

Communication

Optimal binding of acetylene to a nitro-decorated metal-organic framework

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Optimal binding of acetylene to a nitro-decorated metal-organic framework

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Supporting Information

ABSTRACT: We report the first example of crystallographic observation of acetylene binding to $-NO_2$ groups in a metalorganic framework (MOF). Functionalisation of MFM-102 with $-NO_2$ groups on phenyl groups leads to a 15% reduction in BET surface area in MFM-102- NO_2 . However, this is coupled to a 28% increase in acetylene adsorption to 192 cm³ g⁻¹ at 298 K and 1 bar, comparable to other leading porous materials. Neutron diffraction and inelastic scattering experiments reveal the role of $-NO_2$ groups, in cooperation with open metal sites, in the binding of acetylene in MFM-102- NO_2 .

Acetylene is an important chemical for the production of polymers and other advanced materials.¹ However, it is highly explosive and cannot be compressed beyond 2 atm at room temperature, thus making its storage and transport a challenge. Acetylene storage is achieved currently by dissolving acetylene gas in acetone under high pressure (equivalent to ~10 atm) in a heavy-duty tank filled with porous materials, such as firebrick.² This enables the transport of acetylene in liquid form. However, such processes are not only costly but also limit the purity of stored acetylene to ~95%, making it unsuitable for many applications unless a secondary purification process is applied. Porous metal-organic frameworks (MOFs) are emerging sorbents for a variety of gases owing to their high porosity, well-defined pore size, their design flexibility and ability to incorporate active binding sites.³ Recently, there has been an increasing interest on the study of MOFs for acetylene storage,⁴ and the introduction of organic functional groups is an efficient approach to increase the gas binding within pores. MOFs incorporating -OH,⁵ -NH₂,⁶ - $CONH-,^7-C \equiv C-,^8 R-CO-R,^9-R,^{10}-OR,^{11}$ pyridine-,¹² pyrimidine-,¹³ pyrazine-,¹³ pyridazine-,¹³ naphthalene¹⁴ groups have been tested for acetylene adsorption. However, molecular insights into the precise role of these moieties on the binding of acetylene is largely lacking, thus restricting the design of improved materials.

Acetylene is relatively electron-rich due to its triple bond, and we argued that MOFs incorporating electro-positive or electron withdrawing groups would be a promising approach to facilitate C_2H_2 binding. The nitro group (-NO₂) is one of the most powerful electron-withdrawing groups. However, the direct visualisation of gas binding to -NO₂ groups in MOFs has not been reported to date and adsorption of acetylene in NO₂-decorated MOFs remains unexplored.¹⁵ Here, we report the study of acetylene adsorption in a family of four iso-structural MOFs (the MFM-102 series) bearing different functional groups, including nitro, amine, and alkane groups. The selection of these functional groups gives a wide coverage in terms of their electron donating and withdrawing power. We found that functionalisation of the parent MFM-102 with NO₂-groups leads to a 16% reduction in the BET surface area in MFM-102-NO₂, but a 28% improvement in acetylene adsorption to 192 cm³ g⁻¹ at 298 K and 1 bar, comparable to the leading materials for acetylene storage. The binding domains for adsorbed acetylene molecules in MFM-102-NO2 have been studied by in situ neutron powder diffraction and inelastic scattering experiments. In comparison, other functional groups (i.e., amine and alkane groups in MFM-102-NH₂ and MFM-111, respectively) have neutral or detrimental effects on acetylene adsorption compared to MFM-102-NO₂. Importantly, we describe the first example of observation of direct binding of acetylene molecules to the -NO₂ groups in a MOF material, leading to the optimal adsorption of this substrate.

 H_4L^1 and H_4L^2 were synthesised using our previously reported methods.¹⁶ Introduction of nitro and amine groups to H_4L^1 yielded H_4L^3 and H_4L^4 , respectively. Single crystals of MFM-102, MFM-111, MFM-102-NO₂ and MFM-102-NH₂ were synthesised from Cu(NO₃)₂·6H₂O and the corresponding ligand in DMF or DMF/DMSO under solvothermal conditions. Single crystal X-ray diffraction analysis indicated that all these MOFs are iso-structural, crystallise in the hexagonal space group R $\bar{3}m$, and adopt a NbO-type structure (Figure 1).

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Figure 1. Views of organic linkers and the crystal structure for MFM-102, MFM-111, MFM-102-NO₂ and MFM-102-NH₂. The added functional groups are highlighted in ball-stick mode. The BET surface area for each MOF is shown at the bottom. (C, dark grey; O, red; N, blue; Cu, turquoise; all coordinated waters and hydrogen atoms are omitted for clarity, except for the hydrogen atoms on the -NH₂ group, green).

The crystal structure of MFM-102-NO, is described here in detail. Two Cu(II) ions are bridged by four carboxylate groups to form a paddlewheel $[Cu_2(OOCR)_4(OH_2)_2]$. This serves as a 4-connected node that is further linked to other 4-connected nodes to construct a 3D NbO-type open structure. All these MOFs are constructed by the alternative packing of 2 types of metal-ligand cages (A and B) (Figure 1). Cage A, constructed by six linkers and six $\{Cu_2\}$ paddlewheels, has a cylindrical shape with a diameter of 14 Å and length of 19 Å. Cage B (length of 32 Å) has a shuttle-shape with 12 $\{Cu_3\}$ paddlewheels residing at the vertices and 6 ligands on the faces. It is noteworthy that the cages in MFM-111, MFM-102-NH₂ and MFM-102-NO₂ are decorated with alkane, -NH₂ and -NO₂ groups, respectively, pointing into both cages, thus providing additional binding sites for gas molecules. Phase purity of each complex has been confirmed by PXRD data (see SI). The coordinated water molecules and solvent molecules in the pores can be removed under heating to generate open Cu(II) sites in the desolvated materials.

 N_2 isotherms at 77 K confirms that desolvated MFM-102, MFM-111, MFM-102-NH₂ and MFM-102-NO₂ show BET surface areas of 3412, 2930, 2928, and 2893 m² g⁻¹, respectively (Figures 1, 2) with introduction of functional groups leading to reduction in porosity. These values are higher than other reported MOFs with NbO-topology, such as NJU-Bai-17 (2423 m² g⁻¹),¹⁷ UTSA-88 (1771 m² g⁻¹),¹⁸ and ZJU-7 (2209 m² g⁻¹).¹⁹



Figure 2. Adsorption isotherms for desolvated MFM-102, MFM-111, MFM-102-NO₂ and MFM-102-NH₂. (a) N₂ at 77 K; (b) C_2H_2 at 298 K; (c) CH₄ at 298 K. Solid and open symbols represent adsorption and desorption, respectively.

Uptakes of C₂H₂ at 273 K and 1 bar were recorded as 292, 261, 251 and 241 cm³ g⁻¹ for MFM-102-NO₂, MFM-102-NH₂, MFM-102 and MFM-111, respectively (Figure S8). Significantly, the C_2H_2 uptake of MFM-102-NO₂ (292 cm³ g⁻¹) is among those of the best-performing MOFs under the same conditions (Table S3), such as NJU-Bai17 (295 cm³ g⁻¹),¹⁷ MFM-188a (297 cm³ g⁻¹ '),7 and FJI-H8 $(277 \text{ cm}^3 \text{ g}^{-1})$.²⁰ Interestingly, although the introduction of NO2-groups to MFM-102 leads to a 15% reduction of BET surface area in MFM-102-NO2, it results in a 28% enhancement on C₂H₂ adsorption under ambient conditions, strongly demonstrating the positive effect of NO2groups on C₂H₂ binding. With similar BET surface areas, MFM-102-NO2, MFM-102-NH2, and MFM-111 provide an excellent platform to directly examine the role of functional group on C₂H₂ adsorption. Compared to the parent MFM-102, introduction of the amine group shows a small increase (5.3%) in adsorption of C_2H_2 , while the alkane group leads a moderate reduction (-12%) in C_2H_2 adsorption. The isosteric heats of C_2H_2 adsorption (Q_{st}) for these MOFs are around 31 to 33 kJ mol⁻¹, comparable to reported MOFs with open Cu(II) sites (Table S₃). The Q_{st} plots shows little variation as 1

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a function of uptake, indicating the presence of cooperativity of host-guest and guest-guest binding.²¹

To establish the role of these functional groups on C_2H_2 binding, adsorption of CH_4 , as a non-interacting gas probe, was also measured. At 298 K and 20 bar, MFM-102 shows a CH_4 uptake of 236 cm³ g⁻¹, which is higher than that for MFM-102-NO₂, MFM-102-NH₂ and MFM-111 (188, 179 and 173 cm³ g⁻¹, respectively). The trend in uptake of CH_4 is consistent with the variation of BET surface areas of these materials, and suggests potential binding interactions between the -NO₂ functional group and unsaturated C_2H_2 .



Figure 3. View of the binding sites for adsorbed C_2D_2 molecules in MFM-102-NO₂. (C, dark grey; O, red; N, blue; Cu, turquoise and C_2D_2 molecules at site I (light blue), site II (orange), site III (light green), site IV (dark green), site V (purple) and site VI (sapphire).

Six independent binding sites (I to VI) for adsorbed C₂D₂ molecules in MFM-102-NO2 have been determined by in situ neutron powder diffraction (NPD) (Figure 3). Sites I and II (occupancies of 0.41 and 0.40, respectively) are located at the open Cu(II) sites with a side-on interaction between the C≡C bond and Cu(II) [Cu-··C=C(centroid) = 3.98(5) and 2.93(8) Å for site I and II, respectively]. Interestingly, sites I and II have very different bonding distance to the open Cu(II) site. A closer examination revealed that site I also forms supramolecular interactions to two aromatic -CH groups from two adjacent phenyl rings [-CH...C=C(centroid) = 3.23(2), 3.48(3)Å] and becomes the most populated location owing to this cooperativity between sites. Site III (occupancy 0.31) is stabilised by a combination of three types of interactions to the host: (i) hydrogen bonds between the $D(\delta^+)$ of C_2D_2 molecules and $O(\delta)$ center of the -NO, group [D...O = 1.99(9), 2.35(6) Å]; (ii) supramolecular interactions between the C=C bond and the -CH group on adjacent NO2-decorated phenyl rings [-CH…C=C(centroid) = 2.47(9), 2.80(4) Å]; (iii) intermolecular dipole interactions between π -electrons on C=C bond (site III) and D-atoms of C₂D₂ at site IV. Site IV (occupancy 0.26) is also stabilised by hydrogen bonds between C_2D_2 molecules and $-NO_2$ groups $[D - O_{NO_2} = 1.69(2) \text{ Å}]$ and a

-CH bond of the NO₂-decorated phenyl ring [- $CH - C \equiv C(centroid) = 3.11(4)$ Å]. Moreover, there is a weak $\pi \cdots \pi$ interaction between C=C bond of C₂D₂(IV) and the NO2-decorated phenyl ring [ring centroid…C=C(centroid) = 4.46(8) Å]. Site V (occupancy = 0.16) is at the window between the cylindrical and spherical cages involving similar side-on mode interactions with the -CH group of the NO₂decorated phenyl ring [-CH - C = C(centroid) = 2.63(5) Å] and the hydrogen bond to the -NO₂ group $[D...ONO_2 = 3.05(10)]$, 3.17(7) Å]. Site VI (occupancy = 0.09) is located in the center of the elongated cage, interacting directly with the -NO₂ group from three surrounding ligands with D...ONO₂ distances ranging from 2.37(1) to 2.56(3) Å. Overall, C_2D_2 molecules at sites III-VI are all directly associated with the -NO₂ groups in the pore, confirming the positive effect of -NO₂ group on achieving optimal acetylene binding.



Figure 4. INS spectra for MFM-102-NO₂ with C_2H_2 loading. Comparison of difference INS plots derived by subtracting INS spectra for C_2H_2 -loaded MFM-102-NO₂ and bare MFM-102-NO₂ spectra (black), with condensed C_2H_2 in the solid state (red).

The binding dynamics of C₂H₂-loaded MFM-102-NO₂ were also studied by in situ inelastic neutron scattering (INS). The INS spectrum of bare MOF shows excellent agreement with that obtained from DFT calculations, thus allowing assignment of vibrational modes (Figure S12). The INS spectrum of C_2H_2 -loaded MFM-102-NO₂ shows a significant increase in intensity (Figures 4 and S11). The INS peaks at 80 and 95 meV (assigned as the asymmetric and symmetric C-H bending mode of C₂H₂, respectively) show significant broadening on adsorption of C₂H₂ with the appearance of shoulders on both sides and a shift to lower energy. In addition, the translational modes of C₂H₂ molecules, represented by the INS peaks at low energy region (below 25 meV), show restricted motion on adsorption, with adsorbed C₂H₂ molecules well-ordered in the pore as these peaks all shift to lower energy but still remain a three-fold feature as found in solid C₂H₂. Moreover, in the difference spectra, peaks at 164 and 189 meV (Figure S12) develop upon inclusion of C₂H₂ molecules in the pore, and this enhancement of both symmetrical and antisymmetrical stretching modes of -NO₂ groups confirms the formation of host-guest interactions between the -NO₂ groups and adsorbed C₂H₂ molecules. Overall, these results are highly consistent with the crystallographic studies showing various binding sites (I-VI) of C₂D₂ and the strong interaction between the -NO₂ group and C₂D₂ molecules (site III-VI) in the pore of MFM-102-NO₂.

Achieving optimal gas adsorption and binding in porous materials requires integration of high porosity and appropriate binding sites. However, introduction of functional groups to MOF pores naturally reduces the porosity of decorated MOFs, leading to a trade-off between these two factors. In this study, the effect of amine, alkane and nitro groups on adsorption of C_2H_2 has been examined in a family of isostructural MOFs showing high BET surface areas. The first example of binding between electron-rich C_2H_2 molecules and electron withdrawing $-NO_2$ groups in the MOF, MFM-102- NO_2 , at crystallographic resolution has been established. The combination of high BET surface area, high density of open Cu(II) sites and accessible NO_2 -groups leads to excellent adsorption capacity of C_2H_2 in MFM-102- NO_2 , making it one of the best-performing acetylene adsorbents to date.

ASSOCIATED CONTENT

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Supporting Information

Synthesis procedures, characterization, and additional analysis of crystal structures. Single crystal data of MFM-102-NO₂ and MFM-102-NH₂ are deposited at Cambridge Crystallographic Data Centre (CCDC) as 1857304 and 1857305, respectively, with NPD data deposited as 1857872 and 1857873 for C₂D₂-loaded MFM-102-NO₂ and activated MFM-102-NO₂, respectively. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

Notes

The authors declare no competing financial interests.

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