening effect as evidenced by a global shift of peaks to slightly higher energy. Indeed, the N–H motion (69 meV) has no detectable changes upon CO$_2$ loading, while the aromatic C–H groups show small changes as confirmed by the difference spectra (Figure 4b), including a small increase in intensity at 116 meV (assigned as out-of-plane C–H bending on the isophthalate ring) and a decrease at 136 meV (assigned as in-plane C–H bending on all phenyl rings). This result is in excellent agreement with the NPD study and reaffirms the conclusion made from the diffraction experiment that direct CO$_2$ binding to the amide groups in the pore is absent.

Analysis of the CO$_2$-MOF interaction energy landscape determined during the GCMC simulation of the isotherm shows that the strongest predicted guest adsorption locations are in agreement with site A, followed by sites around the periphery of cage A corresponding to sites B–E (Figure S21). As in the NPD and INS studies, no strong adsorption was observed in the regions surrounding the N–H group.

In summary, a (3,6)-connected pyrimidyl isophthalate acylamide decorated MOF with a rare eca-toppingology has been synthesized. The amide-functionalized MOF exhibits high CO$_2$ uptake capacities and selectivity over CH$_4$ and N$_2$. Although it was anticipated that the amide moieties would actively participate in gas adsorption, the NPD and INS data reveal otherwise. The strongest binding site for both adsorbed CO$_2$ and CD$_4$ molecules is at the phenyl-isophthalate rings, and there is an absence of direct binding between adsorbed gas molecules and the pendent amide group in the pore. This has been confirmed by INS which shows retention of vibrational motion of the amide group upon CO$_2$ binding. This study indicates that introduction of functional groups in MOF structures may not necessarily result in the formation of strong binding sites for gas molecules. Future investigation of the impact of a combination of functional groups and pore geometry is currently underway.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08059.

Synthesis procedures, characterization, and additional analysis of crystal structures (CCDC-1452775, 1481610, and 1504702 contain the supplementary crystallographic data for this paper) (PDF) Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**

(1) Allendorf, M. D.; Stavila, V. CrystEngComm 2015, 17, 229.


