

Square Grid and Pillared Square Grid Coordination Polymers – Fertile Ground for Crystal Engineering of Structure and Function

Stephen D. Burd^a, Patrick S. Nugent^a, Mona H. Mohamed^{ab}, Sameh K. Elsaid^{ab}, and Michael J. Zaworotko^{*a}

Abstract: Square grid coordination polymers (CPs) based upon four-connected metal centres linked by linear bifunctional ligands such as 4,4'-bipyridine were first reported in 1990 and the study of their pillared variants began in 1995. It was quickly realized by crystal engineers that the modularity of such CPs creates families of related compounds or platforms which in turn affords opportunities for systematic study of structure/function relationships in the context of catalysis, magnetism and porosity. This review covers the historical development of this important class of CPs before addressing recent studies of variants which incorporate 4,4'-bipyridine and related linkers to facilitate control over pore size and inorganic anion pillars to enable strong interactions with polarizable molecules such as CO₂. Such pillared CPs offer relatively low cost, high stability and modularity. When these features are coupled with superior performance vs. other classes of porous materials in the context of carbon capture and other gas separations involving CO₂, they are likely to gain increased attention in the future.

Keywords: Carbon capture · Coordination polymer · Crystal engineering · Network · Porosity

Introduction

The study of the influence of molecular structure upon crystal packing, crystal structure and physicochemical properties is called *crystal engineering*.^[1] Whereas crystal engineering until recently tended to focus upon design of structure, it is now becoming evident that when the nature of the molecules or ions in a crystal structure renders aspects of the structure amenable to design, systematic control over bulk properties becomes feasible. In this context, *coordination polymers* (CPs)^[2] exemplify the power of crystal engineering to create custom-designed materials from first principles. CPs are typically comprised of metal cations, metal cluster molecular building blocks^[3] (MBBs) or metal-organic polyhedral supermolecular building blocks^[4] (SBBs). The MBBs or SBBs serve the geometric role of the node in a network and they are connected by

organic molecules, inorganic anions and/or metal complexes which serve as linkers. The design of CPs begins by judiciously selecting the right combination of metal/MBB/SBB and linker to afford control of the symmetry and dimensions of the structure. Diamondoid networks formed from tetrahedral metal centres and linear linkers such as 4,4'-bipyridine represent early examples of success in terms of structure design.^[5] However, it was the use of metal cluster MBBs that afforded framework solids with unprecedented permanent porosity^[6] as exemplified by HKUST-1^[7] and MOF-5.^[8] When permanent porosity is coupled with the inherent modularity of CPs, the resulting *metal-organic materials* (MOMs),^[6,8,9] also known as *porous coordination polymers*, PCPs,^[10] or, if all linkers are organic in nature, *metal-organic frameworks*, MOFs,^[11] become relevant to several contemporary challenges related to the environment and energy: i) reducing the cost of energy consumption associated with commodity production (e.g. through improved heterogeneous catalytic processes^[12] or through physisorption that will enable improved separation methods);^[13] ii) enabling more efficient, less-polluting means of energy production (e.g. carbon capture)^[14] and transportation (e.g. methane or hydrogen storage for vehicular transport);^[15] iii) development of electrically conductive porous materials (e.g. for use in physisorptive heat pumps, photoca-

talysis, environmental sensing and solar energy).^[16] In this contribution we review the development of one of the first generations of MOMs, square grid CPs,^[12b,17] and their pillared variants.^[18] Even though the prototypes of these compounds were first reported in 1990^[17] and 1995,^[18a] respectively, they remain at the cutting edge of MOMs research in terms of both design and properties because they offer extraordinary diversity in terms of composition along with exquisite control over pore size and functionality. Such a high degree of control over structure allows for systematic study of structure/function in a manner that represents a paradigm shift from the screening approaches traditionally used in materials science. Two specific classes of MOM are detailed herein:

Square Grid CPs

The prototypical square grid CP, [Zn(bipy)₂(H₂O)₂]_nSiF₆ (bipy = 4,4'-bipyridine), was reported by Robson and co-workers in 1990^[17] and is based upon the widely studied [M(pyridine)₄X₂] MBB (Fig. 1a). [M(pyridine)₄X₂] moieties in [Zn(bipy)₂(H₂O)₂]_nSiF₆ serve the role of four-connected square nodes that are linked at their vertices by bipy ligands. The cationic [Zn(bipy)₂(H₂O)₂]_n CP square grids contain nanoscale cavities (Fig. 1b) that facilitate two-fold inclined interpenetration of the CP networks (Fig. 1b). SiF₆²⁻ (SIFSIX) anions lie in the channels that are

*Correspondence: Prof. Dr. M. J. Zaworotko
Tel.: +1 813 974 3451

E-mail: xtal@usf.edu

^aUniversity of South Florida
Department of Chemistry
4202 E. Fowler Ave., CHE 205
Tampa, FL 33620, USA

^bAlexandria University
Chemistry Department, Faculty of Science
P.O. Box 426 Ibrahimia
Alexandria, 21321, Egypt

formed by the interpenetrated square grid CPs. Interpenetration is also a common feature in diamondoid CPs and angular or flexible linkers can result in corrugated grids which exhibit parallel interpenetration.^[19]

Studies concerning the properties of two-dimensional (2D) interpenetrated grids have tended to focus upon their magnetic behaviour and porosity. In 1995 the first observation of spin crossover in a porous CP^[20] was reported for the inclined interpenetrated material $[\text{Fe}(\text{bpe})_2(\text{NCS})_2]_n \cdot \text{CH}_3\text{OH}$, (bpe = 1,2-bis(4-pyridyl)ethene), while a 2002 study^[21] conducted upon an isostructural variant, $[\text{Fe}_2(\text{azbp})(\text{NCS})_4]_n \cdot (\text{guest})$, (guest = methanol, ethanol, propanol; azbp = 4,4'-azopyridine), revealed that adsorbed guest species could modulate spin crossover behaviour. Subsequent studies on related materials further elucidated the relationship between supramolecular interactions and cooperative magnetism.^[21,22]

Post-synthetic modification (PSM) of 2D interpenetrated grids aimed at enhancing their functionality and providing insight into structure/function relationships has been demonstrated *via* both anion-mediated transformation and anion exchange. PSM *via* anion substitution afforded access to new CPs whereas the latter allowed for systematic comparison of the properties (*e.g.* adsorption, catalysis) of isostructural variants. Kitagawa and co-workers^[23] demonstrated that $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]_n (\text{SiF}_6)$ undergoes a reversible structural transformation upon exchange of SiF_6^{2-} with SO_4^{2-} or PF_6^- . Indeed, anion or solvent exchange of the parent material results in its transformation into one of three CPs. The parent compound and its derivatives are interconvertible, *i.e.* each may be modified under specific conditions to form any of the others. Another interpenetrated variant, $[\text{Cu}(\text{bpgly})_2(\text{H}_2\text{O})_2]_n (\text{SiF}_6)$, (bpgly = meso- α,β -di(4-pyridyl)glycol), readily exchanges SiF_6^{2-} for NO_3^- while retaining its structure. The SiF_6^{2-} and NO_3^- analogues each adsorb light alcohol vapors and exhibit catalytic properties comparable to a related homogeneous system.^[24] The difference in adsorption and catalytic properties observed between the variants was attributed to the effect upon pore size imparted by the varying size of the counterions.

The relationship between structure and synthetic conditions in 2D interpenetrated grids has also been examined. In a noteworthy demonstration of control over supramolecular isomerism,^[1a] Chung and co-workers^[25] reported the synthesis and characterization of three CPs having the formula $[\text{Co}(\text{mpe})_2(\text{NCS})_2]_n$, (mpe = 1-methyl-1',2-bis(4-pyridyl)ethane). Each supramolecular isomer was obtained in pure form through variation of pre-synthet-

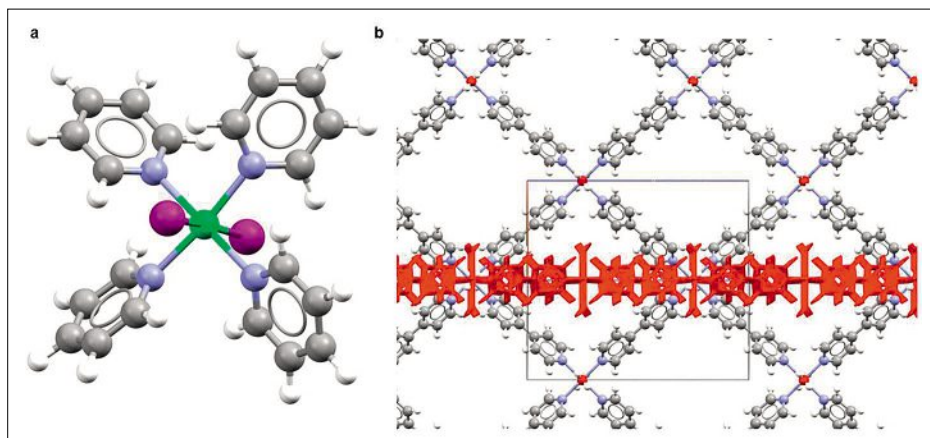


Fig. 1. a) $[\text{M}(\text{pyridine})_4\text{X}_2]\text{MBB}$, b) crystal structure of $[\text{Zn}(\text{bipy})_2(\text{H}_2\text{O})_n]$ square grid coordination polymers exhibiting two-fold inclined interpenetration.

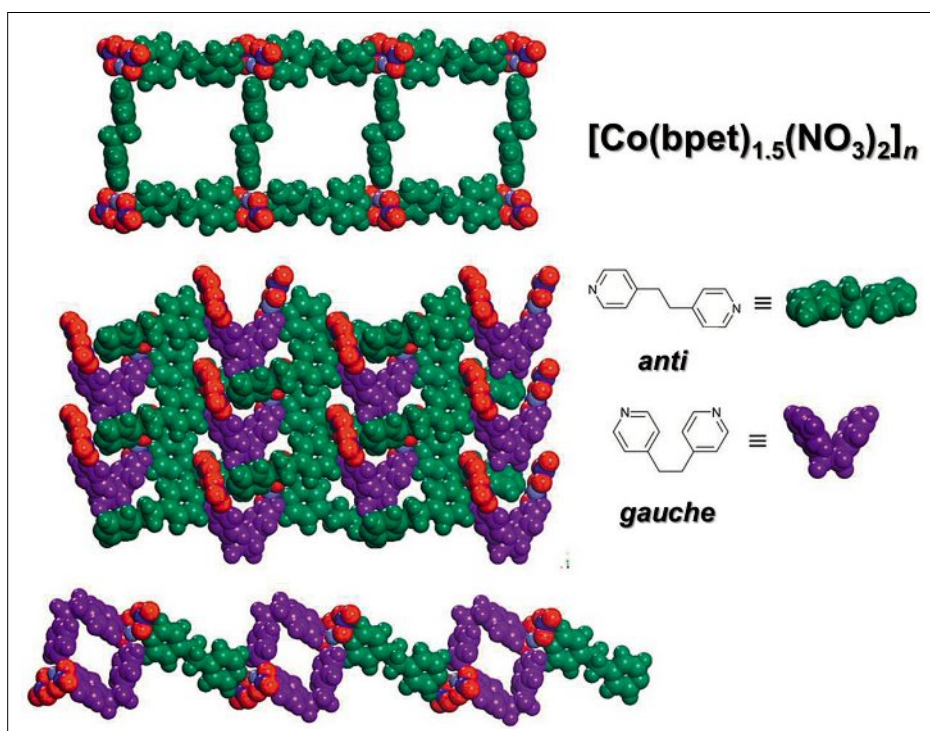


Fig. 2. Supramolecular isomerism in $[\text{Co}(\text{bpet})_{1.5}(\text{NO}_3)_2]_n$ yields three completely different networks with the same molecular formula.

ic (concentration, diffusion rate) or post-synthetic conditions. This set of supramolecular isomers consisted of both 2D interpenetrated and non-interpenetrated forms of square grids. Zaworotko and co-workers also showed control over supramolecular isomerism by exploiting conformational freedom in 1,2-bis(4-pyridyl)ethane (bpet) in $[\text{Co}(\text{bpet})_{1.5}(\text{NO}_3)_2]_n$ to yield three isomeric CPs (Fig. 2) that result from linking the three-connected Co(II) centres: chains, ladders, and bilayers.^[26]

The generation of non-interpenetrated square grid CPs that contain large cavities was first demonstrated by Fujita and co-workers in 1994.^[12b] Fujita's prototypical compound, $[\text{Cd}(\text{bipy})_2(\text{NO}_3)_2]_n$ (Fig. 3a), serves as a heterogeneous catalyst for cyanosilylation of aldehydes and is perhaps the first example of the use of a

MOM in the context of heterogeneous catalysis. Furthermore, $[\text{Cd}(\text{bipy})_2(\text{NO}_3)_2]_n$ forms clathrates with aromatic organic molecules and its square cavity exhibits shape-selective inclusion since it preferentially clathrates *o*-dibromobenzene over its *meta*- and *para*-isomers. A related study by Zaworotko and co-workers^[27] reported square grid CPs of formula $[\text{Ni}(\text{bipy})_2(\text{NO}_3)_2]_n$ that were prepared in the presence of a variety of guest molecules such as pyrene, naphthalene, chlorobenzene, *o*-dichlorobenzene, benzene, toluene, anisole and nitrobenzene (Fig. 3b). This study revealed that, depending on host-guest stoichiometry, the CPs exhibited clay-like behaviour with stacking distance between adjacent square grids varying from 6 to 8 Å. Moreover, the guest molecules in some of these CPs form

complementary noncovalent networks by interacting with each other *via* aromatic stacking interactions. The noncovalent networks of guest molecules were found to interpenetrate the square grid CP networks and were seen to be responsible for the orientation and stacking distance of adjacent CP networks.

A lesson learned from these studies is that the controllable and modular nature of square grid CPs makes them a family or platform of compounds that retains its network structure but is highly amenable to systematic modification through metal, ligand and/or counterion substitution. The use of extended ligands to further develop this platform was demonstrated in elegant fashion by Fujita and co-workers, who synthesized expanded variants of 4,4'-bipyridine and prepared CPs with cavity dimensions of up to 20 Å (Fig. 3c,d).^[28] The expanded variants were observed to retain structure even after removal of the guest molecules and they established how pore size can be readily controlled through the length of the linker in a CP platform. In addition to pore size control, pore functionality (chemistry) can also be controlled. Three approaches have thus far been applied: decoration of the linker with a chiral moiety to form a homochiral network;^[29] incorporation of carboxylate anions into the square cavity;^[30] substitution of the axial ligand. Numerous properties have been studied for square grid CPs including guest exchange,^[31] catalysis,^[32] gas sorption,^[33] spin crossover,^[34] magnetism,^[35] and luminescence.^[36]

In the late 1990s a new class of square grid CPs based upon dicarboxylate linkers and $[M_2(COO)_4]$ 'paddlewheel' MBBs was reported by Yaghi and co-workers (Fig. 4a).^[37] The prototypal such network, which was based upon 1,4-benzenedicarboxylate, was given the designation MOF-2 and represented one of the first examples of a permanently porous MOM.^[38] MOF-2 (Fig. 4b) was quickly followed by carboxylate-linked compounds such as HKUST-1^[7] and MOF-5^[8] that triggered a revolution in materials chemistry because they were found to exhibit unprecedented permanent porosity. The diversity of commercially available or readily synthesizable carboxylate ligands enabled carboxylate-based MOMs to dominate the field for the past decade but this subject is not the focus of this review. However, a relatively small subset of carboxylate-based MOMs, *i.e.* square grid CPs based upon dicarboxylate linkers and 'paddlewheel' MBBs, parallels research activity in the area of bipyridyl-linked square grid CPs and is addressed herein. In addition to the coordination chemistry around the node being different, there is one other salient difference between the two classes of

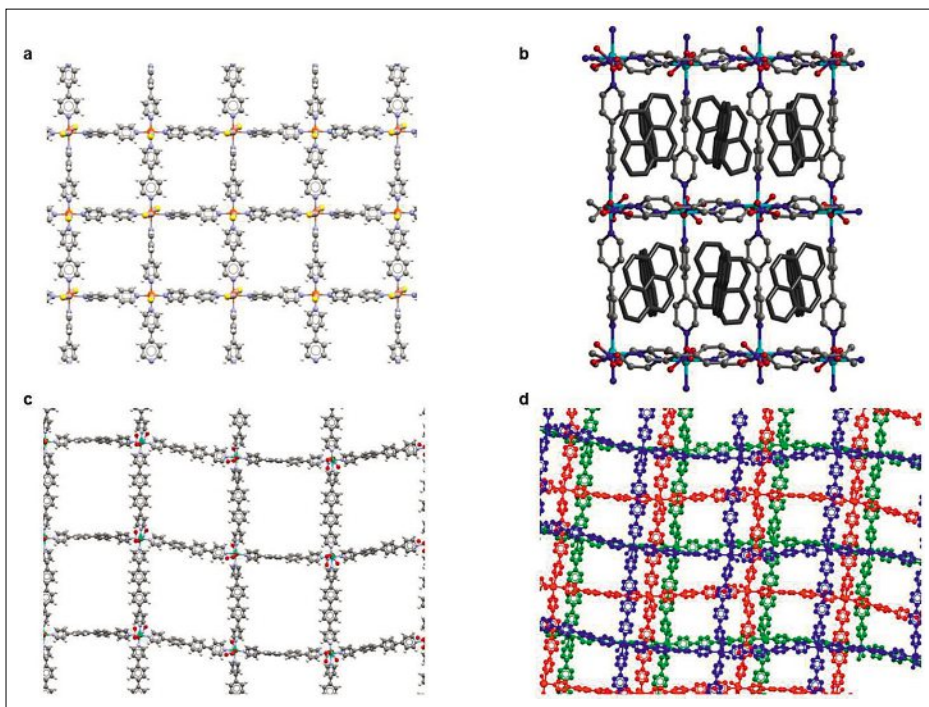


Fig. 3. a) Structural representation of $[Cd(bipy)_2(NO_3)_n]$, b) pyrene guest molecules in $[Ni(bipy)_2(NO_3)_2]_n$, c) crystal structure of a 20 Å pore in $[Cd(bbp)_2(NO_3)_2]_n$ (bbp = 4,4'-bis(4-pyridyl) biphenyl), d) layered sheets of c). Solvent molecules omitted for clarity.

square grid CPs: whereas bipyridyl-linked square grid CPs are cationic, carboxylate-linked square grid CPs based upon divalent metals are likely to be uncharged.^[39] This has important implications when addressing the chemistry used for cross-linking or pillaring of square grid CPs which is delineated in the next section. A summary of the types of bifunctional linker ligands that have been used to form square grid CPs is presented in Scheme 1.

Square Grid CPs that are Cross-linked by Linear Pillars

Square paddlewheel moieties and octahedral metal cations that are bonded to four pyridyl moieties serve the same structural role in the context of square grid CPs. Furthermore, both MBBs have open sites that are available for pillaring in the third dimension to afford three-dimensional (3D) primitive cubic (**pcu**) nets (three-letter codes used herein are defined by the RCSR database^[40]). However,

CPs based upon square paddlewheels are with very few exceptions uncharged and when cross-linked or pillared by neutral organic molecules such as 4,4'-bipyridine^[41] and 1,4-diazabicyclo[2.2.2]octane^[42] they generate neutral **pcu** nets as exemplified by DMOF-1^[43] (Fig. 4c). The size, shape, and physicochemical characteristics of the pores in such nets can be rationally tuned by judicious selection of both types of organic linker.^[42] For example, Nguyen and co-workers^[44] reported a series of Zn-based MOFs using functionalized 4,4'-ethynylene-dibenzoic acid linkers and 4,4'-bipyridine pillars that exhibited permanent porosity with Brunauer–Emmett–Teller (BET) surface areas of 650 m² g⁻¹ and 280 m² g⁻¹ for the dimethyl and dibromosubstituted ligands, respectively. Numerous examples of this MOM platform have been synthesized and many have been characterized in the context of their gas sorption and catalytic properties.^[41,45] Such compounds

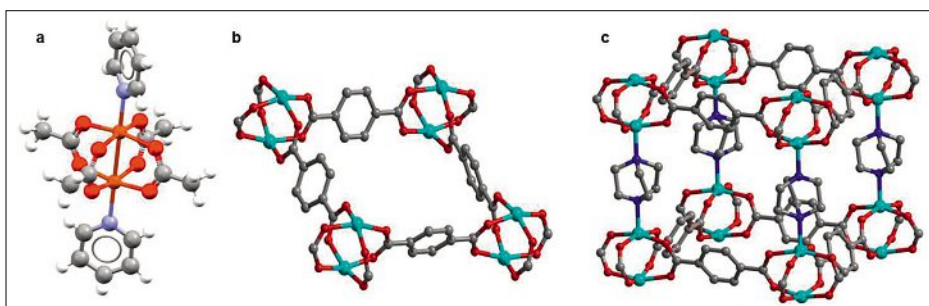
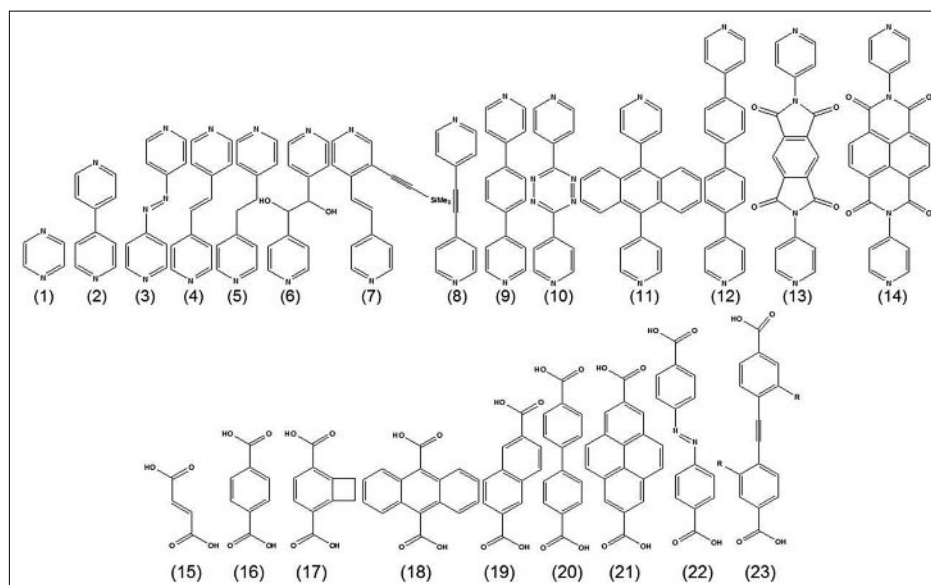


Fig. 4. a) $M_2(COO)_4$ paddlewheel MBB, b) crystal structure of MOF-2 and c) DMOF-1. Solvent molecules omitted for clarity. Colour code: C (grey), O (red), N (blue), Zn (teal).



Scheme 1. Diversity of dipyridyl- and dicarboxylate-based linkers used for the formation of square grid CPs. (1) Pyrazine, (2) 4,4'-bipyridine, (3) 4,4'-azo-bis(pyridine), (4) 1,2-bis(4-pyridyl)ethene, (5) 1,2-bis(4-pyridyl)ethane, (6) 1,2-di(pyridine-4-yl)ethane-1,2-diol, (7) 3-[[trimethylsilyl]ethynyl]-4-[2-(4-pyridinyl)ethenyl]pyridine, (8) 1,2-bis(4-pyridyl)ethyne, (9) 1,4-bis(4-pyridyl)benzene, (10) 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine, (11) 4-(9-(pyridin-4-yl)anthracen-10-yl)pyridine, (12) 4,4'-bis(4-pyridyl)biphenyl, (13) N,N'-bis(4-pyridyl)pyromellitic diimide, (14) N,N'-di(pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide, (15) fumaric acid, (16) terephthalic acid, (17) 1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid, (18) anthracene-9,10-dicarboxylic acid, (19) naphthalene-2,6-dicarboxylic acid, (20) 4,4'-biphenyldicarboxylic acid, (21) pyrene-2,7-dicarboxylic acid, (22) 4,4'-azodibenzoic acid, (23) 4,4'-(1,2-ethynediyl)bis(3-substituted benzoic acid).

represent prototypical examples of porous MOMs which contain saturated metal centres (SMCs) and exclusively organic linkers. Though this family of MOMs is capable of exhibiting high surface area, it does not typically exhibit high selectivity and/or uptake in the context of industrially relevant gases such as CO_2 , CH_4 , and H_2 . This is because such MOMs do not typically exhibit strong sorbent-sorbate interactions when compared to those exhibited by MOMs with unsaturated metal centres (UMCs) or, in the context of CO_2 , amine functionality. However, they remain eminently suitable for studying the effects of pore size and organic functionality upon gas adsorption.

Numerous reports have addressed how MOMs with UMCs (Fig. 5a) can enhance gas selectivity and uptake^[14a] since their empty metal orbitals have the ability to chemically interact with CO_2 molecules. MgDOBDC (DOBDC = 2,5-dihydroxyterephthalate), the Mg variant of MOF-74^[46] and CPO-27-Zn,^[47] exemplifies the profound impact that UMCs can exert upon carbon capture.^[48] Indeed, MgDOBDC is a benchmark MOM in terms of its high CO_2 uptake (35.2 wt%) and CO_2 heat of adsorption (Q_{st}) (42 kJmol^{-1}) at 298 K and 1 atm. The enhanced interaction of MgDOBDC with CO_2 molecules was attributed to the presence of Mg UMCs that, when coupled with decreased framework density vs. other MOF-74 variants, results in unrivalled CO_2 uptake. However, UMCs

have drawbacks: large energy demands for activation and regeneration; they typically bind more strongly to water molecules than to the target gas; selectivity can rapidly decrease with increased sorbate loading due to saturation of the UMCs. Indeed, MgDOBDC exhibits drastically decreased separation performance after just one to two separation cycles under humid conditions.^[49] In contrast, MOMs with SMCs rely upon weaker molecular recognition forces (physisorption) and such MOMs have also been widely screened for CO_2 adsorption and separations. Zeolitic imidazolate frameworks (ZIFs)^[50] are perhaps the best known class of MOMs with SMCs in this context. However, the relatively weak sorbent-sorbate interactions which are present in ZIFs lead to low selectivity for CO_2 vs. CH_4 , as well as to relatively low CO_2 uptake under ambient conditions.

Square grid CPs that are pillared by inorganic anions represent an alternate approach for the systematic study of selective

gas sorption to that offered by the presence of UMCs or neutral 3D nets based upon exclusively organic linkers. Such CPs also tend to exhibit pcu topology based upon six-connected saturated metal centre (SMC) nodes (Fig. 5b), however the electrostatics of their inorganic anions have the potential to drive gas selectivity in a manner similar to that of UMCs but without strong binding to water molecules. The prototypical example of such a pillared MOM platform, $[\text{Zn}(\text{bipy})_2(\text{SiF}_6)]_n$ (**SIFSIX-1-Zn**), contains SiF_6^{2-} pillars^[18a] and its Cu analogue, $[\text{Cu}(\text{bipy})_2(\text{SiF}_6)]_n$ (**SIFSIX-1-Cu**)^[18b] (Fig. 6a and 7b), was subsequently found to display relatively high CH_4 uptake. The nature of such MOMs affords even more opportunities for fine-tuning than square grid CPs because whereas they also offer control over pore size (by contracting or expanding the linker)^[51] and node (by substituting the SMC, *e.g.* Fe, Co, Ni, Cu, Zn and Cd), they can be fine-tuned by modifying the pillar (*e.g.* by use of other MF_6^{2-} anions).^[52] 3D MOMs with inorganic anion pillars remained relatively unstudied in the context of gas sorption until recently, presumably because their SMCs were viewed as being unlikely to offer strong selectivity and uptake. We have addressed this matter in a series of recent studies which reveal that certain inorganic anions can exhibit strong affinity towards CO_2 that rivals that of UMCs and amine groups.^[52,53] Modification of the anionic pillar *via* substitution of SiF_6^{2-} for GeF_6^{2-} , PF_6^- , and NO_3^- was reported by Noro *et al.* in 2002.^[23] This paper established the principle of tunability of the pillar. Modulation of pore size through isorecticular expansion or contraction in such pcu networks offers an opportunity for systematic investigation of the impact of pore size and chemistry in the context of important gas separations. A crystal engineering approach to generate new variants of these pcu nets facilitated our initial study of the effect of pore size upon CO_2/CH_4 selectivity.^[53a] We observed that a smaller pore/lower surface area/denser material (**SIFSIX-1-Cu**) adsorbs CO_2 with stronger affinity and better separation performance than its expanded, less dense isorecticular counterpart, $[\text{Cu}(\text{bpe})_2(\text{SiF}_6)]_n$ (**SIFSIX-4-Cu**, bpe = 1,2-bis(4-bipyridyl)ethene). Specifically,

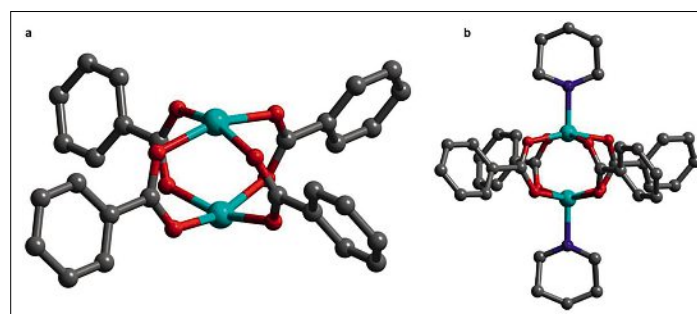


Fig. 5. a) Paddlewheel MBB with unsaturated metal centres (UMCs), b) paddlewheel MBB with saturated metal centres (SMCs).

SIFSIX-1-Cu adsorbs $\sim 118 \text{ cc g}^{-1} \text{ CO}_2$ under ambient conditions and exhibits a 50:50 CO_2/CH_4 selectivity of ~ 10.5 across the full loading range (as calculated by Ideal Adsorbed Solution Theory, IAST^[54]) whereas **SIFSIX-4-Cu** adsorbs much less CO_2 ($\sim 70 \text{ cc g}^{-1}$) and exhibits lower CO_2/CH_4 selectivity (~ 8). The increase in separation performance was attributed to smaller pore size enabling stronger electrostatic interactions between the electronegative fluorides and CO_2 molecules. It should also be noted that **SIFSIX-1-Cu** exhibits high CO_2 uptake in the general context of porous MOMs, especially among those with SMCs.^[14a]

In a separate study, we evaluated the impact upon CO_2 selectivity caused by substitution of the SiF_6^{2-} pillar in **SIFSIX-1-Cu** by TiF_6^{2-} (**TIFSIX**) and SnF_6^{2-} (**SNIFSIX**) *via* IAST calculations based upon pure gas adsorption isotherms, which revealed selectivity enhancements for 50:50 CO_2/CH_4 and 10:90 CO_2/N_2 gas mixtures,^[52] respectively. These mixture compositions mimic those found in biogas and post-combustion flue gas, respectively. **TIFSIX-1-Cu** (Fig. 6b) and **SNIFSIX-1-Cu** (Fig. 6c) adsorb ~ 106 and $\sim 94 \text{ cc g}^{-1}$ of CO_2 at 298 K and 1 atm and exhibit selectivities of 11.2 and 12.1 for 50:50 CO_2/CH_4 and 29.5 and 21.9 for 10:90 CO_2/N_2 , respectively. Both variants exhibit higher CO_2/CH_4 selectivities than **SIFSIX-1-Cu** (50:50 CO_2/CH_4 selectivity of 10.5 and 10:90 CO_2/N_2 selectivity of 26.5), while **TIFSIX-1-Cu** also exhibits higher CO_2/N_2 selectivity than **SIFSIX-1-Cu**. These observations were attributed to the greater polarizability of Ti^{4+} compared to Si^{4+} which in turn affords stronger interactions between CO_2 and the non-bonded equatorial fluorine atoms of the pillars.

These two studies prompted us to address how contraction of pore size might impact gas separation performance. $[\text{Zn}(\text{pyr})_2\text{SiF}_6]_n$,^[51b,55] pyr = pyrazine, (**SIFSIX-3-Zn**) (Fig. 7a) was found to exhibit exceptionally high heat of adsorption (Q_{st}) for CO_2 (45 kJ mol^{-1}) and in effect creates a thermodynamic and kinetic ‘sweet spot’ for CO_2 separations in process relevant applications like natural gas upgrading (5:95 CO_2/CH_4), biogas treatment (50:50 CO_2/CH_4), and post/pre-combustion carbon capture (10:90 CO_2/N_2 , 30:70 CO_2/H_2 , respectively).^[53c] **SIFSIX-3-Zn** exhibits 50:50 CO_2/CH_4 selectivity of 231 and 10:90 CO_2/N_2 selectivity of 1818, exceeding the performance of MgDOBDC (50:50 CO_2/CH_4 selectivity of 137)^[56] and an industrially used sorbent, zeolite 13X (50:50 CO_2/CH_4 selectivity of 103, 10:90 CO_2/N_2 selectivity of 420).^[57] Unparalleled selectivities for 5:95 CO_2/CH_4 (~ 200) and 30:70 CO_2/H_2 ($\sim 1,800$) gas mixtures were determined by IAST and validated by gas mixture experiments under process rel-

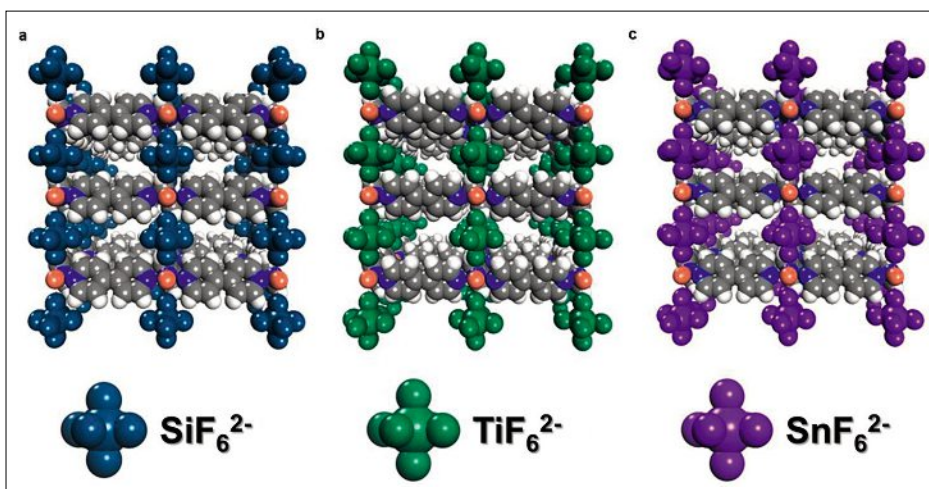


Fig. 6. Anionic pillar substitution in: a) $\text{Cu}(\text{bipy})_2\text{SiF}_6$ (**SIFSIX-1-Cu**), b) $\text{Cu}(\text{bipy})_2\text{TiF}_6$ (**TIFSIX-1-Cu**), c) $\text{Cu}(\text{bipy})_2\text{SnF}_6$ (**SNIFSIX-1-Cu**). Colour code: C (grey), N (blue), Cu (pink), H (white).

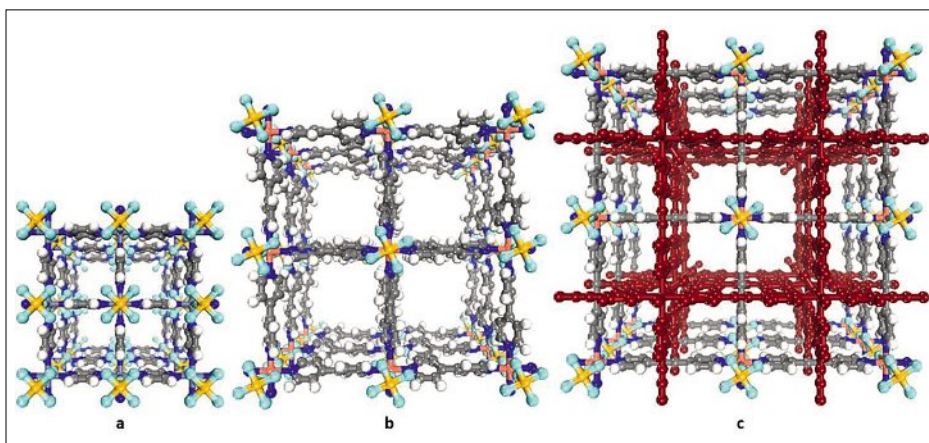


Fig. 7. C-axis view of: a) $\text{Zn}(\text{pyr})_2\text{SiF}_6$ (**SIFSIX-3-Zn**), b) $\text{Cu}(\text{bipy})_2\text{SiF}_6$ (**SIFSIX-1-Cu**), c) $\text{Cu}(\text{dpa})_2\text{SiF}_6$ (**SIFSIX-2-Cu-i**). Solvent molecules omitted for clarity. Colour code: C (grey), N (blue), Si (yellow), F (light blue), H (white), Cu (pink), Zn (purple).

evant conditions (50:50 CO_2/CH_4 , 10:90 CO_2/N_2 , 30:70 CO_2/H_2). **SIFSIX-3-Zn** also exhibits CO_2 saturation at a relatively low pressure ($\sim 0.3 \text{ atm}$), which approximates the partial pressure of CO_2 in post-combustion flue gas ($\sim 0.1 \text{ atm}$). Increasing the adsorption temperature to 338 K had little effect on CO_2 uptake and recycling experiments revealed reversible adsorption/desorption over many cycles with no loss of capacity. **SIFSIX-3-Zn** is therefore a superior sorbent for CO_2 vs. other porous materials under a variety of process relevant conditions.

In addition to judicious selection of the linker for pore size control and the anionic pillar for gas binding, **pcu** frameworks have the potential to be tuned *via* interpenetration. Whereas shorter linkers (*i.e.* pyrazine, 4,4'-bipyridine) have not been found to exhibit interpenetration when forming **pcu** networks, expanded linkers such as 1,2-bis(4-pyridyl)acetylene (bpa), may form doubly interpenetrated **pcu** networks.^[58] Control of pore size *via* interpenetration allowed us to compare the gas adsorption properties of the interpenetrat-

ed form of $[\text{Cu}(\text{bpa})_2(\text{SiF}_6)]_n$ (**SIFSIX-2-Cu-i**; BET surface area = $735 \text{ m}^2 \text{ g}^{-1}$) (Fig. 7c) with those of its non-interpenetrated polymorph (**SIFSIX-2-Cu**; BET surface area = $3140 \text{ m}^2 \text{ g}^{-1}$). In keeping with the adsorption relationship between **SIFSIX-1-Cu** and **SIFSIX-4-Cu**, the smaller pore/lower surface area/denser **SIFSIX-2-Cu-i** exhibits much higher CO_2 uptake ($\sim 121 \text{ cc g}^{-1}$ vs. $\sim 41 \text{ cc g}^{-1}$) when compared to **SIFSIX-2-Cu**. Indeed, the volumetric CO_2 uptake of **SIFSIX-2-Cu-i** approaches that of MgDOBDC (151 vs. 163 v/v), a material with far higher BET surface area (735 vs. $\sim 1500 \text{ m}^2 \text{ g}^{-1}$) which also possesses UMCs. Moreover, **SIFSIX-2-Cu-i** displays greatly enhanced 50:50 CO_2/CH_4 and 10:90 CO_2/N_2 selectivity in comparison to **SIFSIX-2-Cu** (140 and 33 vs. 13.7 and 5.3, respectively), which is attributed to increased sorbent–sorbate interactions in narrow pores vs. wide pores. The importance of the exceptional selectivity of several of these **SIFSIX** compounds is in some ways overshadowed by another feature: their relative water stability and hydrophobicity when compared to that

of most MOMs with UMCs,^[53a] **SIFSIX-2-Cu-i** and **SIFSIX-3-Zn** preferentially adsorb CO₂ over H₂O, a hitherto unprecedented finding in MOMs or zeolites.^[53c] Furthermore, **SIFSIX-2-Cu-i** is stable in water and thermally stable up to 573 K whereas **SIFSIX-3-Zn** undergoes a reversible phase change in the presence of water and is thermally stable up to 523 K.

Square Grid CPs Pillared by Angular Linkers

Square grid networks pillared by angular inorganic anions are much less explored than those based upon linear pillars.^[59] Historically, SO₄²⁻ has been the most widely used angular inorganic linker in CPs.^[60] [Cu(4,4'-bpy)(H₂O)₃(SO₄)_n·2H₂O (4,4'-bpy = 4,4'-bipyridine) and [Cu(bpe)(H₂O)(SO₄)_n] consist of four-connected metal nodes with two coordinated bipyridyl linkers (bpy or bpe) and two metals bridged *via* SO₄²⁻. A uninodal, six-connected net of formula [Cu(4-DPDS)₂(SO₄)₂·1.5H₂O·CH₃OH]_n (4-DPDS = 4,4'-bipyridinedisulfide), containing SO₄²⁻ linkers was also reported, wherein each Cu²⁺ centre bonds to four 4-DPDS linkers to form double-stranded chains of [Cu(4-DPDS)₂]_n. Strands are linked by SO₄²⁻ anions and the six-coordinate distorted octahedral environment affords a two-dimensional non-interpenetrated net. This net does not exhibit **pcu** topology due to the flexibility of 4-DPDS and the angular SO₄²⁻ linker.^[59c]

Other angular oxyanions such as CrO₄²⁻ and MoO₄²⁻ were unexplored as pillars until recently^[61] and remain nearly unexplored in the context of CPs in general. Indeed, a Cambridge Structural Database (CSD)^[62] survey revealed just three reports concerning MoO₄²⁻ acting as a linker and no examples for CrO₄²⁻. In this context, our group has recently studied pillaring of square grids using CrO₄²⁻ or MoO₄²⁻ (Fig. 8).^[53b] The resulting CPs, [M(bpe)₂(M'O₄)_n] (M = Co or Ni; M' = Cr or Mo), **CROFOUR-1-Ni** and **MOOFOUR-1-Ni**, respectively, are the prototypical examples of six-connected **mmo** topology nets. This new uninodal topology results from SMC nodes (Co or Ni) linked by bpe into square grids that are pillared by M'O₄²⁻ anions in an angular manner (112°). Adjacent square grids are thereby oriented in such a fashion that they self-catenate, while helical chains of alternating 6-c SMCs and M'O₄ pillars extend along the [001] direction (Fig. 8c, Fig. 9). These are the first six-connected nets with 4⁸·6⁷ topology and have been assigned the three-letter code **mmo** in the RCSR database. Each node metal is bound to four equatorial pyridyl groups (M–N ~2.12 Å) and to two axial M'O₄²⁻ pillars (Ni–O ~2.04

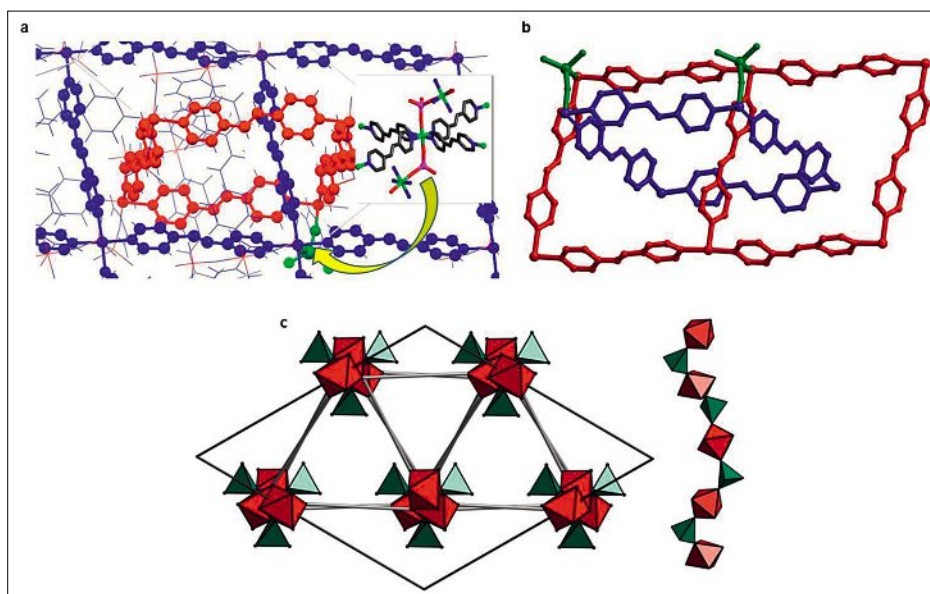


Fig. 8. a) and b) Schematic representations of the self-catenation of square grids in an **mmo** net. c) Polyhedral representation of a 6-c **mmo** net along [001] (left) and a chiral helix of alternating octahedral SMCs (red) and M'O₄ moieties (green) (right).

Å and ~2.03 Å for **CROFOUR-1-Ni** and **MOOFOUR-1-Ni**, respectively). These MOMs retain crystallinity even when immersed in water for months, boiling water for one day, 0.1 M NaOH for a week, or 0.01 M HCl for one day. Our experience with SiF₆²⁻ pillared nets prompted us to evaluate the gas sorption properties of **MOOFOUR-1-Ni** and **CROFOUR-1-Ni**. The pores contain energetically favourable sites for CO₂ binding at low loading and exhibit exceptionally high Q_{st} at zero loading and 298 K: 56 and 50 kJ mol⁻¹ for **MOOFOUR-1-Ni** and **CROFOUR-1-Ni**, respectively. Such values exceed even those of most MOMs with UMCs such as HKUST-1,^[14a] MIL-53(Al),^[63] Mg-MOF-74,^[48] Co-MOF-74^[48] and Ni-MOF-74.^[48] IAST calculations for CO₂/CH₄ in a 50:50 mixture at 298 K revealed zero coverage selectivities of 182 and 170 for **MOOFOUR-1-Ni** and **CROFOUR-1-Ni**, respectively. The corresponding values at 1 atm were found to be 40 and 25. The zero loading CO₂/N₂ selectivities for a 10:90 mixture were found to be 1820 and 1240 for **MOOFOUR-1-Ni** and **CROFOUR-1-Ni**, respectively, and they decrease to 86 and 195 at 1 atm. Whereas MOMs are known that exhibit higher CO₂ uptake, we are unaware of any that exhibit such high selectivity at low loading. The CO₂/N₂ selectivity in the context of post-combustion capture, calculated as the ratio of wt% of CO₂ adsorbed at 0.15 bar to that of N₂ adsorbed at 0.75 bar, was revealed to be 67 and 62 for **MOOFOUR-1-Ni** and **CROFOUR-1-Ni**, respectively. These values surpass those of most MOMs that contain UMCs including Mg-MOF-74 (44 at 303 K) and some amine-grafted MOMs. These observations were attributed to

strong quadrupole–quadrupole interactions between CO₂ and MO₄²⁻ and further suggest the importance of inorganic anions in the crystal engineering and sorption behaviour of porous CPs.

In summary, square grid CPs and their pillared variants have been known since 1990 and 1995, respectively, yet they remain underexplored as platforms when compared to the vast landscape of structures represented by carboxylate-based CPs and MOFs. However, their amenability to design using crystal engineering principles means that exquisite control over pore size and pore chemistry is possible. Furthermore, they represent relatively inexpensive, facile-to-synthesize, robust structures, which make them eminently suited for systematic studies of gas sorption in such a manner that ‘apple vs. apple’ comparisons are feasible. This appealing crystal engineering opportunity has enabled several recent studies that focused upon pillared square grid CPs as CO₂ adsorb-

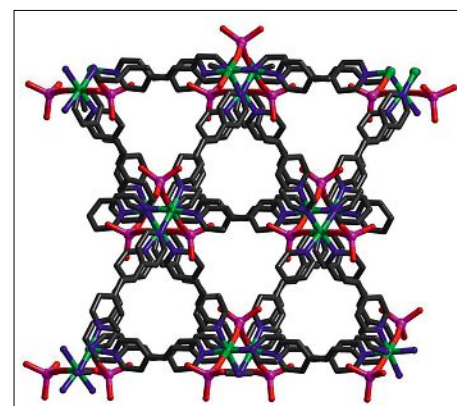


Fig. 9. A view of **MOOFOUR-1-Ni** structure along [001], H atoms omitted for clarity.

bents and shown that they offer favourable performance even in the context of CPs or MOFs with UMCs or amine groups. Given their inherently modular nature and the many inorganic anions that remain unexplored in the context of CPs, it seems likely that both of these CP platforms represent a class of hybrid organic–inorganic materials that will have strong future relevance in terms of both fundamental and applied research.

Received: March 20, 2013

- [1] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; b) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311; c) G. R. Desiraju, *Angew. Chem., Int. Ed.* **2007**, *46*, 8342.
- [2] S. R. Batten, S. M. Neville, D. R. Turner, 'Coordination Polymers: Design, Analysis and Application', Royal Society of Chemistry, Cambridge, **2009**.
- [3] a) G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792; b) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schroder, *Coord. Chem. Rev.* **1999**, *183*, 117.
- [4] a) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 1833; b) J. J. Perry, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400; c) A. J. Cairns, J. A. Perman, L. Wojtas, V. C. Kravtsov, M. H. Alkordi, M. Eddaoudi, M. J. Zaworotko, *J. Am. Chem. Soc.* **2008**, *130*, 1560; d) B. L. Chen, N. W. Ockwig, F. R. Fronczek, D. S. Contreras, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 181; e) J. Park, S. Hong, D. Moon, M. Park, K. Lee, S. Kang, Y. Zou, R. P. John, G. H. Kim, M. S. Lah, *Inorg. Chem.* **2007**, *46*, 10208.
- [5] M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, *23*, 283.
- [6] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. Yazaydin, J. T. Hupp, *J. Am. Chem. Soc.* **2012**, *134*, 15016.
- [7] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.
- [8] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
- [9] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.
- [10] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- [11] L. R. Macgillivray, 'Metal-Organic Frameworks: Design and Application', John Wiley & Sons, **2010**.
- [12] a) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248; b) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151.
- [13] J. R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869.
- [14] a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724; b) J. R. Li, Y. G. Ma, M. C. McCarthy, J. Sculley, J. M. Yu, H. K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **2011**, *255*, 1791; c) J. R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477.
- [15] a) D. Collins, H.-C. Zhou, *J. Mater. Chem.* **2007**, *17*, 3154; b) U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle Arndt, *J. Mater. Chem.* **2006**, *16*, 626.
- [16] G. Givaja, P. Amo-Ochoa, C. J. Gomez-Garcia, F. Zamora, *Chem. Soc. Rev.* **2012**, *41*, 115.
- [17] R. W. Gable, B. F. Hoskins, R. Robson, *Chem. Commun.* **1990**, *23*, 1677.
- [18] a) S. Subramanian, M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127; b) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem., Int. Ed.* **2000**, *39*, 2082.
- [19] a) O.-S. Jung, S. H. Park, D. C. Kim, K. M. Kim, *Inorg. Chem.* **1998**, *37*, 610; b) M. J. Plater, M. R. S. Foreman, A. M. Z. Slawin, *J. Chem. Res.* **1999**, *74*.
- [20] J. A. Real, E. Andres, M. C. Munoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* **1995**, *268*, 265.
- [21] G. J. Halder, K. W. Chapman, S. M. Neville, B. Moubaraki, K. S. Murray, J. F. Letard, C. J. Kepert, *J. Am. Chem. Soc.* **2008**, *130*, 17552.
- [22] a) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2009**, *131*, 12106; b) S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, P. D. Southon, J. D. Cashion, J. F. Letard, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2008**, *130*, 2869; c) S. M. Neville, B. Moubaraki, K. S. Murray, C. J. Kepert, *Angew. Chem., Int. Ed.* **2007**, *46*, 2059.
- [23] S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568.
- [24] S. Wang, L. Li, J. Zhang, X. Yuan, C. Y. Su, *J. Mater. Chem.* **2011**, *21*, 7098.
- [25] D. M. Shin, I. S. Lee, D. Cho, Y. K. Chung, *Inorg. Chem.* **2003**, *42*, 7722.
- [26] T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers, M. J. Zaworotko, *Angew. Chem., Int. Ed.* **1997**, *36*, 972.
- [27] K. Biradha, A. Mondal, B. Moulton, M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.* **2000**, 3837.
- [28] a) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem., Int. Ed.* **2000**, *39*, 3843; b) K. Biradha, M. Fujita, *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 201; c) M. Fujita, M. Aoyagi, K. Ogura, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1799; d) K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 15.
- [29] N. G. Pschirer, D. M. Ciurtin, M. D. Smith, U. H. F. Bunz, H. C. zur Loye, *Angew. Chem., Int. Ed.* **2002**, *41*, 583.
- [30] a) O. Fabelo, J. Pasan, L. Canadillas-Delgado, F. S. Delgado, C. Yuste, F. Lloret, M. Julve, C. Ruiz-Perez, *CrystEngComm* **2009**, *11*, 2169; b) O. Fabelo, J. Pasan, F. Lloret, M. Julve, C. Ruiz-Perez, *CrystEngComm* **2007**, *9*, 815.
- [31] a) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem., Int. Ed.* **2002**, *41*, 3395; b) K. Uemura, S. Kitagawa, K. Fukui, K. Saito, *J. Am. Chem. Soc.* **2004**, *126*, 3817.
- [32] O. Ohmori, M. Fujita, *Chem. Commun.* **2004**, 1586.
- [33] H. Kajiro, A. Kondo, K. Kaneko, H. Kanoh, *Int. J. Mol. Sci.* **2010**, *11*, 3803.
- [34] a) C. J. Adams, J. A. Real, R. E. Waddington, *CrystEngComm* **2010**, *12*, 3547; b) J. B. Lin, W. Xue, B. Y. Wang, J. Tao, W. X. Zhang, J. P. Zhang, X. M. Chen, *Inorg. Chem.* **2012**, *51*, 9423.
- [35] J. A. Real, G. Demunno, M. C. Munoz, M. Julve, *Inorg. Chem.* **1991**, *30*, 2701.
- [36] G. J. McManus, J. J. Perry, M. Perry, B. D. Wagner, M. J. Zaworotko, *J. Am. Chem. Soc.* **2007**, *129*, 9094.
- [37] M. Eddaoudi, H. L. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391.
- [38] H. Li, M. Eddaoudi, T. L. Groy, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571.
- [39] a) M. E. Braun, C. D. Steffek, J. Kim, P. G. Rasmussen, O. M. Yaghi, *Chem. Commun.* **2001**, 2532; b) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4900.
- [40] a) M. O'Keeffe, O. M. Yaghi, *Chem. Rev.* **2012**, *112*, 675; b) M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* **2008**, *41*, 1782.
- [41] B. Q. Ma, K. L. Mulfort, J. T. Hupp, *Inorg. Chem.* **2005**, *44*, 4912.
- [42] H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. Eur. J.* **2005**, *11*, 3521.
- [43] D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem., Int. Ed.* **2004**, *43*, 5033.
- [44] T. Gadzikwa, B. S. Zeng, J. T. Hupp, S. T. Nguyen, *Chem. Commun.* **2008**, 3672.
- [45] T. Gadzikwa, G. Lu, C. L. Stern, S. R. Wilson, J. T. Hupp, S. T. Nguyen, *Chem. Commun.* **2008**, 5493.
- [46] N. L. Rosi, J. Kim, M. Eddaoudi, B. L. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504.
- [47] P. D. C. Dietzel, R. E. Johnsen, R. Blom, H. Fjellvag, *Chem. Eur. J.* **2008**, *14*, 2389.
- [48] S. R. Caskey, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2008**, *130*, 10870.
- [49] A. Kizzie, A. Wong-Foy, A. Matzger, *Langmuir* **2011**, *27*, 6368.
- [50] a) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 3875; b) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939.
- [51] a) M. J. Lin, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, *CrystEngComm* **2009**, *11*, 189; b) K. Uemura, A. Maeda, T. K. Maji, P. Kanoo, H. Kita, *Eur. J. Inorg. Chem.* **2009**, 2329.
- [52] P. Nugent, V. Rhodus, T. Pham, B. Tudor, L. Wojtas, K. Forrest, B. Space, M. J. Zaworotko, *Chem. Commun.* **2013**, *49*, 1606.
- [53] a) S. D. Burd, S. Ma, J. A. Perman, B. J. Sikora, R. Q. Snurr, P. K. Thallapally, J. Tian, L. Wojtas, M. J. Zaworotko, *J. Am. Chem. Soc.* **2012**, *134*, 3663; b) M. H. Mohamed, S. K. Elsaidi, L. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space, M. J. Zaworotko, *J. Am. Chem. Soc.* **2012**, *134*, 19556; c) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, M. J. Zaworotko, *Nature* **2013**, *495*, 80.
- [54] A. L. Myers, J. M. Prausnitz, *AIChE J.* **1965**, *11*, 121.
- [55] P. Kanoo, S. K. Reddy, G. Kumari, R. Haldar, C. Narayana, S. Balasubramanian, T. K. Maji, *Chem. Commun.* **2012**, *48*, 8487.
- [56] Z. Herm, J. Swisher, B. Smit, R. Krishna, J. Long, *J. Am. Chem. Soc.* **2011**, *133*, 5664.
- [57] S. Cavenati, C. A. Grande, A. E. Rodrigues, *J. Chem. Eng. Data* **2004**, *49*, 1095.
- [58] M. J. Lin, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, *CrystEngComm* **2011**, *13*, 776.
- [59] a) D. Bradshaw, J. E. Warren, M. J. Rosseinsky, *Science* **2007**, *315*, 977; b) L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *CrystEngComm* **2003**, *5*, 190; c) J. H. Luo, M. C. Hong, R. H. Wang, D. Q. Yuan, R. Cao, L. Han, Y. Q. Xu, Z. Z. Lin, *Eur. J. Inorg. Chem.* **2003**, 3623.
- [60] D. Hargman, R. P. Hammond, R. Haushalter, J. Zubieta, *Chem. Mater.* **1998**, *10*, 2091.
- [61] a) R. N. Devi, J. Zubieta, *Inorg. Chim. Acta* **2002**, *332*, 72; b) Y. Gong, T. Liu, W. Tang, F. Wu, W. Gao, C. Hua, *J. Solid State Chem.* **2007**, *180*, 1476; c) M. C. Laskoski, R. L. LaDuca, R. S. Rarig, J. Zubieta, *J. Chem. Soc., Dalton Trans.* **1999**, 3467.
- [62] a) F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 380; b) F. H. Allen, W. D. S. Motherwell, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 407.
- [63] S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2009**, *131*, 6326.