Check for updates

View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: O. A. Serra, A. B. Galaço, K. T. de Oliveira, M. C. Donatoni and R. I. Walton, *Chem. Commun.*, 2019, DOI: 10.1039/C9CC03721G.

Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION
Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen *et al.*
Reactivity differences of $Sc_3N@C_{2n}$ ($2n$ = 68 and 80). Synthesis of the first methanofullerene derivatives of $Sc_3N@D_{5h}$-C_{80}

175 YEARS

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

Please do not adjust margins

View Article Online
DOI: 10.1039/C9CC03721G

Journal Name

COMMUNICATION

Ion-exchange resin as a new tool for characterisation of coordination compounds and MOFs by NMR spectroscopy

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ayla Roberta Borges da Silva Galaço,[a] Kleber Thiago de Oliveira,[b] Maria Carolina Donatoni,[b] Richard I. Walton[c] and Osvaldo Antonio Serra[a,d*]

Published on 17 June 2019. Downloaded by American University of Beirut on 6/22/2019 10:26:18 PM.

ChemComm Accepted Manuscript

^{1}H and ^{13}C NMR spectroscopy is used to investigate the organic constituents of metal complexes, MOFs and coordination compounds synthesised under solvothermal and precipitation conditions. The elucidation of the ligands in paramagnetic compounds bearing $Cu^{2+}(d^9)$, Gd^{3+} (f^7), Eu^{3+} (f^6), $Fe^{3+}(d^5)$, ions after treatment with a cationic exchange resin is possible. We prove the efficiency of two post-synthesis linker modifications on diamagnetic IRMOF-3 Zn^{2+} (d^{10}) with ethyl isocyanate and benzyl bromide.

The compositional analysis of coordination compounds, which now includes the large class of coordination polymers and metal-organic frameworks, can be challenging in the absence of single crystal data. Many compounds bearing transition metal and lanthanoid cations have relevant applications in chemistry and apart from being present in biological systems, these ions can also combine with thousands of organic ligands, to result in compounds that deserve intense scientific study.[1-3] The paramagnetic effect limits investigation by nuclear magnetic resonance (NMR) and limits the use of this very elucidative technique to shed light on chemical structures.[4] The usual strategy to analyse complexes containing paramagnetic ions is to add a strong acid or base to the complex, to cleave the M-L bonds and to release the ion and the ligands.[5] However, this protocol can partially or completely destroy the organic ligand, to culminate in very difficult and unreliable analysis. A second situation where analysis of ligand chemistry is challenging is when metal-organic frameworks (MOFs) have been subjected to post-synthesis modification: here, a proportion of the ligand is chemically modified, and often long-range order and crystallinity is lost. Furthermore, reactive functionality is introduced that may be destroyed on acid or base treatment. MOFs represent a large class of porous compounds and they offer enormous structural diversity and several possibilities to create materials with specific properties;[6-12] hence accurate chemical analysis is needed for characterisation. Because the syntheses are carried out at high temperatures, for various days, some ligands may decompose, to generate new unexpected structures.[13,14,15]

In this communication, we demonstrate that ^{1}H and ^{13}C NMR spectroscopy can be employed to characterise complexes and metal organic frameworks (MOFs) of paramagnetic ions without the need to use conventional strong acid or base during chemical processing. We determine the ligands present in the previously reported samples of MOFs and coordination complexes containing paramagnetic $Cu^{2+}(d^9)$, $Eu^{3+}(f^6)$ and $Gd^{3+}(f^7)$, Figure 1. We also report a study using a diamagnetic $Zn^{2+}(d^{10})$ MOF, to which two different post-synthesis modifications are performed. Here, we propose a soft procedure based on a cationic ion exchange resin to determine the organic constituents of coordination compounds and MOFs, Figure 2. The metal ions bind to the resin sulfonyl groups ($-SO_3$) through electrostatic interactions, to release hydrogen ions to the medium. Resins displaying negative groups, such as $-SO_3^-$, are classified as strongly acid cationic.[16-17] They were first used to purify water and to separate ions, and they played an important role during the Manhattan Project, which dealt with uranium purification.[18] In recent years, synthetic polymeric ion exchangers have been applied as efficient adsorbents in industrial wastewater treatment because they are easy to remove and to regenerate for repeated use. Our group has employed the Dowex 50WX12 ion exchange resin to dissolve and to analyse rare earth trimetaphosphates.[19]

In this study, we used a strongly acid cationic ion exchange resin to analyse the organic constituents of paramagnetic compounds (Figure 2). To this end, the solid samples of complexes or MOFs were mixed with the ion-exchange resin, to

---

[a] University of São Paulo, Chemistry Department, FFCLRP, Ribeirão Preto, Av. Bandeirantes, 3900, 14040-901, Ribeirão Preto – SP, Brazil *oserra@usp.br
[b] Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, 13565-905, Brazil.
[c] University of Warwick, Department of Chemistry, Coventry CV4 7AL, U.K
[d] Universidade Federal do ABC, CCNH, Av. dos Estados, 5001, 09210-580, Santo André – SP, Brasil

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Please do not adjust margins

View Article Online
DOI: 10.1039/C9CC03721G

Published on 17 June 2019. Downloaded by American University of Beirut on 6/22/2019 10:26:18 PM.

result in protonation of the anionic ligand (L) and release in its acid form (HL) with trapping of the cations by the resin. This was carried out in either D_2O or deuterated DMF or DMSO, depending on the solubility of HL, and after separation from the resin, the solutions were analysed by ^{1}H NMR and ^{13}C NMR spectroscopy. The process is depicted in Figure 2. Compound HKUST-1 ($Cu_3(btc)_2$) (btc = benzene-1,3,5-tricarboxylate) was the first to be subjected to this protocol.[20] The resin captured the Cu^{2+} ions, to release benzene-1,3,5-tricarboxylic acid, which was then analysed by ^{1}H NMR and ^{13}C NMR (Figure 3). The solvents, acids and water, were deuterated; the ion exchange resin Dowex 50WX12 with 200-400 mesh and exchange capacity of 1.7 meq/mL was employed.

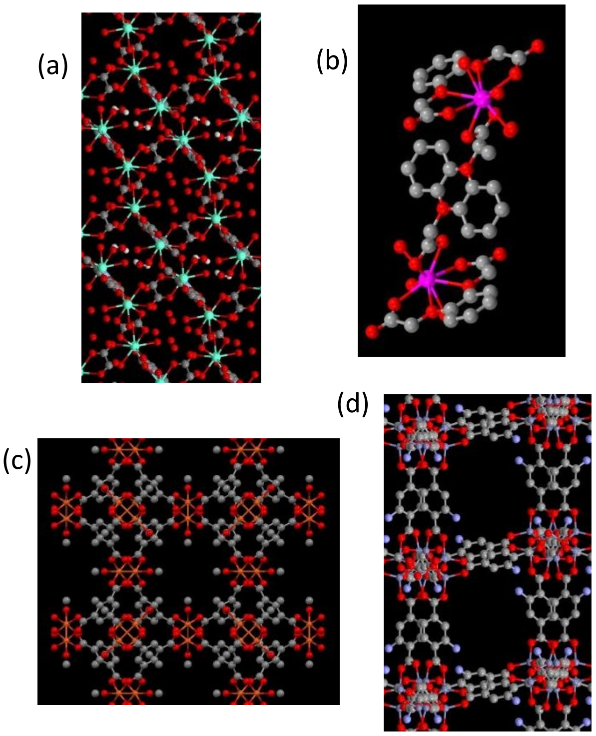


Figure 1: Structure of (a) $[Eu_2(ptc)_2{\cdot}5H_2O{\cdot}(H_2O)]_n$ (b) $[Gd(ofd){\cdot}8H_2O]$ (c) HKUST-1 $[(Cu_2(btc)_3)]_n$ (d) IRMOF-3 $[Zn_4O(bdc\text{-}NH_2)_3]_n$. Oxygen atoms are shown in red, carbon atons grey, and the metals as the third colour in each panel. See text for definition of liagnds ptc, ofd, btc and bdc.

We treated the Dowex 50WX12 cation exchanger with DCl 1.0 mol.L^{-1} solution three times, washed it with D_2O four times, and dried it at 25 °C after filtration. Subsequently, we added 0.5 mL of the treated resin (≈ an excess of 20 times), 0.5 mL of deuterated *N*,*N*-dimethylformamide, and 0.5 mL of D_2O to 10 mg of MOF in a screw-caped recipient. After two days, the solution was filtered off into an NMR-tube and analysed at 400 and 100 MHz for ^{1}H and ^{13}C NMR, respectively.

The ^{1}H NMR signal at 8.7± 0.02 ppm (Figure 3a) perfectly fitted with the signal expected for benzene-1,3,5-tricarboxylic acid and was corroborated with a commercial standard (Figure 3b). Similarly, treatment of 10 mg of the MOF$[Eu_2(ptc)_2{\cdot}5H_2O){\cdot}H_2O]_n$ (ptc = 2,4,6-pyridinetricarboxylate) by the same protocol allowed us to determine the presence of the ligand (for details see the SI).[21]

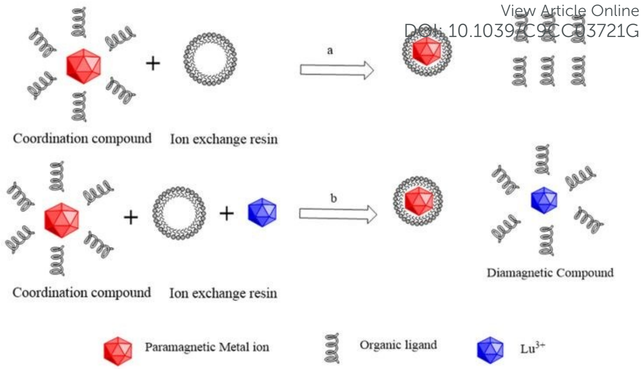


Figure 2: Illustration of paramagnetic ions bonded to an ion exchange resin – (a) non-strongly bonded ligands; (b) strongly bonded ligands.

The PXRD (Figure S11) indicates the presence of at least one impurity. However, this is not unreacted 2,4,6-ptc. The TGA (Figure S2) is in agreement with the bulk composition; the impurity phase(s) must be present in small amounts, or are polymorphs of the major phase.

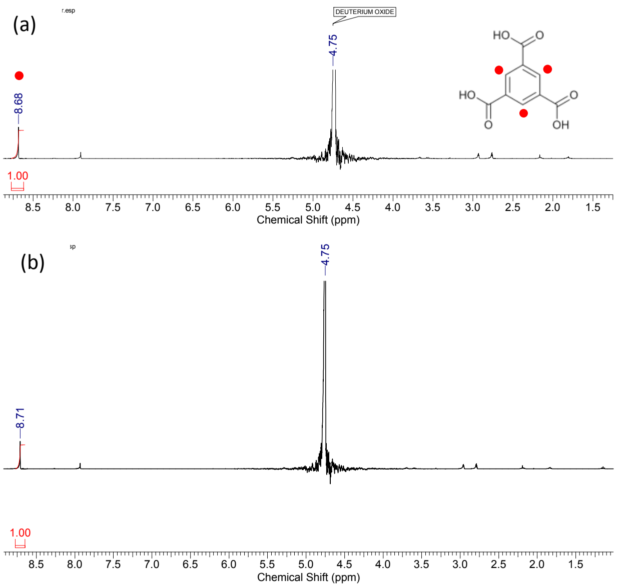


Figure 3: ^{1}H NMR of benzene-1,3,5-tricarboxylate in D_2O from (a) **MOF HKUST-1** after treatment with the resin and (b) commercial standard obtained from Aldrich.

The ^{1}H NMR signal at 8.78 ppm indicated the presence of C-H in the benzene ring (Figure 4a). The signals at 128.1, 142.8, 150.1, 166.5 and 166.7 ppm present in the ^{13}C NMR analysis confirmed the presence of pyridine tricarboxylic acid (Figure S17). We recorded the ^{1}H NMR spectra of the ligands released from the Cu^{2+} and Eu^{3+} MOFs and compared them with the standard ligands. We measured the T_1 from the $\nu_{1/2}$ of the signals at 8.68 ppm (H_2btc) and 8.78 (H_3ptc) (see SI, Fig S25). The same values were obtained for both released and standard ligands with 1.25 Hz for H_2btc (T_1 = 254 ms) and 1.37 Hz for H_3ptc (T_1 = 232 ms). All these results indicate the absence of paramagnetic ions in solution after the ion exchange treatment.

ChemComm Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C9CC03721G

Published on 17 June 2019. Downloaded by American University of Beirut on 6/22/2019 10:26:18 PM.

ChemComm Accepted Manuscript

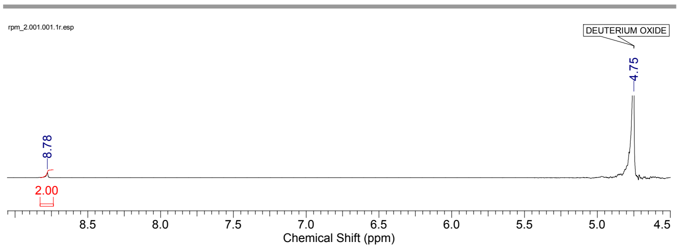


Figure 4: ^1H NMR of pyridine tricarboxylic acid (**H_3ptc**). Signal relative to **ptc** emerged at 8.78 ppm.

The Gd^{3+} ion has seven unpaired electrons, which makes its coordination compounds strongly paramagnetic. We synthesised the coordination compound $Gd_2(ofd)_3{\cdot}8H_2O$ (ofd = o-phenylenedioxydiacetate) in order to test the efficiency of the ion-exchange towards such a compound (SI).[22] In this case, the resin does not exchange the cation due to the high binding affinity between $Gd^{3+}$and the organic ligand. In order to release the Gd^{3+} from the coordination complex, we exchanged it with Lu^{3+} (f^{14}). Among rare earth cations, diamagnetic Lu^{3+} provides the highest stability constants with most organic ligands. Therefore, accomplishing the resin treatment described above, the Gd^{3+} goes to the resin and the Lu^{3+} diamagnetic coordination compound can equally be analysed by NMR, Figure 2b.

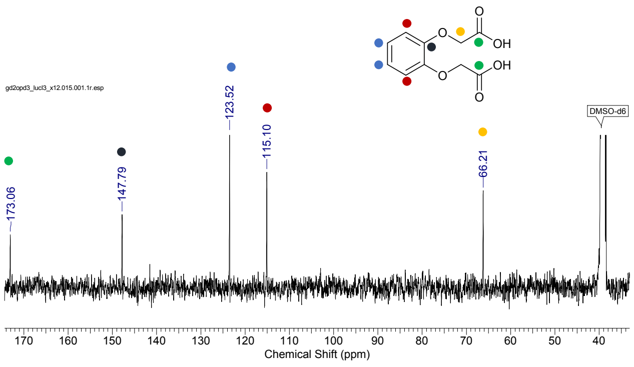


Figure 5: ^{13}C NMR of *o*-phenylenedioxydiacetic acid from the $Gd_2(ofd)_3{\cdot}8H_2O$ complex.

Analysis of the ^{13}C NMR spectra (Figure 5) allowed us to assign the chemical shifts at 115.1, 123.5, and 147.7 ppm to the aromatic ring carbons. The signal at 66.6 ppm corresponds to aliphatic carbon, and the signal at 173.1 ppm referred to the C=O carbon. The strong paramagnetism of compounds containing Gd^{3+} leads to broad NMR peaks. If Gd^{3+} exchange for Lu^{3+} is not satisfactory, NMR peak broadening occurs even if only a small amount of gadolinium is present in the medium. We also analysed the stable MOF MIL-53 $[Fe(OH)_{0.2}F_{0.8}(bdc)]$ containing paramagnetic Fe^{3+}, by using the same procedure, and the ligand bdc (benzene-1,4-dicarboxylate) was confirmed as its acid by ^1H NMR and ^{13}C NMR spectroscopy. The data are presented in Figure S18 in the SI.

"Post-synthetic" modification of MOFs can provide a method for introducing functional groups into the materials, generating a greater range of physical and chemical properties than could be achieved by direct synthesis alone.[23,24] After the reaction the MOFs often become polycrystalline in nature and, therefore, determination of the modification becomes a challenge in the absence of crystallographic methods. To analyse the post modification method, we first synthesised the well-known IRMOF-3 ($(Zn_4O(bdc\text{-}NH_2)_3)$) (bdc-$NH_2$ = 2-amino-benzene-1,4-dicarboxylate) and then functionalised it with ethyl isocyanate (IRMOF-3-EISCN) (details in the SI).[25-26] Treatment of 10 mg of the IRMOF-3-EISCN was done using the ion-exchange protocol outlined before. The ^1H NMR signals at 1.48 ppm indicated the presence of CH_3 group, whereas the signals at 3.50 ppm attested to the presence of CH_2 group and NH at 8.65 ppm (Figure 6a). Finally, the ^{13}C NMR chemical shifts at 16.2, 35.02 and 151.6 ppm confirmed the success of the post-synthetic modification (Figure S14).

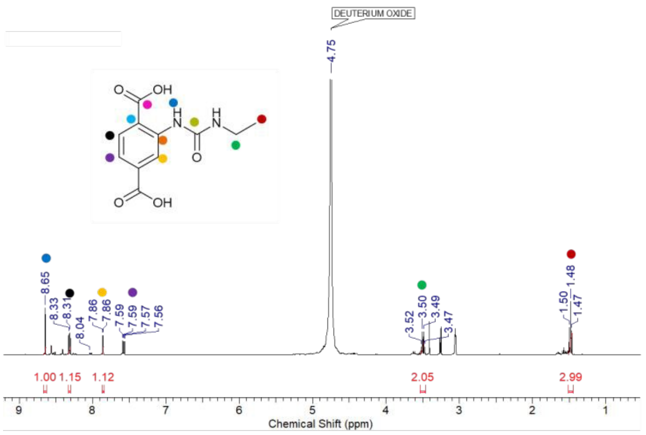


Figure 6: ^1H NMR of the MOF IRMOF-3 post-synthesis functionalised with ethyl isocyanate.

It is expected that the ligands in the centre of the crystal will be difficult to reach during functionalisation, so only partial modification occurs. By NMR it was possible to quantitatively determine the amount of effective post modification. Integrating the signals of the H at 7.59 ppm (1H) and 8.03 ppm (0.13 H), respectively, unmodified and modified compound, we found the value of 11.5% of modified ligand, Figure 7, in accordance with the TGA analysis (11.3%), (details in the SI). Another post-synthetic modification was performed, with benzyl bromide, one not previously reported, and was confirmed by the synthesis of the monomer standard as illustrated in Scheme 1 (synthesis described in the SI). The ^1H NMR signals at 5.07 ppm indicated the presence of CH_2 group, which allowed us to confirm the post modification. The signals between 7 to 8 ppm are attributed to the ^1H at the benzene rings, Figure 8. For quantitative determination of the post-modification, the integration of the signals at 7.65 (1H 0.22) and 8.34 (1H 0.71) lead to the value of 23.3%, Figure 5S(b), in agreement with the value found by TGA, 24%, SI.

In summary, the use of cationic ion exchange resin to remove the paramagnetic ions proved to be a useful tool to elucidate the ligands present in MOFs and coordination compounds. Unmodified organic constituents were determined in all cases.

Please do not adjust margins

Published on 17 June 2019. Downloaded by American University of Beirut on 6/22/2019 10:26:18 PM.

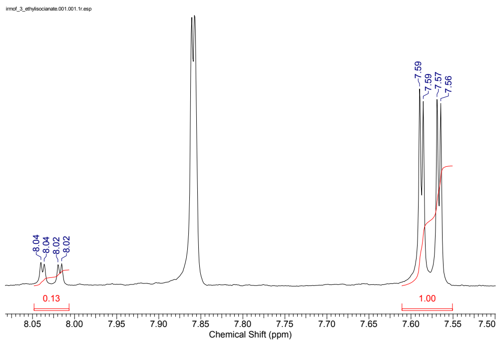
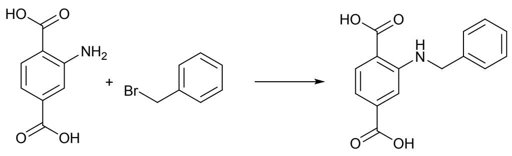


Figure 7: ^{1}H NMR Quantitative determination of post-functionalisation (IRMOF-3-EISCN).



Scheme 1: Functionalisation of 2-aminoterephthalic acid with benzyl bromide.

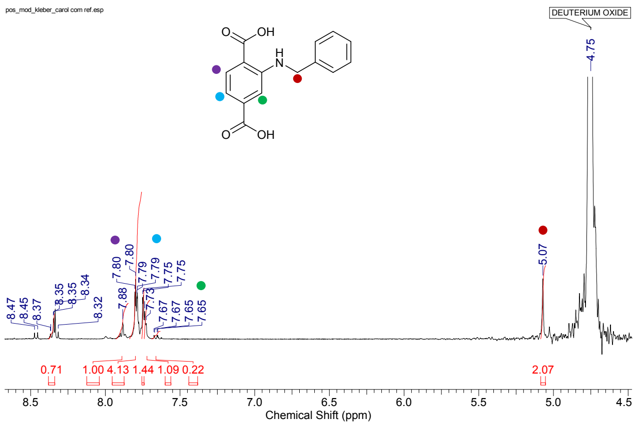


Figure 8: ^{1}H NMR of the MOF IRMOF-3 post functionalised with benzyl bromide.

This method was then applied to post-synthetically modified MOFs and proved to give accurate quantification of ligand functionalisation. The experimental protocol described here opens many possibilities for the analysis of coordination compounds and MOFs and in future work we will extend the method to a greater variety of materials.

We acknowledge the Brazilian agencies CAPES, FAPESP, and CNPq for financial support and scholarships. We would also like to thank Vinicius Palaretti for NMR analysis.

Conflicts of interest

There are no conflicts to declare.

Notes and references

View Article Online
DOI: 10.1039/C9CC03721G

1 N. B. D. Lima, A. I. S. Silva, S. M. C. Gonçalves and A. M. Simas, *J. Lumin.*, 2016, **170**, 505–512.

2 J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926–940.

3 B. B. C. Holanda, R. B. Guerra, A. O. Legendre, D. F. Almeida, T. F. C. Fraga-Silva, Â. C. Finato, J. Venturini and G. Bannach, *Thermochim. Acta*, 2017, **647**, 47–54.

4 F. Rastrelli and A. Bagno, *Chem. - A Eur. J.*, 2009, **15**, 7990–8004.

5 Z. Wang and S. M. Cohen, *J.Am.Chem.Soc.*, 2007, **129**, 12368-12369.

6 H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, *Science*, 2013, **541**, 1230444.

7 Z. Ni and R. I. Masel, *J Am Chem Soc.*, 2006, 12394–12395.

8 T. R. Cook, Y. R. Zheng and P. J. Stang, *Chem. Rev.*, 2016, **113**, 734–777.

9 N. Stock and P. Biswas,*Chem. Rev.*, 2012, **112**, 933-969.

10 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.

11 Y. Takashima, V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto and S. Kitagawa, *Nat. Commun.*, 2011, **2**, 168.

12 J. Seo, D. Whang, H. Lee, S. Jun, J. Oh, Y. Jeon and K. Kim, *Nature.*, 2000, **404**, 982–986.

13 Z. Min, M. A. Singh-Wilmot, C. L. Cahill, M. Andrews and R. Taylor, *Eur. J. Inorg. Chem.*, 2012, 4419–4426.

14 G. Huang, P. Yang, N. Wang, J. Z. Wu and Y. Yu, *Inorganica Chim. Acta.*, 2012, **384**, 333–339.

15 Y. Y. Yang, S. B. Zai, W. T. Wong and S. W. Ng, *Acta Crystallogr. Sect. E Struct. Reports Online.*, 2005, **61**, 1912–1914.

16 C. Harland, *Ion exchange: Theory and practice*, Royal Society of Chemistry, Cambridge 2nd edn., 1994.

17 A. Zagorodni, *Ion exchange materials Properties and Applications*, Kidlington, Elsevier BV, 1nd edn., 2007.

18 K. C, Sole, M. B, Mooiman, E, Hardwick, *Separation & Purification Reviews.*, 2018, **47**, 159-78.

19 O. A, Serra, E. Giesbrecht, *J. Inorg. Nucl. Chem.*, 1968, **30**, 793–99.

20 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.

21 W. Hongsheng, Z. Xiaoquing, L. Mingli, S. Wei and C. Peng, *Chin. J. Chem.*, **30**, 2097-102.

22 Y. Jiang, X-S. Wu, X. Li, J-H. Song and Y-Q. Zou, *J. Coord. Chem.*, 2010, **63**, 36-45.

23 K. K, Tanabe, S. M, Cohen, *Chem. Soc. Rev..*, 2011, **40**, 498-519.

24 Z, Wang and S. M, Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315-1329.

25 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J, O'Keefe. Wachter, O. M. Yaghi, *Science.*, 2002, **295**, 469-472.

26 E. Dugan, Z. Wang, M. Okamura, A. Medina, S. M. Cohen, *Chem.Commun.*, 2008, 3366-3368.

ChemComm Accepted Manuscript