Metal Organic Framework

Crystalline Stacked Molecular Containers

Ramanathan Vaidhyanathan

X-ray crystallography is the most comprehensive character-ization tool to gain a molecular level understanding of a range of crystalline materials. One of the recent areas in which research with the aid of crystallography has exploded, is the metal organic frameworks (MOFs). These are porous crystal-line solids with exceptionally large surface areas capable of showing good promise in gas storage and gas separation applications. Here, we have captured the potential of crystal-lography as a tool to provide direct observation of gas mol-ecules trapped in the pores of the MOF and how such data serves to quantify the interactions that hold the gas within the pores. Insights from this have immediate and far reaching implication for design of gas-selective porous solids in future. The article is written in a highly simplified form, being tutorialistic in parts and we then move on to a case study and decsribe one of the state-of-the-art crystallography applica-tions.

"Simple is beautiful" – C N R Rao

Metal organic frameworks (MOFs) can be described as metals or metal clusters connected together by organic ligands into infi-nitely long structures (*Figure* 1). These appear as single crystals.

A single crystal comprises of what is called a unit cell, which can be seen as a single brick in a wall. The entire wall is the crystal. Just as how a wall has many bricks stacked, a crystal will have millions of such unit cells stacked together in 3D. The molecular composition, arrangement and orientation within this single box or unit cell is exactly the same as what it is in every box that is stacked. This makes single crystals highly ordered structures (*Figure 2*).

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Figure 1 (top) (a). A metal organic framework representing the linking of OZn_4 clusters by organic ligand, terephthalate or 1,4-benzenedicarboxylate – Unit cell. **(b)** The same cube extended in a 3D lattice in a crystal – stacked cubes.
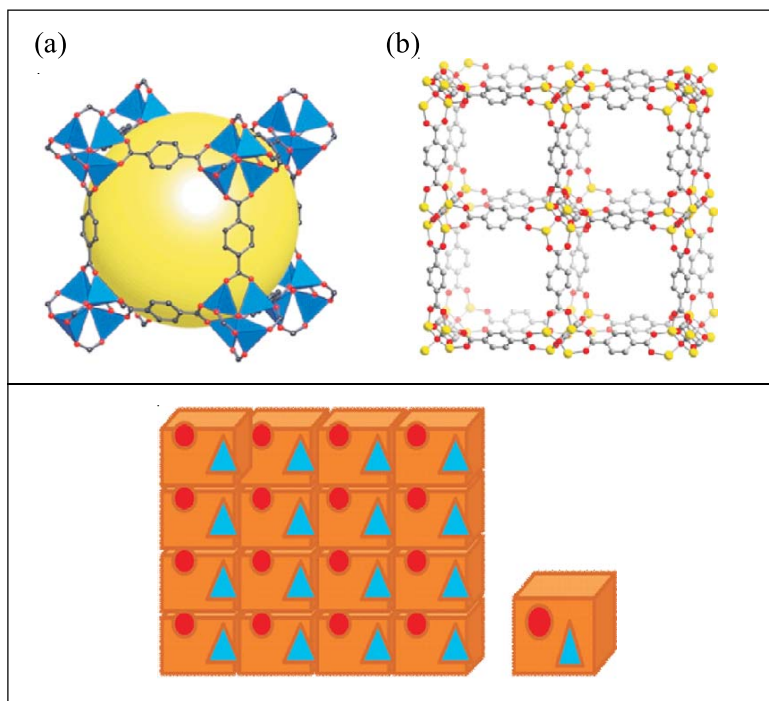
Figure 2 (bottom). Schematic representation of a single crystal and a unit cell that makes up the single crystal. The orange brick represents the unit cell, the red and blue the atoms or molecules inside it. The entire stack represents the crystal.

In an MOF, if a cube is built by connecting metal centres with organic linkers and if one such cube forms a unit cell *Figure* 1, then the single crystal will have millions of such MOF cubes stacked in three-dimensions. The advantage of a single crystal is its ability to diffract incident X-rays constructively in certain specific directions. At the atomic level, during such an X-ray diffraction, it is the electrons surrounding an atom that interact with or diffract the incident X-rays and since these atoms are arranged in an orderly fashion in a crystal, the diffracted X-rays will interact with each other constructively, following a mathematical rule. This is defined by Bragg's law (*Figure* 3).

In this figure, we denote incident X-rays of wavelength λ, as 1 and 2; diffracted X-rays as 1′ and 2′; interplanar distance as d; angle of incidence as θ; and $\angle AZB = \angle CZB = \theta$. Implies AB = BC, means, waves in 1′ will be in phase with 2′ (crest to crest), i.e., AB + BC = 2AC. If this is equal to the integral number of wavelengths,
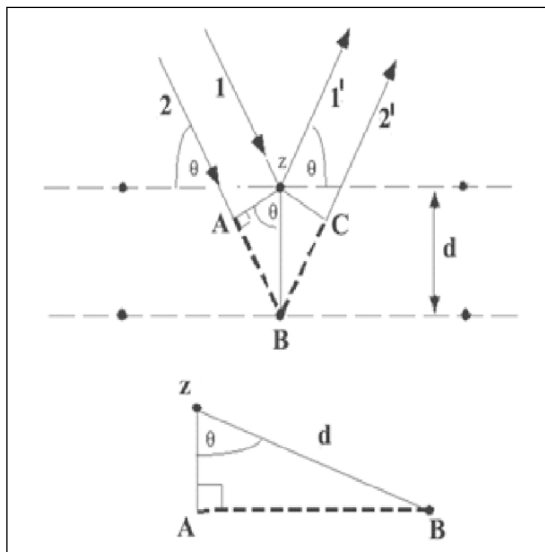
$$2AC = n\,\lambda.$$

By definition,

$$AB/d = \sin\theta.$$

Therefore,

$$2d \sin\theta = n\lambda.$$

This is Bragg's law. Essentially, this conveys that if the path difference between two different diffracted rays matches an integer multiple of the incident X-rays' wavelength, then a constructive interference will occur.

So, what is the advantage of this? If we manage to collect or project the diffracted X-rays or, more precisely, the resultant of the X-rays that have interacted among themselves, either constructively or destructively, then one can observe a series of bright spots which are ordered on the screen on a dark background (*Figure* 4).

Now, these ordered spots directly represent the arrangement of atoms within the single crystal and, in turn, the arrangement of atoms within the unit cells (the brick). Now, rotating the crystal against an incident X-ray beam and continuously collecting the photographs of the resulting X-ray diffraction will offer a series of images with ordered bright spots. When many such images are
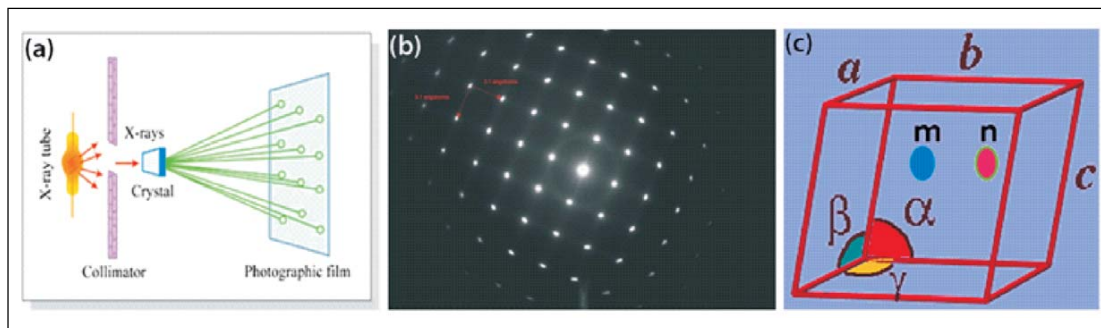
Figure 4. (a) Schematic illustration of X-ray diffraction experiment; (b) A diffraction photograph of the diffracted image collected using an image plate detector. (c) A representation of how the atomic coordinates can serve as addresses to atoms within a unit cell. For example, $m = 0.4a, 0.2b, 0.3c = x_1,y_1,z_1$; $n = 0.8a$, $0.9b, 0.1c = x_2,y_2,z_2$, would mean if you travel $0.4 \times a$ times along a-axis and $0.2 \times b$ times along b-axis and $0.3 \times c$ times c-axis, you will reach the position of atom m within the box, i.e., unit cell. Note: the distances between the atoms m and n can be estimated from the lattice parameters and the atomic coordinates as: $D = \sqrt{(a\Delta x)^2 + (b\ \Delta y)^2 + (c\ \Delta z)^2 + 2bc\Delta y\Delta z \cos\alpha + 2ac\Delta x\Delta z \cos\beta + 2ab\Delta x\Delta y \cos\gamma}$.

combined, one can back-calculate the arrangement of the atoms within the unit cell. As mentioned earlier, the electrons surrounding the atoms are what diffract the X-ray. Given that each atom has a specific atomic number associated with it, the diffraction from a specific type of atom, say carbon or fluorine or silver will be unique. This uniqueness directly relates to the intensity of the spots observed on the screen. From this, now, both the orientation and arrangement of the atoms within the unit cell as well as the types of atoms in it or, in other words, the composition of the unit cell can be identified. Now, if we represent this unit cell with three unique orthogonal lengths and angles between them (a, b and c and α, β, γ are called lattice parameters), the position and the symmetry relation between the atoms filling up the box or unit cell can be identified.

Structural Aspects of Metal Organic Frameworks

Now, let's come back to MOFs. MOFs being single crystals, the entire chemical composition and structure of the MOF can be obtained with molecular precision. So, what is special about MOF? Alternative to the way MOF was defined earlier, MOF can be seen
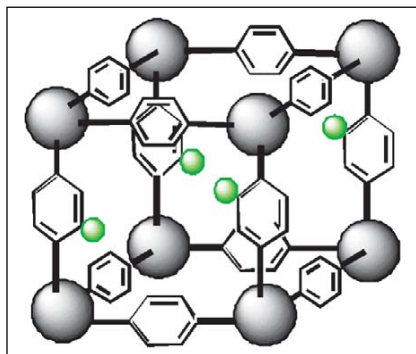
Figure 5. Illustration of a metal cubic unit of a metal organic framework showing the metal (grey spheres) linked by an organic ligand with phenyl backbone. The green spheres represent the side functionalities on the ring. Now, consider the green sphere as: CF_3 – the pore is hydrophobic; NH_2 – the pore is basic; OH – the pore is phenolic; SO_3H – the pore is acidic. Thus, the pore can get specific chemical nature by design. Note: Due to the very crystalline nature of the MOF, the green spheres will be symmetrically repeated on other phenyl rings. However, this has not been shown for clarity.

as metal-oxide cubes, wherein oxide anions with -2 charges have been replaced by an organic linker carrying the same charge. This makes the dimensions of the cube much larger depending on the length of the organic linker (*Figure* 5). This increasing the dimensions of the unit cell is what makes MOFs interesting and useful. When the organic linkers are much longer (6–10 Å) than the oxide anions (2 Å), this creates pores or spaces within the cube. And, since in a single crystal of an MOF we have millions of cubes, then it creates millions of such nanospaces in the cubes. Also, each edge of such an expanded cube serves as a surface for adsorption, which means that MOFs can have exceptionally large surface areas. It turns out that these spaces have dimensions that match the van Der Waal dimensions of gases, solvent molecules such as water, DMF, methanol etc., and when the organic linker is long enough, it can even accommodate large guest molecules like metal-complexes.

In addition to these nanospaces, another tuneable feature of an MOF is the back bone of the organic linker. For example, if we have an organic linker with a phenyl ring, there can be a variety of functional groups that can be attached to this ring and when the structure is rightly oriented, this functional group can line the walls of the pore and, thereby, impart its chemical nature to the pore itself (*Figure* 6).

One of the closest counterparts to MOFs include the zeolites, which are generally aluminosilicates. These can again be compared to metal oxides and can be visualized as being formed by
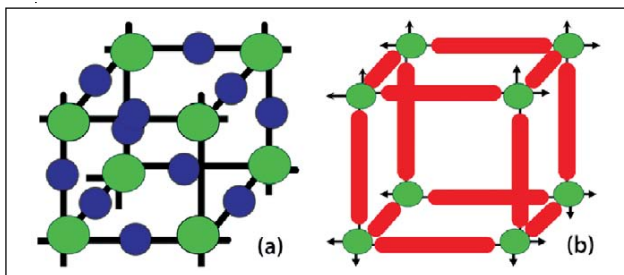
replacing the oxide anions of a metal oxide by silicate units. These also form expanded structures with well-defined spaces or pores. However, one can immediately realize that the possibility of introducing organic functional groups on the framework of these zeolites is restricted, if not impossible. This makes MOFs highly interesting and applicable for gas separation, storage, sensing, guest-dependent properties etc.

Recently, there is burgeoning interest in using MOFs as 'stacked molecular containers' to trap certain interesting guest molecules and visualize the host-guest interactions directly using single crystal X-ray diffraction techniques. To our knowledge, there is no other technique that can give molecular level data or insights as precise as this approach. In the following part of this article, we will see a case study where this methodology using MOF has been exploited thoroughly in order to directly observe some extremely sought out host-guest interactions within a crystalline lattice of the MOF.

Carbon dioxide is clearly identified as a greenhouse gas and its anthropogenic emissions have to be curtailed. One of the major sources of CO_2 emission includes the burning of coal and fossil fuels for generating power. This produces a post-combustion gas stream with about 5–25% CO_2 in it which gets released into the atmosphere. In the last few decades, industries have made an attempt to capture this CO_2 using liquid amines. The 'absorbed' CO_2, being an acidic gas, reacts with the basic amines to form '*Carbamates*' (reaction schematic shown below). The CO_2 captured this way is later released by heating at 120–150 °C for permanent dumping underground – sequestration.

Reversible reaction forming carbamate:
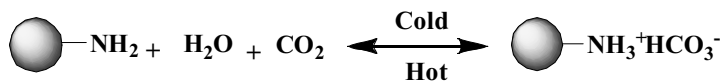
Undesirably, these liquid amines acting as CO_2 scrubbers have severe shortcomings such as being corrosive, volatile and unstable over time. Also, the regeneration of the CO_2 during sequestration requires high temperature (150 °C) which could consume up to 30% of the power produced by the coal burning power generation company, which is totally unacceptable. To address these issues, enormous research is being done in developing superior materials for capturing CO_2.

Solid state materials such as zeolites, carbon powder, mesoporous clays can be functionalized with amines to do the job, but again, the amines can leach out as it is just loaded as a guest. One interesting approach is to anchor amine groups as side groups on an organic ligand via covalent bonds and, if we can develop MOFs using such ligands, there is a good chance of making the amines protrude into the pores (*Figure* 4). When CO_2 is captured in such pores via 'adsorption', (note: it is not absorption), the amine could interact to hold them strong. However, when such a scenario is created, how do we know if the amine is rightly oriented? Do we know if it forms a carbamate? Do we know if it is just a physical interaction or is it a chemical bond? Can we quantify such interactions?

Crystallography is the way to go. Recently, an MOF, Zinc-(3-aminotriazolato)-oxalate, with amine lined walls was made and it was evaluated from 'adsorption isotherms' that it was very selective to CO_2. And a 'Clausius–Clayperon' fit (*Box* 1) to the isotherms indicated that the heat of adsorption associated with the CO_2 and the MOF was quite high (40kJ/mol), but the facile desorption as observed from the isotherm indicated pure physical interaction rather than chemical reaction involving carbamate formation (*Figure* 7).
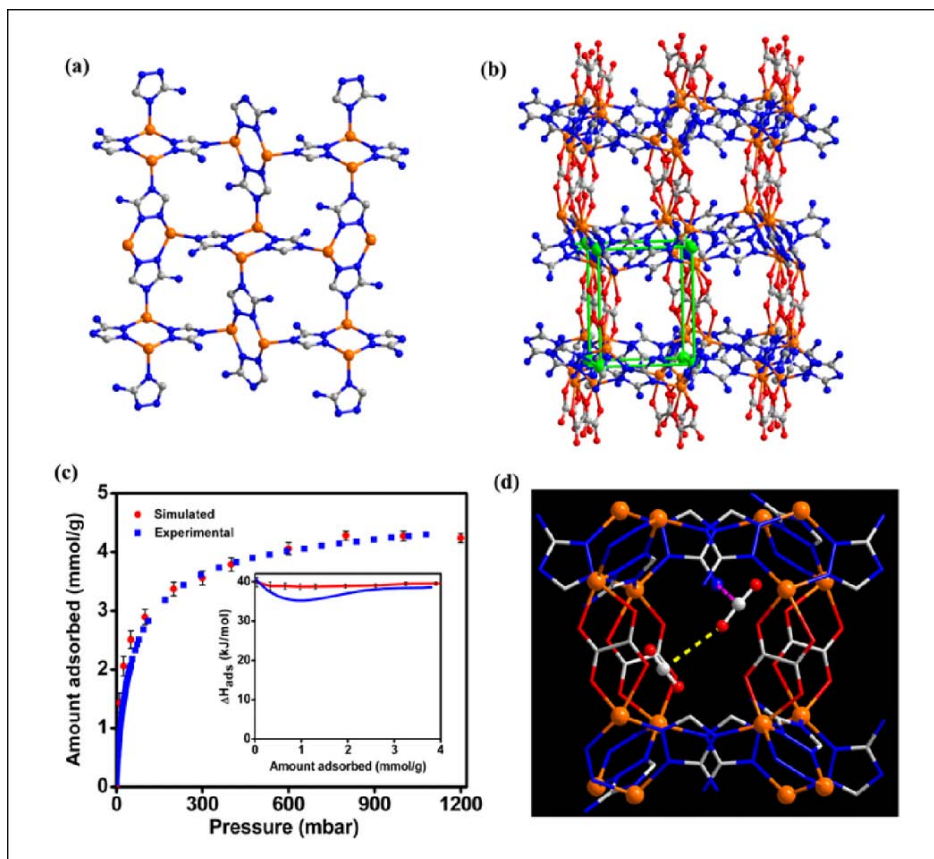
Figure 7. (a) Structure of an MOF solved using single crystal diffraction. The solid has a 3-D network of pores lined with free amine groups. (b) The Zn-Aminotriazolate layer is pillared by the oxalate groups in red. Green outlines the pores. Framework has a regular 6-connected a-Po topology. Cavity size: $4.0 \times 4.0 \times 4.0$ Å. (c) CO_2 adsorption isotherm collected at 273K, inset showing the heat of adsorption vs. uptake plot. (d) Single crystal structure of a pore in the MOF showing CO_2 located in two different crystallographic sites. One interacts with the amine group of the framework and could be responsible for the high energy (40kJ/mol) adsorption site, while the other one, sandwiched between the oxalate, corresponds to an energy of 28kJ/mol as estimated from the simulations. Note the T-shaped CO_2-CO_2 dimers. Color scheme: Zn- orange; O - red; C-grey; N- blue.

This, now presents a suitable model system to evaluate the potential of amine groups in such solids to act as functional adsorption sites to trap CO_2. Considering the single crystal nature of the MOF and the fact that CO_2 could be located within the pores of such MOFs at low temperatures (below 195K), an experiment was carried out to crystallographically locate the CO_2 within the small pores of this MOF and to identify amine-CO_2

Box 1. The Clausius–Clapeyron Equation

This equation relates the vapor pressure of a liquid or a gas to the change in temperature. The mathematical expression of this relation is given below. Experiments showed that the pressure P, enthalpy of vaporization, ΔH_{ads}, and temperature T are related,

$$P = A \exp (-\Delta H_{ads}/RT),$$

where R (= 8.3145 J mol^{-1} K^{-1}) and A are the gas constant and unknown constant. This is known as the Clausius–Clapeyron equation. If P_1 and P_2 are the pressures at two temperatures T_1 and T_2, the equation has the form:

$$\ln \left(\frac{P_1}{P_2} \right) = \left(\frac{\Delta H_{ads}}{R} \right) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

In an experiment, the adsorption isotherms can be recorded at different temperatures and the data can be plugged into this equation to calculate the ΔH_{ads}.

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interactions which are universally attractive from a capture point of view.

For this purpose, the crystal was loaded into a capillary and the capillary was evacuated to make sure that any trapped guests such as solvent from moisture or synthesis was removed from the pores – *activation*. The activated or degassed MOF was then exposed to a stream of CO_2 and the capillary was sealed under it. Now, this capillary was mounted on to a single crystal diffractometer and X-ray diffraction was performed on the crystal that was cooled to 150K. Hurray! The CO_2 was well located in the pore (*Figure* 7d). Even better, there were two CO_2 molecules within each pore and one of them was proximal to the amine group of the framework. The other was oriented in a right geometry to interact with this CO_2. This dual site model could be nicely correlated with the heat of adsorption vs. CO_2 loading plot that was obtained from the adsorption experiments. The HOA plot showed that there was an initial strong CO_2–framework interaction (*Box* 2) (40kJ/mol) and this slowly died down as more CO_2 was loaded but after some more loading it again increased and reached a constant value. This could be interpreted as the first site closer to the amine being a high-energy site and once that starts filling up, it is able to


Box 2. CO_2–Framework Interaction

This is the interaction between the functional groups that comprise the ZnAtzOx (zinc 3-amino-1,2,4 triazolato oxalate) framework (host) and the extra-framework CO_2 molecules (guest) trapped within the nanospaces of the framework. In this case, there seems to be significant interactions between the -NH_2 (part of the aminotriazole unit) groups of the framework and the CO_2 molecules. The origin for these interactions is due to the delta negative charge associated on the nitrogen atoms of the NH_2 caused by the presence of lone pairs and the delta positive charge associated with carbon atoms of the CO_2 molecule arising from the polarization of the CO_2 molecules trapped within the framework. The polarization is caused by a combination of electrostatic and dispersive forces felt along the walls of the framework.

co-operatively assist the filling up of the second site, where the CO_2 sits and is able to interact with the CO_2 filled earlier via a *T-shaped* dimer geometry. The T-shaped CO_2–CO_2 interaction is highly prevalent in low temperature solid phases of CO_2. The bond distances and non-bonded close contacts between the amine and the CO_2 that there is no true chemical bond in this case and this is consistent with a physisorption (no chemisorptions) that was observed during the CO_2 isotherm measurements.

Further, the crystallographic model was used as an excellent high level input for a computer simulation and from this, a theoretical CO_2 adsorption isotherm could be simulated using Grand Canonical Monte–Carlo methods (GCMC) (*Figure* 8). Using the density

Figure 8 (a). The comparison of the CO_2 adsorption isotherm that was simulated using GCMC methods with the experimental 273K isotherm. (b) The CO_2 positions determined from DFT–MD simulations represented as electron probabilities and the single crystal X-ray diffraction determined positions represented as sticks.
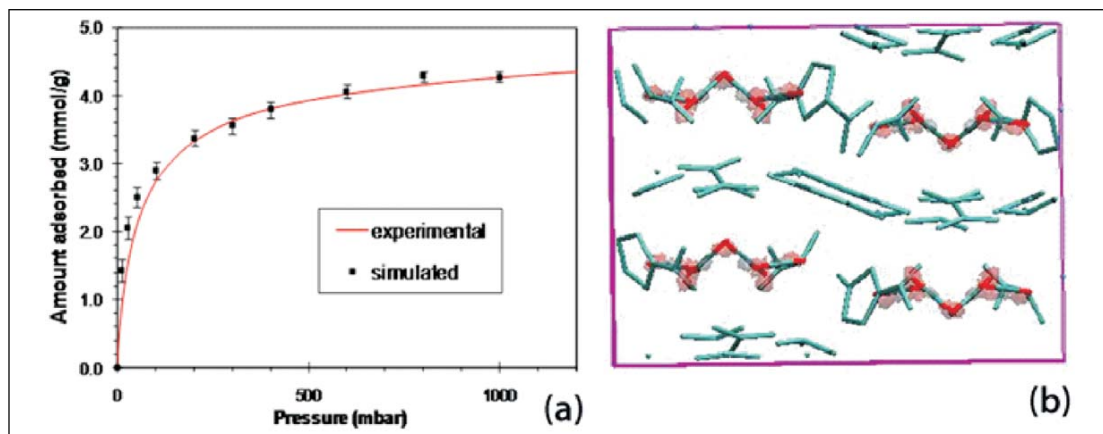
functional theory (DFT), the molecular positions of the CO_2 could be modelled and compared with the crystallographically located CO_2 positions.

The advantage of doing this comes from the ability of the DFT simulations to quantify the energy types (dispersion vs. electrostatic) and amounts involved in the interaction between the amine and the CO_2 molecules. A detailed description of this is presented in the original article [1].

Suggested Reading

[1]   Ramanathan Vaidhya-nathan, Simon S Iremon-ger, George K H Shimizu, Peter G Boyd, Saman Alavi and Tom K Woo, Direct observation and quantification of CO_2 binding within an amine-functionalized nanoporous solid, *Science*, Vol.330, pp.650–653, 2010.

[2]   Hiroyasu Furukawa, Kyle E Cordova, Michael O'Keeffe and Omar M Yaghi, The chemistry and applications of metal-organic frameworks, *Science*, Vol.341, 2013.

[3]   Hong-Cai 'Joe' Zhou and Susumu Kitagawa, Metal–organic frameworks (MOFs), *Chem. Soc. Rev.*, Vol.43, p.5415, 2014.

[4]   Recent advances in carbon dioxide capture with metal-organic frameworks, *Greenhouse Gas Sci. Technol.*, Vol.2, p.239, 2012.

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