Metal–Organic Frameworks

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A Water-Stable Cationic Metal–Organic Framework as a Dual Adsorbent of Oxoanion Pollutants

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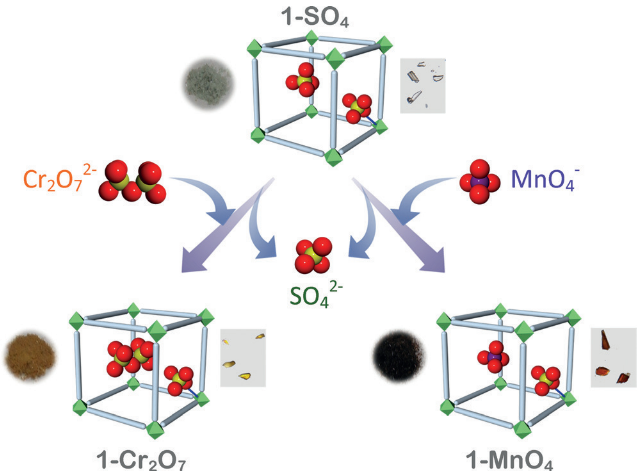
Abstract: *A three-dimensional water-stable cationic metal–organic framework (MOF) pillared by a neutral ligand and with Ni^{II} metal nodes has been synthesized employing a rational design approach. Owing to the ordered arrangement of the uncoordinated tetrahedral sulfate (SO_4^{2-}) ions in the channels, the compound has been employed for aqueous-phase ion-exchange applications. The compound exhibits rapid and colorimetric aqueous-phase capture of environmentally toxic oxoanions (with similar geometries) in a selective manner. This system is the first example of a MOF-based system which absorbs both dichromate ($Cr_2O_7^{2-}$) and permanganate (MnO_4^-) ions, with the latter acting as a model for the radioactive contaminant pertechnetate (TcO_4^-).*

Water pollution has become a pressing global concern and the sequestration of toxic contaminants present in water streams has attracted significant research attention. In particular, the widespread growth of modern industry has meant that the segregation of heavy-metal contaminants from industrial effluents has become a pertinent problem.[1] Several inorganic pollutants, present in the form of oxoanions, feature prominently in the list from the Environment Protection Agency (EPA) of priority pollutants.[2] Attempts have been made to capture and remove these species from water streams through the development of materials and/or methods for selective entrapment. In particular, much research has focused on the separation of Cr^{VI} ions, generated, for example, from chromium plating, pigment synthesis, and leather tanning, because of the severe health hazards posed by its predominant ionic form.[3] Similarly, the presence of pertechnetate (TcO_4^-) ions in radioactive waste vitrification poses serious disposal issues because of the long half-life and facile mobility of the ions.[4] Although several techniques, such as ion exchange, adsorption, and photocatalytic reduction, have been trialed for this purpose,[5] in general the preferred routes have applied ion-exchange pathways owing to cost, sensitivity, simplicity, and selectivity considerations.[6] The limitations of the currently employed ion exchangers, such as slow process kinetics and poor selectivity, actuates the development of newer materials or optimization of the performance of the currently studied adsorbents.

Metal–organic frameworks (MOFs), built from organic linkers and metal ions, have evolved as an important class of porous materials.[7] The fact that the pore size and surface of MOFs can be easily tuned renders these compounds suitable for selective sorption and separation applications.[8] As a subclass, cationic MOFs have attracted significant attention as anion receptors/separators because of the confinement of substitutable uncoordinated anionic species.[9] Generally, such frameworks are fabricated from neutral N-donor ligands wherein the residual charge-balancing ions reside in the void spaces.[10] Although porous cationic materials, including MOFs, have been explored for several applications as anion-exchange hosts, the development of MOFs as adsorbents for toxic oxoanion capture is still in the early stages, both in terms of design strategies and loading capacities.[11] We sought to develop an efficient route to construct cationic MOFs for the trapping of oxoanions encountered in wastewater streams by employing water-compatible building blocks of metal salts (for example, metal sulfates or metal phosphates) to overcome the common drawback of poor hydrolytic stability in systems built from neutral ligands. We further hypothesized that the tetrahedral geometry of the exchangeable uncoordinated anion (such as SO_4^{2-} or PO_4^{3-}) would facilitate its substitution by the target anions, as both monovalent and multivalent heavy-metal oxoanion targets have a tetrahedral geometry. Additionally, use of a multidentate neutral ligand would help to keep such anions free



Scheme 1. Schematic representation of the capture of heavy-metal oxoanions by **1**-SO_4 with concurrent loss of SO_4^{2-} ions. Photographs of the different phases and crystals of the materials are shown with each representation.

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within the porous network and lead to the formation of higher dimensional coordination polymers.

After combination of all of these aspects and carrying out experiments to validate the hypothesis, herein we report a water-stable, three-dimensional cationic MOF $[\{Ni_2(L)_3(SO_4)(H_2O)_3\}\cdot(SO_4)\cdot x(G)]_n$ (**1′**-SO_4; L = tris(4-(1H-imidazol-1-yl)phenyl)amine; G = DMF, H_2O), built from a tripodal neutral ligand and containing free sulfate ions. MOF **1**-SO_4 (guest-free phase) acts as a fast and selective adsorbent for the capture of both monovalent and divalent tetrahedral oxoanions, namely dichromate and permanganate ions, with the latter acting as a model for radioactive pertechnetate anions (Scheme 1). Adsorption of these anions by MOF **1**-SO_4 can be detected by the naked eye.

Compound **1′**-SO_4 was synthesized solvothermally by heating a mixture of ligand (L) and $NiSO_4\cdot x H_2O$ at 90 °C for 48 h. Single-crystal X-ray diffraction (SC-XRD) studies revealed that the compound crystallized in the *C*2/*c* space group.[14] The asymmetric unit consists of one full and two half Ni^{II} ions, three L units, one coordinated sulfate (SO_4^{2-}) ion, three water molecules, and one uncoordinated SO_4^{2-} ion (Figure 1 a; Figures S1–S2 in the Supporting Information). Application of the ADSYM subroutine confirmed that no additional symmetry could be applied to the model. Although all Ni^{II} ions are octahedral, there are two different coordination modes (Figure S3). One Ni center (Ni1; Figure S2) is coordinated by four nitrogen atoms from four independent L units, one H_2O molecule, and one SO_4^{2-} ion (coordinated through the O atom). Four independent ligands coordinate to Ni2 and Ni3 centers along with two water molecules. The free sulfate ions are held inside the porous cavities by weak noncovalent interactions with the framework components (Figure S4). PLATON calculations revealed that the total empty volume of the compound is 4592.8 $Å^3$, which corresponds to 24.6 % of the total volume. Uncoordinated SO_4^{2-} ions are aligned along the *c*-axis within the pore channels (Figure 1 b; Figure S5–S8). It is noteworthy that although metal–sulfate-based open frameworks are well known,[12a–e] coordination polymers having free sulfate ions are uncommon[12f–h] and structures containing both free and ligated SO_4^{2-} ions, as in the present case, are even rarer.[12i–j] Powder X-ray diffraction (PXRD) patterns (Figure S9) and elemental analysis confirmed the bulk phase purity of the compound.

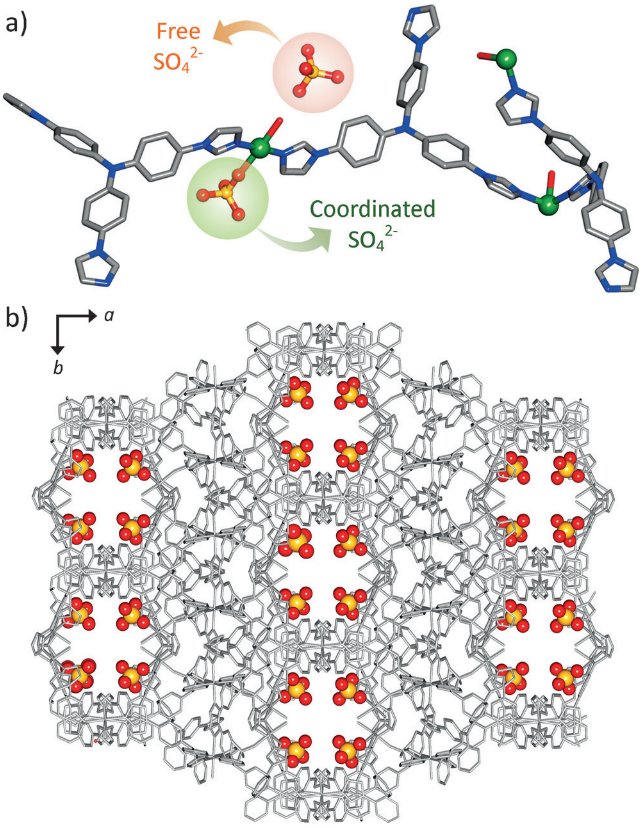

Figure 1. a) Asymmetric unit of the crystal structure of **1**-SO_4.[14] b) Overall packing in **1**-SO_4 viewed along the *c*-axis highlighting the alignment of free SO_4^{2-} ions, with the framework shown as a stick model and SO_4^{2-} ions shown in space-filling mode. H atoms omitted in (a) and (b) for clarity. Atom colors: C = gray, N = blue, Ni = green, O = red, S = yellow. In (b), the complete framework is shown in gray.

Thermogravimetric analysis (TGA) revealed that there is loss of free guest molecules within the framework and coordinated water molecules up to about 250 °C (Figure S10). PXRD patterns recorded upon heating the compound at higher temperatures confirmed the structural integrity of the compound (Figure S11). At higher temperatures, subtle variations in the PXRD patterns were detected, probably on account of slight structural changes accompanied by the loss of coordinated water molecules.

We sought to harness the ionic functionality imparted by the cationic framework to investigate the anion exchange and loading properties of **1**-SO_4. Owing to the hydrolytic stability, robust 3D architecture, and channelized alignment of the free SO_4^{2-} ions, the ability of **1**-SO_4 to trap dichromate ions was initially investigated. Crystals of **1**-SO_4 were dipped into an aqueous solution of $K_2Cr_2O_7$ and the exchange process was monitored by PXRD, FTIR, and UV/Vis absorption spectroscopic techniques. The partial decoloration of the solution and the change in color of the crystals were evident to the naked eye (Figure 2 a) within 6 h of commencement of the exchange process, and almost complete decoloration of the solution was detected after 72 h to yield **1**-Cr_2O_7 (in which SO_4^{2-} ions had been exchanged for $Cr_2O_7^{2-}$; Figure S12–13).

PXRD patterns suggested the retention of both crystallinity and the integrity of the framework after the exchange process (Figure S14). As a result of weak diffraction, SC-XRD studies could not be performed despite repeated attempts. FTIR spectroscopy and energy-dispersive X-ray (EDX) spectra confirmed the inclusion of dichromate ions, with new bands corresponding to Cr–O stretching modes appearing at about 950 and 770 cm^{-1} in the FTIR spectrum (Figure S15) and a comprehensive distribution of chromium in the elemental mapping profiles (Figure S16–S17). The UV/Vis absorption spectrum of **1**-Cr_2O_7 dispersed in deionized water overlapped well with that of the $K_2Cr_2O_7$ solution (Figure S18), thereby corroborating the inclusion of dichromate ions within the framework. Time-dependent UV/Vis absorption spectra of the supernatant solution during the exchange process corresponded well with the color changes evident for **1**-SO_4 (Figure 3 a; Figure S19). The presence of sulfur in the EDX analysis and incomplete disappearance of

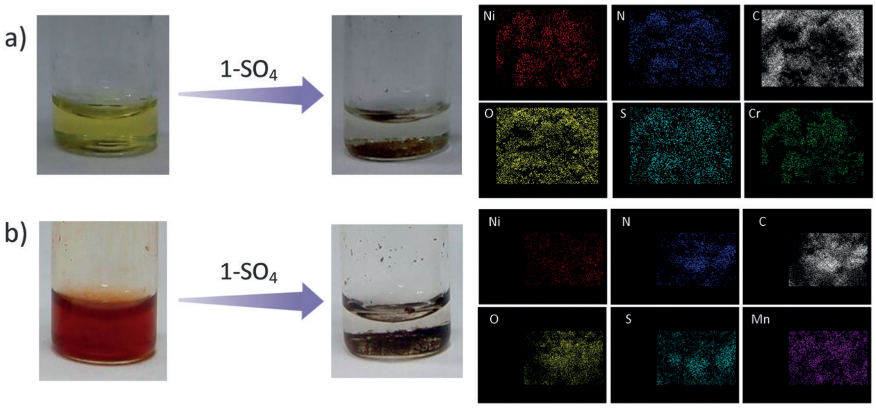

Figure 2. Photographs showing the decoloration of a) $K_2Cr_2O_7$ and b) $KMnO_4$ solutions upon addition of **1**-SO_4 and the corresponding EDX mapping profiles of **1**-Cr_2O_7 and **1**-MnO_4.

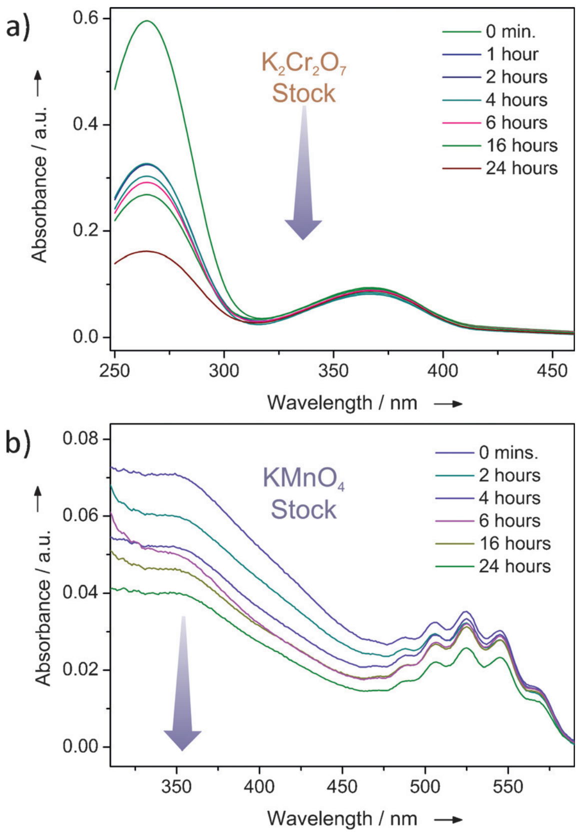

Figure 3. UV/Vis absorption spectra of the supernatant solution remaining after a) $Cr_2O_7^{2-}$ exchange or b) MnO_4^- exchange within **1**-SO_4 crystals at various time intervals. The arrows indicate the change in the absorption spectra with time.

the band corresponding to SO_4^{2-} ions in the FTIR spectrum implied the exchange of only the free SO_4^{2-} ions in the framework. We believe that the anion exchange process leads to occupation of the positions of the free sulfate ions (aligned in the porous channels) by $Cr_2O_7^{2-}$ ions. We suggest that this swap is possible because one-half of the dichromate ion has a tetrahedron-like geometry, even though the entire ion itself is not tetrahedral in shape. The other half of the dichromate anion could then reorganize itself in the free space as the anion position is directed towards the pore. By using inductively coupled plasma atomic emission spectroscopy (ICP-AES), the loading capacity of the MOF for dichromate ions was calculated to be about 166 $mg\,g^{-1}$, which is among the highest reported values for MOF-based materials.[11t]

Although anion exchange is important, selective inclusion of a target anion has greater relevance and is more challenging. To test the selectivity of the system for dichromate capture, **1**-SO_4 was dipped into an aqueous mixture of $K_2Cr_2O_7$ and a salt of either ClO_4^-, NO_3^-, BF_4^-, or $CF_3SO_3^-$ ions (separate experiments carried out for each ion). FTIR spectroscopy was employed to study preferential anion uptake. Careful analysis revealed that in all cases, $Cr_2O_7^{2-}$ was selectively incorporated inside the porous matrix over other competing anions (Figure S20). The bands corresponding to the competing anions were absent in the FTIR spectra, whereas the characteristics bands for $Cr_2O_7^{2-}$ were present for all mixtures. These results validated the hypothesis of employing tetrahedral exchangeable anions for targeted capture of oxoanions of heavy metals.

Additionally, the order of uptake affinities for the anions examined in this work was studied by using FTIR spectroscopy (Figure S21). Qualitatively, this uptake order was estimated to be: $Cr_2O_7^{2-} > NO_3^- \approx ClO_4^- > BF_4^- > CF_3SO_3^-$. ClO_4^- and BF_4^- ions, having similar tetrahedral geometries, exhibit comparatively lower uptake compared to dichromate.[11n,13] To check if **1**-SO_4 could function as a reversible absorbent, we attempted to desorb the loaded $Cr_2O_7^{2-}$ ions and replace them by SO_4^{2-} ions. Although desorption was visible to the naked eye through color changes of both the supernatant and the solid (Figure S22), FTIR spectra suggested that for replacement of dichromate ions with SO_4^{2-} ions, desorption was partial (Figure S23). ICP-AES analysis was performed to quantify these observations and the desorption corresponding to 45 μM of Na_2SO_4 was found to be about 94 $mg\,g^{-1}$. Additionally, the framework was also found to be stable in the desorbed phase (Figure S22). Furthermore, the desorbed phase of **1**-Cr_2O_7 could be used as a $Cr_2O_7^{2-}$ adsorbent, re-adsorbing the same amount of $Cr_2O_7^{2-}$ desorbed in the first cycle.

Similarly, **1**-SO_4 was probed as an adsorbent for pertechnetate ion trapping by studying its response towards its congener the permanganate anion. Crystals of **1**-SO_4 were dipped in an aqueous solution of $KMnO_4$ and rapid decoloration of the solution with a simultaneous change in the color of the crystals from pale-green to dark-red was observed (see Figure 2b for supernatant color change and Figure 1 for crystal color change; Figure S12). Like in the case of $Cr_2O_7^{2-}$ exchange, almost complete decoloration was noted after 72 h, giving rise to the exchanged phase **1**-MnO_4. Several attempts to obtain a crystal structure of **1**-MnO_4 by SC-XRD were unsuccessful as a result of weak diffraction of the crystals, precluding investigation of the exchange process by crystallography. PXRD patterns confirmed that the integrity of the framework was retained (Figure S14). EDX mapping was in good agreement with the inclusion of the permanganate ions and the presence of sulfur confirmed the exchange of only the free anions (Figure S24–S25). Time-dependent UV/Vis absorption spectra of the supernatant solution during the exchange process corresponded with the visually evident changes, with a gradual decrease of the intensity of the absorption band at $\lambda = 540$ nm (Figure 3 b; Figure S19). The selective entrapment of MnO_4^- was explored by dipping **1**-SO_4 into an aqueous solution of $KMnO_4$ containing salts of either ClO_4^-, NO_3^-, BF_4^- or $CF_3SO_3^-$ ions. FTIR spectra confirmed that competing anions were not included and suggested the selective uptake of permanganate ions (Figure S26). These results further confirm our hypothesis that a tetrahedral substitutable anion acts as a facilitator for the capture of toxic-metal oxoanions. An experiment to understand the preferential uptake between MnO_4^- and $Cr_2O_7^{2-}$ was undertaken by dipping **1**-Cr_2O_7 in an aqueous solution of $KMnO_4$ and separately by dipping **1**-MnO_4 in a $K_2Cr_2O_7$ solution. This process was monitored by FTIR spectroscopy and the results suggested that the framework had a higher affinity for MnO_4^- ions (Figure S27). PXRD patterns suggested the retention of crystallinity even after the second exchange process, reconfirming the stability of the framework (Figure S28).

In conclusion, we have synthesized a rigid water-stable 3D cationic MOF containing free SO_4^{2-} ions. The compound is an unusual example of a MOF-based dual adsorbent for permanganate ions and the environmental pollutant dichromate, with the former acting as a model for the radioactive-contaminant pertechnetate (TcO_4^-). In both cases, anion exchange is rapid and selective with visual colorimetric changes, rendering the compound a potential real-time sensor. In comparison with other MOF-like systems, this compound exhibits a moderately high uptake capacity of about 166 $mg\,g^{-1}$ for $Cr_2O_7^{2-}$ ions. We believe that these results offer a strategically simple method for the construction of heavy-metal-ion adsorbents and will contribute positively to the development of MOF-based aqueous-phase sorbents.

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[1] F. Fu, Q. Wang, *J. Environ. Manage.* **2011**, *92*, 407–418.

[2] L. H. Keith, W. A. Teillard, *Environ. Sci. Technol.* **1979**, *13*, 416–423.

[3] a) M. Costa, C. B. Klein, *Crit. Rev. Toxicol.* **2006**, *36*, 155–163; b) L. Khezami, R. Capart, *J. Hazard. Mater.* **2005**, *123*, 223–231; c) A. Zhitkovich, *Chem. Res. Toxicol.* **2005**, *18*, 3–11.

[4] a) J. G. Darab, P. A. Smith, *Chem. Mater.* **1996**, *8*, 1004–1021; b) E. A. Katayev, G. V. Kolesnikov, J. L. Sessler, *Chem. Soc. Rev.* **2009**, *38*, 1572–1586.

[5] a) T. H. Boyer, P. C. Singer, *Environ. Sci. Technol.* **2008**, *42*, 608–613; b) D. Parasuraman, A. K. Sarker, M. J. Serpe, *ChemPhysChem* **2012**, *13*, 2507–2515.

[6] a) A. Bhatnagar, M. Sillanpaa, *Chem. Eng. J.* **2010**, *157*, 277–296; b) L. M. Blaney, S. Cinar, A. K. Sengupta, *Water Res.* **2007**, *41*, 1603–1613.

[7] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Watcher, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; b) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213–1214; c) S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695–704; d) P. Ramaswamy, N. E. Wong, G. K. H. Shimizu, *Chem. Soc. Rev.* **2014**, *43*, 5913–5932; e) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815–5840; f) S. S. Nagarkar, A. V. Desai, S. K. Ghosh, *Chem. Asian J.* **2014**, *9*, 2358–2376; g) D. Bradshaw, S. El-Hankari, L. Lupica-Spagnolo, *Chem. Soc. Rev.* **2014**, *43*, 5431–5443.

[8] a) K. L. Mulfort, O. K. Farha, C. L. Stern, A. A. Sarjeant, J. T. Hupp, *J. Am. Chem. Soc.* **2009**, *131*, 3866–3868; b) A. Demessence, D. M. D'Alessandro, M. L. Foo, J. R. Long, *J. Am. Chem. Soc.* **2009**, *131*, 8784–8786; c) Z. Zhang, W. Y. Gao, L. Wojtas, S. Ma, M. Eddaoudi, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2012**, *51*, 9330–9334; *Angew. Chem.* **2012**, *124*, 9464–9468; d) B. Joarder, S. Mukherjee, A. K. Chaudhari, A. V. Desai, B. Manna, S. K. Ghosh, *Chem. Eur. J.* **2014**, *20*, 15303–15308; e) J. Duan, M. Higuchi, R. Krishna, R. Kiyonaga, Y. Tsutsumi, Y. Sato, Y. Kubota, M. Takata, S. Kitagawa, *Chem. Sci.* **2014**, *5*, 660–666; f) Z.-H. Xuan, D.-S. Zhang, Z. Chang, T.-L. Hu, X.-H. Bu, *Inorg. Chem.* **2014**, *53*, 8985–8990; g) B. Li, H.-M. Wen, H. Wang, H. Wu, T. Yildirim, W. Zhou, B. Chen, *Energy Environ. Sci.* **2015**, *8*, 2504–2511; h) G. Chang, M. Huang, Y. Su, H. Xing, B. Su, Z. Zhang, Q. Yang, Y. Yang, Q. Ren, Z. Bao, B. Chen, *Chem. Commun.* **2015**, *51*, 2859–2862.

[9] a) H. Fei, D. L. Rogow, S. R. J. Oliver, *J. Am. Chem. Soc.* **2010**, *132*, 7202–7209; b) A. Schoedel, L. Wojtas, S. P. Kelley, R. D. Rogers, M. Eddaoudi, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **2011**, *50*, 11421–11424; *Angew. Chem.* **2011**, *123*, 11623–11626; c) J.-P. Ma, Y. Yu, Y.-B. Dong, *Chem. Commun.* **2012**, *48*, 2946–2948; d) Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang, X.-H. Bu, *Chem. Sci.* **2013**, *4*, 3678–3682; e) S. Hou, Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Inorg. Chem.* **2013**, *52*, 3225–3235; f) B. Manna, B. Joarder, A. V. Desai, A. Karmakar, S. K. Ghosh, *Chem. Eur. J.* **2014**, *20*, 12399–12404; g) D.-m. Chen, W. Shi, P. Cheng, *Chem. Commun.* **2015**, *51*, 370–372; h) A. Karmakar, A. V. Desai, B. Manna, B. Joarder, S. K. Ghosh, *Chem. Eur. J.* **2015**, *21*, 7071–7076; i) B.-Q. Song, X.-L. Wang, Y.-T. Zhang, X.-S. Wu, H.-S. Liu, K.-Z. Shao, Z.-M. Su, *Chem. Commun.* **2015**, *51*, 9515–9518.

[10] a) A. Karmakar, A. V. Desai, S. K. Ghosh, *Coord. Chem. Rev.* **2015**, *307*, 313–341; b) S. Muthu, J. H. K. Yip, J. J. Vittal, *J. Chem. Soc. Dalton Trans.* **2001**, 3577–3584; c) J. H. Wang, M. Li, D. Li, *Chem. Sci.* **2013**, *4*, 1793–1801; d) J.-Y. Cheng, P. Wang, J.-P. Ma, Q.-K. Liu, Y.-B. Dong, *Chem. Commun.* **2014**, *50*, 13672–13675; e) A. Aijaz, P. Lama, P. K. Bharadwaj, *Inorg. Chem.* **2010**, *49*, 5883–5889; f) B. Manna, A. V. Desai, S. K. Ghosh, *Dalton Trans.* **2016**, DOI: 10.1039/c5dt03443d.

[11] a) K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **2000**, *122*, 6834–6840; b) S.-i. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H.

Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583; c) D. T. Tran, P. Y. Zavalij, S. R. J. Oliver, *J. Am. Chem. Soc.* **2002**, *124*, 3966–3968; d) B. H. Hamilton, T. A. Wagler, M. P. Espe, C. J. Ziegler, *Inorg. Chem.* **2005**, *44*, 4891–4893; e) M. Du, X.-J. Zhao, J.-H. Guo, S. R. Batten, *Chem. Commun.* **2005**, 4836–4838; f) T. K. Maji, R. Matsuda, S. Kitagawa, *Nat. Mater.* **2007**, *6*, 142–148; g) S. R. J. Oliver, *Chem. Soc. Rev.* **2009**, *38*, 1868–1881; h) H. Fei, S. R. J. Oliver, *Angew. Chem. Int. Ed.* **2011**, *50*, 9066–9070; *Angew. Chem.* **2011**, *123*, 9232–9236; i) G. V. Kolesnikov, K. E. German, G. Kirakosyan, I. G. Tananaev, Y. A. Ustynyuk, V. N. Khrustalev, E. A. Katayev, *Org. Biomol. Chem.* **2011**, *9*, 7358–7364; j) H. Fei, M. R. Bresler, S. R. J. Oliver, *J. Am. Chem. Soc.* **2011**, *133*, 11110–11113; k) R. Cao, B. D. McCarthy, S. J. Lippard, *Inorg. Chem.* **2011**, *50*, 9499–9507; l) R. Custelcean, P. V. Bonnesen, N. C. Duncan, X. Zhang, L. A. Watson, G. V. Berkel, W. B. Parson, B. P. Hay, *J. Am. Chem. Soc.* **2012**, *134*, 8525–8534; m) C. Fang, Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Inorg. Chem.* **2012**, *51*, 3923–3925; n) S. Wang, P. Yu, B. A. Purse, M. J. Orta, J. Diwu, W. H. Casey, B. L. Phillips, E. V. Alekseev, W. Depmeier, D. T. Hobbs, T. E. Albrecht-Schmitt, *Adv. Funct. Mater.* **2012**, *22*, 2241–2250; o) P.-F. Shi, B. Zhao, G. Xiong, Y.-L. Hou, P. Cheng, *Chem. Commun.* **2012**, *48*, 8231–8233; p) H. Fei, C. S. Hen, J. C. Robins, S. R. J. Oliver, *Chem. Mater.* **2013**, *25*, 647–652; q) X. Li, H. Xu, F. Kong, R. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 13769–13773; *Angew. Chem.* **2013**, *125*, 14014–14018; r) B. Manna, A. K. Chaudhari, B. Joarder, A. Karmakar, S. K. Ghosh, *Angew. Chem. Int. Ed.* **2013**, *52*, 998–1002; *Angew. Chem.* **2013**, *125*, 1032–1036; s) H.-R. Fu, Z.-X. Xu, J. Zhang, *Chem. Mater.* **2015**, *27*, 205–210; t) Q. Zhang, J. Yu, J. Cai, L. Zhang, Y. Cui, Y. Yang, B. Chen, G. Qian, *Chem. Commun.* **2015**, *51*, 14732–14734; u) A. J. Howarth, Y. Liu, J. T. Hupp, O. K. Farha, *CrystEngComm* **2015**, *17*, 7245–7253.

[12] a) A. Choudhury, J. Krishnamoorthy, C. N. R. Rao, *Chem. Commun.* **2001**, 2610–2611; b) J. N. Behera, K. V. Gopalkrishnan, C. N. R. Rao, *Inorg. Chem.* **2004**, *43*, 2636–2642; c) A. C. Sudik, A. R. Millward, N. W. Ockwig, A. P. Cote, J. Kim, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 7110–7118; d) P. Ramaswamy, N. N. Hegde, R. Prabhu, V. M. Vidya, A. Datta, S. Natarajan, *Inorg. Chem.* **2009**, *48*, 11697–11711; e) D. Zhang, Y. Lu, D. Zhu, Y. Xu, *Inorg. Chem.* **2013**, *52*, 3253–3258; f) L. Carlucci, G. Ciani, D. M. Proserpio, *Chem. Commun.* **2004**, 380–381; g) B. Wu, J. Liang, Y. Zhao, M. Li, S. Li, Y. Liu, Y. Zhang, X.-J. Yang, *CrystEngComm* **2010**, *12*, 2129–2134; h) C. R. Murdock, D. M. Jenkins, *J. Am. Chem. Soc.* **2014**, *136*, 10983–10988; i) H. A. Habib, A. Hoffmann, H. A. Hoppe, G. Steinfeld, C. Janaik, *Inorg. Chem.* **2009**, *48*, 2166–2180; j) G. Seeber, G. J. T. Cooper, G. N. Newton, M. H. Rosnes, D.-L. Long, B. M. Kariuki, P. Kogerler, L. Cronin, *Chem. Sci.* **2010**, *1*, 62–67.

[13] a) I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090; *Angew. Chem.* **2004**, *116*, 2116–2142; b) I. Ravikumar, P. Ghosh, *Chem. Soc. Rev.* **2012**, *41*, 3077–3098.

[14] CCDC 1422306 (**1′**-SO_4) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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