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Metal–organic frameworks for applications in remediation of oxyanion/cation-contaminated water

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Water pollution is an issue that should be carefully monitored and addressed. A major source of water pollution originates from high temperature industrial processes such as fossil fuel combustion and solid waste incineration. This waste typically contains high levels of oxyanion/cation forming elements which are particularly hazardous due to their inherent solubility in water and their resulting bioavailability. One approach for oxyanion/cation removal from water involves using an adsorbing medium to soak up and remove pollutants. Metal–organic frameworks (MOFs) offer an interesting platform for water remediation. MOFs are structurally diverse, porous materials that are constructed from metal nodes bridged by organic ligands. This highlight will focus on oxyanion/cation (PO_4^{3-}, AsO_4^{3-}, SeO_3^{2-}, SeO_4^{2-}, UO_2^{2+}) removal from aqueous solutions using MOFs as contaminant-selective sponges. The mechanism of adsorption in different frameworks will be explored to gain insight into some design features that are important for MOFs to be used in applications to help alleviate water pollution.

1. Introduction

Environmental pollution is a global issue that needs to be mitigated.[1] While pollutants can enter our environment from natural sources, the major causes of pollution arise from anthropogenic sources such as industrial waste, resource mining, the use of fertilizers and pesticides, burning of fossil fuels and radioactive waste produced from nuclear power generation.[2] The amount of air and water pollution on earth is increasing daily due to urbanization, industrialization and the steady increase in world population.[1] Given that humans need clean air and drinkable water to survive, pollution prevention and – perhaps more importantly at this stage – environmental remediation is of utmost importance.

Water pollutants can generally be divided into two categories, organic and inorganic, based on chemical composition. Common organic pollutants include solvents,[3] polyaromatic hydrocarbons (PAHs),[4] detergents,[5] dyes,[6] and pesticides/

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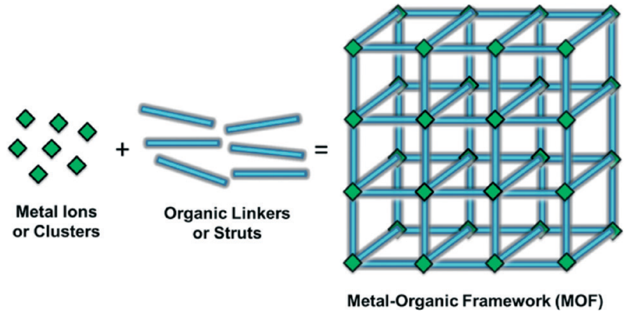
insecticides/herbicides.[7] Inorganic pollutants are generally more persistent in the environment than organic contaminants[8] and consist of metal and metalloid species which often rapidly oxidize to oxyanions and oxycations in industrial waste due to the high temperatures and varying pH conditions used in industrial processes.[9] Given that inorganic oxyanions/cations are charged molecules, they tend to be highly soluble in water making them a very bioavailable form of pollution.[10] It is therefore extremely problematic if these pollutants are allowed to enter our water supply since many inorganic oxyanions/cations are toxic to humans and wildlife at ppm or even ppb level concentrations.[9]

Many technologies have been explored and successfully used for the removal of oxyanions and cations from wastewater including co-precipitation,[11] chemical reduction to less soluble species,[12] reverse osmosis,[13] bioreactors[14] and vertical flow wetlands.[15] These methods and processes however, are not ideal since they require the construction of complex and space consuming facilities and they incur high start-up and maintenance costs.[9] An alternative method for oxyanion/cation remediation from water involves the use of a permanently porous adsorbent material. Common adsorbents that have been studied include iron oxides,[16] aluminium oxide,[17] activated carbons[18] and zeolites.[19] There are a few drawbacks associated with these adsorbents however, including: (1) low to moderate surface areas that limit the number of sites available for adsorption and (2) lack of tunability making specific anion/cation selectivity difficult to achieve.

Metal–organic frameworks (MOFs) (Scheme 1) offer an interesting alternative platform for use as adsorbents in wastewater remediation applications. MOFs are structurally diverse, porous materials that are composed of metal nodes bridged by organic linkers. Using rational design, the chemical and physical properties of MOFs can be elegantly tuned and materials with very high surface areas,[20] high porosity, and high stability can be obtained.[21] As a result, MOFs have shown promise in a wide variety of potential applications,



Scheme 1 Simplified representation of a MOF where metal ions/clusters are connected by organic linkers to give a three dimensional framework.

including catalysis,[22] sensing,[23] adsorption, storage, and release of gases,[24] chemical separations,[25] deactivation of chemical warfare agents,[26] light harvesting,[27] as well as in the removal of toxic materials from air and water.[28] For wastewater remediation and adsorption applications, MOFs with permanent porosity can be designed and the size, shape, and chemical composition of the pores can be tuned to promote the uptake of specific analyte molecules with high affinity, high selectivity and in ideal cases, both.[29] Research on the use of MOFs in oxyanion/cation wastewater remediation is still in its infancy, but with the recent advent of MOFs that are highly stable in water, under varying pH conditions, such as Zr-[21b,30] and Hf-based[31] MOFs, as well as MILs[32] and azolate-based[33] frameworks, this area of research is quickly expanding. It is important to learn from early examples of MOFs used for the removal of oxyanion/cations from water in order to understand the possible mechanisms of adsorption in MOFs and to determine design criteria necessary for synthesizing new MOFs that are highly effective for remediation of polluted solutions. MOFs have also been studied for the removal of hazardous organic materials from water,[34] anion exchange[35] and separation[36] and sulfate encapsulation,

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complexation, and extraction,[37] but these examples are beyond the scope of this highlight. Likewise, sorptive removal of nitrate and perchlorate from water are outside the scope.[38] Herein, we discuss examples of MOFs studied for applications in the adsorption and removal of phosphates, arsenates, selenates, selenites and uranyl from aqueous solutions. Examples are divided into two categories based on the predicted (and in some cases confirmed) mode of analyte adsorption: (1) adsorption enabled by metal nodes and (2) adsorption facilitated by organic linkers. While there are many more examples of adsorption on the nodes when considering oxyanion remediation, adsorption mechanisms involving both metal nodes and/or organic linkers are important to consider when designing materials for wastewater clean-up. Table 1 shows the MOFs that will be discussed, highlighting the metal nodes and organic linkers that make up the frameworks.

2. Adsorption facilitated by metal nodes

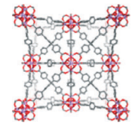
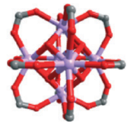
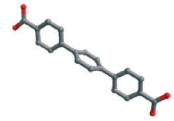
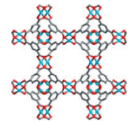
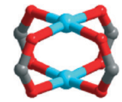
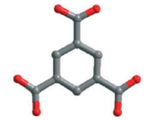
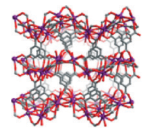
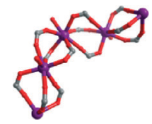
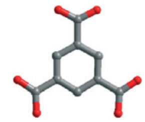
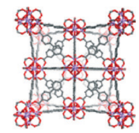
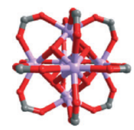
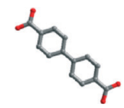
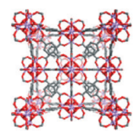
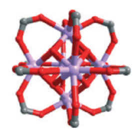
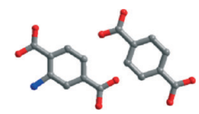
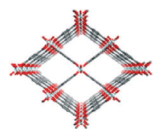
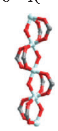
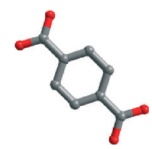
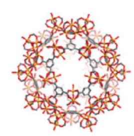
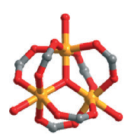
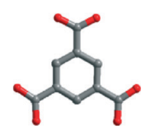
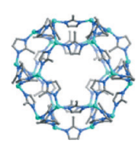
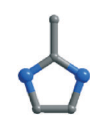
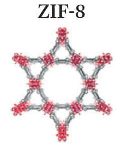
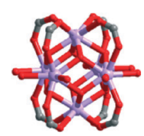
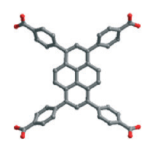
2.1 Phosphates and phosphorus containing compounds

Phosphates and organic phosphorus compounds are widely used in fertilizers, detergents, and pesticides.[39] The production and prevalent use of phosphorus-containing products results in significant contamination of agricultural runoff, and of municipal and industrial wastewater.[39] Consistent with its role as a primary component of teeth and bones, phosphate is acutely toxic to humans only at relatively high doses (3 g kg^{-1} was found to be lethal in pigs),[40] but a more pertinent issue caused by excess phosphate in water is eutrophication.[41,42] As a result, the removal of excess phosphates from water is of significant environmental concern.

Gu and coworkers reported the first example of adsorptive removal of organophosphorus compounds from water using a Zr-based MOF, UiO-67 (Table 1).[43] It is well known that hydrous zirconia has an affinity for compounds containing phosphate and phosphonic acid functional groups due to strong interactions between surface Zr–OH groups and the oxygen functionality of these phosphorus-containing contaminants.[44] Indeed, a combination of Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis performed on samples of UiO-67 following adsorption of organophosphorus compounds, glyphosate and glufosinate, suggest that terminal Zr–OH groups (present due to missing linker defects[45] within the MOF – Fig. 1) are responsible for adsorption of the organophosphorus compounds through the formation Zr–O–P bonds. The less reactive bridging –OH groups in the node may conceivably also contribute to the adsorption, but this was not confirmed.[43]

In a similar study, the adsorptive removal of phosphate anions from water using Zr-MOFs UiO-66 and UiO-66-NH_2 was explored.[46] A modest increase in adsorption capacity was observed in UiO-66-NH_2 at neutral pH (265 mg g^{-1} *vs.* 237 mg g^{-1} in UiO-66) suggesting that hydrogen bonding and electrostatic interactions between the amino functionality

Table 1 Metal–organic framework (MOF) structures highlighting the metal node and organic linker constituents. Zr: light purple; Cu: light blue; Tb: dark purple; Fe: yellow; Zn: teal; O: red; C: grey; N: blue

MOF	Metal node	Organic linker
 UiO-68	 $Zr_6O_4(OH)_4$	 TPDC
 HKUST-1	 Cu_2	 BTC
 MOF-76(Tb)	 TbOH	 BTC
 UiO-67	 $Zr_6O_4(OH)_4$	 BPDC
 UiO-66/UiO-66-NH_2	 $Zr_6O_4(OH)_4$	 NH_2-BDC and BDC
 MIL-53(Al/Fe)	 AlOH or FeOH	 BDC
 MIL-100(Fe/Al/Cr)	 $Fe_3O(OH)_3$	 BTC
 ZIF-8	 Zn	 MeIM
 NU-1000	 $Zr_6O_4(OH)_8(H_2O)_4$	 TBAPy

(most likely ammonium under the conditions used) and phosphate anions (HPO_4^{2-} or $H_2PO_4^-$) may lead to enhanced adsorption. The primary adsorption mechanism however, was attributed to interactions between the Zr(IV) and the

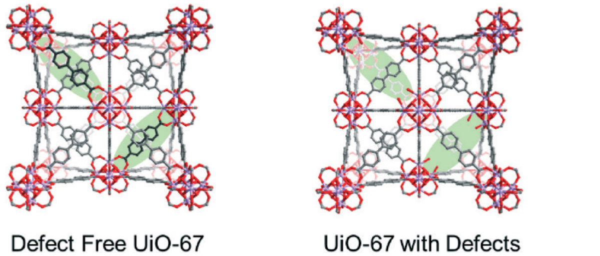


Fig. 1 Defect free UiO-67 and an idealized representation of missing linker defects in UiO-67 giving rise to terminal Zr–OH groups on select Zr_6 nodes. Zr: light purple; O: red; C: grey.

phosphate anion,[46] forming Zr–O–P bonds similar to those observed in UiO-67.[43] It is therefore possible that the increased affinity for phosphate anions observed in UiO-66-NH_2 compared to UiO-66 is a consequence of an increase in missing linker defects in the functionalized framework giving rise to more terminal and sorbate-displaceable node hydroxo ligands. (Note that at neutral pH, terminal aqua ligands (at defect sites or on eight-connected nodes; see bottom center entry in Table 1) are largely converted to hydroxo ligands. Thus each missing linker creates a pair of defects (one on each node), with each defect site consisting of a pair of hydroxo ligands bound to a single zirconium ion.) The synthesis of Zr-MOFs with large numbers of defects may therefore be a worthwhile strategy for increasing oxyanion adsorption capacity. The number of defects (and hence the number of terminal –OHs present) can be controlled *via* the choice of acid modulator and the choice of reaction time (synthesis time).[47] Lin and coworkers discovered that when UiO-66 is exposed to much higher concentrations of phosphate (*i.e.*, >25 000 ppm instead of 50 ppm phosphate in the form of either H_3PO_4 or Na_3PO_4), the BDC linkers of UiO-66 are extracted from the MOF and replaced with PO_4^{3-} linkers.[48] This linker replacement gives rise to porous, amorphous, and remarkably chemically robust materials (ZrPhos and ZrOxyPhos) having the same crystal shape morphology as the parent UiO-66. In turn, these daughter materials have been shown to be effective for the removal of Sr, Pu, Np and U from high-level nuclear waste.

2.2 Arsenic oxyanions

Arsenic is a highly toxic metalloid that enters our waterways *via* erosion, runoff from orchards as well as from wastewater generated by glass and electronics production.[49] Chronic ingestion of arsenic through contaminated drinking water can lead to stomach pain, nausea, partial paralysis, blindness and cancer.[49] The United States Environmental Protection Agency (EPA) has mandated that levels of arsenic in drinking water be less than 10 ppb to be considered safe for consumption.[49] Arsenic primarily exists as arsenite ($H_xAsO_3^{3-x}$) and arsenate ($H_xAsO_4^{3-x}$) in water and it is these forms that are the major focus of remediation.[50]

There have been a handful of studies performed on adsorption and removal of arsenate from water using MOFs. Both MIL-53(Al)[51] and MIL-53(Fe)[52] (Table 1) have been explored for arsenate removal and in both cases, the adsorption of arsenate was attributed to interactions between the oxyanion and trivalent metal sites in the framework. A detailed experimental and computational study of the mechanism of adsorption of *organo*arsenic compounds by MIL-100-(Fe) similarly showed the importance of open metal sites.[53] In this study, the adsorption of *p*-arsanilic acid on MIL-100-(Cr), MIL-100(Al) and MIL-100(Fe) was explored to understand the effect of changing the metal node on analyte adsorption. It was found that MIL-100(Fe) had the highest adsorption capacity—a consequence of the much higher lability of water coordinated to the iron node *versus* aluminum or chromium. Bond lability in the different MIL derivatives was estimated using DFT calculations and the Fe–O–As binding motif (Fig. 2) was confirmed by FTIR.

The adsorption of trace arsenate from water by the Zn-based MOF ZIF-8 (Table 1) has been examined.[54] The authors claim a high adsorption capacity for ZIF-8 (76 mg g^{-1}) for arsenate removal, while also establishing a low equilibrium concentration[55] (9.8 ppb). This is the highest adsorption capacity of any material reported for arsenate removal with such low equilibrium concentration. Prior to arsenate adsorption, the surface of ZIF-8 presents terminal Zn–OH sites produced by the dissociative adsorption of water. After adsorption of arsenate, analysis of the O 1s region of the wide-scan XPS spectrum shows a significant decrease in the peak attributed to Zn–OH and a new peak attributed to Zn–O–As binding. This Zn–O–As binding could occur in a monodentate or bridging fashion on the surface of ZIF-8 (Fig. 3). Similar to the MIL derivatives that were studied for arsenate[51,52] and organoarsenic[53] adsorption, and Zr-MOFs studied for phosphate removal,[43,46] the adsorption of arsenate on ZIF-8 demonstrates the importance of open metal sites or more specifically, the presence of metal sites with substitutionally labile ligands, for the adsorption of oxyanions.

2.3 Selenium oxyanions

Selenium is a naturally occurring element that is essential in very low concentrations (<40 μg per day causes selenium deficiency) but can also be toxic at concentrations only

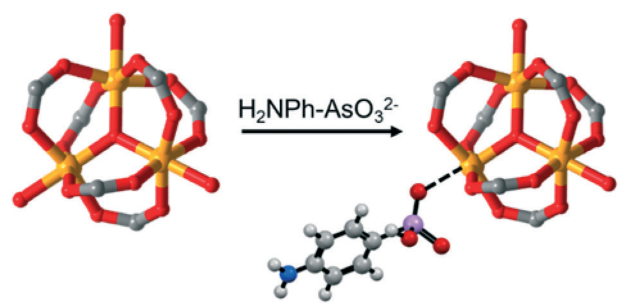


Fig. 2 Proposed adsorption mechanism for *p*-arsanilic acid on the node of MIL-100(Fe). As: light purple; Fe: yellow; O: red; C: grey; N: blue; H: white.

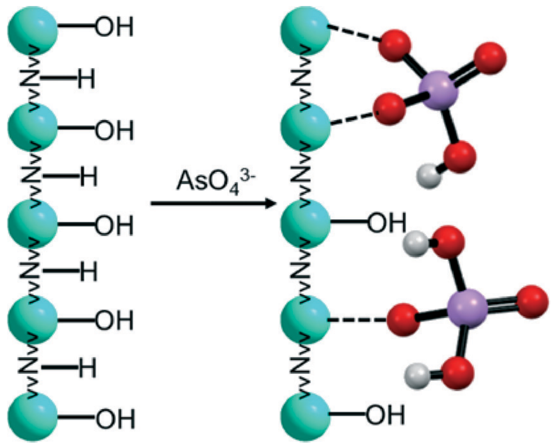


Fig. 3 Proposed adsorption mechanism of arsenate on the surface of ZIF-8 occurring in a monodentate or bridging fashion. Zn: teal; As: light purple; O: red, H: white.

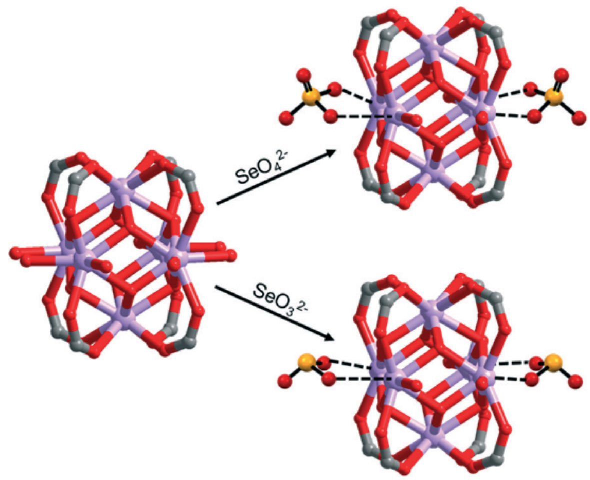


Fig. 4 Adsorption of selenate and selenite on the Zr_6 node of NU-1000. Zr: light purple; Se: yellow; O: red; C: grey.

moderately higher (>400 μg per day).[56] Selenium enters our drinking water in many different ways such as erosion of natural deposits, agricultural runoff, discharge from petroleum refineries and mining, as well as *via* flue gas desulfurization processes.[57] The U.S. EPA recognizes the potential dangers associated with selenium ingestion and has mandated the maximum level for selenium in consumable drinking water to be no greater than 50 ppb.[58] Selenium primarily exists as selenite ($H_xSeO_3^{2-x}$) and selenate ($H_xSeO_4^{2-x}$) in water making these anions the primary focus of remediation efforts.[59]

Our group recently reported the adsorption of selenate and selenite by a series of Zr-based MOFs.[60] NU-1000 (Table 1) was shown to have the highest adsorption capacities (102 mg g^{-1} and 62 mg g^{-1} for selenite and selenate respectively) as well as the fastest uptake rates of all the Zr-MOFs studied. Two important design features contribute to the success of NU-1000 as an adsorbent for selenium oxyanions: (1) the large 30 Å apertures of the framework help facilitate fast diffusion and adsorption of selenate and selenite throughout the framework, and (2) the presence of labile hydroxyl and water ligands on the Zr_6 node of NU-1000 allow for facile binding of the selenium oxyanions to the Zr_6 node in bridging Zr–O–Se–O–Zr configurations (Fig. 4). These adsorption configurations were confirmed by diffuse reflectance infrared spectroscopy (DRIFTS) and pair distribution function (PDF) analysis of X-ray total scattering data. The use of metal nodes containing labile ligands available for substitution is another strategy for creating adsorption anchors within a MOF. Unlike missing linker defects or anchors present only on the external surface of a MOF, this strategy allows for adsorption to occur uniformly throughout the framework.

3. Adsorption facilitated by organic linkers

Uranium is a naturally occurring element that is present at low concentrations in nearly all soil, rock and water.[61] Uranium is commonly extracted and concentrated through mining and refining processes for use in nuclear power generation. These processes produce waste which can be distributed back into the environment by wind and water. Exposure to uranium, through contaminated drinking water for example, can lead to increased cancer risk, liver damage, or both, and chronic ingestion can lead to internal irradiation and chemical toxicity.[61] As a consequence, the U.S. EPA has set the acceptable limit for uranium levels in drinking water to be no higher than 30 ppb.[61] It should be noted that while the removal of uranium from waste streams and mine drainage is important for human health, the extraction of uranium from seawater is potentially important for nuclear fuel production. An adsorbent material that could effectively remove uranium from wastewater[62] might also be useful for uranium extraction applications.[63]

The first example of a MOF studied for application in uranium extraction from water was reported in 2013 by Carboni and coworkers.[64] The Zr-MOF UiO-68 was used due to its inherent water stability (owing in part to strong Zr(IV)–O bonds between linkers and nodes)[65] and its large apertures that can facilitate the adsorption or diffusion of species up to 10 Å in diameter.[66] To enhance the affinity of UiO-68 for the uranyl cation (UO_2^{2+}), phosphorylurea groups were added to the terphenyldicarboxylate linker; *N*-diphenylphosphorylurea functional groups are known to be capable of extracting actinides and lanthanides from aqueous solutions.[67] The resulting UiO-68 derivatives named UiO-68-P(O)$(OEt)_2$ and UiO-68-P(O)$(OH)_2$ (Table 1) were shown to adsorb uranyl from water and seawater with adsorption capacities as high as 217 mg g^{-1} and 188 mg g^{-1}, respectively. Given that these capacities are equivalent to the binding of one uranyl cation for every two phosphorylurea groups, an adsorption mechanism was proposed whereby two phosphorylurea groups present on adjacent terphenyldicarboxylate linkers form a binding pocket for each linear uranyl complex (Fig. 5). This mechanism was supported by DFT calculations which show

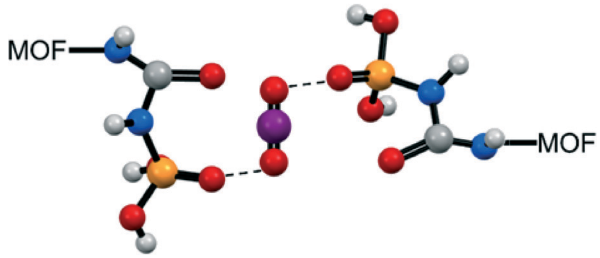


Fig. 5 Ball and stick representation of phosphorylurea functional groups showing how the binding pocket is formed inside UiO-68-P-(O)(OH)$_2$ for the adsorption of uranyl. U: purple; P: yellow; N: blue; O: red; C: grey; H: white.

that monodentate binding of each of two phosphorylurea ligands to one uranyl is a thermodynamically favourable motif.

HKUST-1[68] and Tb-MOF-76[69] (Table 1) were also explored for adsorption and removal of uranium from water. In HKUST-1, adsorption was attributed to both coordination (with free carboxylate groups) as well as charge-dipole interactions between uranyl and the benzenetricarboxylate linker. The effect of MOF surface charge was probed by monitoring uranyl adsorption as a function of pH. An observed increase in uranyl dication adsorption upon raising the solution pH from 2 to 6 was ascribed to the MOF surface becoming more negatively charged. In addition, adsorption *via* coordination of uranyl to oxygen atoms of the benzenetricarboxylate linker, most likely on the surface of HKUST-1, was proposed as an additional adsorption mode since it is known that carboxylates have an affinity for uranyl.[70] Surface charges and electrostatic interactions were also reasoned to facilitate uranyl adsorption by Tb-MOF-76. The pH dependence of uranyl uptake is supportive of this type of adsorption mechanism.[70]

The use of organic linkers in a MOF to promote analyte adsorption has been shown to be a successful strategy. Adsorption mediated by surface charge and electrostatic interactions may be important in some instances but to increase affinity, selectivity and overall adsorption capacity, the use of organic linkers that form a binding pocket inside the cavity of a MOF is of particular interest. The construction of an analyte binding pocket with specific size and shape, as well as the incorporation of functional groups which are known to have an affinity for a particular analyte, could prove to be a useful strategy for creating ideal sorbents. A similar strategy has been employed with discrete molecules[37c] and is akin to the manner in which the substrate-binding sites of enzymes achieve chemical specificity.

4. Summary and outlook

Although research on remediation of oxyanion/cation-contaminated water using MOFs is just beginning to grow and expand, there is much to be learned from the studies discussed here. The use of organic linkers containing functional groups known to have a strong affinity for specific analytes has been shown to be a successful approach for analyte adsorption. While perhaps more synthetically challenging, the use of linkers containing functional groups that can self-assemble and create a strong binding pocket inside the cavity of a MOF may help to increase analyte binding affinity and selectivity. One potential limitation is progressive width-attenuation of MOF channels by the assembled structures, resulting in slow analyte diffusion and uptake rate; however, MOFs with hierarchical pore structure, such as NU-1000 (Table 1), may help since larger pores can host the self-assembled binding pocket while smaller pores remain unobstructed to facilitate rapid diffusion. Additionally, coordination to metal nodes has been shown to be a particularly successful approach for adsorption of oxyanions. Taking advantage of missing-linker defects and external-surface defects is one approach to achieving oxyanion coordination by node metal-ions, while the use of nodes with lower linker connectivity[71] (and hence the presence of labile ligands) is another. In summary, a combination of water stability, large pores and apertures (for ion transport), organic linker functionality (for coordination and selectivity), and open metal sites (for coordination and in some cases selectivity) may give rise to MOFs that are ideal sorbents for oxyanion/oxycation removal from water thus creating another intriguing, practical application for metal–organic frameworks.

Going forward, computational evaluation of MOFs that are known,[72] as well as hypothetical MOFs, may help advance research in this area. High-throughput screening can be performed on MOFs prior to testing analyte adsorption and even prior to MOF synthesis to expedite the discovery and development of highly effective adsorbents.

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Notes and references

1 N. Middleton, *The Global Casino: An Introduction to Environmental Issues*, Routledge New York, 2013.
2 R. Fuge, *Essentials of Medical Geology*, ed. O. Selinus, Springer Netherlands, 2013, ch. 4, pp. 59–74.
3 H. Bi, X. Xie, K. Yin, Y. Zhou, S. Wan, L. He, F. Xu, F. Banhart, L. Sun and R. S. Ruoff, *Adv. Funct. Mater.*, 2012, **22**, 4421–4425.
4 M. Tobiszewski and J. Namieśnik, *Environ. Pollut.*, 2012, **162**, 110–119.
5 B. G. Plósz, L. Benedetti, G. T. Daigger, K. H. Langford, H. F. Larsen, H. Monteith, C. Ort, R. Seth, J.-P. Steyer and P. A. Vanrolleghem, *Water Sci. Technol.*, 2013, **67**, 1–15.
6 M. Tichonovas, E. Krugly, V. Racys, R. Hippler, V. Kauneliene, I. Stasiulaitiene and D. Martuzevicius, *Chem. Eng. J.*, 2013, **229**, 9–19.

7 *Environmental Pollution by Pesticides*, ed. C. A. Edwards, Plenum New York, 1973.
8 M. A. Hashim, S. Mukhopadhyay, J. Narayan Sahu and B. Sengupta, *J. Environ. Manage.*, 2011, **92**, 2355–2388.
9 G. Montes-Hernandez, N. Concha-Lozano, F. Renard and E. Quirico, *J. Hazard. Mater.*, 2009, **166**, 788–795.
10 H. Rüdel, C. Díaz Muñiz, H. Garelick, N. G. Kandile, B. W. Miller, L. Pantoja Munoz, W. J. G. M. Peijnenburg, D. Purchase, Y. Shevah, P. van Sprang, M. Vijver and J. P. M. Vink, *Environ. Sci. Pollut. Res.*, 2015, **22**, 7405–7421.
11 (*a*) D. M. Roundhill and H. F. Koch, *Chem. Soc. Rev.*, 2002, **31**, 60–67; (*b*) T. R. Harper and N. V. Kingham, *Water Environ. Res.*, 1994, **64**, 200–203.
12 L. E. Eary and D. Rai, *Environ. Sci. Technol.*, 1988, **22**, 972–977.
13 K. R. Fox and T. J. Sorg, *J. - Am. Water Works Assoc.*, 1987, **79**, 81–84.
14 Q. Luo, T. K. Tsukamoto, K. L. Zamzow and G. C. Miller, *Mine Water Environ.*, 2008, **27**, 100–108.
15 F. D. Mooney and C. Murray-Gulde, *Environ. Geosci.*, 2008, **15**, 131–141.
16 (*a*) L. S. Balistrieri and T. T. Chao, *Soil Sci. Soc. Am. J.*, 1987, **51**, 1145–1151; (*b*) L. S. Balistrieri and T. T. Chao, *Geochim. Cosmochim. Acta*, 1990, **54**, 739–751; (*c*) M. Duc, G. Lefèvre, M. Fédoroff, J. Jeanjean, J. C. Rouchaud, F. Monteil-Rivera, J. Dumonceau and S. Milonjic, *J. Environ. Radioact.*, 2003, **70**, 61–72; (*d*) K. Mitchell, R.-M. Couture, T. M. Johnson, P. R. D. Mason and P. Van Cappellen, *Chem. Geol.*, 2013, **342**, 21–28.
17 (*a*) C. P. Johnston and M. Chrysochoou, *J. Hazard. Mater.*, 2015, **281**, 56–63; (*b*) Y. T. Chan, W. H. Kuan, T. Y. Chen and M. K. Wang, *Water Res.*, 2009, **43**, 4412–4420; (*c*) N. Bleiman and Y. G. Mishael, *J. Hazard. Mater.*, 2010, **183**, 590–595.
18 (*a*) S. K. Gupta and K. Y. Chen, *J. - Water Pollut. Control Fed.*, 1978, **50**, 493–506; (*b*) C. P. Huang and L. K. Fu, *J. - Water Pollut. Control Fed.*, 1984, **56**, 233–242; (*c*) R. Mahmudov and C. P. Huang, *Sep. Purif. Technol.*, 2011, 77, 294–300.
19 H. Figueiredo and C. Quintelas, *J. Hazard. Mater.*, 2014, **274**, 287–299.
20 (*a*) O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydın and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016–15021; (*b*) H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O'Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424–428; (*c*) R. Grünker, V. Bon, P. Müller, U. Stoeck, S. Krause, U. Mueller, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2014, **50**, 3450–3452.
21 (*a*) O. V. Gutov, W. Bury, D. A. Gomez-Gualdron, V. Krungleviciute, D. Fairen-Jimenez, J. E. Mondloch, A. A. Sarjeant, S. S. Al-Juaid, R. Q. Snurr, J. T. Hupp, T. Yildirim and O. K. Farha, *Chem. – Eur. J.*, 2014, **20**, 12389–12393; (*b*) T. C. Wang, W. Bury, D. A. Gómez-Gualdrón, N. A. Vermeulen, J. E. Mondloch, P. Deria, K. Zhang, P. Z. Moghadam, A. A. Sarjeant, R. Q. Snurr, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 3585–3591.
22 (*a*) J. Lee, O. K. Farha, J. Roberts, K. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459; (*b*) J. Gascon, A. Corma, F. Kapteijn, F. X. Llabrés and I. Xamena, *ACS Catal.*, 2014, **4**, 361–378; (*c*) T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982–5993.
23 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125.
24 (*a*) M. Dincă and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766–6779; (*b*) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504; (*c*) O. K. Farha, A. Ö. 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.
25 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
26 (*a*) M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, O. K. Farha and J. T. Hupp, *Angew. Chem., Int. Ed.*, 2014, **53**, 497–501; (*b*) M. J. Katz, S.-Y. Moon, J. E. Mondloch, M. H. Beyzavi, C. J. Stephenson, J. T. Hupp and O. K. Farha, *Chem. Sci.*, 2015, **6**, 2286–2291; (*c*) J. E. Mondloch, M. J. Katz, W. C. Isley III, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp and O. K. Farha, *Nat. Mater.*, 2015, **14**, 512–516; (*d*) P. Nunes, A. C. Gomes, M. Pillinger, I. S. Gonçalves and M. Abrantes, *Microporous Mesoporous Mater.*, 2015, **208**, 21–29; (*e*) E. López-Maya, C. Montoro, L. M. Rodríguez-Albelo, S. D. Aznar Cervantes, A. A. Lozano-Pérez, J. L. Cenís, E. Barea and J. A. R. Navarro, *Angew. Chem., Int. Ed.*, 2015, **54**, 6790–6794.
27 (*a*) C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 15858–15861; (*b*) M. C. So, G. P. Wiederrecht, J. E. Mondloch, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2015, **51**, 3501–3510; (*c*) C. A. Kent, D. Liu, L. Ma, J. M. Papanikolas, T. J. Meyer and W. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 12940–12943; (*d*) J.-L. Wang, C. Wang and W. Lin, *ACS Catal.*, 2012, **2**, 2630–2640.
28 (*a*) E. Barea, C. Montoro and J. A. R. Navarro, *Chem. Soc. Rev.*, 2014, **43**, 5419–5430; (*b*) J. B. DeCoste and G. W. Peterson, *Chem. Rev.*, 2014, **114**, 5695–5727; (*c*) N. A. Khan, Z. Hasan and S. H. Jhung, *J. Hazard. Mater.*, 2013, **244–245**, 444–456.
29 (*a*) G. Férey, *Chem. Soc. Rev.*, 2007, **37**, 191–214; (*b*) H. Furukawa, K. E. Cordova, M. O. O'Keefe and O. M. Yaghi, *Science*, 2013, **341**, 1230444; (*c*) H.-L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351–3370.
30 (*a*) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851; (*b*) G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye, C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068–4071; (*c*) J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 10294–10297; (*d*) W. Morris, B. Volosskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa,

D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443–6445; (*e*) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 10307–10310.
31 (*a*) S. Jakobsen, D. Gianolio, D. S. Wragg, M. H. Nilsen, H. Emerich, S. Bordiga, C. Lamberti, U. Olsbye, M. Tilset and K. P. Lillerud, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 125429; (*b*) M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2014, **136**, 15861–15864; (*c*) V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, *CrystEngComm*, 2013, **15**, 9572–9577.
32 (*a*) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042; (*b*) P. Horcajada, S. Surblé, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Grenéche, I. Margiolaki and G. Férey, *Chem. Commun.*, 2007, 2820–2822.
33 (*a*) M. Eddaoudi, D. F. Sava, J. F. Eubank, K. Adil and V. Guillerm, *Chem. Soc. Rev.*, 2015, **44**, 228–249; (*b*) K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186–10191; (*c*) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875–3877; (*d*) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939–943.
34 Z. Hasan and S. H. Jhung, *J. Hazard. Mater.*, 2015, **283**, 329–339.
35 (*a*) H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202–7209; (*b*) P.-F. Shi, B. Zhao, G. Xiong, Y.-L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231–8233; (*c*) H.-R. Fu, Z.-X. Xu and J. Zhang, *Chem. Mater.*, 2015, **27**, 205–210.
36 R. Custelcean and B. A. Moyer, *Eur. J. Inorg. Chem.*, 2007, 1321–1340.
37 (*a*) R. Custelcean, B. A. Moyer, V. S. Bryantsev and B. P. Hay, *Cryst. Growth Des.*, 2006, **6**, 555–563; (*b*) B. Wu, J. Liang, Y. Zhao, M. Li, S. Li, Y. Liu, Y. Zhang and X.-J. Yang, *CrystEngComm*, 2010, **12**, 2129–2134; (*c*) B. A. Moyer, R. Custelcean, B. P. Hay, J. L. Sessler, K. Bowman-James, V. W. Day and S.-O. Kang, *Inorg. Chem.*, 2013, **52**, 3473–3490.
38 H. Fei, D. L. Rogow and S. R. J. Oliver, *J. Am. Chem. Soc.*, 2010, **132**, 7202–7209.
39 U.S. EPA, *Environmental Impacts- Phosphorus*, http://www.epa.gov/oecaagct/ag101/impactphosphorus.html (accessed June 2015).
40 R. R. Martin, G. R. Lisehora, M. Braxton Jr and P. J. Barcia, *JAMA, J. Am. Med. Assoc.*, 1987, **257**, 2190–2192.
41 V. H. Smith, *Environ. Sci. Pollut. Res.*, 2003, **10**, 1–14.
42 Eutrophication is defined as excessive plant and algal growth caused by an increase (or excess) of one or more growth factors required for photosynthesis such as sunlight, carbon dioxide, and/or nutrients.
43 X. Zhu, B. Li, J. Yang, Y. Li, W. Zhao, J. Shi and J. Gu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 223–231.
44 G. Liu and Y. Lin, *Anal. Chem.*, 2005, **77**, 5894–5901.
45 UiO-67 ideally has 12-connected nodes but more typically, UiO-type MOFs contain missing linker defects giving rise to 10- or 11-connected nodes. UiO-MOFs can also have defects resulting from missing nodes but these are not discussed in this highlight.
46 K.-Y. A. Lin, S.-Y. Chen and A. P. Jochems, *Mater. Chem. Phys.*, 2015, **160**, 168–176.
47 (*a*) H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532; (*b*) F. Vermoortele, B. Bueken, G. Le Bars, B. Van de Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock and D. E. De Vos, *J. Am. Chem. Soc.*, 2013, **135**, 11465–11468.
48 C. W. Abney, K. M. L. Taylor-Pashow, S. R. Russell, Y. Chen, R. Samantaray, J. V. Lockard and W. Lin, *Chem. Mater.*, 2014, **26**, 5231–5243.
49 U.S. EPA, *Arsenic in Drinking Water*, http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/index.cfm (accessed June 2015).
50 T. S. Y. Choonga, T. G. Chuaha, Y. Robiaha, F. L. Gregory Koaya and I. Azni, *Desalination*, 2007, **217**, 139–166.
51 J. Li, Y.-N. Wu, Z. Li, M. Zhu and F. Li, *Water Sci. Technol.*, 2014, **70**, 1391–1397.
52 T. A. Vu, G. H. Le, C. D. Dao, L. Q. Dang, K. T. Nguyen, Q. K. Nguyen, P. T. Dang, H. T. K. Tran, Q. T. Duong, T. V. Nguyen and G. D. Lee, *RSC Adv.*, 2015, **5**, 5261–5268.
53 J. W. Jun, M. Tong, B. K. Jung, Z. Hasan, C. Zhong and S. H. Jhung, *Chem. – Eur. J.*, 2015, **21**, 347–354.
54 J. Li, Y.-N. Wu, Z. Li, B. Zhang, M. Zhu, X. Hu, Y. Zhang and F. Li, *J. Phys. Chem. C*, 2014, **118**, 27382–27387.
55 The equilibrium concentration is the final concentration of analyte in the water being treated after adsorption.
56 (*a*) World Health Organization, *Trace elements in human nutrition and health*, World Health Organization, Geneva, 1996; (*b*) P. M. Chapman, *Hum. Ecol. Risk Assess.*, 1999, **5**, 1123–1138; (*c*) F. M. Fordyce, Selenium Deficiency and Toxicity in the Environment, in *Essentials of Medical Geology: Revised Edition*, ed. O. Selinus, B. Alloway, J. A. Centeno, R. B. Finkelman, R. Fuge, U. Lindh and P. Smedley, Elsevier, London, 2005, pp. 375–416.
57 A. D. Lemly, *Ecotoxicol. Environ. Saf.*, 2004, **59**, 44–56.
58 U.S. EPA, *Basic Information about Selenium in Drinking Water*, http://water.epa.gov/drink/contaminants/basicinformation/selenium.cfm (accessed June 2015).
59 J. A. Plant, D. G. Kinniburgh, P. L. Smedley, F. M. Fordyce and B. A. Klinck, *Treatise Geochem.*, 2003, **9**, 17–66.
60 A. J. Howarth, M. J. Katz, T. C. Wang, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 7488–7494.
61 U.S. EPA, *Radiation Protection*, http://www.epa.gov/radiation/radionuclides/uranium.html, (accessed June 2015).
62 (*a*) M. R. L. Nascimento, O. Fatibello-Filho and L. A. Teixeira, *Miner. Process. Extr. Metall. Rev.*, 2004, **25**, 129–142; (*b*) A. C. Q. Ladeira and C. R. Gonçalves, *J. Hazard. Mater.*, 2007, **148**, 499–504.
63 (*a*) J. Kim, C. Tsouris, R. T. Mayes, Y. Oyola, T. Saito, C. J. Janke, S. Dai, E. Schneider and D. Sachde, *Sep. Sci. Technol.*,

2012, **48**, 367–387; (*b*) G. Tian, S. J. Teat, Z. Zhang and L. Rao, *Dalton Trans.*, 2012, **41**, 11579–11586; (*c*) P. S. Barber, S. P. Kelley and R. D. Rogers, *RSC Adv.*, 2012, **2**, 8526–8530.

64 M. Carboni, C. W. Abney, S. Liu and W. Lin, *Chem. Sci.*, 2013, **4**, 2396–2402.

65 (*a*) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851; (*b*) M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632–6640.

66 A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. – Eur. J.*, 2011, **17**, 6643–6651.

67 E. Matrosov, E. Goryunov, T. Baulina, I. Goryunova, P. Petrovskii and E. Nifant'ev, *Dokl. Chem.*, 2010, **432**, 136–139.

68 Y. Feng, H. Jiang, S. Li, J. Wang, X. Jung, Y. Wang and M. Chen, *Colloids Surf., A*, 2013, **431**, 87–92.

69 W. Yang, Z.-Q. Bai, W.-Q. Shi, L.-Y. Yuan, T. Tian, Z.-F. Chai, H. Wang and Z.-M. Sun, *Chem. Commun.*, 2013, **49**, 10415–10417.

70 S. H. Choi and Y. C. Nho, *Radiat. Phys. Chem.*, 2000, **57**, 187–193.

71 S.-Y. Moon, Y. Liu, J. T. Hupp and O. K. Farha, *Angew. Chem., Int. Ed.*, 2015, **54**, 6795–6799.

72 Y. G. Chung, J. Camp, M. Haranczyk, B. J. Sikora, W. Bury, V. Krungleviciute, T. Yildirim, O. K. Farha, D. S. Sholl and R. Q. Snurr, *Chem. Mater.*, 2014, **26**, 6185–6192.