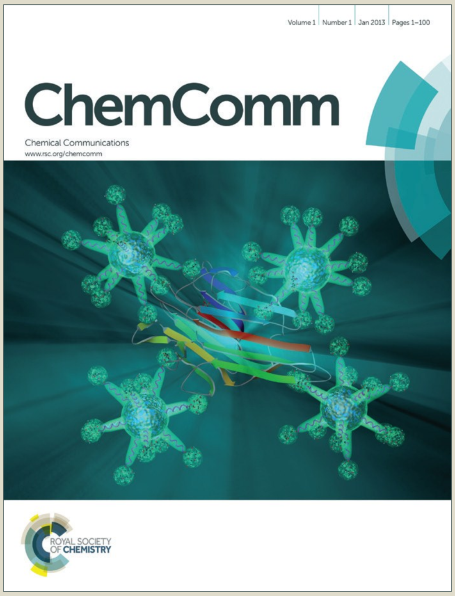
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

ChemComm

FEATURE ARTICLE

Finely Tuning MOFs towards High-performance Post-combustion CO_2 Capture Materials

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qian Wang [a], Junfeng Bai*[a], Zhiyong Lu[b], Yi Pan[a], Xiaozeng You[a]

CO_2 capture science and technology, particularly for the post-combustion CO_2 capture, has become one of very important research fields, due to great concern of global warming. Metal-organic frameworks (MOFs) with one unique feature of structural fine-tunability, unlike the traditional porous solid materials, can provide many and powerful platforms to explore high-performance adsorbents for the post-combustion CO_2 capture. Until now, several strategies for finely tuning MOFs' structures have been developed, in which considering the larger quadrupole moment and polarizability of CO_2, metal ion change (I), functional groups attachment (II) and functional groups insertion (III) functionalize the pore surface; whereas targeting the smaller kinetic diameter of CO_2 over N_2, framework interpenetration (IV), ligand shortening (V), and coordination site shifting (VI) contract the pore size of frameworks to improve their CO_2 caption properties. In this review, from the viewpoint of synthetic materials scientists/chemists, we would like to introduce and summarize them based upon recent work published by other groups and us.

Introduction

Global warming is one of the greatest environmental concerns facing our mankind today.[1-6] The major factors inducing global warming is the excessive emission of CO_2 due to industrial revolution contributed previously by developed nations and currently and in near future both developed nations and developing countries, such as China and India, *et al*.[1-9] The perfect solution is to seek for the alternative green energy, such as solar energy, hydrogen energy and so on.[2,7,9-11] However, before the success of that, we should reduce CO_2 emission by green technology, restrict our behaviors towards lowering energy consumption or capture CO_2 by CCS technology (carbon capture and sequestration).[3,7,10-14]

Qian Wang

Qian Wang received her BS in chemistry from the Henan University in 2009 and her MS in inorganic chemistry from the East China Normal University in 2012. She is now in the PhD program of the School of Chemistry & Chemical Engineering at Nanjing University under the guidance of Professor Junfeng Bai. Her research focuses on the design and synthesis of microporous metal-organic frameworks (MOFs) and the gas storage and separation properties, especially methane storage and post-combustion carbon dioxide capture.

Junfeng Bai

Junfeng Bai obtained PhD degree from Nanjing University in 2000 under the guidance of Professor Xiaozeng You. After two years of postdoctoral work with Professor Manfred Scheer at University of Karlsruhe, he joined the chemistry faculty of Nanjing University in 2003 as a Professor. He was a winner of Education Ministry's New Century Excellent Talents (2004), the First Prize of Henry Fok Education Fund (2005) and the Jiangsu Province innovative talents (2006). His main research interests are the synthesis and applications of MOFs.

---

[a] State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: bjunfeng@nju.edu.cn
[b] College of Mechanics and Materials, Hohai University, Nanjing 210098, China

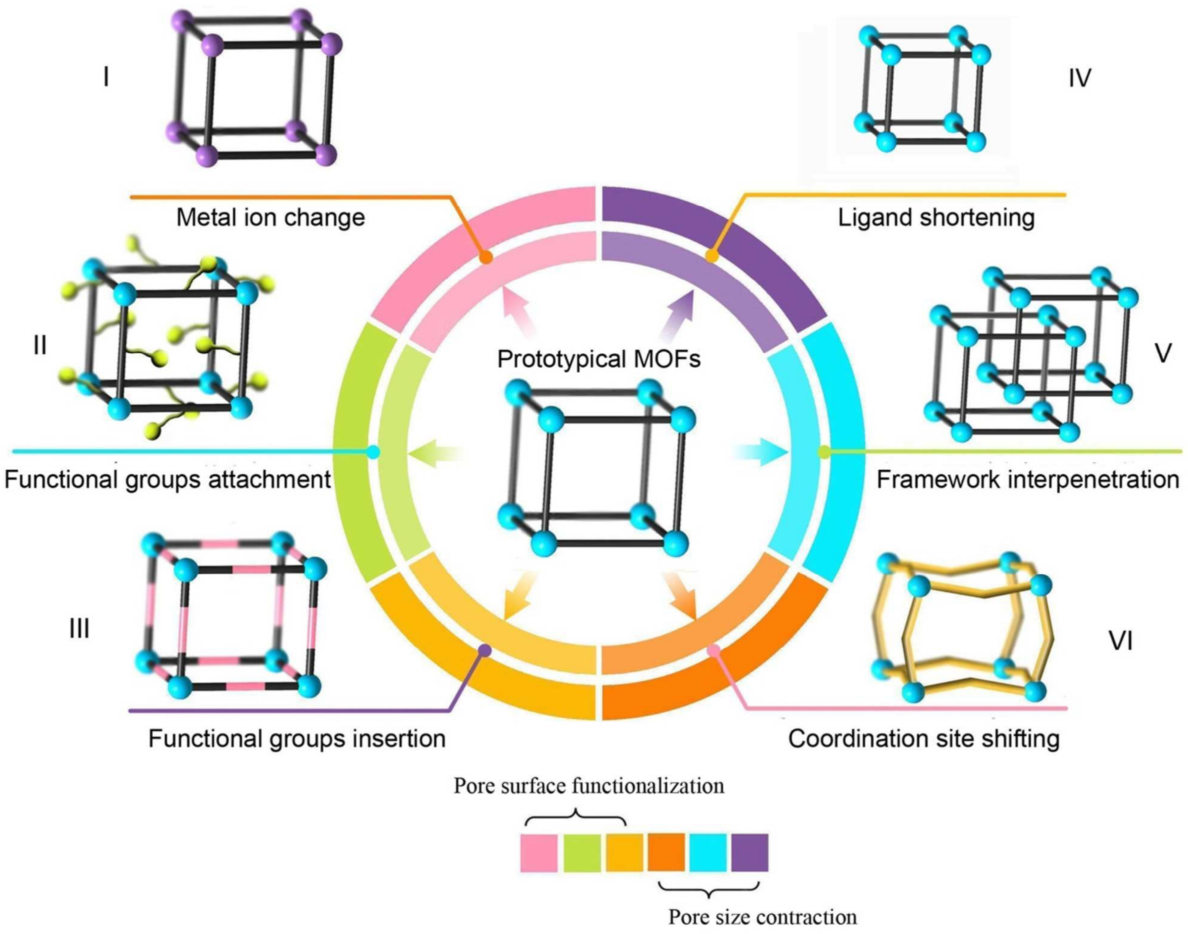


Fig. 1 Schematic drawing of six strategies for fine tuning of MOFs' structures with the prototypical MOFs

CCS technology includes post-combustion capture, pre-combustion capture and Oxy-fuel combustion.[3,12,13,15] The post-combustion CO_2 release, which is generally produced from post-combustion flue gas of power plants with 73-77% of N_2, 15-16% of CO_2 and 5-7% of H_2O, *et al*. as well as the total pressure as ~ 1 bar, is considered to be a great proportion of global disposal of CO_2 and the intensive investigations of its capture is ongoing in the world.[3,7-9,16] Conventional CCS technologies for post-combustion CO_2 capture which are based upon chemisorptions by amine-solution systems encounter problems of high energy input and corrosion of pipelines in its capture process.[7,9,17,18] Therefore, porous solid materials, such as zeolite and activated carbon, have been developed.[19,20] However, lower surface area and large negative water effect of zeolites restrict their application and activated carbons have larger surface area, but show lower selectivity for CO_2 capture.[9,19,21]

Zhiyong Lu

Zhiyong Lu was born in Sichuan province of China in 1987. He received his BS in chemistry from the Sun Yat-sen University in 2009 and PhD in inorganic chemistry from Nanjing University under the guidance of Professor Junfeng Bai in 2015. *Currently, he is working as a lecturer at Hohai University. His research interest focuses on the design and syntheses of porous materials for gas storage and separation.*

Metal-organic frameworks (MOFs) have emerged as a new class of porous solid materials with interesting features, such as high porosity, rational design, tunability,[22-31] and have experienced rapid development in these two decades.[8,9,19,21,32-36] Previously, more attention has been paid on the construction and characterization of diverse MOFs.[37-45] Recently, several research groups, including my group, started to systematically investigate the construction of MOFs to improve their CO_2 capture properties.[9,46-49]

For post-combustion CO_2 capture, considering the quadrupole moment and polarizability of CO_2 that is larger than that of N_2, strategies of metal ion change (I), functional groups attachment (II) and functional groups insertion (III) have been developed for functionalizing MOFs to improve their properties (Fig. 1).[8,9,20,21,33,46,47,50,51] On the other hand, to target the smaller kinetic diameter of CO_2 over N_2, strategies of ligand shortening (IV), framework interpenetration (V) and coordination site shifting (VI) have been used to finely contract the pore size of MOFs for optimizing their adsorption (Fig. 1).[9,48-51] In this review, we would like to summarize them based upon recent work including others and us.

Metal ion change in MOFs

Many MOFs possess the exposed metal cation sites in frameworks.[9,19,21,46,51-55] Such binding sites are beneficial to the close interaction of guest molecules to the pore surface, which facilitates to improve affinity and preferential adsorption of the frameworks towards CO_2 over N_2 in the post-combustion capture because of the larger quadrupole moment and polarizability of CO_2 molecules (CO_2: 43.0×10^{-27} esu^{-1} cm^{-1} and 29.1×10^{-25} cm^{-3}; N_2: 15.2×10^{-27} esu^{-1} cm^{-1} and 17.4×10^{-25} cm^{-3}).[9,21] Several groups have made great effort in this regard, such as, Yaghi, Férey and Long.[56-64] Many structural types, such as MIL-53,[59-61,65,66] MOF-74,[46,54,57,58,67-70] M-BTT[62-64] and HKUST-1[71-74] et al have been designed.

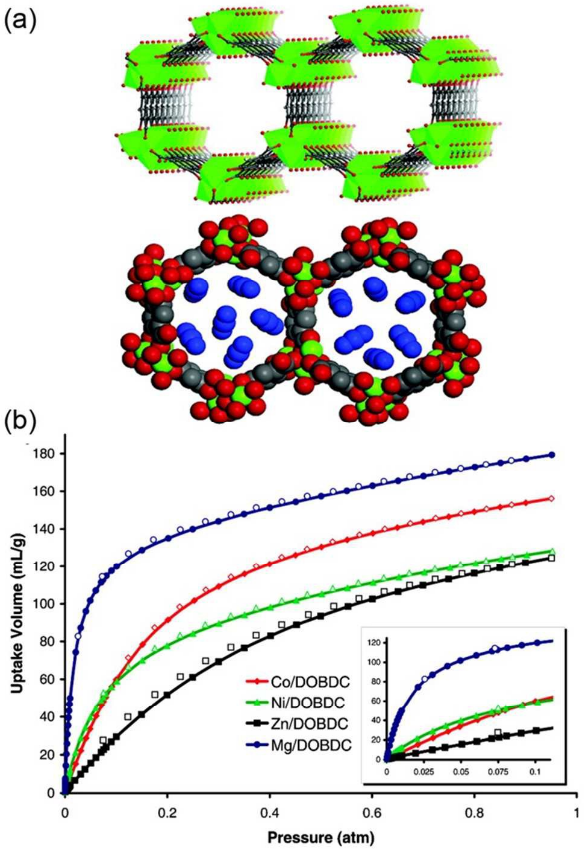


Fig. 2 (a) The structure of the series of MOF-74-X (X = Zn, Co, Ni, Mg) with 1D hexagon channels (up, ball-stick; down, space-filling); and (b) the CO_2 adsorption isotherms of the MOF-74-X series (X = Zn, Co, Ni, Mg) at 296 K and 0–1 bar pressure range. Reprinted with permission from ref. 46. Copyright 2008 American Chemical Society.

The series of MOF-74-X (X = Zn, Co, Ni, Mg) vividly reveals how metal ion in MOFs affects the adsorption capacity, binding strength and material stability *et al.* of MOFs.[9,21,46,67,75] The first example was reported by Yaghi's group with the name of MOF-74, which was synthesized from 2,5-dihydroxy-1,4-benzene-dicarboxylate (DHBDC) and Zn ions.[46,56] Then isostructural MOF-74-Co (named as CPO-27-Co) and MOF-74-Ni (CPO-27-Ni) were presented by Dietzel's group, subsequently.[46,68,69] All these MOFs are constructed by the same organic ligands and similarly infinite and linear metal-oxygen secondary building units (SBUs), which generate the honeycomb-type frameworks with one-dimensional hexagonal channels embedded by a high density of exposed metal sites after the removal of guest molecules (Fig. 2a).[21,46] Different to the transition metals, Mg, a lighter and harder metal, was then chosen to construct the new isostructural MOF, MOF-74-Mg, by Matzger and co-workers.[46] MOF-74-Mg shows an uptake amount of CO_2 (19.1 wt %) which is twice than that of any other materials in the MOF-74 series at 0.1 atm and 296 K.[46] Eliminating the weight effect of different metal ions, the CO_2 adsorption uptakes of this MOF series at 0.1 atm and 296 K (Fig. 2b) would be 4 for MOF-74-Zn (perhaps due to less thermal stability), 7 for MOF-74-Co/Ni, and 12 for MOF-74-Mg, respectively, if it is converted to the number of CO_2 molecules per unit cell (UC).[46] Moreover, the zero-coverage adsorption enthalpies of CO_2 in this series are also affected by different metal ions dramatically, which are varied from the lowest level for MOF-74-Zn, to 37 kJ/mol for MOF-74-Co, to 41 kJ/mol for MOF-74-Ni, and to 47 kJ/mol for MOF-74-Mg.[46] More importantly, the highest adsorption uptake at low pressures and zero-coverage adsorption enthalpies of MOF-74-Mg among these MOFs are attributed to the higher partial positive charge on the Mg^{2+} metal centers which is resulted from the increased ionic character of Mg-O bonds.[46] Consequently, it could facilitate the greater degree of polarization on the adsorbed CO_2 molecules.[9,21]

Exposed metal ion sites in MOFs are beneficial for improving the affinity and selectivity of frameworks towards CO_2 over N_2 in the post-combustion capture. Notably, some drawbacks still exist in these MOFs, such as less ease activation/regeneration in some particular cases[19,49] and less water stability[49,67] in general.

Functional groups attachment in MOFs

Another popular strategy for the enhancement of CO_2–MOF interactions is to attach polar functional groups on the walls of MOFs.[9,19,21,29,51,58,76-78] The first utilization of such strategy was Yaghi and co-workers with the research of the family of IRMOF-1.[29,58,77-83] Then this idea was extended to other series of MOFs, such as UiO-66, MIL-53, and NOTT-101 structure types made by Cohen's,[84] Stock's,[85] and Schröder's groups,[86,87] respectively. The polar functional groups favorable to optimize CO_2 adsorption behaviors commonly include amine, hydroxyl, nitryl, cyan, halide, sulfo, and carboxyl functionalities.[9,21] Generally, the enhancement of affinity of frameworks toward CO_2 highly depends on the polarizing strength of the functional groups.[9]

Due to the commercial availability,[9] large numbers of metal-organic frameworks with aromatic amine functionalized ligands have been designed, and many of them have been systematically studied for exploring polar functional group effect on the selective CO_2 adsorption at low pressures.[78,83,88,89] Typically, two MOFs of isostructural $Zn_4O(NH_2\text{-BDC})$ (IRMOF-3, NH_2-BDC = NH_2-1,4-benzenedicarboxylate) and prototype $Zn_4O(BDC)$ (IRMOF-1, BDC = 1,4-benzenedicarboxylate) designed by Yaghi's group,[83,90] provide a good example in this field. The aromatic amine functionalized IRMOF-3, shows a more rapid adsorption at its initial occurrence and a higher uptake of CO_2 at the special pressure. And its heat of adsorption for CO_2 is also higher than that of prototype IRMOF-1.[9,83,90]

There are many examples in this regard. $-NO_2$ functionalized ZIF-78 discovered by Banerjee *et al.*,[89] which exhibits GME topology, also shows a higher CO_2 adsorption uptake and selectivity for CO_2 over N_2 (Table 2) than those of other isoreticular ZIFs in the series of ZIF-68, ZIF-69, ZIF-79, and ZIF-81. Furthermore, $Zn(OH\text{-BDC})(TED)_{0.5}$ (OH-BDC = 2-OH-terephthalic acid, TED = triethylenediamine) with the BDC ligand modified by a hydroxyl (–OH) group, reported by Li's group,[88] also exhibits a higher adsorption uptake of CO_2 than that of the parent MOF $Zn(BDC)(TED)_{0.5}$.

More interestingly, in the series of MTV-MOF-5 which may be considered as the next-generation MOFs for the post-combustion CO_2 capture,[78] different functionalities are incorporated into MOFs to afford selective CO_2 properties which were not simply linear sum of their constituents.

Meanwhile, it should be noticed that functional groups attachment into MOFs may lead to some occupancy of space in pores or cavities, and then reduce the surface areas and free volume of MOFs.[19,89,91]

Functional groups insertion in MOFs

In order to alleviate problems mentioned above, an optional strategy that is the functional groups insertion in MOFs which we called and initially explored by our group. The functionality insertion implies to decorate MOFs with desired functional groups which are inserted into backbones of organic parts in MOFs instead of the original ones with similar shapelike.[19,45,47,58,63,92-105] Up to now, the polar functional groups frequently reported to be used in such strategy involve –NH–CO– functionality by our group[47,94,97,100] and N heteroatom by Li's group[92]. In this strategy, both the polarization of pore surface of MOFs and preserving the intrinsic porosity from the parent frameworks are almost realized which helps to investigate the tunability of MOFs more finely.

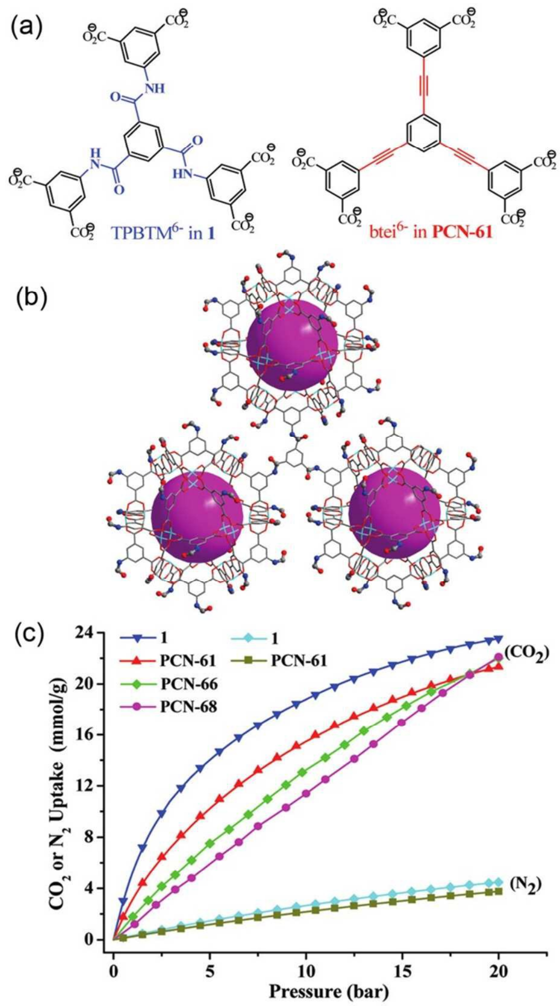


Fig. 3 (a) The designed organic ligand, H_6TPBTM, (left) based upon the parent organic linker, H_6BTEI, (right); and (b) the porous structure of NJU-Bai0 with the pore surface decorated by the inserted polar amide group; and (c) the gravimetric excess CO_2 and N_2 adsorption isotherms of NJU-Bai0 (expression of 1 in figure) and PCN-6X series at 298 K and 0–20 bar pressure range. Reprinted with permission from ref. 47. Copyright 2011 American Chemical Society.

NJU-bai0 represents a typical example in this respect.[47] In its structure, the square $[Cu_2(O_2CR)_4]$ paddle-wheels is connected through 1,3-benzenedicarboxylate moieties, giving the formation of extra-large and highly symmetrical 24-connected faceted polyhedra or supermolecular building blocks (SBBs) which are further 3- connected at each of their 24 vertices by the organic moieties at 5-position of isophthalate groups to afford the (3, 24)-connected nets or

Table 1 The porosity and selective CO_2/N_2 adsorption of NJU-Bai0 and the prototype, PCN-61[47]

MOF	Pore size[a]			Pore volume[b]	BET[c]	CO_2 uptake (0.15 bar, 298 K)		N_2 uptake (0.75 bar, 298 K)		$-Q_{st,\ n=0}$ (CO_2)[d]	Selectivity at 298 K	
	Cub-O_h (Å)	T-T_d (Å)	T-O_h (Å)	(cm^3/g)	(m^2/g)	mmol/g	wt %	mmol/g	wt %	(kJ/mol)	IAST[e]	Eq.[f]
NJU-Bai0	12	11.6	18.7	1.27	3160	0.95	4.0	0.24	0.67	26.3	22	19.8
PCN-61	12	11.8	18.8	1.37	3350 [3000]	0.56	2.4	0.19	0.53	22	15	14.7

[a] The pore size is defined as the diameter of sphere representing the void inside the polyhedron; [b] The total pore volume is calculated from N_2 gas adsorption isotherm at 77 K; [c] The value in square bracket is taken from another reference; [d] The determination of adsorption enthalpy for CO_2 at zero-loadings is estimated by applying the virial equation using the adsorption isotherms; [e] IAST selectivity for CO_2 over N_2 in the CO_2:N_2 (50:50) binary mixture at 1 bar calculated from adsorption isotherm of each pure gas at 298 K; [f] Adsorption selectivity for CO_2 over N_2 is calculated from the pure-component adsorption isotherms at 298 K based upon the equation of S = (q1/q2)/(p1/p2)[9].

---

rht-type MOF (Fig. 3b). Its overall structure can be viewed as three types of cages: cuboctahedra (cubOh), truncated tetrahedral (T-Td), and truncated octahedral (T-Oh) packed in three-dimensional space.[47,104] In comparison to PCN-61, the polarity of pore surface of NJU-Bai0 is greatly enhanced by the substitution of the –NH–CO– groups in NJU-Bai0 for the –C=C– groups in PCN-61. However, notably, the pore size, surface area, and the number of open Cu^{II} sites of NJU-Bai0 are almost not reduced, compared with those of PCN-61 (Table 1).[47] With the enhanced pore surface polarity, the adsorption capacity for CO_2 at 298 K and 0.15 bar of NJU-Bai0 is up to 4.0 wt %, largely higher than that of 2.4 wt % of PCN-61 under the identical conditions (Fig. 3c).[47] In addition, the initial slope of the CO_2 adsorption isotherm at 298 K of NJU-Bai0 was observed steeper than that of PCN-61, which implies the stronger affinity toward CO_2 of NJU-Bai0 than that of its prototype PCN-61.[47] And the CO_2 adsorption isosteric heat at zero-coverage, associated to the affinity of frameworks toward CO_2, also increases from the 22 kJ/mol for PCN-61 to the 26.3 kJ/mol for NJU-Bai0.[47] Furthermore, the CO_2 adsorption selectivity for the equimolar mixture of CO_2/N_2 at 298 K and 1 bar is calculated based upon experimental single component isotherms by IAST (ideal adsorption solution theory) as 15 for PCN-61 and 22 for NJU-Bai0, varying with the similar trend.[47] Inherently, the enhanced CO_2 adsorption of NJU-Bai0 is directly attributed to the enhanced pore surface polarity of framework by the polar –CO–NH– group inserted. Moreover, we also investigated other prototypical MOFs experimentally and theoretically, further confirming the beneficial effect of enhancing pore surface polarity by inserting polar –CO–NH– group to improve CO_2 adsorption properties of MOFs (Table 2).[94,97,100]

Despite the fact that the incorporated open metal sites or organic polarizing sites in MOFs enhance the affinity of frameworks towards CO_2, both of them have some drawbacks in the design of MOFs applied to the post-combustion CO_2 capture, such as less ease activation/regeneration and water stability issues, *et al.* Consequently, targeting the difference of kinetic diameters of CO_2 and N_2 gas molecules: CO_2, 3.30 Å; N_2, 3.64 Å, finely tuning pore size to control the adsorption performances for the post-combustion CO_2 capture of MOFs may be more fruitful. This will be discussed in detail in the following sections.

Ligand shortening in MOFs

The simplest strategy of contracting the pore size to improve adsorption performances for post-combustion CO_2 capture of MOFs is the ligand shortening in MOFs.[48,49,58] Typically, contracting the pore size of MOFs facilitates the better overlap of attractive potential fields between the opposite pore walls, leading to the enhancement of affinity of pore walls toward adsorbed gases.[49,58] When the pore size is large enough to permit the larger size of gas (*e.g.* N_2 gas in the post-combustion CO_2 capture[9]) to readily diffuse into, the separation of such two kind of gases will depend on their different equilibrium adsorptions due to their different interactions with frameworks.[50,51,106] And, while the pore size is slightly larger than the kinetic diameter of the larger size of gas molecules, the kinetic separation of such two kinds of gases will rely on the different limitation of diffusing rate of gases, which was dominantly caused by the steric hindrance of pores.[50,51,106] Furthermore, if the pore size is reduced to the right size just between the kinetic diameters of such two kinds of gas molecules (*e.g.* CO_2, 3.30 Å; N_2, 3.64 Å),[9] the narrowed pore will allow the small size of gas molecules to diffuse into but exclude the large size of ones completely, resulting in the size-excluded effect separation of different gases in MOFs.[50,51,106]

Recently, motivated by the study of CO_2 removal from flue gases, the contraction of pore size in MOFs by shortening the length of organic ligands was proposed, and then it was used to enhance the adsorption performances for CO_2 post-

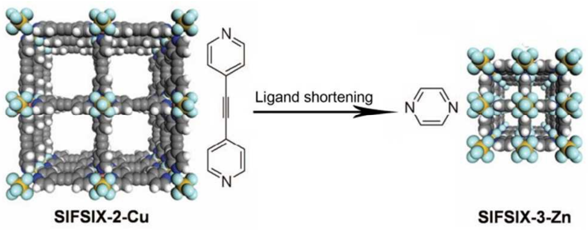


Fig. 4 The designed MOF, SIFSIX-3-Zn, based upon the prototype one, SIFSIX-2-Cu, by the organic ligand shortening, with the pore size of 1D square channels in SIFSIX-3-Zn dramatically reduced. Copyright 2013 Nature Publishing Group.

combustion capture of MOFs.[49]

As a typical example, the isostructural series, SIFSIX-2-Cu and SIFSIX-3-Zn, with saturated metal centers were reported by Zaworotko's group.[49] In their work, 4,4'-dipyridylacetylene and pyrazine were used as one of the organic ligands of both SIFSIX-2-Cu and SIFSIX-3-Zn, respectively (Fig. 4).[49] For both structures, metal ions are connected through organic 4,4'-dipyridylacetylene or pyrazine ligands with the formation of two-dimensional layers in SIFSIX-2-Cu or SIFSIX-3-Zn. These 2D layers are further pillared by SiF_6^{2-} anions ('SIFSIX') in the third dimension giving the 3D primitive cubic topological frameworks with one-dimensional square channels aligned by a periodic array of SiF_6^{2-} pillars.[49] However, with the pyrazine whose length is shorter than 4,4'-dipyridylacetylene, the Langmuir surface area and pore size of SIFSIX-3-Zn dramatically decrease to 250 m^2/g (from CO_2 gas adsorption isotherm at 298 K and low pressure) and 3.84 Å (given as diagonal dimensions), compared with those of 3370 m^2/g (from N_2 gas adsorption isotherm at 77 K and low pressure) and 13.05 Å of SIFSIX-2-Cu correspondingly.[49] On the contrary, owing to the contracted pore size, the CO_2 adsorption uptake of SIFSIX-3-Zn at 298 K and 0.1 bar increase up to 9.5 wt %, compared with that of 1.0 wt % of the prototype, SIFSIX-2-Cu, under the same experimental conditions (Fig. 5).[49] In addition, the adsorption enthalpy for CO_2 at zero-loadings has also increased from 22 kJ/mol of SIFSIX-2-Cu to 45 kJ/mol of SIFSIX-3-Zn.[49] And the CO_2 adsorption selectivity of SIFSIX-3-Zn over N_2 in CO_2:N_2 (10:90) binary mixture at 1 bar is 1818, calculated by IAST based upon adsorption isotherm of each pure gas at 298 K, which is extraordinarily larger than that of 13.7 for SIFSIX-2-Cu.[49] Significantly, all these results are attributed to the reduced pore size in the SIFSIX-3-Zn by shortening the length of organic ligands, which is helpful to strengthen the overlap of attractive potential fields among the opposite pore walls to optimize the performances of MOFs for CO_2 separation from N_2 gas.[49]

Obviously, the reduction of pore size by shortening the length of organic ligands for the construction of MOFs helps to significantly tune the CO_2 adsorption properties for the post-combustion CO_2 capture. Furthermore, contracting the pore size of MOFs also helps to reduce the extent of frameworks exposed upon the humid environment, which, thus, generally enhances the water stability of the obtained MOFs.[76,107]

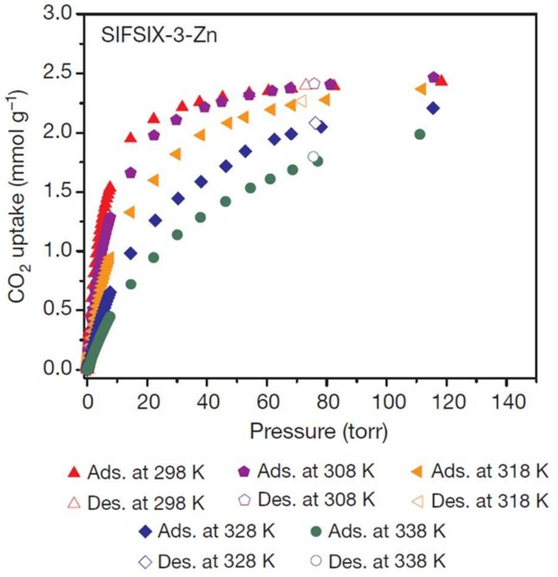


Fig. 5 The CO_2 adsorption isotherms of SIFSIX-3-Zn at different temperatures and the low pressure range. Copyright 2013 Nature Publishing Group.

Framework interpenetration in MOFs

For the longer length of organic ligands to build MOFs, an alternative strategy for contracting the pore size to improve the performances of CO_2 adsorption of MOFs is to control the framework interpenetration in MOFs. This strategy means the intergrowth of two or more frameworks, in which frameworks are maximally displaced from each other.[55] Previously, the approach was developed to the storage of H_2 gas in a series of Zn_4O carboxylates with the cubic topology by Yaghi's group[25,55] and for the separation of small molecules in the primitive cubic topological family of paddle-wheel cluster $M_2(COO)_4$ bicarboxylates pillared by bidentate linkers by Zhou's and Chen's group, respectively[108-113]. Recently, this strategy is extended for CO_2 capture, particularly, the CO_2 removal from flue gas.[49,114]

One good example is a polymorph series, SIFSIX-2-Cu and SIFSIX-2-Cu-i, which was also reported by Zaworotko's group (Fig. 6).[49] By interpenetration, the pore size of SIFSIX-2-Cu-i is reduced to 5.15 Å from that of 13.05 Å for SIFSIX-2-Cu.[49] Upon the contraction of pore size by framework interpenetration, the uptake amount of CO_2 adsorption isotherm of SIFSIX-2-Cu-i at 298 K and 0.1 bar is up to 7.1 wt %, which is greatly higher than that of its parent MOF, SIFSIX-2-Cu (Fig. 7). Also, the enthalpy of CO_2 adsorption at zero loadings increases from 22 kJ/mol of SIFSIX-2-Cu to 31.9 kJ/mol of SIFSIX-2-Cu-i. Besides, the CO_2 adsorption

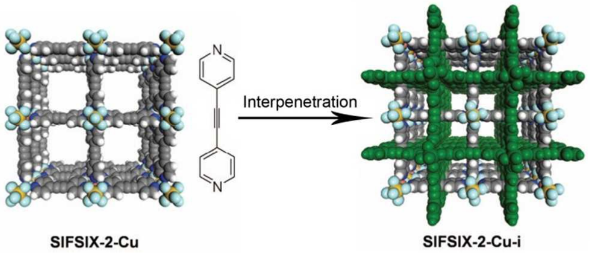


Fig. 6 The designed MOF, SIFSIX-2-Cu-i, based upon the prototype one, SIFSIX-2-Cu, by the framework interpenetration, with the pore size of 1D square channels in SIFSIX-2-Cu-i significantly reduced. Copyright 2013 Nature Publishing Group.

selectivity over N_2 in the CO_2:N_2 (10:90) binary mixture calculated by IAST based upon adsorption isotherm of each pure gas at 298 K is 13.7 for SIFSIX-2-Cu and 140 for SIFSIX-2-Cu-i, respectively, with the similar tunability.[49] It is noted that the optimized CO_2 adsorption properties of SIFSIX-2-Cu-i are attributed to the reduced pore size by framework interpenetration in MOFs.[49]

The framework interpenetration in MOFs is of much significance for the pore size contraction to enhance the performances for CO_2 adsorption of MOFs. However, accompanied with the reduction of pore size, the framework density of MOFs simultaneously increases by the interpenetration of frameworks.[25] In some cases, thus, the BET surface area and gravimetric adsorption density of adsorbed gas in MOFs decrease,[25,114] which correspondingly interrupts the gas adsorption behaviors of MOFs.

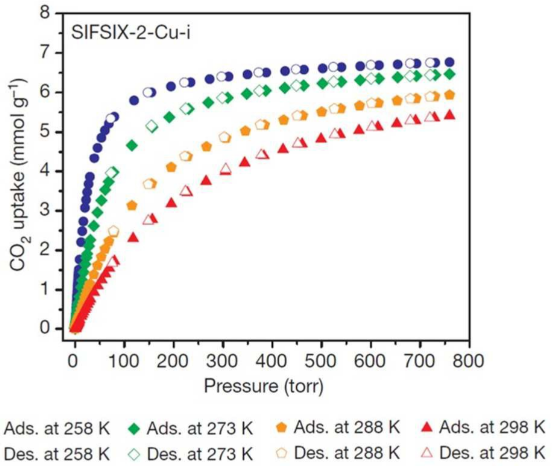


Fig. 7 The CO_2 adsorption isotherms of SIFSIX-2-Cu-i at different temperatures and the low pressure range. Copyright 2013 Nature Publishing Group.

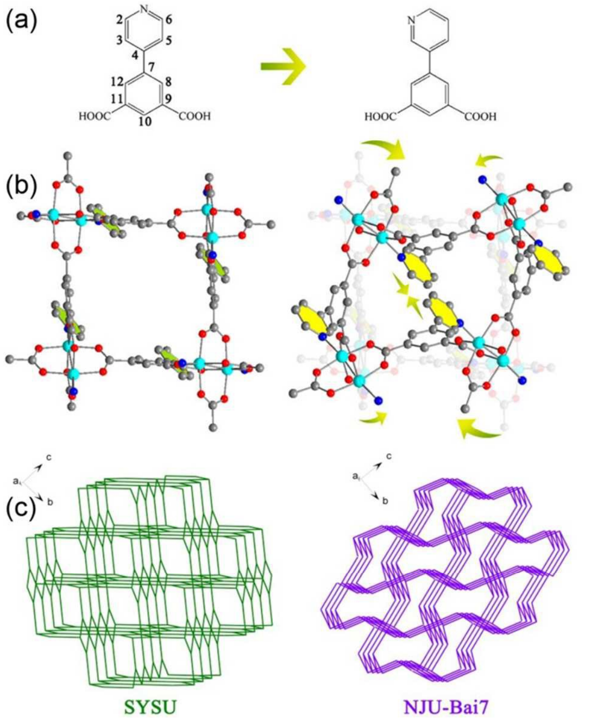


Fig. 8 (a) The designed organic ligand (right) by shifting the coordination site, N, based upon the parent organic linker (left); and (b) the finely-tuned channels in NJU-Bai7 (right) compared with those in the prototype, SYSU (left), with the pore size in NJU-Bai7 greatly reduced; and (c) the topological networks of SYSU (left) and NJU-Bai7 (right), with the tuned pores in NJU-Bai7 observed obviously. Reprinted with permission from ref. 48. Copyright 2013 American Chemical Society.

Coordination site shifting in MOFs

Considering issues mentioned above, another strategy of the coordination site shifting in MOFs is employed for contracting pore size to tune the CO_2 adsorption properties of MOFs by our group. The approach simply changes the coordination position of some coordinating functional groups of organic ligands in the MOFs (Fig. 8a).[48,115,116] Shifting the coordination sites of organic ligands could contract the pore size of MOFs without remarkably decreasing the BET surface area.[48]

NJU-Bai7 is the initial example in this context.[48] In its structure, $Cu_2(COO)_4$ paddle-wheel units are connected by the carboxyl groups of organic ligands to form the 2D sql topological layers, which are further linked by the pyridin-3-yl at the 5-position of isophthalic acid to give the (3,6)-connected 3D MOFs with one-dimensional open channels (Fig. 8).[48] Compared with 6.3 × 6.3 Å^2 for its prototype, SYSU, the pore size of NJU-Bai7 decreases significantly to 3.4 × 3.4 Å^2 (considering Van der Waals radius of atoms) by shifting the N

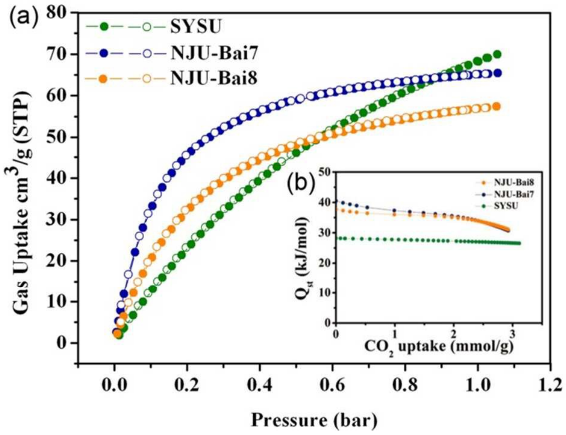


Fig. 9 The CO_2 adsorption isotherms of SYSU, NJU-Bai7 and NJU-Bai8 at 298 K and 0–1 bar pressure range, with the CO_2 adsorption enthalpy of SYSU, NJU-Bai7 and NJU-Bai8 in the inset. Reprinted with permission from ref. 48. Copyright 2013 American Chemical Society.

coordination sites. However, the BET surface area of 1155 m^2/g of NJU-Bai7 remains approximately equal to that of 1100 m^2/g of the parent SYSU.[48] Significantly, the CO_2 adsorption uptakes at 298 K and 0.15 bar of NJU-Bai7 is 7.4 wt % after the contraction of pore size by coordination sites shifting in MOFs, greatly higher than 3.5 wt % for SYSU (Fig. 9).[48] In addition, the CO_2 adsorption enthalpy at zero loadings also displays the similar variation from 28.2 kJ/mol for SYSU to 40.5 kJ/mol for NJU-Bai7.[48] Moreover, the adsorption selectivity for CO_2 over N_2, calculated upon the ratio of initial slopes of their adsorption isotherms at 273 K, also increases from 25.5 for SYSU to 97.1 for NJU-Bai7.[48] Notably, all these different results are attributed to the reduced pore size in NJU-Bai7 by shifting the coordination sites, which is close to the kinetic diameter of CO_2 (3.3 Å) but slightly smaller than that of N_2 (3.64 Å),[48] inducing the size-exclusive effect separation of two gases in the MOF.

Contracting the pore size by coordination sites shifting is useful for improving the performances for the post-combustion CO_2 capture of MOFs. Nevertheless, it needs to be further investigated and developed.

Table 2 Summary of selective CO_2 adsorption properties of some typical platforms for exploring the tunablity of MOFs

MOF	Surface area[a] (m^2/g)	CO_2 uptake[c]		N_2 uptake[c]		$-Q_{st,\ n=0}$ (CO_2)[d] (kJ/mol)	Selectivity[e] (CO_2/N_2)	Pressure (bar)		Temp (K)	Ref.
		mmol/g	wt %	mmol/g	wt %			CO_2	N_2		
MOF-74-Mg	1495	5.36	19.1	-	-	47	-	0.1	-	296	46
	1800	5.90	20.6	0.67	1.83	-	44	0.15	0.75	303	9
		5.30	18.9	0.51	1.40	-	52.3	0.15	0.75	313	9
		4.56	16.7	0.39	1.08	-	58.8	0.15	0.75	323	9
		3.85	14.5	0.31	0.87	-	61.1	0.15	0.75	333	9
MOF-74-Ni	936	4.62	16.9	0.78	2.14	-	30	0.15	0.75	298	9
	1070	2.64	10.4	-	-	41	-	0.1	-	296	46
MOF-74-Co	957	3.76	14.2	-	-	-	-	0.15	-	298	9
	1080	2.66	10.5	-	-	37	-	0.1	-	296	46
SIFSIX-3-Zn	250[b]	2.43	9.7	-	-	45	-	0.15	-	298	49
		2.39	9.5	-	-		1818[f]	0.1	0.9	298	49
SIFSIX-2-Cu-i	735	2.3	9.2	0.16	0.45	31.9	71.9	0.15	0.75	298	49
		1.73	7.1	-	-		140[f]	0.1	0.9	298	49
NJU-Bai7	1155	1.82	7.4	0.13	0.36	40.5	70	0.15	0.75	298	48
		-	-	-	-		97.1[g]	-	-	273	
MOF-74-Zn	-	1.87	7.6	-	-	-	-	0.15	-	296	9
	816	1.32	5.5	-	-	-	-	0.1	-	296	46
Bio-MOF-11	1040	1.3	5.4	0.1	0.28	45	65	0.15	0.75	298	9
NJU-Bai8	1103	1.23	5.1	0.12	0.33	37.7	51.3	0.15	0.75	298	48
		-	-	-	-		111.3[g]	-	-	273	
NJU-Bai0	3160	0.95	4.0	0.24	0.67	26.3	19.8	0.15	0.75	298	47
							22[f]	0.5	0.5		
$[Cu(bpy\text{-}1)_2(SiF_6)]$	1468	0.84	3.6	0.24	0.67	27	17.5	0.15	0.75	298	117
SYSU	1100	0.82	3.5	0.12	0.33	28.2	34.2	0.15	0.75	298	48
		-	-	-	-		25.5[g]	-	-	273	
Zif-78	620	0.78	3.3	0.13	0.36	-	30	0.15	0.75	298	9
						-	50.1[h]	-	-		9
PCN-61	3350	0.56	2.4	0.19	0.53	22	14.7	0.15	0.75	298	47
							15[f]	0.5	0.5		

Table 2 (continued)

MOF	Surface area[a]	CO$_2$ uptake[c]		N$_2$ uptake[c]		$-Q_{st, n=0}$ (CO$_2$)[d]	Selectivity[e]	Pressure (bar)		Temp	Ref.
	(m^2/g)	mmol/g	wt %	mmol/g	wt %	(kJ/mol)	(CO$_2$/N$_2$)	CO$_2$	N$_2$	(K)	
[Cu(bpy-2)$_2$(SiF$_6$)]	2718	0.52	2.2	0.21	0.58	21	12.4	0.15	0.75	298	117
NJU-Bai3	2690	0.49	2.1	-	-	36.5	-	0.15	-	298	94
		1.5	6.2	0.2	0.56		37.5	0.15	0.75	273	
Zif-79	810	0.36	1.6	0.10	0.28	-	18	0.15	0.75	298	89
							23[h]	-	-		
SIFSIX-2-Cu	3140	0.36	1.6	0.16	0.45	22	11.3	0.15	0.75	298	49
		0.23	1.0	-	-		13.7[f]	0.1	0.9	298	49
Zif-68	1090	0.31	1.3	0.09	0.25	-	17.2	0.15	0.75	298	89
							18[h]	-	-		
Zif-70	1730	0.27	1.2	0.10	0.28	-	13.5	0.15	0.75	298	89
							16[h]	-	-		

[a] Unless otherwise stated, the value is calculated as BET surface area from N$_2$ gas adsorption isotherm at 77 K; [b] The surface area is calculated based upon the Langmuir model from CO$_2$ gas adsorption isotherm at 298 K; [c] Uptake is estimated from adsorption isotherms in cases where the value not specially reported; [d] The determination of adsorption enthalpies for CO$_2$ at zero-loadings is estimated by applying the virial or Clausius-Clapeyron equation using the adsorption isotherms, not directly related to values of *Pressure* and *Temp*; [e] When not specially noted, adsorption selectivity of CO$_2$ over N$_2$ is calculated from the pure-component isotherms by dividing the mass of CO$_2$ adsorbed at the pressure of value in Pressure (CO$_2$) by the mass of N$_2$ adsorbed at the pressure of the value in Pressure (N$_2$) according to the equation of S = (q1/q2)/(p1/p2)[9]; [f] IAST selectivity for CO$_2$ over N$_2$ in the CO$_2$:N$_2$ binary mixture at 1 bar calculated from adsorption isotherm of each pure gas; [g] Selectivity for CO$_2$ over N$_2$ determined by the ratio of initial slopes based upon the isotherms; [h] Selectivity for CO$_2$ over N$_2$ calculated by Herry's law based upon the adsorption isotherms.

Conclusion and Perspective

MOFs have emerged as the powerful platforms for exploring more promising materials for the post-combustion CO$_2$ capture. In this review, we have summarized main strategies for finely tuning of MOFs' structures toward high performance, in which metal ion change, functional groups attachment, and functional groups insertion are used to modulate the pore surface properties of MOFs and ligand shortening, framework interpenetration, and coordination site shifting contract the pore size of MOFs.

To further develop MOFs for the real-world application of the post-combustion CO$_2$ capture, we should design MOFs with combined features of higher CO$_2$ adsorption uptakes at 0.15 bar and better selectivity, higher water stability and lower regeneration penalty, *et al.*, which, but, is still a big challenge. In addition, large-scale synthesis and efficient packing in a real industrial adsorber of MOFs are also the crucial issues for their industrial applications, which need to be further intensively investigated. However, despite the fact that these difficulties should be overcome, we believe in the near future that MOFs are promising for industrial applications for the CO$_2$ removal from the flue gas.

Acknowledgements

This work is supported by the Major State Basic Research Development Programs (Grant 2011CB808704) and the National Natural Science Foundation of China (21371091). In addition, Prof. Junfeng Bai would like to thank professor Michael J. Zaworotko for many discussions concerning about MOFs.

Appendix

For clarity, some mathematical relations between metrics for *Loading* and *Pressure* in figures taken from literature are listed, respectively:

1 × cm^3/g = 1 × mL/g = 1/22.4 × mmol/g;

1 × bar ≈ 1 × atm = 760 × torr.

References

1 E. J. Stone, J. A. Lowe and K. P. Shine, *Energy Environ. Sci.*, 2009, **2**, 81-91.

2 M. Z. Jacobson, *Energy Environ. Sci.*, 2009, **2**, 148-173.

3 F. M. Orr, *Energy Environ. Sci.*, 2009, **2**, 449-458; J. A. Mason, T. M. McDonald, T. H. Bae, J. E. Bachman, K. Sumida, J. J. Dutton, S. S. Kaye and J. R. Long, *J Am Chem Soc*, 2015, **137**, 4787-4803; J. M. Huck, L.-C. Lin, A. H. Berger, M. N. Shahrak, R. L. Martin, A. S. Bhown, M. Haranczyk, K. Reuter and B. Smit, *Energy Environ. Sci.*, 2014, **7**, 4132-4146.

4 S. Chu, *Science*, 2009, **325**, 1599-1599.

5 T. R. Karl and K. E. Trenberth, *Science*, 2003, **302**, 1719-1723.
6 M. Z. Jacobson, *Nature*, 2001, **409**, 695-697.
7 A. Goeppert, M. Czaun, G. K. S. Prakash and G. A. Olah, *Energy Environ. Sci.*, 2012, **5**, 7833-7853.
8 J. R. Li, Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H. K. Jeong, P. B. Balbuena and H. C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791-1823.
9 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781; R. Poloni, K. Lee, R. F. Berger, B. Smit and J. B. Neaton, *J Phys Chem Lett*, 2014, **5**, 861-865.
10 M. I. Hoffert, K. Caldeira, G. Benford, D. R. Criswell, C. Green, H. Herzog, A. K. Jain, H. S. Kheshgi, K. S. Lackner, J. S. Lewis, H. D. Lightfoot, W. Manheimer, J. C. Mankins, M. E. Mauel, L. J. Perkins, M. E. Schlesinger, T. Volk and T. M. L. Wigley, *Science*, 2002, **298**, 981-987.
11 S. Pacala and R. Socolow, *Science*, 2004, **305**, 968-972.
12 M. A. Habib, M. Nemitallah and R. Ben-Mansour, *Energy & Fuels*, 2013, **27**, 2-19.
13 L.-C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhown, M. W. Deem, M. Haranczyk and B. Smit, *Nat Mater*, 2012, **11**, 633-641.
14 R. S. Haszeldine, *Science*, 2009, **325**, 1647-1652.
15 M. Kanniche, R. Gros-Bonnivard, P. Jaud, J. Valle-Marcos, J. M. Amann and C. Bouallou, *Appl. Therm. Eng.*, 2010, **30**, 53-62.
16 C. E. Wilmer, O. K. Farha, Y.-S. Bae, J. T. Hupp and R. Q. Snurr, *Energy Environ. Sci.*, 2012, **5**, 9849-9856.
17 E. B. le Bouhelec, P. Mougin, A. Barreau and R. Solimando, *Energy & Fuels*, 2007, **21**, 2044-2055.
18 R. H. Weiland, J. C. Dingman and D. B. Cronin, *J. Chem. Eng. Data*, 1997, **42**, 1004-1006.
19 Y. Liu, Z. U. Wang and H.-C. Zhou, *Greenhouse Gases: Science and Technology*, 2012, **2**, 239-259.
20 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058-6082.
21 Z. J. Zhang, Y. G. Zhao, Q. H. Gong, Z. Li and J. Li, *Chem. Commun.*, 2013, **49**, 653-661.
22 J. J. Perry Iv, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400-1417.
23 M. O'Keeffe, *Chem. Soc. Rev.*, 2009, **38**, 1215-1217.
24 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375.
25 O. K. Farha and J. T. Hupp, *Acc. Chem. Res.*, 2010, **43**, 1166-1175.
26 D. J. Tranchemontagne, Z. Ni, M. O'Keeffe and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2008, **47**, 5136-5147.
27 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705-714.
28 D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257-1283.
29 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469-472.
30 H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2007, **129**, 5314-+.
31 M. H. Alkordi, Y. L. Liu, R. W. Larsen, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 12639-+.
32 A. U. Czaja, N. Trukhan and U. Muller, *Chem. Soc. Rev.*, 2009, **38**, 1284-1293.
33 Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868-2899.
34 J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308-2322.
35 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
36 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 974-+.
37 O. K. Farha, A. Özgür Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944-948.
38 Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstey and M. Schroder, *Chem. Commun.*, 2009, DOI: 10.1039/B900013E, 1025-1027.
39 Q. R. Fang, D. Q. Yuan, J. Sculley, J. R. Li, Z. B. Han and H. C. Zhou, *Inorg. Chem.*, 2010, **49**, 11637-11642.
40 D. F. Sun, S. Q. Ma, Y. X. Ke, D. J. Collins and H. C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 3896-3897.
41 L. Song, J. Zhang, L. Sun, F. Xu, F. Li, H. Zhang, X. Si, C. Jiao, Z. Li, S. Liu, Y. Liu, H. Zhou, D. Sun, Y. Du, Z. Cao and Z. Gabelica, *Energy Environ. Sci.*, 2012, **5**, 7508-7520.
42 Y. He, Z. Guo, S. Xiang, Z. Zhang, W. Zhou, F. R. Fronczek, S. Parkin, S. T. Hyde, M. O'Keeffe and B. Chen, *Inorg. Chem.*, 2013, **52**, 11580-11584.
43 Z. X. Chen, S. C. Xiang, T. B. Liao, Y. T. Yang, Y. S. Chen, Y. M. Zhou, D. Y. Zhao and B. L. Chen, *Cryst. Growth Des.*, 2010, **10**, 2775-2779.
44 J. Jia, F. Sun, Q. Fang, X. Liang, K. Cai, Z. Bian, H. Zhao, L. Gao and G. Zhu, *Chem. Commun.*, 2011, **47**, 9167-9169.
45 D. Zhao, D. J. Timmons, D. Q. Yuan and H. C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123-133.
46 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870-10871.
47 B. S. Zheng, J. F. Bai, J. G. Duan, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **133**, 748-751.
48 L. Du, Z. Lu, K. Zheng, J. Wang, X. Zheng, Y. Pan, X. You and J. Bai, *J. Am. Chem. Soc.*, 2013, **135**, 562-565.
49 P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Q. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80-84.
50 J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
51 Y. S. Bae and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2011, **50**, 11586-11596.
52 P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, DOI: 10.1039/B810574J, 5125-5127.
53 P. D. C. Dietzel, V. Besikiotis and R. Blom, *J. Mater. Chem.*, 2009, **19**, 7362-7370.
54 W. Zhou, H. Wu and T. Yildirim, *J. Am. Chem. Soc.*, 2008, **130**, 15268-15269.
55 J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem. Int. Ed.*, 2005, **44**, 4670-4679.
56 N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504-1518.
57 D. Britt, D. Tranchemontagne and O. M. Yaghi, *Proc. Nat. Acad. Sci. U.S.A.*, 2008, **105**, 11623-11627.
58 J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304-1315.
59 C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Férey, *J. Am. Chem. Soc.*, 2002, **124**, 13519-13526.
60 S. R. Miller, P. A. Wright, C. Serre, T. Loiseau, J. Marrot and G. Ferey, *Chem. Commun.*, 2005, DOI: 10.1039/B506677H, 3850-3852.

61 G. Ferey, M. Latroche, C. Serre, F. Millange, T. Loiseau and A. Percheron-Guegan, *Chem. Commun.*, 2003, DOI: 10.1039/B308903G, 2976-2977.

62 M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown and J. R. Long, *Angew. Chem. Int. Ed.*, 2007, **46**, 1419-1422.

63 K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly and J. R. Long, *Chemical Science*, 2010, **1**, 184-191.

64 M. Dincǎ and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172-11176.

65 E. V. Anokhina, M. Vougo-Zanda, X. Wang and A. J. Jacobson, *J. Am. Chem. Soc.*, 2005, **127**, 15000-15001.

66 S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon and F. Kapteijn, *J. Am. Chem. Soc.*, 2009, **131**, 6326-6327.

67 A. Ö. Yazaydın, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198-18199.

68 P. D. C. Dietzel, Y. Morita, R. Blom and H. Fjellvåg, *Angew. Chem. Int. Ed.*, 2005, **44**, 6354-6358.

69 P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom and H. Fjellvag, *Chem. Commun.*, 2006, DOI: Doi 10.1039/B515434k, 959-961.

70 J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, 2011, **4**, 3030-3040.

71 M. Kramer, U. Schwarz and S. Kaskel, *J. Mater. Chem.*, 2006, **16**, 2245-2248.

72 J. I. Feldblyum, M. Liu, D. W. Gidley and A. J. Matzger, *J. Am. Chem. Soc.*, 2011, **133**, 18257-18263.

73 L. Xie, S. Liu, C. Gao, R. Cao, J. Cao, C. Sun and Z. Su, *Inorg. Chem.*, 2007, **46**, 7782-7788.

74 L. J. Murray, M. Dinca, J. Yano, S. Chavan, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7856-7857.

75 K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2012, **24**, 3153-3167.

76 H. Jasuja, Y.-g. Huang and K. S. Walton, *Langmuir*, 2012, **28**, 16874-16880.

77 N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, DOI: Doi 10.1039/B203193k, 401-404.

78 H. X. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, **327**, 846-850.

79 Z. X. Zhao, Z. Li and Y. S. Lin, *Ind. Eng. Chem. Res.*, 2009, **48**, 10015-10020.

80 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276-279.

81 M. Eddaoudi, H. L. Li and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 1391-1397.

82 S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 14176-+.

83 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998-17999.

84 S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700-7702.

85 S. Biswas, T. Ahnfeldt and N. Stock, *Inorg. Chem.*, 2011, **50**, 9518-9526.

86 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schroder, *J. Am. Chem. Soc.*, 2009, **131**, 2159-2171.

87 X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schröder, *Angew. Chem. Int. Ed.*, 2006, **45**, 7358-7364.

88 Y. Zhao, H. Wu, T. J. Emge, Q. Gong, N. Nijem, Y. J. Chabal, L. Kong, D. C. Langreth, H. Liu, H. Zeng and J. Li, *Chem. Eur. J.*, 2011, **17**, 5101-5109.

89 R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875-+.

90 D. Farrusseng, C. Daniel, C. Gaudillère, U. Ravon, Y. Schuurman, C. Mirodatos, D. Dubbeldam, H. Frost and R. Q. Snurr, *Langmuir*, 2009, **25**, 7383-7388.

91 E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon and F. Kapteijn, *Langmuir*, 2011, **27**, 3970-3976; R. Babarao, C. J. Coghlan, D. Rankine, W. M. Bloch, G. K. Gransbury, H. Sato, S. Kitagawa, C. J. Sumby, M. R. Hill and C. J. Doonan, *Chem. Commun.*, 2014, **50**, 3238-3241.

92 B. Li, Z. Zhang, Y. Li, K. Yao, Y. Zhu, Z. Deng, F. Yang, X. Zhou, G. Li, H. Wu, N. Nijem, Y. J. Chabal, Z. Lai, Y. Han, Z. Shi, S. Feng and J. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 1412-1415.

93 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **132**, 38-39.

94 J. Duan, Z. Yang, J. Bai, B. Zheng, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 3058-3060.

95 X. S. Wang, S. Q. Ma, K. Rauch, J. M. Simmons, D. Q. Yuan, X. P. Wang, T. Yildirim, W. C. Cole, J. J. Lopez, A. de Meijere and H. C. Zhou, *Chem. Mater.*, 2008, **20**, 3145-3152.

96 A. Demessence, D. M. D’Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784-8786.

97 Z. Lu, L. Du, B. Zheng, J. Bai, M. Zhang and R. Yun, *CrystEngComm*, 2013, **15**, 9348-9351.

98 D. F. Sun, S. Q. Ma, J. M. Simmons, J. R. Li, D. Q. Yuan and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 1329-1331.

99 D. Sun, Y. Ke, D. J. Collins, G. A. Lorigan and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 2725-2734.

100 B. Zheng, Z. Yang, J. Bai, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 7025-7027.

101 Z. Lu, L. Du, K. Tang and J. Bai, *Cryst. Growth Des.*, 2013, **13**, 2252-2255.

102 Y. Liu, J.-R. Li, W. M. Verdegaal, T.-F. Liu and H.-C. Zhou, *Chem. Eur. J.*, 2013, **19**, 5637-5643.

103 J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 5516-5521.

104 D. Zhao, D. Yuan, D. Sun and H.-C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 9186-9188.

105 M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2011, **112**, 782-835.

106 R. T. Yang, *Adsorbents: Fundamentals and Applications*, John Wiley & Sons, Inc., 2003.

107 S. S. Han, S.-H. Choi and A. C. T. van Duin, *Chem. Commun.*, 2010, **46**, 5713-5715.

108 B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.*, 2007, **46**, 8490-8492.

109 Z. Zhang, S. Xiang, K. Hong, M. C. Das, H. D. Arman, M. Garcia, J. U. Mondal, K. M. Thomas and B. Chen, *Inorg. Chem.*, 2012, **51**, 4947-4953.

110 B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky, C. Liang, H. Zhu and S. Dai, *Inorg. Chem.*, 2007, **46**, 8705-8709.

111 M. Xue, S. Ma, Z. Jin, R. M. Schaffino, G.-S. Zhu, E. B. Lobkovsky, S.-L. Qiu and B. Chen, *Inorg. Chem.*, 2008, **47**, 6825-6828.

112 B. L. Chen, S. Q. Ma, F. Zapata, F. R. Fronczek, E. B. Lobkovsky and H. C. Zhou, *Inorg. Chem.*, 2007, **46**, 1233-1236.

113 B. L. Chen, S. C. Xiang and G. D. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115-1124.

114 S. K. Elsaidi, M. H. Mohamed, L. Wojtas, A. Chanthapally, T. Pham, B. Space, J. J. Vittal and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2014, **136**, 5072-5077.
115 S. Xiang, J. Huang, L. Li, J. Zhang, L. Jiang, X. Kuang and C.-Y. Su, *Inorg. Chem.*, 2011, **50**, 1743-1748.
116 J. F. Eubank, L. Wojtas, M. R. Hight, T. Bousquet, V. C. Kravtsov and M. Eddaoudi, *J. Am. Chem. Soc.*, 2011, **133**, 17532-17535.
117 S. D. Burd, S. Q. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2012, **134**, 3663-3666.