JOHNSON MATTHEY
TECHNOLOGY REVIEW

247th American Chemical Society National Meeting and Exposition: Part II

Metal organic framework coverage from the ACS spring conference on 'Chemistry and Materials for Energy'

Reviewed by Ian Casely

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH, UK

Email: ian.casely@matthey.com

Introduction

American Chemical Society National Meetings and Expositions are held twice a year in spring and autumn and constitute the largest gathering of chemical scientists at any point in the conference calendar. This year the 247th meeting (1) was held from 16th–20th March 2014, hosted at the Dallas Convention Centre, Texas, USA. The overarching theme of the conference was Chemistry and Materials for Energy which was reflected in the focus of the Plenary and Kavli Foundation sponsored Lectures.

This selective review will focus on metal organic frameworks (MOFs), covering a range of synthetic and applied work. Part I of this review covered a range of biomass related work and was published previously (2).

Stability and Purification

MOFs are a relatively new class of highly ordered crystalline solids consisting of metal ions or metal-oxo clusters linked together by organic linkers (3). The resulting highly porous structures contain numerous accessible channels and pores which make them interesting candidates for myriad applications including gas separation and storage, catalysis and sensing.

Jared DeCoste (Leidos Inc, USA) presented an overview of the use of MOFs in air purification of toxic chemicals and in particular focused on efforts to overcome the common issue of water stability applied to real situations (4). Current focus on respiratory protection masks is concerned not just with chemical weapons protection in military applications but also toxic industrial chemicals in a much broader context, including ammonia, carbon monoxide and volatile sulfur and phosphorous gases. Typically activated carbon has been widely used and modern formulations involve impregnating the carbon with a range of different metal salts and amines to optimise the range of protection. Although the performance of any sorbent for the removal of toxic chemicals is critical, they also need to withstand high humidity and temperature during storage as well as in use (with no decrease in their efficacy) and be robust to rough handling without creating dust. MOFs have garnered much interest for respiratory applications recently as they typically have highly porous structures which makes them ideal for gas sorption, they are highly tuneable in terms of metals, linkers and incorporated functional groups and can show significant thermal stability.

The water stability of MOFs has been studied extensively, but great focus has been placed on copper-1,3,5-benzenetricarboxylate ($Cu_3(BTC)_2$) referred to as Cu-BTC probably due to its superior chemical removal capabilities and that its water degradation is on a slow timescale making it conducive to systematic study. The adsorption capacity of Cu-BTC has been experimentally found to be between 27–32 mmol g^{-1} at 298 K and to occur

via two energetically distinct processes, with water molecules firstly coordinating to the metal site and subsequently filling the pores. Water coordinates to the metal centres along the Cu-Cu axis in the bimetallic paddlewheel structure and results in a colour change from dark purple to light blue as the dehydrated material is exposed to moisture. At 40% relative humidity (RH) and 313 K very little degradation occurs over 28 days, whereas at 90% RH and 298 K the structure is almost completely destroyed within two weeks. This process was tracked by X-ray diffraction (XRD) which showed a new structure had been formed, as well as infrared (IR) showing the formation of protonated carboxylic acid groups and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) which showed the presence of numerous aromatic and carboxylic acid resonances remote from the Cu centres.

In Cu-BTC, ligand functionalisation is not as simple as just changing the functional groups on the linker due to increased steric hindrance and unfavourable reaction conditions during synthesis. Therefore post-synthesis modification needs to be used and one approach has used plasma-enhanced chemical vapour deposition (PECVD) using perfluoroalkanes to coat the surface and pores of Cu-BTC, thereby enhancing the water stability (5). Material treated in this way displays superhydrophobicity by floating on water and also shows an increased contact angle on a pressed pellet from around 60º to 120º, **Figure 1**.

Incorporation of these hydrophobic fluorinated groups renders the material stable in liquid water over 24 h compared to the complete degradation of untreated Cu-BTC and the ammonia removal capacity was not affected. After ageing at 100% RH and 313 K for three days this material showed an ammonia removal capacity almost five times greater than the untreated material, due to the structure being more robust over time.

Post Synthetic Modifications

One of the big challenges in current MOF research is chemists having at their disposal enough synthetic routes to access any desired new materials and structures. Common problems with traditional techniques such as solvothermal synthesis are a limit on the type of functional ligands that can be used. Incorporating coordinatively unsaturated metal centres can be difficult due to reaction with many multitopic
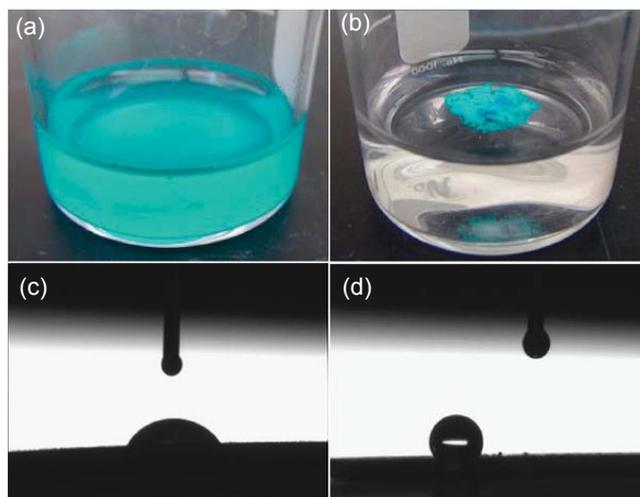

Fig. 1. Pictures of Cu-BTC: (a) dispersed in water; (b) treated with C_2F_6-plasma, repelling and floating on top of water. Contact angle images of: (c) Cu-BTC; and (d) C_2F_6-plasma-treated Cu-BTC with 2 µl droplet of water (Reprinted with permission from (4). Copyright (2014) American Chemical Society)

linkers and in some cases difficulty in controlling the arrangement of metals and linkers as the low-energy structure is not always the desired product.

A number of different procedures have been developed to mitigate these issues and recently post-synthetic modification of the linker or metal has proven successful. Joseph Hupp (Northwestern University, USA) presented work on solvent assisted linker exchange (SALE), a straightforward technique whereby a parent MOF crystal is exposed to the desired linker in a carefully chosen solvent where the aim is to produce a new MOF material possessing the topology of the parent structure but incorporating the linkers from the reaction solution (6). A challenging target in this area is the incorporation of a variety of longer linkers into a structure and pillared-paddlewheel MOFs have proven to be a facile means by which to study this. **Scheme I** shows the range of linkers examined and structures formed, starting from solvent-assisted linker exchanged material-5 (SALEM-5) which was itself formed by SALE from a previously isolated MOF *via* exchange with linker L1, creating pillars approximately 9 Å long. In particular, this work aimed to investigate the incorporation of longer linkers and the effect of pK_a of the conjugate acid of the pillar.

Reaction of SALEM-5 with a four-fold excess of the 11 Å long pillar L3 was conducted in dimethylformamide (DMF) and after 24 h at 100°C, ^{1}H NMR spectroscopy

(a)

(b)
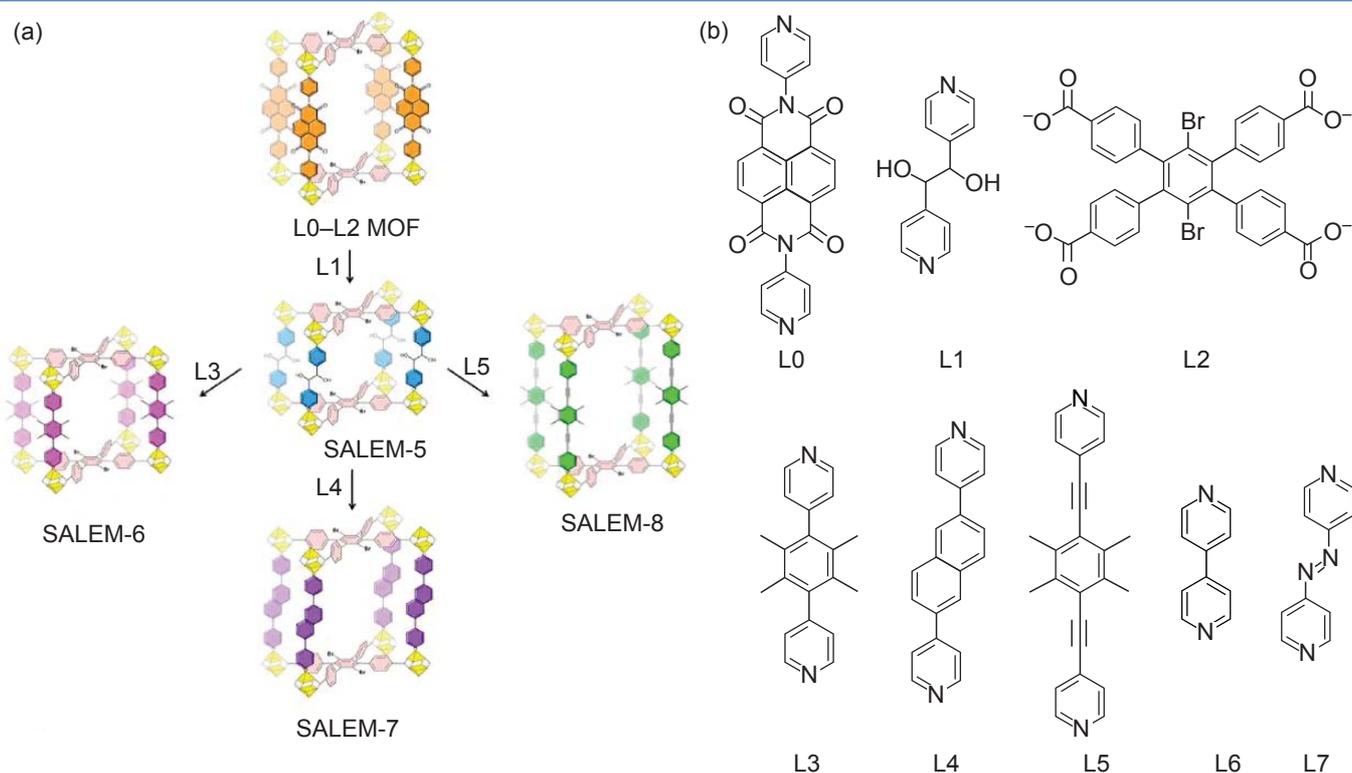
Scheme I. (a) Summary of the SALE reactions performed on the SALEM-5 system; (b) representation of structures of linkers used in the experiments (Reprinted with permission from (6). Copyright (2013) American Chemical Society)

showed that quantitative exchange of the parent linker had occurred. Powder XRD analysis of the product showed it to still be highly crystalline and that the first reflection peak had shifted from $2\theta = 5.6°$ to $4.76°$, suggesting a larger unit cell which would be consistent with incorporation of the larger linker. Following this, similar reactions were run but using the longer linkers L4 (14 Å) and L5 (17 Å) to probe the limits of the SALE process. By using L4 a steady increase in the amount of product SALEM-7 was seen by ^{1}H NMR spectroscopy and a maximum ligand exchange of 90% could be achieved over the course of four days by regularly changing the reaction solution with fresh linker. Following this trend, the reaction with the longest linker L5 proceeded very slowly, likely due to the large degree of strain associated with incorporation of such a large pillar and only approached >90% exchange and formation of SALEM-8 after two weeks. Consistent with the previous XRD data, the first reflection in SALEM-7 and SALEM-8 lies at decreasingly lower angles of $2\theta = 4.20°$ and $3.72°$, respectively, consistent with an increase in unit cell as pillar length is increased.

Following this, the effect of linker pK$_a$ was examined as a factor affecting the success of a SALE reaction. The higher the conjugate acid pK$_a$ of a linker, the stronger the metal (in this case zinc) linker bond which leads to more energetically favourable structures. Therefore, mixed linker experiments were conducted whereby SALEM-5 was exposed to mixtures of pairs of different pillars, such that the pairs had different lengths and pK$_a$ values. The first pair comprised L6 and L7 in equimolar amounts, L6 is shorter than L7 (7 Å *vs.* 9 Å) but has a higher conjugate acid pK$_a$ (4.44 *vs.* 3.62) and over the course of the reaction L6 was able to replace almost all of the L1 pillars in the starting SALEM-5. In line with expectations, L7 was only minimally incorporated and this is probably due to its larger steric demands and lower affinity for the metal centre. In contrast, exposure of SALEM-5 to a mixture of L3 (11 Å, pK$_a$ = 4.86) and L6 (7 Å, pK$_a$ = 4.44) showed rapid exchange with L3 and a maximum incorporation of L6 of 11%. This is despite L6 being significantly shorter than L3 (as such it should face a lower kinetic diffusion barrier into the SALEM-5 structure) and seems to indicate that the stronger L3-Zn interaction is the main driving force of the reaction. This result, coupled with other studies starting from different SALEM compounds with longer pillars and larger pores, show that although linker

length is an important consideration to the outcome of a SALE reaction, it is equally important to consider the relative pK_a values of the linkers involved to gain an understanding of the eventual direction or success of a SALE reaction.

An alternative and much less developed technique is the post-synthetic metathesis of metal nodes within the MOF structure so that robust MOFs which would otherwise be difficult to synthesise can be accessed. A common problem of MOFs is their limited chemical stability and much work is ongoing trying to make robust MOFs containing synthetically useful hard Lewis base carboxylate functionalities in conjunction with hard Lewis acids such as trivalent iron or chromium or tetravalent titanium and zirconium ions. However, incorporation of these higher valent metals is less predictable or controllable and few examples have been obtained, particularly as single crystals.

Tian-Fu Liu (Texas A&M University, USA) presented work on MOF postsynthetic metathesis and oxidation (PSMO) in single crystal to single crystal transformations to obtain otherwise inaccessible chemically stable materials by following two design rules: (a) start from a template MOF containing labile M-ligand bonds; and (b) exchange with metal ions which can access high oxidation states whilst maintaining the same metal coordination environment. Towards this end, the authors synthesised a Mg-MOF, porous coordination network (PCN)-426-Mg, by reaction of magnesium nitrate and the 2,3,6-trimethyl-1,4-benzoquinone perylene tetracarboxylate (TMQPTC) ligand (depicted in **Scheme II**) under solvothermal conditions at 100ºC for 24 h (7). The Mg-O bond in these type of structures is more labile than other similar common coordination bonds and single crystal XRD studies reveal the Mg ion is octahedrally coordinated as part of an oxo-trinuclear cluster more commonly found in iron and chromium compounds.

With the PCN-426-Mg template material in hand, direct metal metathesis reactions with trivalent Fe and Cr salts were attempted, using both hydrated and anhydrous precursors. Energy-dispersive X-ray spectroscopy (EDS) showed that only partial metal exchange had occurred, 87% for Fe and only a trace amount for Cr. This is largely due to Fe^{3+} and Cr^{3+} having very low ligand exchange rates and in the case of Cr^{3+} this renders it almost kinetically inert. These harder Lewis acidic metal ions also possess larger hydrolysis equilibrium constants which results in a more acidic environment being produced during the course of the reaction which damages the skeleton of the Mg-MOF template.

Consequently the analogous exchange reactions and oxidation using anhydrous divalent metal salts iron(II) chloride ($FeCl_2$) or chromium(II) chloride ($CrCl_2$) was investigated due to their much higher ligand exchange rates and small hydrolysis equilibrium constants. Reaction of the PCN-426-Mg crystals with the Fe or Cr reagent rapidly produced a pronounced colour change and in the case of Fe^{2+} for example, resulted in a change from colourless to purple within 20 min and reached complete conversion in 3 h. Following this
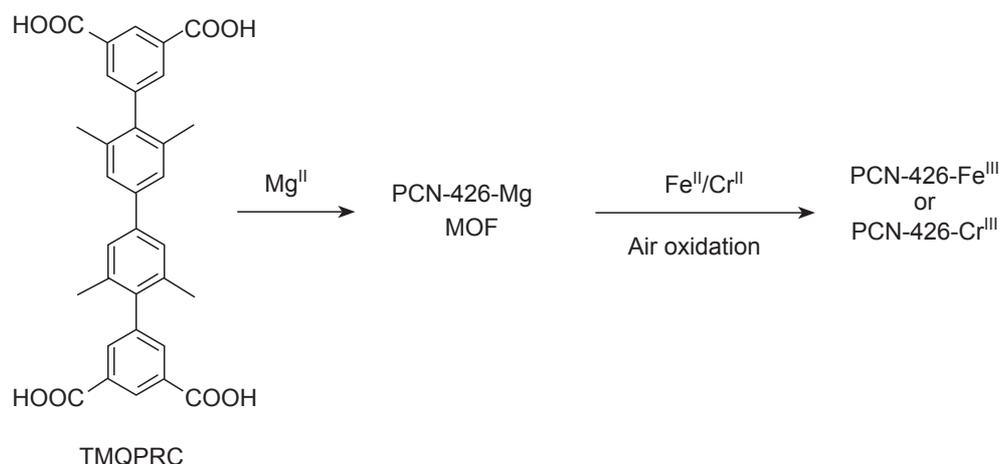
Scheme II. Synthetic route to synthesise PCN-426-Mg MOF template and subsequent PSMO reactions to access stable Fe(III) and Cr(III) analogues (Adapted from (7))

first exchange step, the product crystals were isolated, washed, suspended in DMF and underwent a very mild oxidation step by bubbling a stream of air through the suspension for 15 min. The colour changes associated with each of these exchange and oxidation steps are shown in **Figure 2**.

Single crystal XRD analysis of the product crystals show that they are isostructural with the starting Mg-template and that the PSMO method has allowed access to otherwise unobtainable Fe^{3+} and Cr^{3+} based MOFs. The PSMO technique is very effective here using the divalent metal ions as it overcomes the problems of slow ligand exchange rates, partial exchange and kinetic inertness encountered with the trivalent ions. This also eliminates the issue of decomposition of the template MOF from acid produced by the higher hydrolysis equilibria of the trivalent ions and additionally benefits from a mild oxidation step which produces very robust MOF materials. This was exemplified by the stability of PCN-426-Cr(III) which remains intact from pH 12 to 4 M hydrochloric acid for at least 12 h.

Molecular Container

An exciting area of materials chemistry is functional materials, particularly those that incorporate photoactive groups acting as valves that can be optically remote controlled, potentially leading to controlled molecule storage/release materials or photon-driven pumps. An elegant example in this field was presented by Christof Wöll (Karlsruhe Institute of Technology, Germany) using a surface mounted MOF (SURMOF) hybrid material, where the MOF component can be grown on
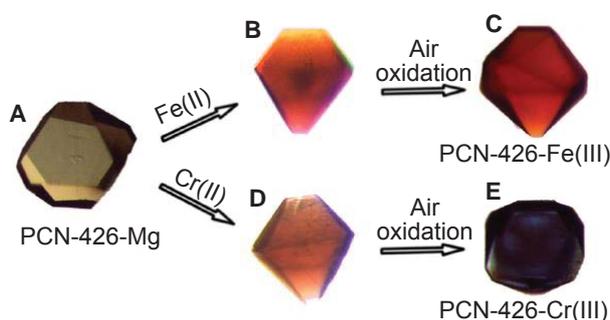
a surface in a very controlled fashion before surface functionalisation enables the MOF channels to be capped with photosensitive molecules (8). This leads to a 'molecular container' in which substrate molecules can be stored and released on demand *via* irradiation, **Figure 3**.

The material consists of two discreet domains, comprising an initial layer of $Cu_2(BPDC)_2(BiPy)$ (BPDC denotes biphenyl-4,4′-dicarboxylic acid and BiPy denotes 4,4′-bipyridine), onto which a second layer of $Cu_2(AB-BPDC)_2(BiPy)$ (AB-BPDC denotes 2-azobenzene biphenyl-4,4′-dicarboxylic acid) where the bipyridine linker used is now functionalised with an azobenzene group. This was achieved by the controlled layer-by-layer growth of each MOF on a suitable substrate. In this case a gold substrate functionalised with a long chain mercapto alcohol was used to help nucleate surface growth and control the SURMOF crystal orientation. This was sequentially immersed in a 0.5 mM solution of copper acetate, washed with ethanol and immersed in a 0.1 mM solution of the appropriate ligand before the process was repeated. Under optimised conditions SURMOF growth was very uniform, giving a film roughness as low as the height of a unit cell, and took 50 cycles to complete for the base layer and 45 cycles for the second covering layer, **Figure 4**.

XRD analysis of the finished material showed that both layers grow almost exclusively in the [001] direction as desired. The bottom layer contains pores of 1.5 nm diameter and can act as a storage medium for gases or small molecules. A quartz crystal microbalance (QCM) was used to determine that the loading of a substrate,

Fig. 2. Optical microscope photographs of: **A** as-synthesised PCN-426-Mg; **B** PCN-426-Mg after metathesis with $FeCl_2$ for 3 h; **C** PCN-426-Fe(III) after metal node oxidation; **D** PCN-426-Mg after metathesis with $CrCl_2$ for 3 h; and **E** PCN-426-Cr(III) after metal node oxidation (Reprinted with permission from (7). Copyright (2014) American Chemical Society)
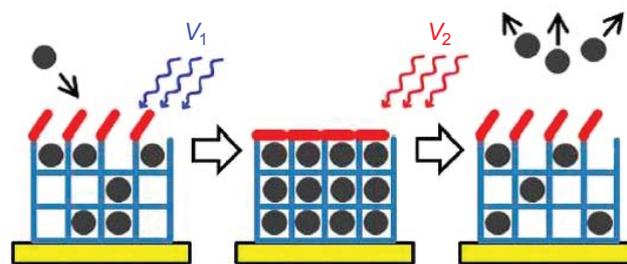

Fig. 3. Optically triggered release from two-component SURMOFs. Porous films composed of two different layers are synthesised on solid surfaces. The bottom layer serves as a reservoir and can be loaded with different molecules, whereas the top layer serves as a valve that can be opened and closed (V_1 = UV light, V_2 = visible light) (Reprinted with permission from (8). Copyright (2014) American Chemical Society)
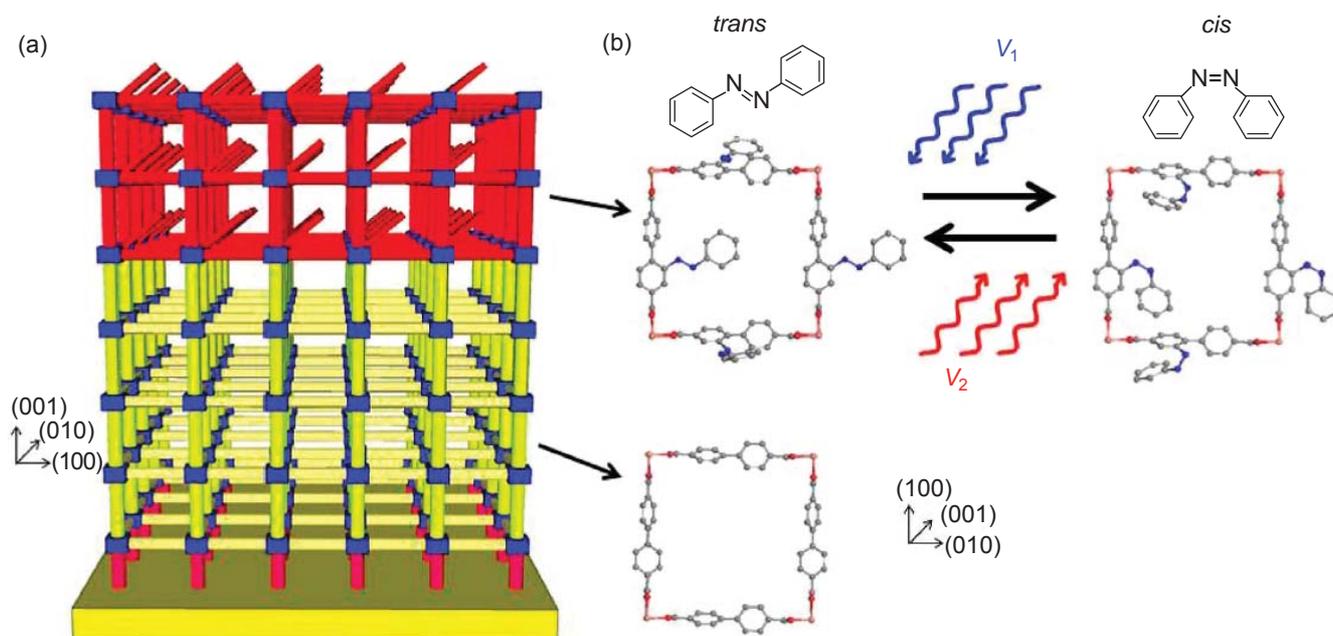
Fig. 4. Sketch of a layered photoswitchable SURMOF: (a) the bottom, passive SURMOF is grown on a gold substrate and an active SURMOF containing photoswitchable azobenzene is grown on top; (b) view of the pore window in the [001] direction. The azobenzene embedded in the MOF structure as well as molecular azobenzene can be switched from the *trans* to the *cis* state by UV light (*V*$_1$) and *vice versa* by visible light (*V*$_2$) (Reprinted with permission from (8). Copyright (2014) American Chemical Society)

in this case butanediol, in the material was 1.9 μg cm^{-2} which corresponds to an absorption capacity of five butanediol molecules per pore. The upper layer contains an azobenzene strut on the MOF linker group which is planar in the resting ground state and allows substrate molecules to be absorbed by the material. Irradiation with ultraviolet (UV) light (365 nm) causes the azobenzene to switch to the *cis* conformation, effectively closing the 'lid' and confining the substrate. Once closed, monitoring by QCM revealed there is very little leakage of the substrate . The subsequent release of the substrate can be controlled by a transition back to the *trans* conformation through thermal treatment or irradiation with visible light (560 nm) and results in complete desorption of the butanediol from the MOF.

Conclusions

This review has taken only a small snapshot of the numerous talks and posters presented on the area of MOFs but the sheer number of presentations demonstrates the breadth of interest in the field. A significant amount of work was directed at fundamental material and method understanding but there were

several examples looking into finding potential applications for these materials and how to overcome some of the associated challenges. For the area of MOFs to transition from academically interesting curiosities to commercially viable materials more work needs to be done to identify and demonstrate their applicability in a number of different areas. Particular challenges to realising this are stability to water and trace impurities under real world operating conditions, as well as cost and performance *versus* the current materials used. Despite this, it is surely only a matter of time until their full potential is realised.

References

1 247th ACS National Meeting & Exposition: http://www.acs.org/content/acs/en/meetings/spring-2014.html (Accessed on 5th June 2014)

2 I. J. Casely, *Johnson Matthey Technol. Rev.*, 2014, **58**, (3), 162

3 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, (2), 673

4 J. B. DeCoste and G. W. Peterson, *Chem. Rev.*, 2014, **114**, (11), 5695

5   J. B. DeCoste, G. W. Peterson, M. W. Smith, C. A. Stone and C. R. Willis, *J. Am. Chem. Soc.*, 2012, **134**, (3), 1486

6   O. Karagiaridi, W. Bury, E. Tylianakis, A. A. Sarjeant, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2013, **25**, (17), 3499

7   T.-F. Liu, L. Zou, D. Feng, Y.-P. Chen, S. Fordham, X. Wang, Y. Liu and H.-C. Zhou, *J. Am. Chem. Soc*, 2014, **136**, (22), 7813

8   L. Heinke, M. Cakici, M. Dommaschk, S. Grosjean, R. Herges, S. Bräse and C. Wöll, *ACS Nano*, 2014, **8**, (2), 1463

The Reviewer

Ian Casely graduated in Chemistry from Imperial College London, UK, in 2005 with subsequent PhD studies at the University of Edinburgh, UK, focused on rare-earth metal *N*-heterocyclic carbene organometallic complex synthesis and reactivity. In 2009 he moved to the University of California Irvine, USA, as a postdoc to work on small molecule activation chemistry and established a project developing the organometallic chemistry of bismuth complexes. Returning to the UK in 2011 to work at the University of Oxford, UK, on Group 4 metal based heterogeneous slurry polymerisation, in July 2012 he joined the PGM Applications group at the Johnson Matthey Technology Centre, Sonning Common, UK. He is now working on the conversion of biomass to chemicals as well as in the area of metal organic framework chemistry.