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Post-synthetic metalation in an anionic MOF for efficient catalytic activity and removal of heavy metal ions from aqueous solution

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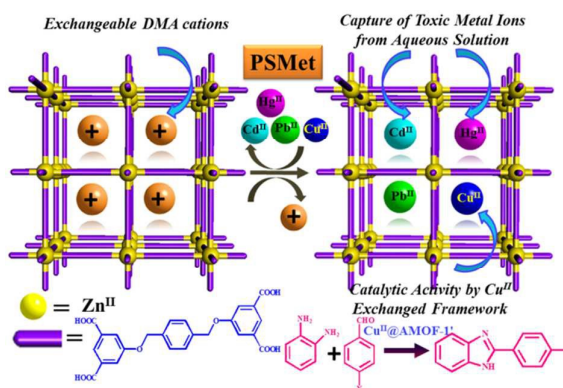
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A new 3D porous anionic MOF (AMOF-1) based on Zn^{II} and flexible tetracarboxylate linker has been synthesized. AMOF-1 showed potential for capture and removal of toxic metal ions from aqueous solution with a detection limit in ppm level. Cu^{II}@AMOF-1 hybrid obtained by post-synthetic metalation is studied as heterogeneous catalyst for the synthesis of benzimidazole derivatives.

The extraordinary modular nature of metal-organic frameworks (MOFs)¹ allow post-synthetic modification (PSM) of the pristine framework to furnish novel properties.² In this regard, Anionic MOFs (AMOFs)³ are particularly interesting since their nanopores can be modified using simple ion-exchange process. However, their tunability gives them an edge over conventional ion-exchangers like zeolite.⁴ Through post-synthetic metalation⁵ (PSMet, a subset of PSM approach), AMOFs can be functionalized suitably for targeted actions via the encapsulation of exogenous metal ions, e.g. sensitization of lanthanide ions⁶, capture of toxic heavy metal pollutants from liquid phase waste⁷ or immobilization of highly Lewis acidic metal sites for catalysis. Herein, we focus our study to exploit an AMOF for such applications.

Environmental pollution by heavy metals like Pb^{II}, Cd^{II} and Hg^{II} is a major threat to human health which continues to increase with rapid industrialization. Thus effective capture and removal of these heavy metal ions from water is of utmost importance.⁸ Although porous solids like activated carbon have been traditionally used to adsorb heavy metal ions, the higher flexibility and structural diversity in MOFs led us to envisage that a suitable AMOF will be much more effective for this purpose. Water stability along with a good detection limit,



Scheme 1: Schematic representation of the AMOF-1 and its applications to capture toxic heavy metal ions and Lewis acidic catalytic activity through PSMet.

preferably in the parts per million (ppm) level^{8d} should be the desired features of the AMOF for efficient capture of heavy metal ions from their aqueous solution.

To realize Lewis acidic catalytic activity in AMOFs, PSMet could be a promising approach where the resulting hybrid would contain unsaturated metal site (UMS)^{9,10} in desolvated state, as in general the pristine AMOF will not fulfil all the coordination sites of the encapsulated metal ions. Furthermore, based on the favourable interaction with the AMOF, the metal ions will be precisely positioned in the framework, thus they would not suffer from leaching during catalysis. The exchanged solid MOF being a heterogeneous catalyst also offers easy removal of catalyst from reaction mixture. In this context we envisioned to exploit Cu^{II} exchanged AMOF as a Lewis acid catalyst for the synthesis of benzimidazole derivatives, which are important intermediates in different organic reactions¹¹ and are also essential for various medicinal applications including antiviral, antiulcer, antifungal, antihypertensive, anticancer and antihistamine activity.¹²

In this communication we report the synthesis and structural characterization of a 3D flexible AMOF

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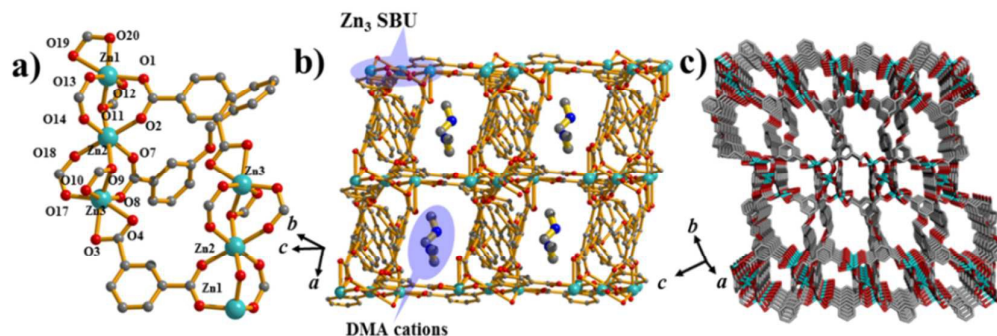


Fig. 1. (a) View of the coordination environment around Zn^{II} centers and the trinuclear SBU. Color Code: C: grey; Zn: cyan; O: red. (b) View of the 3D framework with the rectangular channel containing DMA cations. (c) View along crystallographic *a* direction showing biporous 3D framework with interconnected channels.

$\{[(\text{NH}_2\text{Me}_2)_2][\text{Zn}_3(\text{L})_2] \cdot 9\text{H}_2\text{O}\}$ (AMOF-1; L = 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diiisophthalic acid) which is exploited for capture and removal of toxic heavy metal ions from water with a detection limit in ppm level. To the best of our knowledge, capture of toxic metals in ppm level by an AMOF is unprecedented. Moreover, PSMet of AMOF-1' (desolvated AMOF-1) with Cu^{II} results in Cu^{II}@AMOF-1' hybrid which is studied as a catalyst for synthesis of benzimidazole derivatives.

Single-crystal X-ray diffraction experiment reveals that AMOF-1 crystallizes in the triclinic $P\bar{1}$ space group and the asymmetric unit contains three crystallographically independent hexa-coordinated Zn(II) centers, two linkers (L1 and L2) and two different dimethyl ammonium (DMA) cations. Three Zn^{II} centers in the anionic framework $[\text{Zn}_3(\text{L})_2]$ are linked to each other through the carboxylate groups of the linker L. Zn1 and Zn2 are connected through different bridging bidentate carboxylate groups (O1, O2; and O13, O14 oxygen atoms) in *syn-syn* fashion. Zn1 and Zn2 are also bridged by μ_2 -oxo bridging (O11 atom) from another carboxylate group. Zn2 and Zn3 are connected similarly (Figure 1a). Such connections result in the formation of a trinuclear $[\text{Zn}_3(\text{CO}_2)_8]$ secondary building unit (SBU). Each of the linkers (L1 and L2) is connected to four $[\text{Zn}_3(\text{CO}_2)_8]$ SBUs and the dihedral angles between two terminal benzene rings of L1 and L2 are 79.8° and 73.9°, respectively.¹⁴ Such spatial orientation of the terminal benzene rings containing carboxylate groups eventually extend the SBUs along the crystallographic *ac* plane. The 2D networks lying in the *ac* plane are further bridged through two crystallographically different L linkers along the *b* direction resulting in a complex 3D framework structure.¹⁴ The framework houses rectangular channels which are occupied by DMA cations (Figure 1b). Also along crystallographic *a* direction, two different channels can be seen which are circumvented by the phenyl rings (Figure 1c). The smaller and the larger channels (pore dimensions are 2.7×2.2 Å² and 4.1×3.6 Å² respectively) are interconnected by the DMA cations containing channels.¹⁴ Topological analysis shows that AMOF-1 is a 2-nodal net and has fluorite type topology with stoichiometry (4-c)2(8-c). The Schläfli symbol of the net is determined as $\{4^{12}.6^{12}.8^4\}\{4^6\}\{2\}$.¹⁴ The solvent water molecules are highly disordered and hence could not be

located crystallographically. The solvent accessible void space of the framework including the DMA cations is 27% of the total cell volume. TGA shows a loss of 11% up to 120 °C, which corresponds to loss of nine guest water molecules and the desolvated framework is stable up to 300 °C.¹⁴ Elemental analysis also supports the formula of AMOF-1 as $\{[(\text{NH}_2\text{Me}_2)_2][\text{Zn}_3(\text{L})_2] \cdot 9\text{H}_2\text{O}\}$. PXRD pattern of AMOF-1' reveals that the PXRD pattern becomes slightly broadened upon desolvation but the structural integrity is maintained (Figure 2a). When solid sample of AMOF-1 was immersed in water for 7 days and the dried sample shows similar PXRD pattern to AMOF-1 suggesting its stability in water.¹⁴

AMOF-1' does not adsorb any N₂ at 77 K probably due to the high diffusion barrier for N₂ into the framework. CO₂ adsorption at 195 K reveals an initial type I uptake of 30 ml/g up to *P* = 0.65 bar followed by a step with a final uptake of 145 ml/g at 1 bar (Figure 2c). The desorption curve does not retrace the adsorption profile and shows a large hysteric sorption profile.

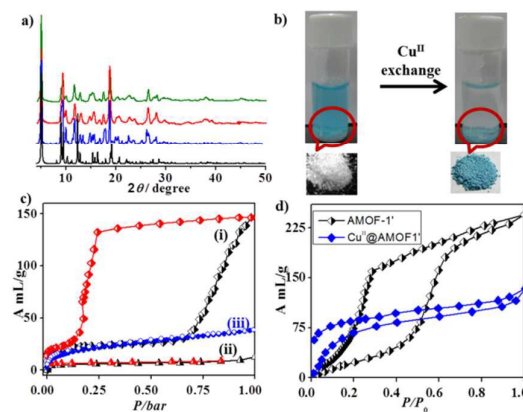


Fig. 2. (a) PXRD patterns; black: simulated; blue: as-synthesized AMOF-1, red: AMOF-1', green: Cu^{II}@AMOF-1' (b) Visible colour change during Cu^{II} exchange in aqueous solution (c) Adsorption isotherms (i) CO₂ of AMOF-1' at 195 K; (ii) N₂ of AMOF-1' at 77 K and (iii) CO₂ of Cu^{II}@AMOF-1' at 195 K; (d) Water vapour adsorption isotherms for AMOF-1' and Cu^{II}@AMOF-1' at 298 K; *P*₀ is the saturated vapour pressure of the adsorbates at respective temperature.

We conjecture that CO₂ molecules first diffuse into the larger pore resulting in the initial uptake. The interaction between polar DMA cations and CO₂ molecules probably induce

diffusion through the interconnected channels thus resulting in stepwise adsorption. The hysteretic adsorption suggests different adsorption sites for CO₂ molecules in the framework. The anionic nature and water stability of the framework motivated us to study the capture and removal of toxic heavy metal ions from their aqueous solution. To check the ability to capture in a very low concentration, we have performed cation exchange by immersing 20 mg AMOF-1' in 20 ml 1 ppm M^{II} solutions.¹⁴ The initial and residual metal ion concentrations were measured through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis, which showed that after 24 hours almost complete removal of heavy metal ions occur (Table 1). Thus AMOF-1' can be used for effective removal of heavy metal ions from waste water with detection limit in ppm level. Time-dependent measurements were performed for Hg^{II} ion which shows within 24 hours almost complete removal (98.7%) occur. To know the uptake capacity of different ions, AMOF-1' was immersed in 0.01(M) solutions of Pb^{II}, Cd^{II} and Hg^{II} and the solutions were stirred for 24 hours.¹⁴ Exchange experiments were also carried out for prolonged time (7 days) to check the maximum uptake capacity. ICP analyses of the exchanged solids suggest that number of Hg^{II}, Pb^{II} and Cd^{II} cations per formula unit are 0.31, 0.26 and 0.29 respectively after 24 hours of exchange reaction, which increases to 0.48, 0.42 and 0.45 after 7 days of exchange.¹⁴ The maximum uptake capacity for Hg^{II}, Pb^{II} and Cd^{II} are 78 mg, 71 mg and 41 mg per g of AMOF-1', respectively. ICP analysis of the exchanging solution does not show presence of Zn^{II} ions which indicate that Zn^{II} ions do not leach out from the framework and do not exchange with the heavy metal cations. On the other hand, NMR analysis of exchanging solution shows presence of DMA cation, clearly advocating that the metal inclusion in the AMOF occurs by cation exchange.¹⁴

Table 1: Results for the heavy metal ion exchange from 1 ppm aqueous solution

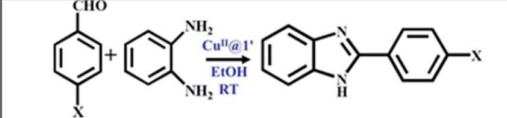
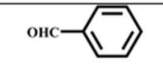
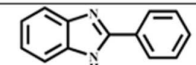
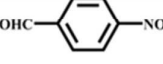
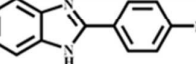
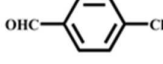
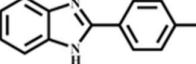
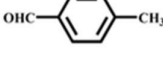
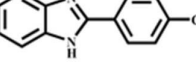
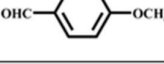
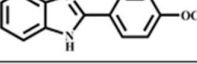
Heavy metal (M ^{II})	Exchange time (hour)	Initial concentration of M ^{II} ions (ppm)	Concentration of M ^{II} ions after exchange(ppm)	Removal efficiency (%)
Hg ^{II}	2	1	0.579	42.1
	6	1	0.326	67.4
	12	1	0.109	89.1
	18	1	0.059	94.1
	24	1	0.013	98.7
Pb ^{II}	24	1	0.024	97.6
Cd ^{II}	24	1	0.018	98.2

Next, we have checked encapsulation of different transition metal ions (M^{II}) ions by immersing AMOF-1' into 0.01(M) solutions of M^{II} for 24 hours.¹⁴ ICP data of the exchanged solids suggest that Cu^{II} ions are exchanged with 49% of the DMA guests, while the extent of exchange for Mn^{II}, Co^{II}, and Ni^{II} are 24, 25, 27% respectively. The DMA cations in the exchanging solution for Cu^{II} exchange experiment were quantified through ICP analysis, which suggests 47% exchange of DMA cations.¹⁴ The higher percentage of Cu^{II} exchange is attributed to the

flexible geometry of Cu^{II} which helps Cu^{II} ions to be accommodated in diverse coordination environments in the nanospace.⁶ Such exchange is also evident as a blue solution of Cu^{II} in water becomes colourless on dipping AMOF-1' in it, while the white solid of AMOF-1' transform into blue coloured Cu^{II}@AMOF-1' (Figure 2b). It is noteworthy that extent of Cu^{II} exchange does not increase after 7 days of exchange.¹⁴ The structural integrity is maintained upon Cu^{II} inclusion as evident from the PXRD patterns (Figure 2a). We conjecture that the Cu^{II} ions replace the DMA cations and would reside near the carboxylate oxygen atoms (see ESI) which can serve as coordination sites for Cu^{II}. The TGA profile of Cu^{II}@AMOF-1' shows continuous weight loss at higher temperature (>150 °C) suggesting the presence of Cu^{II} bound water molecules.

The Cu^{II} inclusion was further validated from the CO₂ adsorption isotherm which shows a type I (Figure 2c) profile without any step. We propose that once Cu^{II} ions replace the DMA cations, the accessibility of the interconnected channels would be restricted resulting in a type I profile without any step/hysteresis. To further investigate the impact of Cu^{II} exchange on the polarity of the pore surfaces, water adsorption measurements were carried out at 298 K for AMOF-1' and Cu^{II}@AMOF-1'. A type IV profile is observed for AMOF-1' which suggests hydrophobic nature of the pore surface (Figure 2d). In Cu^{II}@AMOF-1', the steeper uptake at low pressure regions compared to that of AMOF-1' (Figure 2d) suggest strong affinity of water molecules to the pore surface, which can be attributed to the presence of open Cu^{II} Lewis acidic sites in Cu^{II}@AMOF-1'.

Table 2: The catalytic reactions and the results with varying substituent on the aldehydes

		
Aromatic aldehyde	Benzimidazole (product)	Conversion (%)
		97
		88
		82
		60
		23

The permanent porosity and presence of UMS in the activated Cu^{II}@AMOF-1' inspired us to use this hybrid as a Lewis acid catalyst for the synthesis of chemically important

benzimidazole compounds (Table 2).¹³ We have carried out reaction of *o*-phenylenediamine with different *p*-substituted benzaldehyde (X= H, NO₂, Cl, CH₃ and OCH₃) at room temperature.¹⁴ The quantitative analysis of product conversion is monitored by GC-MS analyser at regular intervals of times. The conversion of products with benzaldehyde (X= H) is 62% after 3 h, after 6 h the product conversion is increased to 97%, suggesting that the conversion is almost complete within 6 h (for X= H). We did not find any detectable amount of the desired benzimidazole product through GC-MS data analysis when homogeneous Cu^{II} catalyst, dehydrated cupric acetate was used as a catalyst under similar conditions as employed for Cu^{II}@AMOF-1'. This reflects the heterogeneous Cu^{II}@AMOF-1' is a superior catalyst than the homogeneous Cu^{II} catalyst.¹⁴ We have carried out reaction of *o*-phenylenediamine and benzaldehyde in the presence of only AMOF-1', which shows no conversion of product even after 12 hours. This suggests that AMOF-1' could not act as a catalyst. The pristine solvated Cu^{II}@AMOF-1' also does not show any catalytic activity as the coordinated water molecules inhibits any Lewis acid catalytic activity.¹⁴ In another reaction using Cu^{II}@AMOF-1' catalyst, we have removed the catalyst after a time period of 3 h by filtration and the reaction mixture was further stirred for additional 3 h. After 6 h, there was no increase in the yield (62%), suggesting that Cu^{II} sites indeed act as the catalytic sites. ICP analysis of the filtrate obtained after removing the solid catalyst from the reaction mixture shows no detectable Cu^{II} ions suggesting that no leaching of Cu^{II} ions occurs during the catalysis. This result indicates that the AMOF-1' stabilizes Lewis acidic Cu^{II} sites on the pore surface. Furthermore, experiments were performed with various aromatic aldehydes having different substituents with reaction time of 6 h (Table 2). Although the conversion of the products are significant for X= H, NO₂ and Cl, the yield is significantly reduced for X= CH₃ and OCH₃ group (the purity of the products is verified through the ¹H NMR measurements of the pure compounds¹⁴). This suggests that an electron withdrawing group at *para* position of aldehyde enhance electrophilic nature of the carbonyl carbon thereby increasing its reactivity, while electron donating methoxy and methyl groups exhibit lesser yield (Table 2). The recyclability experiment¹⁴ was studied with benzaldehyde (X = H), which suggest that the solid catalyst could be reused for at least 3 cycles.

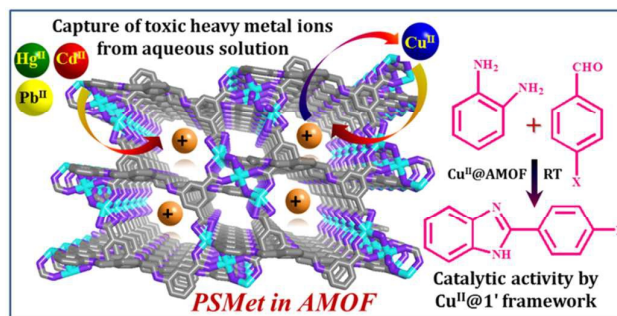
In conclusion, we have developed a new porous AMOF that allows easy access of desired exogeneous cations and offers a unique way to post-synthetically modify the AMOF. The AMOF effectively capture toxic metal ions from their aqueous solutions. The Cu^{II} exchanged AMOF shows good catalytic activity towards the synthesis of benzimidazole derivatives at room temperature. Such PSMet in water stable AMOFs will ensue a new route to capture toxic metal ions from industrial waste water. Suitable AMOF would also act as the platform to immobilize different cationic groups to obtain versatile targeted functions.

Notes and references

‡ The CCDC number of AMOF-1 is 1431244.

- 1 Themed Issue: Metal-organic Frameworks, *Chem. Rev.*, 2012, **112**, 673-1268.
- 2 (a) S. M. Cohen, *Chem. Rev.* 2012, **112**, 970–1000; (b) W. M. Bloch, R. Babarao, M.R. Hill, C. J. Doonan and C. J. Sumbly, *J. Am. Chem. Soc.*, 2013, **135**, 10441-10448; (c) C. K. Brozek and M. Dinca, *J. Am. Chem. Soc.*, 2013, **135**, 12866-12891; (d) D. Sun, F. Sun, X. Deng and Z. Li, *Inorg. Chem.*, 2015, **54**, 8639-8643; (e) D. Sun, W. Liu, M. Qiu, Y. Zhang and Z. Li, *Chem. Commun.*, 2015, **51**, 2056-2059; (f) J. S. Costa, P. Gamez, C. A. Black, O. Roubeau, S. J. Teat and J. Reedijk, *Eur. J. Inorg. Chem.*, 2008, 1551-1554.
- 3 (a) E. Quartapelle Procopio, F. Linares, C. Montoro, V. Colombo, A. Maspero, E. Barea and J. A. R. Navarro, *Angew. Chem. Int. Ed.*, 2010, **49**, 7308-7311; (b) J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen and G. Qian, *Angew. Chem. Int. Ed.*, 2012, **51**, 10542-10545; (c) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **131**, 8376-8377; (d) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586-10589; (e) J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno and P. K. Thallapally, *J. Am. Chem. Soc.*, 2012, **134**, 9581-9584; (f) S. Yang, G. S. B. Martin, J. J. Titman, A. J. Blake, D. R. Allan, N. R. Champness and M. Schröder, *Inorg. Chem.*, 2011, **50**, 9374-9384; (g) J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen and G. Qian, *Nat Chem*, 2013, **4**: 2719.
- 4 P. Vanelderen, J. Vancauwenbergh, B. F. Sels and R. A. Schoonheydt, *Coord. Chem. Rev.*, 2013, **257**, 483-494.
- 5 (a) J.D. Evans, C. J. Sumbly and C. J. Doonan, *Chem. Soc. Rev.*, 2014, **43**, 5933.
- 6 S. Bhattacharyya, A. Chakraborty, K. Jayaramalu, A. Hazra and T. K. Maji, *Chem. Commun*, 2014, **50**, 13567-13570.
- 7 (a) B. J. Zhu, X. Y. Yu, Y. Jia, F. M. Peng, B. Sun, M. Y. Zhang, T. Luo, J. H. Liu and X. J. Huang, *J. Phys. Chem. C* 2012, **116**, 8601–8607; (b) J. He, K. K. Yee, Z. Xu, M. Zeller, A. D. Hunter, S. S. Y. Chui and C. M. Che, *Chem. Mater.* 2011, **23**, 2940 – 2947.
- 8 (a) S. B. Maity, S. Banerjee, K. Sunwoo, Jong Seung Kim and P. K. Bharadwaj, *Inorg. Chem.* 2015, **54**, 3929-3936; (b) K. K. Yee, N. Reimer, J. Liu, S. Y. Cheng, S. M. Yiu, J. Weber, N. Stock and Z. Xu, *J. Am. Chem. Soc.* 2013, **135**, 7795–7798; (c) X. P. Zhou, Z. T. Xu, M. Zeller and A. D. Hunter, *Chem. Commun.* 2009, 5439–5441; (d) T. Liu, J.-X. Che, Y.-Z. Hu, X.-W. Dong, X.-Y. Liu and C.-M. Che, *Chem. Eur. J.* 2014, **20**, 14090-14095.
- 9 (a) B. Chen, M. Eddaoudi, T. M. Reineke, J. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.* 2000, **122**, 11559; (b) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* 2005, **117**, 4823; *Angew. Chem. Int. Ed.* 2005, **44**, 4745; (c) A. Hazra, P. Kanoo and T. K. Maji, *Chem. Commun.*, 2011, **47**, 538.
- 10 (a) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.* 2008, **130**, 10870; (b) X.-L. Yang, C. Zou, Y. He, M. Zhao, B. Chen, S. Xiang, O'Keeffe and C.-D. Wu, *Chem. Eur. J.* 2014, **20**, 1447-1452.
- 11 Y. Bai, J. Lu, Z. Shi and B. Yang, *Synlett* 2001, 544–546.
- 12 (a) D. G. O'Sullivan and A. K. Wallis, *J. Med. Chem.* 1972, **15**, 103–104; (b) P. W. Erhardt, *J. Med. Chem.* 1987, **30**, 231 – 237; (c) G. L. Gravatt, B. C. Baguley, W. R. Wilson and W. A. Denny, *J. Med. Chem.* 1994, **37**, 4338–4345.
- 13 (a) N. Zheng, K.W. Anderson, X. H. Huang, H. N. Nguyen and S. L. Buchwald, *Angew. Chem.* 2007, **119**, 7653–7656; (b) M. Shen and T. G. Driver, *Org. Lett.* 2008, **10**, 3367–3370; (c) L. C. R. Carvalho, E. Fernandes, M. M. B. Marques, *Chem. Eur. J.* 2011, **17**, 12544–12555; (d) A. Dutta, J. Mondal, A. K. Patra and A. K. Bhaumik, *Chem. Eur. J.*, 2012, **18**, 13372-13378.
- 14 See ESI.

Graphical abstract



An anionic MOF shows the potential of capture toxic metal ions from water and the Cu^{II}@AMOF hybrid obtained through post-synthetic metalation is used as a Lewis acid catalyst.