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## Crystalline metal-organic frameworks (MOFs): synthesis, structure and function

Metal-organic frameworks (MOFs) are a class of hybrid network supramolecular solid materials comprised of organized organic linkers and metal cations. They can display enormously high surface areas with tunable pore size and functionality, and can be used as hosts for a range of guest molecules. Since their discovery, MOFs have experienced widespread exploration for their applications in gas storage, drug delivery and sensing. This article covers general and modern synthetic strategies to prepare MOFs, and discusses their structural diversity and properties with respect to application perspectives.

Received 16 July 2013  
Accepted 26 October 2013

### 1. Introduction

Crystalline metal-organic frameworks (MOFs) are one of the most important classes of porous materials, which find widespread utilization in adsorption, separation, catalysis, magnetism, sensing and drug delivery (Bellussi *et al.*, 2013; Férey, 2008; Lalonde *et al.*, 2013; Rosi *et al.*, 2002). MOFs are typically constructed by connecting secondary building units (SBUs) with organic spacers to create diverse networks. The organic spacers or the metallic SBUs can be altered to control the pore environment of the MOF, which controls its interactions with adsorbates, which ultimately enables its utilization for a particular application. An enormous amount of research has been carried out on MOFs over the last two decades. Transition metals (*e.g.* Cu, Zn), alkaline earth elements (*e.g.* Sr, Ba), *p*-block elements (*e.g.* In, Ga), actinides (*e.g.* U, Th), even mix metals have been used for the synthesis of MOFs (Cui *et al.*, 2012; Kong *et al.*, 2012; Shultz *et al.*, 2009; Stavila *et al.*, 2012; Mallick *et al.*, 2012; Dey *et al.*, 2012; Kim *et al.*, 2003). Since MOF structure depends on the choice of metals and ligands, various organic ligands of different shape and size have also been utilized to control the architecture. A noteworthy aspect in MOF chemistry is the direct structure–property relationship, which is a hallmark of this research area.

So far, MOFs have been extensively used for adsorption and separation of gases, *viz.* N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> *etc.*, due to their porous nature (Han *et al.*, 2009; Rowsell & Yaghi, 2004). A huge number of nonporous MOFs are also reported in the literature, having other important applications, *e.g.* magnetism, luminescence and sensors, depending on the type of metals and ligands. Functionalization of MOFs with various diverse organic links has been used for selective adsorption and separation of different gases from gas mixtures (Czaja *et al.*, 2009; Li *et al.*, 2009). One such example is MOFs having open metal sites, which have been used to enhance H<sub>2</sub> adsorption (Kong *et al.*, 2012). Similarly amino-functionalized MOFs have been used for selective CO<sub>2</sub> adsorption (Pachfule

*et al.*, 2011; An *et al.*, 2009; Panda *et al.*, 2011). A number of review articles have been written on the topic of MOFs, highlighting almost all aspects of this exciting research area (Ricco *et al.*, 2013; O’Keeffe & Yaghi, 2012). Hence, instead of focusing on one particular aspect we have attempted in this *Feature Article* to prepare an overview of the three most critical aspects of the field, namely synthesis, structure and properties.

## 2. Synthesis

A summary of the various approaches for MOF preparation is illustrated in Fig. 1. Most MOF syntheses are liquid-phase syntheses, where separate metal salt and ligand solutions are mixed together or solvent is added to a mixture of solid salt and ligand in a reaction vial. Selection of a solvent for these liquid-phase reactions can be based on different aspects such as reactivity, solubility, redox potential, stability constant *etc.* Solvent also plays an important role in determining the thermodynamics and activation energy for a particular reaction. Apart from liquid-phase synthesis, researchers have also attempted solid-phase syntheses of MOFs, because it is quicker and easier, but solid-state synthesis always faces difficulties obtaining single crystals, and thereby determining product structure, which is otherwise quite easy in solution-

phase reactions. The slow evaporation method is a regular process of crystallization which has been applied for the last few decades to prepare MOF crystals. Although routine synthesis of MOFs involves solvothermal methods, other methods such as microwave-assisted synthesis, electrochemical synthesis, mechanochemical synthesis and sonochemical synthesis have been applied as alternatives for MOF synthesis.

### 2.1. The slow evaporation method

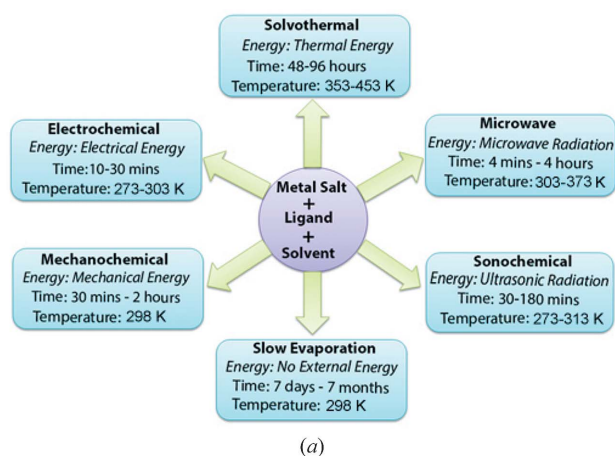
The slow evaporation method is a conventional method to prepare MOFs, which mostly does not need any external energy supply. Although this method is sometimes preferred because it is a room-temperature process, its major disadvantage remains that it requires more time compared with other well known conventional methods. In the slow evaporation method, a solution of the starting materials is concentrated by slow evaporation of the solvent at a fixed temperature, mostly at room temperature. Sometimes the process involves a mixture of solvents, which can increase the solubility of the reagents and can make the process faster by quicker evaporation of low-boiling solvents (Du *et al.*, 2005; Halper *et al.*, 2006; Ohi *et al.*, 2004; Yoo *et al.*, 2011).

### 2.2. Solvothermal synthesis

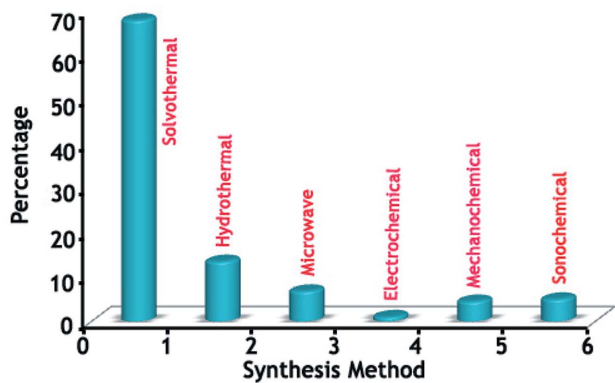
Solvothermal reactions are carried out in closed vessels under autogenous pressure above the boiling point of the solvent. Many starting materials can undergo quite unexpected chemical changes under solvothermal conditions, which are often accompanied by the formation of nanoscale morphologies that are not achievable by conventional methods. In most cases, high-boiling organic solvents have been used for solvothermal reactions. The most commonly used organic solvents are dimethyl formamide, diethyl formamide, acetonitrile, acetone, ethanol, methanol *etc.* Mixtures of solvents have also been used to avoid problems of differing solubility for the different starting materials. Solvothermal reactions can be carried out in different temperature ranges, depending on the requirement of the reaction. Generally, glass vials are used for lower temperature reactions, while reactions performed at temperatures higher than ~ 400 K require Teflon-lined autoclaves (Wang & Ying, 1999). The hydrothermal method has been used successfully for the synthesis of an enormous number of inorganic compounds and inorganic organic hybrid materials.

### 2.3. Microwave-assisted synthesis

Microwave-assisted synthesis provides a very rapid method for the synthesis of MOFs. Microwave-assisted procedures have been used extensively to produce nanosize metal oxides (Lagashetty *et al.*, 2007). Such processes involve heating a solution with microwaves for a period of about an hour to produce nanosized crystals. The microwave-assisted synthesis has been termed ‘microwave-assisted solvothermal synthesis’ for the preparation of MOFs. The quality of the crystals obtained by microwave-assisted processes are generally the



(a)



(b)

**Figure 1**  
(a) Synthesis conditions commonly used for MOF preparation; (b) indicative summary of the percentage of MOFs synthesized using the various preparation routes.

same as those produced by the regular solvothermal processes, but the synthesis is much quicker (Bux *et al.*, 2009; Hindelang *et al.*, 2012; Liang & D'Alessandro, 2013; Zornoza *et al.*, 2011; Klinowski *et al.*, 2011).

#### 2.4. Electrochemical synthesis

Although there is a possibility to prepare large MOF crystals under mild conditions by changing the pH/solvent at room temperature, for certain applications and for the sake of fast reproducible production of large amounts of MOF samples, the development and understanding of new mild and rapid synthetic methods is ongoing. Electrochemical synthesis, being one such process, does not require metal salts and offers continuous production of MOF crystals, which is a major advantage in an industrial process. The basic principle relies on providing the metal ion by anodic dissolution into synthesis mixtures that include organic linkers and electrolytes (Martinez Joaristi *et al.*, 2012).

#### 2.5. Mechanochemical synthesis

Mechanochemical synthesis is a solvent-free synthesis method for MOFs. Mechanochemistry is the process of performing a chemical reaction by applying mechanical force. Construction of bonds through simple, economical and environmentally friendly mechanochemical routes is of considerable interest in modern synthetic chemistry. Recently, mechanochemical syntheses have been efficiently employed for the rapid synthesis of MOFs using liquid-assisted grinding (LAG), where a small amount of solvent is added into a solid reaction mixture (Beldon *et al.*, 2010). Friščić and co-workers have shown that by varying the added solvent in a LAG process, they could obtain one-dimensional, two-dimensional and three-dimensional coordination polymers from the same reaction mixture. This strategy was applied further for the synthesis of some zeolitic imidazolate frameworks (ZIFs; Friščić *et al.*, 2013).

#### 2.6. Sonochemical synthesis

Sonochemistry is a phenomenon by which molecules undergo chemical change due to the application of intensive ultrasonic radiation (20 kHz–10 MHz). Ultrasound induces chemical or physical changes due to a cavitation process involving the formation, growth and instantaneous collapse of bubbles in a liquid, which creates local hot spots of a short lifetime with high temperature and pressure. The extreme conditions can promote chemical reactions by immediate formation of a surplus of crystallization nuclei. Sonochemical methods can generate homogeneous nucleation centres and a considerable reduction in crystallization time compared with conventional hydrothermal methods. MOF-5 synthesis using sonochemical irradiation in 1-methyl-2-pyrrolidinone (NMP) can produce 5–25  $\mu\text{m}$  crystals in 30 min, which is similar to MOF-5 synthesized *via* solvothermal or microwave methods (Arul Dhas *et al.*, 1998; Aslani & Morsali, 2009; Carson *et al.*, 2011; Dharmarathna *et al.*, 2012; Jung *et al.*, 2010; Kim *et al.*, 2011; Mohanty *et al.*, 2009; Son *et al.*, 2008).

### 3. Structure

Lack of control over the structural integrity of traditional solid-state materials like zeolites and activated carbons is related to the fact that the starting materials do not maintain their arrangement due to poor correlation between reactants and products. By contrast, MOFs can be obtained using rigid molecular building blocks under reaction conditions that maintain their structural integrity throughout the synthesis regime. In this context, reticular synthesis can be described as the process of assembling judicious primary building blocks to form SBUs which predetermine ordered structures held together by strong coordination bonds. In a nutshell, with this strategy it is possible to control the overall coordination number of the inorganic and organic building units, and it then becomes important to identify the networks that can be expected to result from a topological point of view.

Typically, MOFs are composed of two types of primary building units or points of extension. One type is essentially organic ligands, which could be multitopic in nature. Another type is a metal atom or finite polyatomic cluster having two or more metal atoms of the same (homometallic, *e.g.*  $\text{Zn}_4\text{O}$ ,  $\text{Zr}_6\text{O}_4$ ) or different type (heterometallic, *e.g.* polyoxometallates). The two types of building units exhibit characteristic roles in the construction of secondary building units (SBUs). These SBUs finally self-assemble in higher dimensions to construct the MOF architecture.

The underlying topology of a structure is described by a net, assigned by a three-letter symbol such as *abc* (*pts*, *soc*, *rht* *etc.*). The details of nets are available as a searchable database known as the Reticular Chemistry Structure Resource (RCSR), having a collection of more than 2000 different nets (O'Keeffe *et al.*, 2008). *TOPOS*, a computer program which identifies underlying nets within a structure, has a huge database of over 70 000 nets (Blatov *et al.*, 2000). A mathematical program called *SYSTRE* has been used to identify new nets that are not included in the RCSR database (Delgado-Friedrichs & O'Keeffe, 2003). Nets with one type of vertex are called uninodal, whereas nets with two types of vertex are bimodal, and so on. The metal-containing building units produced during synthesis are generally polygonal or polyhedral. Although organic building units have predetermined shape and geometry, their flexibility often determines the final architecture. Hence, it is vital to identify all vertices and edges rather than just identifying the nets. In particular, all types of network structures (organic, inorganic or organic–inorganic hybrid materials) possess inherent nets, and the interest of researchers drives them for topological construction of MOF networks based on rational assembly of building units in different dimensions.

For example, a prototypical metal-organic framework, MOF-5, possess  $\text{ZnO}_4$  tetrahedra [ $(\text{Zn}_4\text{O})_{\text{O}_{12}}$  octahedral SBU] joined by benzene dicarboxylate (BDC) ligands, resulting in a three-dimensional cubic network structure with interconnected pores of 8 Å aperture and 12 Å pore diameter (Fig. 2; Li *et al.*, 1999). On the other hand, simply changing the inorganic building block from  $\text{Zn}_4\text{O}$  to  $\text{Cr}_3\text{O}$ , keeping the

same organic building block, results in a drastic change in structure from MOF-5 to MIL-101, a versatile type of mesoporous solid containing large cages (diameter  $\sim 3$  nm) with both pentagonal and hexagonal windows (Fig. 2; Férey *et al.*, 2005). Changing the organic ligand from linear BDC to triangular BTC (benzene tricarboxylic acid) and a paddle-wheel SBU  $\text{Cu}_2(\text{CO}_2)_4$  results in one of the most studied MOFs, *viz.* HKUST-1 (Chui *et al.*, 1999). A view of the cubic unit cell of HKUST-1 reveals  $\sim 1$  nm-sized channels with fourfold symmetry (Fig. 2). The nano-channels intersect to provide a three-dimensional connected network with a honeycomb arrangement of large hexagonal-shaped windows. Concisely, a suitable choice of inorganic building blocks has been explored to provide diverse SBUs along with precise control over predictable network topologies. Moreover, imparting functionality to the BDC linker opens up further possibilities to obtain a class of versatile crystalline porous

materials with tailor-made properties for numerous industrially relevant applications. In a nutshell, marriage between organic and inorganic building blocks has been realised to explore a variety of MOFs with predicted topology and nets previously unrevealed in the field of extended solids.

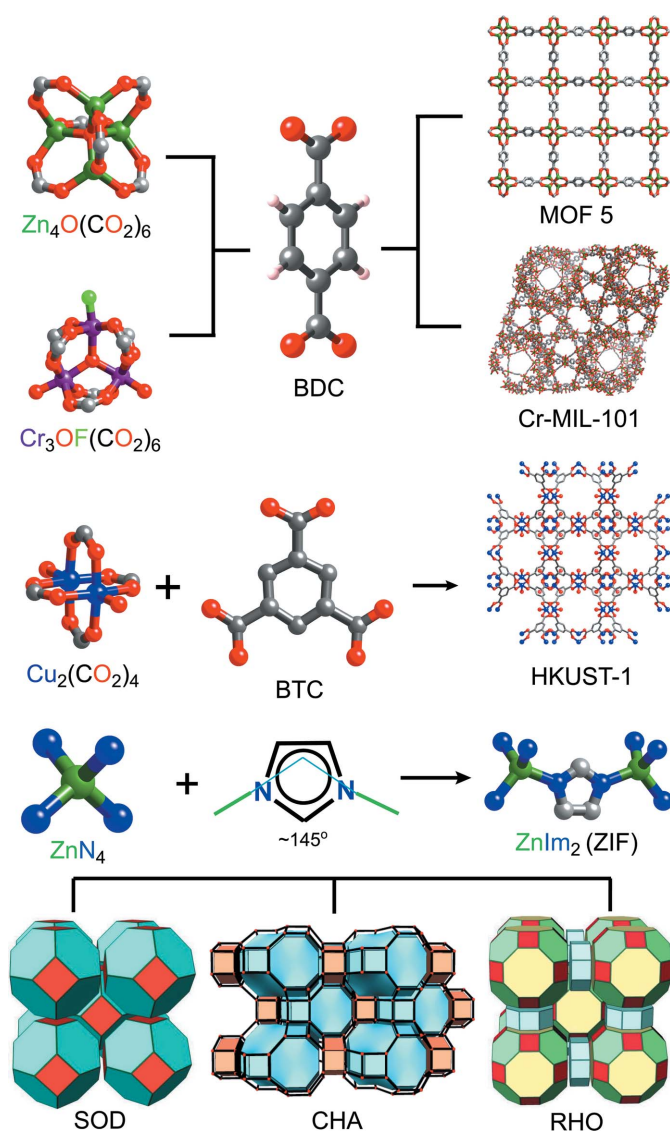
Zeolite imidazolate frameworks (ZIFs) are three-dimensional structural analogues of zeolites, commonly based on nets of linked  $\text{CoN}_4$  or  $\text{ZnN}_4$  tetrahedra *via* imidazolate bridges to make an  $M$ –imidazolate– $M$  angle close to  $145^\circ$  (Fig. 2) which is comparable to the Si–O–Si angle in many zeolites (Banerjee *et al.*, 2008; Park *et al.*, 2006). Subtle changes in reaction conditions (*e.g.* temperature, time, concentration, additives or structure-directing agents) can result in drastic changes in the three-dimensional structures of ZIFs, which changes the network topology and properties, while keeping both the metal and imidazolate the same. On the other hand, simple changes in linker functionality and polarity have resulted in a vast class of ZIFs with tunable porosity and properties. In addition, incorporation of multiple imidazolates in a single ZIF has been demonstrated, which opens up innumerable combinatorial possibilities of transition metal ion and functional imidazoles in the realisation of novel architectures and topologies, which is still undeveloped in zeolite chemistry.

#### 4. Properties

Gases are important for energy production, and hence storage tanks are an essential requirement for effective storage of gases. Several options are available for storing gases effectively, but these mostly require high-pressure tanks and multi-stage compressors. Such methods are highly expensive for practical uses and there is a need for them to be substituted by simple and cheaper solutions. In an attempt to overcome these issues and to find safer storage methods, several materials, like zeolites or activated porous carbons, have been studied for gas storage. However, MOFs have outperformed most of these traditional materials in terms of gas storage and separation. Easy synthetic procedures, high surface area, wide opportunities for functionalization and tuneable pore structures make MOFs preferable compared with other porous materials. This section reviews studies of storage applications for important gases like  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{NO}$ , hydrocarbons *etc.* within MOFs, with a brief description of the factors responsible for effective storage.

##### 4.1. Hydrogen storage in MOFs

Hydrogen ( $\text{H}_2$ ) is considered as a possible ideal source of energy due to its large gravimetric heat of combustion ( $120 \text{ MJ kg}^{-1}$ ). However, due to its low density in the gaseous state ( $0.08 \text{ kg m}^{-3}$ ), its storage at ambient temperature and pressure is difficult. Low volumetric storage density of  $\text{H}_2$  hinders its use as a fuel and therefore effective storage materials need to be explored. The United States Department of Energy (DOE) set gravimetric and volumetric storage targets for  $\text{H}_2$  in 2010 (6 wt%,  $45 \text{ g L}^{-1}$ ) and 2015 (9 wt%,



**Figure 2**  
Examples of secondary building units (SBUs) and topologies reported in MOFs and ZIFs.



81 g L<sup>-1</sup>). H<sub>2</sub> storage in porous MOFs is influenced by several factors such as very high surface area, functionalized polar groups, light weight, open metal centres and specific weak interactions. It has been proven that MOF materials possess the required underlying characteristics to act as high H<sub>2</sub> uptake materials by physisorption, and they can be the best option to reach the set DOE targets in the near future. More than 300 MOFs have been tested so far for their H<sub>2</sub> uptake capacity. One of the benchmark H<sub>2</sub> storage materials is MOF-177, which is constructed from [Zn<sub>4</sub>O] clusters and 4,4',4''-benzene-1,3,5-triyltribenzoate (BTB) to form a (6, 3) net (Wong-Foy *et al.*, 2006). Due to its high BET surface area (~5000 m<sup>2</sup> g<sup>-1</sup>) and large pore volume (1.59 cm<sup>3</sup> g<sup>-1</sup>), it shows a gravimetric H<sub>2</sub> uptake of 7.5 wt% at 70 bar and 77 K. Another famous zinc carboxylate based MOF, MOF-5 (IRMOF-1), possesses a BET surface area of 3800 m<sup>2</sup> g<sup>-1</sup> and takes up 7.1 wt% of H<sub>2</sub> at 40 bar and 77 K. There are other MOFs which are also well known for H<sub>2</sub> storage, such as MOF-210, MIL-101, HKUST-1, NU-100, PCN-12, NOTT-102 and MOF-205 (Wang *et al.*, 2008b; Lin *et al.*, 2009; Farha *et al.*, 2010; Furukawa *et al.*, 2010). Generally, MOFs with open metal sites provide high surface area which facilitates stronger interaction between the metal ion nodes and H<sub>2</sub> molecules. This is the principal reason behind the high H<sub>2</sub> uptake in this promising class of materials. In addition, theoretical calculations have suggested that doping MOFs with metal ions could enhance the H<sub>2</sub> uptake capacity.

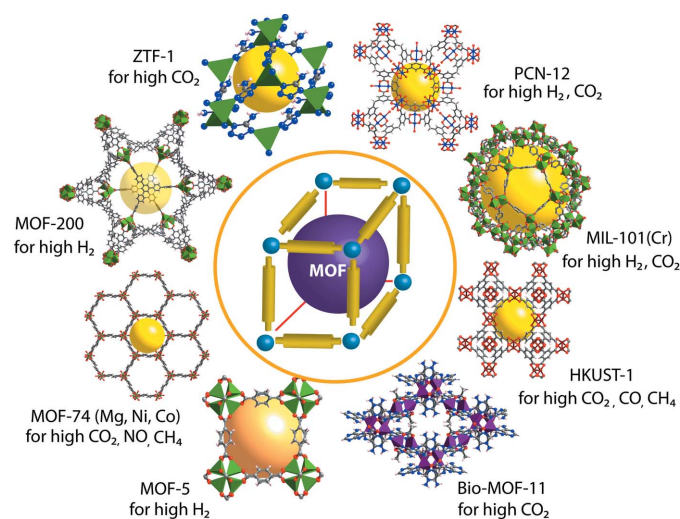
#### 4.2. CO<sub>2</sub> storage in MOFs

The rising level of atmospheric CO<sub>2</sub> is one of the hottest topics worldwide (Sumida *et al.*, 2012; Sakakura *et al.*, 2007), and its consequence is considered to provide a major threat towards living beings. The emission from coal, oil and natural gas due to rapid industrial development is mostly responsible for the rising CO<sub>2</sub> level in the atmosphere. Earlier, zeolites and activated porous carbons were explored for CO<sub>2</sub> adsorption, and other classes of porous materials, like MOFs, have now picked up attention as potential adsorbents. Very high internal surface area with polar functional groups decorating the pores provides opportunities for high CO<sub>2</sub> uptake capacity in MOFs. For example, MOF-210 is the highest surface area (10450 m<sup>2</sup> g<sup>-1</sup>) MOF known to date, constructed from 4,4',4''-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate (H<sub>3</sub>BTE), biphenyl-4,4'-dicarboxylate (H<sub>2</sub>BPDC), and zinc(II)nitrato hexahydrate (Furukawa *et al.*, 2010). Due to its ultrahigh surface area, the CO<sub>2</sub> uptake value of MOF-210 is 2400 mg g<sup>-1</sup> (74.2 wt%, 50 bar at 298 K) which exceeds that of any other porous material, such as MOF-177 or MIL-101(Cr) (60 and 56.9 wt%, respectively; Wong-Foy *et al.*, 2006; Férey *et al.*, 2005). MOF-200 has a similar CO<sub>2</sub> uptake as MOF-210 under similar experimental conditions. Other well known MOFs, such as NU-100 (69.8 wt%, 40 bar at 298 K), Mg-MOF-74 (68.9 wt%, 36 bar at 278 K), MOF-5 (58 wt%, 10 bar at 273 K), and HKUST-1 (19.8 wt%, 1 bar at 298 K), also show considerably higher CO<sub>2</sub> uptake compared with other solid materials.

Also, it has been proven experimentally and by calculations that the presence of polar groups such as -NH<sub>2</sub> or free N-containing organic heterocyclic residues on the pores is helpful for high CO<sub>2</sub> uptake compared with unfunctionalized analogues. One of the best examples, BioMOF-11, demonstrates the effects of an N heterocycle, and its CO<sub>2</sub> uptake of 15.2 wt% (at 1 bar and 298 K) exceeds any other MOF in the same category (An *et al.*, 2009). Another of this category is ZTF-1 (Fig. 3), which shows high CO<sub>2</sub> uptake (14.4 wt%, 1 bar at 298 K; Panda *et al.*, 2011) due to the presence of free -NH<sub>2</sub> as well as uncoordinated N on a tetrazole molecule within the framework. Recently, the location of CO<sub>2</sub> molecules within a MOF structure has been identified crystallographically, which helps to understand further the structural relationship between the host and guest molecules (Vaidhyanathan *et al.*, 2010). This will probably motivate new strategies to design functionalized MOFs for higher CO<sub>2</sub> uptake.

#### 4.3. CH<sub>4</sub> storage in MOFs

Methane is another potential fuel, as natural gas contains about 95% of methane. Methane has a comparable gravimetric heat of combustion (50.0 MJ kg<sup>-1</sup>) to gasoline (44.5 MJ kg<sup>-1</sup>). For methane, MOFs have already achieved the DOE target of 180 v/v at ambient temperature and pressure (< 35 bar), but improving further the methane storage capacity is still an active area of interest (Konstas *et al.*, 2012). Noro *et al.* (2000) reported the first methane sorption study in MOFs. In 2007, Zhou and co-workers showed methane uptake of 16 wt% (35 bar) in [PCN-14 Cu<sub>2</sub> (adip)] MOF, with BET surface area 1753 m<sup>2</sup> g<sup>-1</sup> (Perry *et al.*, 2007; Wang *et al.*, 2008a). The CH<sub>4</sub> adsorption capacity of MOF-177 is 22 wt% at 298 K and 100 bar, which is the largest adsorption uptake of CH<sub>4</sub> among all dry solid materials (Wong-Foy *et al.*, 2006). Other MOFs such as HKUST-1 (15.7 wt% at 150 bar), MIL-101 (14.2 wt% at 125 bar), IRMOF-1 [228 cm<sup>3</sup>(STP) g<sup>-1</sup> at 298 K



**Figure 3**  
Schematic representation of important reported MOFs which are known for high gas storage properties.

and  $\sim 36$  bar] also show considerably high methane uptake capacity (Fig. 3). In the case of Ni-MOF-74 [ $190 \text{ cm}^3(\text{STP}) \text{ g}^{-1}$  (298 K, 35 bar)], open metal sites are the dominating factor responsible for the high methane capacity (Wu *et al.*, 2009). Other important hydrocarbons like benzene, toluene, xylene and linear hydrocarbons have also been effectively separated from liquid mixtures by trapping inside MOFs.

#### 4.4. CO and NO storage in MOFs

Separation of hazardous gases like CO and NO from gas mixtures is very important, and MOFs with pores compatible with the kinetic diameter of these gases could be useful for this purpose. So far, the capture of CO in MOFs has not been achieved experimentally; it is believed that the interaction between the CO dipole and the open metal sites of MOFs are the dominating factor for the sorption performance. In order to achieve better selectivity, some chemical modification needs to be adopted into these porous materials. On the other hand, MOFs have been used for ultrahigh selectivity of NO gas over other gases, for example Cu-SIP-3 and Zn(TCNQ-TCNQ)(bipy) (Shimomura *et al.*, 2010). Usually these two MOFs are nonporous in nature and they do not absorb gases like Ar, N<sub>2</sub>, CO<sub>2</sub> *etc.*, but above gate-opening pressure ( $> 275$  mbar) they take up NO gas ( $\sim 9$  NO molecules per formula unit at 1 bar). On reduction of the pressure, the desorption path is not like adsorption. This is due to strong coordination to coordinatively unsaturated metal sites (CUMs) in the case of Cu-SIP-3, while for [Zn(TCNQ-TCNQ)(bipy)], charge transfer plays a crucial role for high NO capture (Allan *et al.*, 2010). Ni- and Co-MOF-74 (Fig. 3) also show very high NO uptake ( $\sim 7.0$  mmol NO per g of activated material) at room temperature (McKinlay *et al.*, 2008).

#### 4.5. MOFs as magnetic materials

Magnetism in solids is of considerable interest due to its widespread applications in electromagnetism, devices and sensing. Recently, researchers have introduced magnetism within MOFs through the use of paramagnetic *3d* transition metal nodes along with suitable organic linkers, subsequently named as MMOFs (magnetic metal-organic frameworks). The MOFs based on first-row transition metals (V, Cr, Mn, Fe, Co, Ni and Cu) have contributed significantly to developing porous molecular magnets (Cheetham & Rao, 2007; Cheetham *et al.*, 2006; Coronado & Mínguez Espallargas, 2013; Kurmoo, 2009; Okawa *et al.*, 2009; Rao *et al.*, 2004). The porous nature of MOFs combined with magnetic properties could find interesting applications for air separation. Another important factor responsible for magnetism in MOFs is the framework structure, which may involve layered geometry with a shorter conjugated distance between the metal clusters. Organic linkers have also been used for the synthesis of MMOFs, where radicals present in the organic linker are responsible for the magnetic properties. Also metal-radical combined approaches have been used to synthesize a variety of magnetic metal-organic materials (Maspocho *et al.*, 2003;

Roques, Maspocho, Luis *et al.*, 2008; Roques, Maspocho, Imaz *et al.*, 2008).

#### 4.6. MOFs as sensors

The use of MOFs as luminescent materials has become an important area of research due to their potential application in small-molecule sensors (Lu *et al.*, 2011; Sun *et al.*, 2013), pH sensors (Harbuzaru *et al.*, 2009), light concentrators for photovoltaic devices, antennae in photo-sensitive bioinorganic compounds and high-technology optics. MOF materials are advantageous because of their hybrid nature, which includes inorganic metal ions, organic linkers and also guest molecules. MOFs can be considered as excellent solid-state luminescent materials since they have structural predictability and well defined environments for the chromophores in crystalline form. Lanthanide metal ions are widely used for the synthesis of luminescent MOFs, due to their electronic transitions from *d* to *f* shells, with accompanying photon emission. Eu and Tb are most attractive lumophores because of their narrow emission (Reddy & Sivakumar, 2013; Cui *et al.*, 2012). The lanthanide metal ions are coordinated by strongly absorbing ligands, which enhances the luminescent properties of the MOFs. Other lanthanides like Dy, Sm, Nd, Gd, Er and Yb are also used as luminescent metal ions. Organic linkers having significant conjugation through extended  $\pi$ -systems are responsible for strong absorption, emission and electronic transition. In the case of organic linkers,  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  electronic transitions are commonly observed. The luminescent properties of transition-metal MOFs only come from the linkers. Different types of effect have been reported, including metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT) and ligand centre luminescence. Naphthalene, anthracene, pyrene, perylene and stilbene types of ligands are most commonly used for luminescent MOF synthesis (Rocha *et al.*, 2011; Zacher *et al.*, 2009; Zhan *et al.*, 2013).

### 5. Conclusion

Already great strides have been made with the synthesis of MOFs and the understanding of these porous classes of material in diverse applications. The synthesis of MOFs has enhanced the scope of crystalline porous compounds with desired properties for applications in sorption, separation, magnetism, sensing, catalysis *etc.* Different synthesis methods have been utilized to prepare MOFs at faster rates as well as in bulk quantities, and the judicious choice of SBUs and ligands makes it possible to design topologically new compounds. Since it is possible to tune pore size and functionality inside the cavities of MOFs, these unique aspects should enable porous MOFs as useful materials for virtually all aspects of storage, separation and catalysis. Since magnetic interaction in porous MOFs depends on metal-to-metal distance and spacers between them, therefore it is also possible to tune the magnetic properties of MOFs by varying ligand length and included solvent molecules. Functionalized MOFs with open

metal sites could enhance H<sub>2</sub> and CO<sub>2</sub> uptake to reach the DOE targets for the benefit of mankind. Thus, the opportunity to utilize MOF architectures is limited only by imagination and our ability to prepare and characterize adequately well designed structures.

CD, TK and AM acknowledge CSIR, New Delhi, India, for a SRF, and BPB acknowledges UGC, New Delhi, India, for a JRF. RB acknowledges CSIR's Five Year Plan (CSC0122) for funding. Financial assistance from BRNS (2011/37C/44/BRNS) is also acknowledged.

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