



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Selective Metal Cation Capture by Soft Anionic Metal-Organic Frameworks via Drastic Single-Crystal-to-Single-Crystal Transformations

Citation for published version:

Tian, J, Saraf, LV, Schwenzer, B, Taylor, SM, Brechin, EK, Liu, J, Dalgarno, SJ & Thallapally, PK 2012, 'Selective Metal Cation Capture by Soft Anionic Metal-Organic Frameworks via Drastic Single-Crystal-to-Single-Crystal Transformations' *Journal of the American Chemical Society*, vol 134, no. 23, pp. 9581-9584. DOI: 10.1021/ja303092m

Digital Object Identifier (DOI):

[10.1021/ja303092m](https://doi.org/10.1021/ja303092m)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Journal of the American Chemical Society

Publisher Rights Statement:

Copyright © 2012 by the American Chemical Society. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Journal of the American Chemical Society*, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <http://dx.doi.org/10.1021/ja303092m>

Cite as:

Tian, J., Saraf, L. V., Schwenzer, B., Taylor, S. M., Brechin, E. K., Liu, J., Dalgarno, S. J., & Thallapally, P. K. (2012). Selective Metal Cation Capture by Soft Anionic Metal–Organic Frameworks via Drastic Single-Crystal-to-Single-Crystal Transformations. *Journal of the American Chemical Society*, 134(23), 9581–9584.

Manuscript received: 30/03/2012; Article published: 25/05/2012

Selective Metal Cation Capture by Soft Anionic Metal–Organic Frameworks via Drastic Single-Crystal-to-Single-Crystal Transformations**

Jian Tian,¹ Laxmikant V. Saraf,¹ Birgit Schwenzer,¹ Stephanie M. Taylor,² Euan K. Brechin,² Scott J. Dalgarno^{3,*} and Praveen K. Thallapally^{1,*}

^[1]Pacific Northwest National Laboratory, Richland, Washington 99352, USA.

^[2]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

^[3]Institute of Chemical Sciences, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK.

^[*]Corresponding authors; P.K.T. e-mail: praveen.thallapally@pnnl.gov; S.J.D. e-mail: s.j.dalgarno@hw.ac.uk

^[**]This work was supported by the EPSRC (ref. EP/I031421/1 and EP/H011234/1), the Laboratory Direct Research, and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (Award KC020105-FWP12152). Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Supporting information:

Sample preparation and characterization, including TGA, PXRD, and EDX data; crystallographic data (CIF); and additional structural figures. This material is available free of charge at <http://pubs.acs.org>

Keywords:

coordination compounds; soft metal-organic frameworks; flexible ligands; dynamic structural changes; magnetic properties

Abstract

Flexible anionic metal-organic frameworks transform to neutral heterobimetallic systems via single-crystal-to-single-crystal processes invoked by cation insertion. These transformations are directed by cooperative bond breakage and formation, resulting in expansion or contraction of the 3D framework by up to 33% due to the flexible nature of the organic linker. These MOFs displays highly selective uptake of divalent transition metal cations (Co^{2+} and Ni^{2+} for example) over alkali metal cations (Li^+ and Na^+).

Introduction

Metal-organic frameworks (MOFs) have been widely investigated because of their potential application in areas such as gas storage/separation,^[1, 2] ion exchange,^[3] magnetism,^[4] catalysis^[5] and non-linear optics.^[6] Flexible MOFs have received particular recent attention as they can exhibit structural transformations upon single-crystal-to-single-crystal (SC-SC) processes triggered by external stimuli,^[7, 8] a feature that can be accompanied by fascinating changes in host-guest behavior,^[9, 10] magnetism^[11] and photochemical reactivity^[12] for example. Such transformations are generally accompanied (or generated) by the removal / addition of guest molecules,^[13] or exchange of coordinated metal ions or counterions,^[14, 15] processes in which framework integrity is often retained. A seminal example of flexible MOF formation is MIL-53 as reported by Feréy and co-workers.^[16] Cell volume in said system varies by approximately 40% between large-pore and narrow-pore forms with respective expansion / contraction of the frameworks during adsorption / desorption of suitable guest molecules. In general SC-SC processes involving the robust rearrangement of framework structures are comparatively rare because single crystals usually fail to maintain their crystallinity upon transformation. Herein we report soft anionic MOFs, constructed from the flexible organic linker tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H_4L , Figure 1A), that act as transition metal (TM) cation receptors via ligand-directing SC-SC structural rearrangement (Figure 1B&1C). These transformations involve incorporation of TM^{2+} cations into the anionic networks to afford neutral and heterobimetallic systems. To the best of our knowledge this represents the first documented report of soft anionic MOFs capturing metal ions in the solid state, the transformations of which involve cooperative bond breaking and formation rather than the more frequently encountered counterion-exchange mechanism.^[3, 14, 15b]

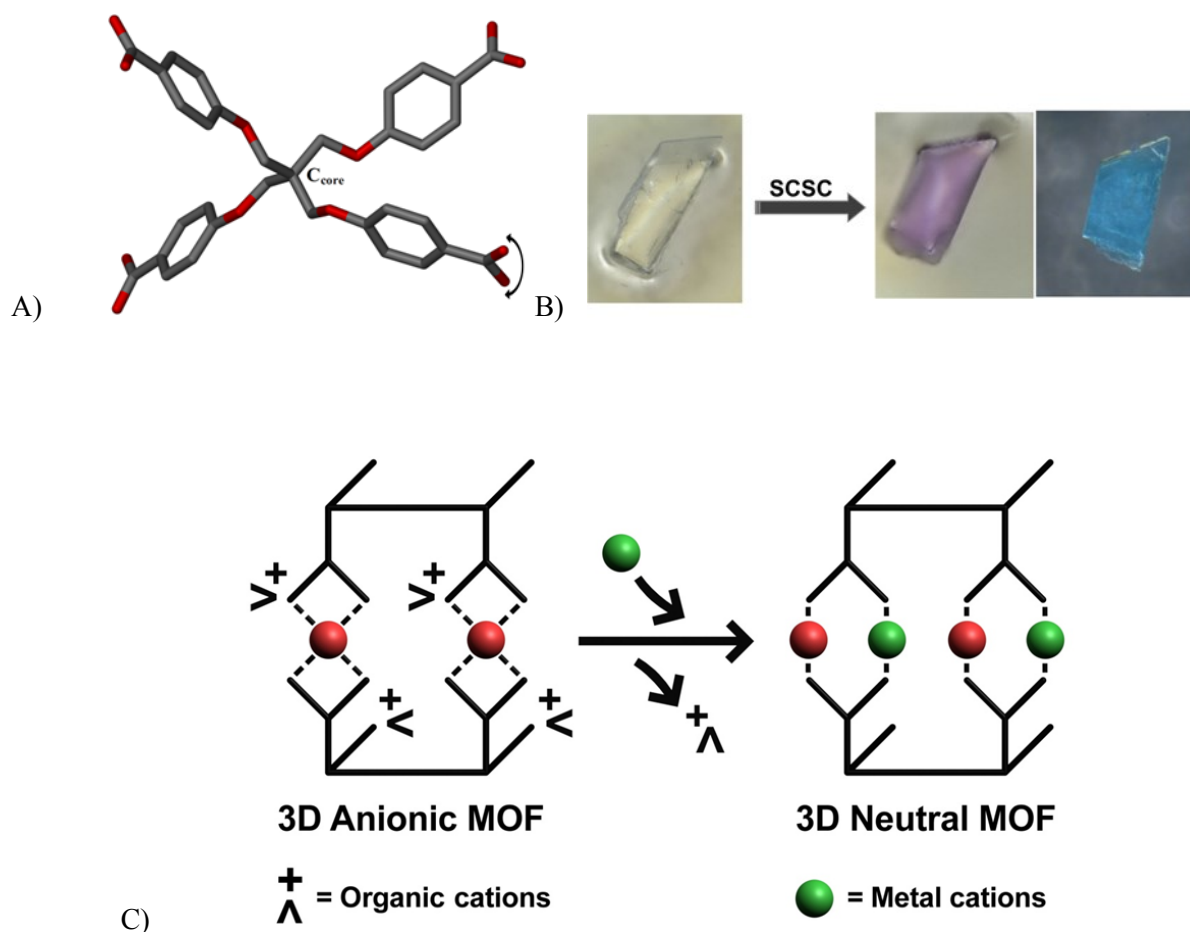


Figure 1. A) Structure of the semi-rigid carboxylate linker Tetrakis[4-(carboxyphenyl)oxamethyl] methane acid (H_4L). Its flexibility arises from twisting of the benzoate moieties around the central quaternary carbon atom (defined as C_{core}) through ethereal links. (C, grey; O: Red); B) Photos of crystals before and after TM^{2+} capture; C) Scheme showing the incorporation of TM^{2+} cations into the anionic networks to afford neutral and heterobimetallic systems via ligand-directing SC-SC structural rearrangement.

Interest in the coordination chemistry of H_4L has been driven by both its flexibility and varied mode of coordination with TMs.^[17] Reaction of H_4L with Zn^{2+} ions under different conditions affords seven isomers based on different Zn clusters that act as secondary building units (SBUs).^[18] Diverse ligand geometries such as tetrahedral, irregular or near-flattened are observed in these solids, and this flexibility arises from twisting of the benzoate moieties around the central quaternary carbon atom (defined as C_{core}) through ethereal links. With this in mind we sought to explore the potential of constructing stimuli-responsive flexible MOFs from H_4L . A series of isostructural anionic MOFs with general formula $[\text{M}_3(\text{L})_2]^{2-} \cdot 2\text{NH}_2(\text{CH}_3)_2^+ \cdot 8\text{DMA}$ ($\text{M} = \text{Co}, \text{Mn}, \text{Cd}$) have recently been reported by Cao and co-workers.^[19] These MOFs crystallize in the triclinic space group $P-1$ and the asymmetric unit comprises one L^{4-} ligand, two crystallographically independent TM^{2+} ions and a $\text{NH}_2(\text{CH}_3)_2^+$

counterion that is generated *in situ* under solvothermal conditions. One of the TM^{2+} ions is in a general position while the other resides on an inversion center with 50% site occupancy. In our hands, two MOFs of general anionic framework formula $[\text{Mn}_3(\text{L})_2]^{2-}$ (**1**) were obtained under solvothermal conditions from differing ratios of DMF and water; these have formulae $[\text{Mn}_3(\text{L})_2]^{2-} \cdot 2\text{NH}_2(\text{CH}_3)_2^+ \cdot 9\text{DMF}$ (**1a**) and $[\text{Mn}_3(\text{L})_2]^{2-} \cdot 2\text{H}_3\text{O}^+ \cdot 12\text{DMF}$ (**1b**) (See experimental section). Single crystal X-ray diffraction (SCXRD) studies reveal that both structures display the same connectivity between Mn_3 SBUs and L^4 linkers, resulting in anionic 3D frameworks with the same topology but disparate counterions (Supporting Information, Figure S1). Although this is the case different conformations of L^4 in the solids results in varied dimensionality in **1a** and **1b**; the unit cell volume of **1a** ($V = 2671 \text{ \AA}^3$) is 14% smaller than that of **1b** ($V = 3052 \text{ \AA}^3$). Overlaying the conformers of L^4 in **1a** and **1b** clearly shows (along the a axis) that two of the four arms of L^4 are more splayed in **1b** than in **1a**, resulting in the a axis of **1b** being 1.7 \AA longer (Supporting Information, Figure S2). Thus, the anionic framework of **1b** can be regarded as an ‘expanded’ form of **1a**. The flexibility of L^4 within these anionic MOFs prompted us to investigate the possibility of exchanging the Mn^{2+} or $\text{NH}_2(\text{CH}_3)_2^+/\text{H}_3\text{O}^+$ ions with other TM^{2+} ions such as Co^{2+} , Cu^{2+} and Ni^{2+} .

A colorless single crystal of **1a** was fixed to the top of a glass fiber and immersed in a 0.2M DMF solution of cobalt(II) nitrate. The crystal did not dissolve and turned to light-purple color within a few hours, indicating penetration of Co^{2+} into the framework. After 24 hours, a deep-purple crystal **2** was obtained and analyzed crystallographically. Surprisingly, the crystal structure of **2** is significantly different from that of **1a** despite the fact that both have the same space group and similar unit cell parameters. The asymmetric unit of **2** comprises one L^4 linker, one aqua ligand and three crystallographically independent $\text{Mn}^{2+}/\text{Co}^{2+}$ ions; two of these reside on inversion centers with 50% site occupancy while the third occupies a general position. In comparison to **1a**, the SBU in **2** becomes neutral by uptake of one TM^{2+} with 50% site occupancy per asymmetric unit. Based on elemental analysis, TGA and energy dispersive X-ray spectroscopy (EDX) studies, the formula of **2** was found to be $\text{MnCo}_3\text{L}_2(\text{H}_2\text{O})_2 \cdot 12\text{DMF}$. This implies that, in addition to insertion of additional Co^{2+} into the framework, partial exchange of Mn^{2+} for Co^{2+} also occurs. Such an insertion / exchange process, proceeding via a SC-SC transformation, must therefore involve the cooperative breakage / formation of metal-carboxylate bonds. This is evidenced by the fact that in moving from **1a** to **2** two of four carboxylate groups in the L^4 ligand have changed their coordination modes: one carboxylate group changes to a bridging rather than chelating mode, while the other changes from chelating bridging mode to a $\mu^3\text{-}\eta^2\text{:}\eta^1$ bridging mode (Figure S3 in the Supporting Information). To better understand the mechanism of the SC-SC transformation we carefully compared structural features of both MOFs. Figure 2 shows extended structures of **1a** and **2** along the b axis. In **1a**, the Mn_3 SBUs align along the c axis and mutually interconnect by L^4 linkers with a short distance (7.0 \AA) between two nearest neighboring clusters. Insertion of Co^{2+} ions in the synthesis of **2** results in linkage of

discrete Mn_3 clusters in **1a** to afford an infinite MnCo chain with a zigzag arrangement along the c axis. One Co^{2+} (Co1 and its symmetry equivalents, s.e.) resides on an inversion center (between the position of two neighboring Mn_3 SBUs in **1a**), is bonded by four carboxylate oxygen atoms from different L^4 linkers and two oxygen atoms from aquo ligands, and is of octahedral geometry. We hypothesize that, in order to connect the inserted Co^{2+} (Co1) and meet the constraints of octahedral geometry, the carboxylate groups coordinated to two nearby terminal Mn^{2+} ions (Mn2 and Mn2A) of the Mn_3 SBUs in **1a** must change their coordination modes with a high degree of cooperativity: the chelating carboxylate groups change to bridging mode, the chelating/bridging carboxylate groups change to $\mu^3\text{-}\eta^2\text{:}\eta^1$ bridging mode, and the bridging carboxylate groups remain the same (Figure 2b). This would mean that the terminal octahedral Mn^{2+} ions of the Mn_3 SBUs in **1a** would become four-coordinate with tetrahedral geometry prior to displacement by the Co^{2+} (Co2 and Co2A) ions. This theory is based on the short Co-O bond lengths (four Co2-O bonds in the range of 1.950 Å – 2.043 Å) that are evident in **2**. The variation in coordination mode of the carboxylate groups is directed by the rotation around C_{core} within the L^4 linker, resulting in a slight change in ligand conformation and an expansion of the entire framework by 6.5% upon going from **1a** to **2**. Single crystals of **1b** also transform to **2** via a similar SC-SC process once being treated in an identical fashion, and in this case the framework contracts by 7.5 %, demonstrating that the L^4 linker can adjust its conformation to allow for either expansion or contraction frameworks of **1**.

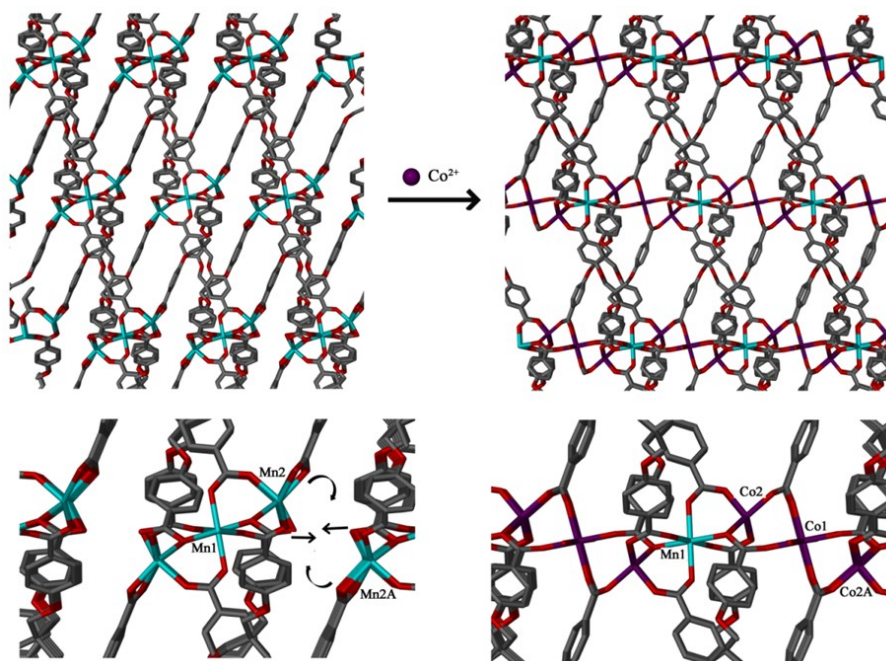


Figure 2. Crystallographic view of the **1a** (left) and **2** (right) structures along the b crystal axis (C, gray; O, red; Mn, cyan; Co, purple). The arrows propose how the carboxylate groups coordinated to two nearby terminal Mn^{2+} ions (Mn2 and Mn2A) of the Mn_3 SBUs in **1a** move cooperatively to connect the inserted Co^{2+} (Co1 as shown in the right figure).

The insertion of Co^{2+} ions into the anionic framework of **1** indicated that other dications such as Zn^{2+} , Mg^{2+} , Cu^{2+} and Ni^{2+} may be accommodated given the degree of ligand versatility observed. Crystals of **1a** were found to capture Cu^{2+} from a DMF solution via a process similar to that of capturing Co^{2+} . An intermediate structure of Cu^{2+} -inserted crystals of **1a** was successfully solved and was found to be isostructural to that of Co^{2+} -inserted analog (Figure S4 in the Supporting Information), but these crystals lose persistently monocrystallinity following completion of the insertion / exchange process over a 24h period. The insertion of either Mg^{2+} or Zn^{2+} into **1a** results in crystal cracking / degradation and loss of single crystallinity, thus preventing further structural analysis. Notably, crystals of **1a** capture Ni^{2+} ions via a SC-SC process that is significantly different to that of either Co^{2+} or Cu^{2+} . Light-green crystals of **3** are obtained after soaking **1a** (or **1b**) in DMF solution of 0.2M nickel (II) nitrate for 24 hrs. SCXRD analysis reveals that **3** retains the same space group (*P*-1) but has a much larger unit-cell volume ($V=3541 \text{ \AA}^3$) than that of **1a**. The asymmetric unit of **3** comprises one L^{4-} linker, four aquo ligands and three crystallographically independent $\text{Mn}^{2+}/\text{Ni}^{2+}$ ions, implying the insertion of Ni^{2+} into the **1a** framework. Combined with elemental analysis, TGA and energy dispersive X-ray spectroscopy (EDX) studies, the formula of **3** was decided to be $\text{Mn}_{1.3}\text{Ni}_{2.7}\text{L}_2(\text{H}_2\text{O})_7(\text{DMF})\cdot 16\text{DMF}$. Comparison of structural features of **1a** and **3** indicates how the SC-SC transformation proceeds. Figure 3a and 3b show views of **1a** and **3** along the *b* axis. The 3D framework of **1a** can be thought as discrete 2D layers interconnected by the carboxylate groups that are coordinated to the terminal Mn^{2+} cations (Mn2 and Mn2A) of Mn_3 SBUs in a chelating coordination mode. The distance between neighboring layers is 11.664 Å. We hypothesize that the chelating carboxylate groups in **1a** are cleaved from the terminal Mn^{2+} cations, and that two proximal (now unbound) carboxylate groups coordinate to an inserted Ni^{2+} cation (Ni1). These would be located at apical positions, with four aquo ligands occupying the equatorial plane of the resulting octahedral geometry. In addition, each terminal Mn^{2+} of the Mn_3 SBU (with a 85% probability) in **1a** is displaced by a Ni^{2+} ion, with two aquo ligands replacing the cleaved chelating carboxylate group in order to maintain octahedral geometry. The overall result of this process would be the trimetallic NiMnNi cluster as the SBU of **3**. It is noted that in order to accommodate the insertion of Ni^{2+} between 2D layers of **1a**, layers in **3** are pushed apart by $\sim 5 \text{ \AA}$, a feature directed by conformational change to the L^{4-} linker. As a result, the *a* axis of **3** is significantly longer than that of **1a**, with an overall expansion of 33% upon SC-SC transformation. It is worthy to mention that attempts to synthesize **2** and **3** by conventional means (by combining mixed metal salts) failed, indicating that cation insertion-induced SC-SC transformations is a feasible method for the generation of new coordination compounds from anionic MOFs constructed of flexible ligands.

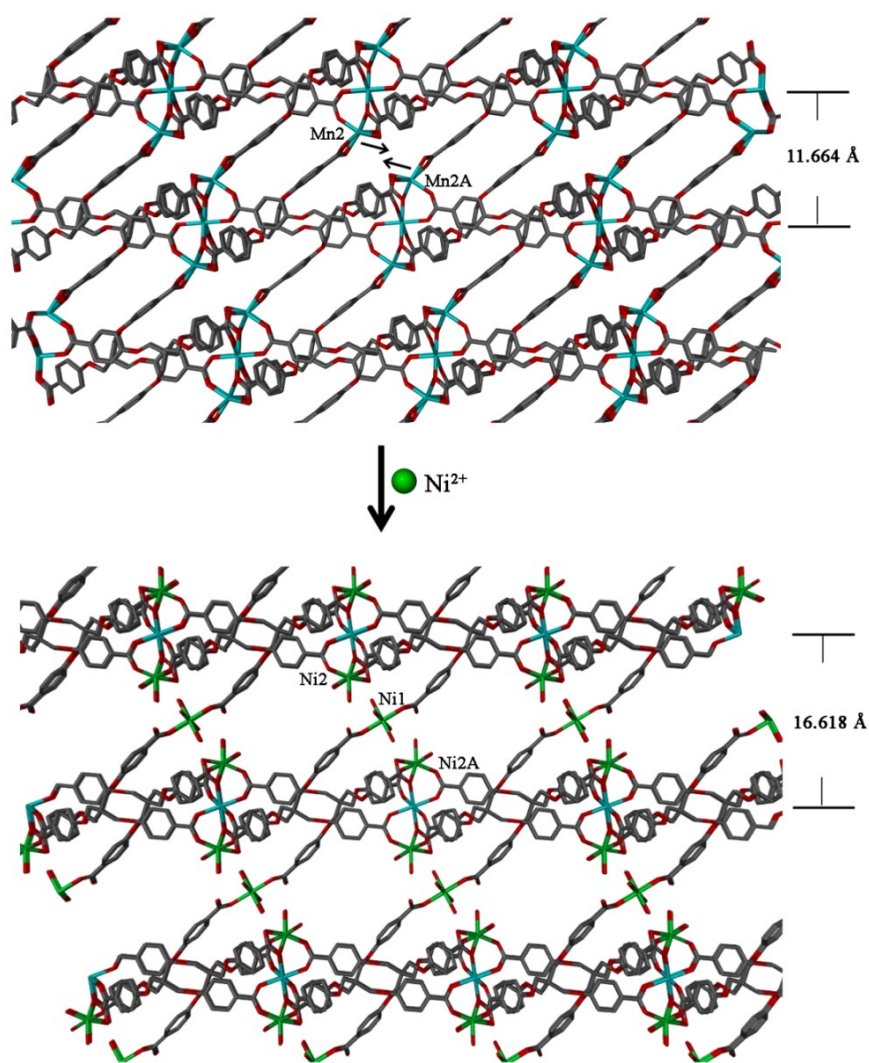


Figure 3. Crystallographic view of **1a** (top) and **3** (bottom) framework structures along the *b* crystal axis (C, gray; O, red; Mn, cyan; Ni, green). The arrows propose how the chelating carboxylate groups coordinated to terminal Mn^{2+} ions (Mn2 and Mn2A) of the Mn_3 SBUs in **1a** adapt to connect the inserted Ni^{2+} (Ni1).

Photometric experiments were conducted in order to establish cation uptake capabilities and kinetics of bulk **1a** over a 48h period (Figure 4). Co^{2+} was used as a suitable probe for uptake experiments based on its stability and UV spectroscopic profile. Framework **1a** was introduced into a 0.2M DMF solution of cobalt(II) nitrate and concentration measured as a function of time; the observed Co^{2+} concentration was found to decrease by 19% and 37% over 8.5 h and 24 h respectively. No significant decrease in Co^{2+} concentration was detected after 24 h, indicating uptake completion. The overall capacity of Co^{2+} uptake for **1a** was found to be $3.12 \text{ mol mol}^{-1}$ and 93 mg g^{-1} , values that correlate with those obtained from SCXRD and EDX analysis. Additional EDX studies were performed in order to evaluate selective uptake / exchange capabilities of **1a** towards a series of divalent metal ions

($\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \gg \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$). It was further demonstrated that **1a** crystals solely capture Cu^{2+} from the DMF solution of Cu^{2+} and Ca^{2+} (with the same molarity), implying that **1a** crystals could be used to sequester divalent cations from a mixture (Table S1). Interestingly **1a** shows highly selective uptake of divalent metal ions in the presence of multiple competing alkali cations such as Li^+ and Na^+ . When crystals of **1a** were immersed in a DMF solution of either lithium or sodium nitrate over a period of three days, powder X-ray diffraction (PXRD) and inductively coupled plasma optical emission spectroscopy (ICP-OES) studies show that the anionic framework of **1a** remains unchanged, but that the $\text{NH}_2(\text{CH}_3)_2^+$ counterions have been fully replaced by Li^+ or Na^+ ions. Subsequent competition reactions were carried out by introducing solid **1a** into DMF solutions containing combinations of either cobalt(II) nitrate or nickel(II) nitrate and lithium nitrate or sodium nitrate. Following cation uptake / exchange, ICP-OES and EDX measurements indicate that either Co^{2+} or Ni^{2+} ions have been sequestered by **1a**, with only trace amounts of Li^+ or Na^+ detected in the resulting solids (Table S2). This result could be explained by the fact that, although an exchange process of $\text{Li}^+ / \text{Na}^+$ with the $\text{NH}_2(\text{CH}_3)_2^+$ counterion is possible during the reaction,^[19] the soft framework of **1a** shows preference for $\text{Co}^{2+} / \text{Ni}^{2+}$ via SC-SC processes due to significantly stronger interaction of carboxylate groups with the TM^{2+} cations.

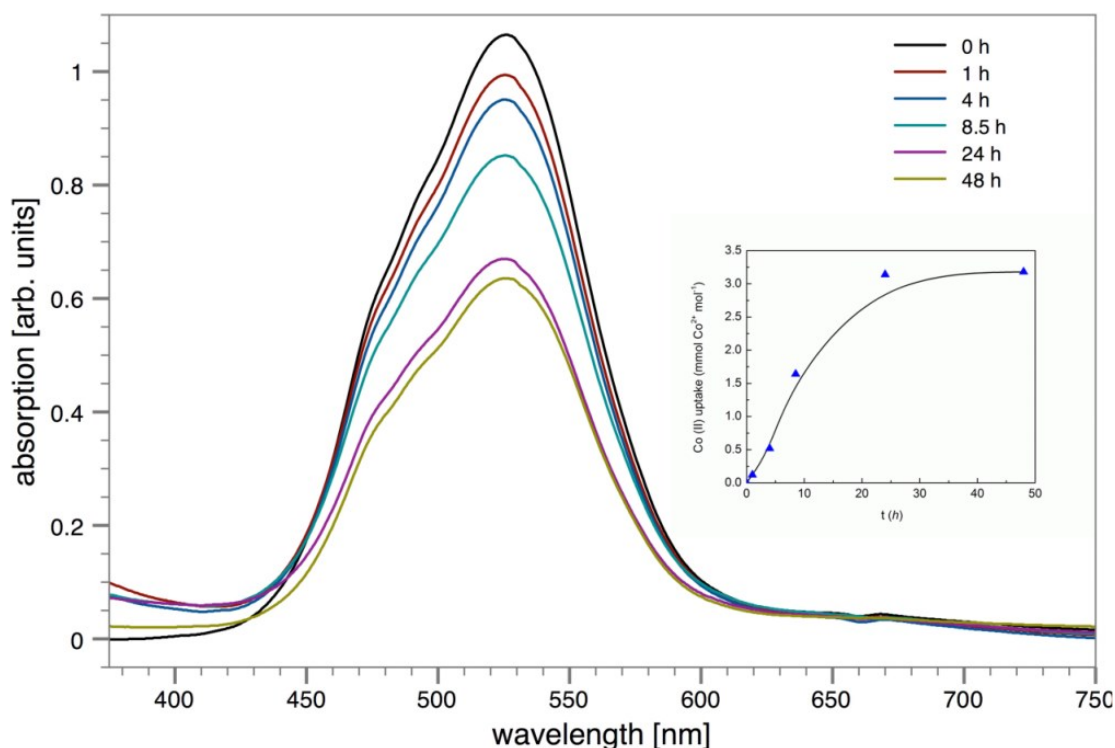


Figure 4. UV-vis absorption spectra of the 10 ml DMF solution of $\text{Co}(\text{NO}_3)_2$ with initial concentration of 0.2 M at various intervals, in which **1a** crystals (0.25mmol) were soaked. (Inset) Plot of uptake of $\text{Co}(\text{II})$ by **1a** crystals over a 48-h period.

The ability to interchange and control metal composition in such systems has clear potential to vary the magnetic properties of a resulting solid.^[4] Magnetic susceptibility measurements were carried out on powdered microcrystalline samples of complexes **1-3** in an applied field of 0.1 T and the data plotted as the $\chi_M T$ product versus temperature in Figure 5. For all compounds the data is somewhat similar – decreasing slowly on decreasing temperature - and is indicative of relatively weak antiferromagnetic interactions between neighbouring metal ions. The χ^{-1} versus T plots (not shown) are linear for each and this permits one to fit to a Curie-Weiss law, $\chi^{-1} = (T - \Theta)/C$, affording Weiss constants (Θ) of -14.4 K (**1**), -10.5 K (**2**) and -9.30 K (**3**). For complex **1** the susceptibility data can be fitted to a simple isotropic Hamiltonian ($\hat{H} = -2J(\hat{S}_{Mn1} \cdot \hat{S}_{Mn2} + \hat{S}_{Mn2} \cdot \hat{S}_{Mn3})$) that describes the system as a series of magnetically isolated Mn1-Mn2-Mn3 linear trimers in which all M...M interactions are equivalent. The solid red line in Figure 5 is the fit with $J_{Mn-Mn} = -1.42 \text{ cm}^{-1}$ and $g = 2.00$. The data for complex **3** can be treated in a similar fashion by assuming isolated linear Ni1-Mn1-Ni2 chains ($\hat{H} = -2J(\hat{S}_{Ni1} \cdot \hat{S}_{Mn1} + \hat{S}_{Mn1} \cdot \hat{S}_{Ni2})$) and non-interacting (paramagnetic) Ni monomers. The solid red line in Figure 5 is the fit with $J_{Ni-Mn} = -1.43 \text{ cm}^{-1}$ and $g = 2.21$. The magnetochemical analysis of Co(II)-based complexes is non-trivial because of the combined effects of spin-orbit coupling and the distortion of the octahedral crystal field. This and the presence of significant crystallographic disorder precludes any meaningful quantitative analysis of the magnetic data for complex **2**.

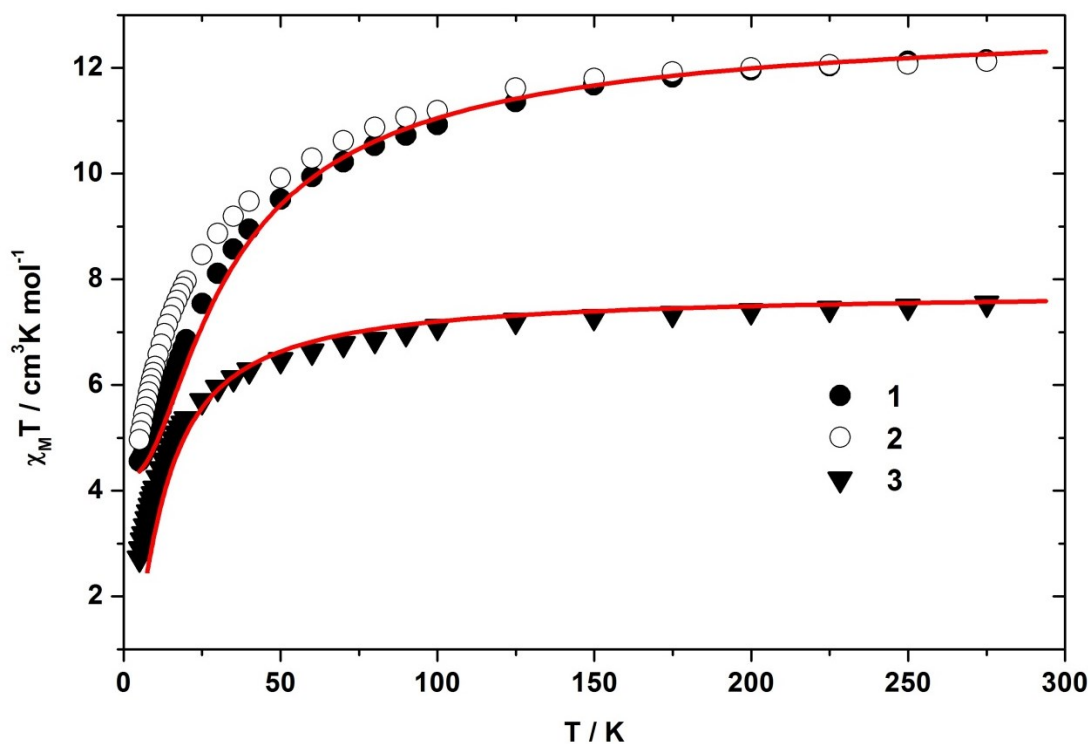


Figure 5. Plot of $\chi_M T$ vs T for complexes **1-3** in an applied field of 0.1 T. The solid red lines are fits of the experimental data to the appropriate model; see text for details.

In summary, we have demonstrated that soft anionic MOFs (**1a** and **1b**) are capable of sequestering metal cations through cooperative SC-SC processes, resulting in novel neutral and heterobimetallic systems with rearranged framework structures. These SC-SC transformations are directed by the adaptation of conformers and coordination modes of the flexible organic carboxylate linker (L^4) in order to meet the coordination environment of inserted / exchanged metal ions, a process involving cooperative breakage / formation of metal-carboxylate coordination bonds in the solid state. These anionic MOFs also exhibit exceptional uptake / exchange selectivity for TM^{2+} ions in the presence of competing alkali metal cations. In stark contrast to the rigid open 3-D frameworks of zeolites, that tend to be less affected by ion exchange, the framework flexibility observed for the soft anionic MOFs reported here holds great potential for the design of selective sensors, selective ion-exchange media and materials for the removal of toxic heavy metal ions, all of which will be the focus of future studies.^[20]

Experimental Section

Syntheses of structures

For all structures, TGA and elemental analysis revealed the amount of solvent in the crystals and were taken into account to decide the formula unit and calculate the yield. **Synthesis of 1a:** Tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H_4L) (30.8 mg, 0.05 mmol) and $MnCl_2 \cdot 4H_2O$ (22 mg, 0.11 mmol) were added to a mixture of *N,N*-dimethylformamide (DMF) (4 mL) and H_2O (100 μ L) in a capped vial, sonicated to mix, and heated to 110°C for 72 h, followed by slow cooling to room temperature over 8 h. The block-like colorless crystals of **1a** were obtained in a 72% yield (based on H_4L). Elemental analysis calcd (%) for **1a** $[Mn_3(L)_2]^{2-} \cdot 2[NH_2(CH_3)_2]^+ \cdot 9DMF$: C, 55.77; H, 5.93; N, 7.19%. Found: C, 55.28; H, 5.84; N, 7.42%. **Synthesis of 1b:** H_4L (30.8 mg, 0.05 mmol) and $MnCl_2 \cdot 4H_2O$ (22 mg, 0.11 mmol) were added to a mixture of *N,N*-dimethylformamide (DMF) (4 mL) and H_2O (1 mL) in a capped vial, sonicated to mix, and heated to 110°C for 24 h, followed by slow cooling to room temperature over 8 h. The bar-shaped colorless crystals of **1b** were obtained in a 68% yield (based on H_4L). Elemental analysis calcd (%) for **1b** $[Mn_3(L)_2]^{2-} \cdot 2H_3O^+ \cdot 12DMF$: C, 53.06; H, 5.98; N, 7.28%. Found: C, 52.09; H, 5.76; N, 6.78%. Note: one of the two solvated protons ($2H_3O^+$) per formula unit balancing the framework charge were found by X-ray diffraction analysis but the other one is suggested by TGA and elemental analysis. **Transformation of 1a (or 1b) to 2 and 3:** The fresh colorless crystals of **1a** (or **1b**) were briefly dried on the filter paper and then were immersed in DMF solution of $Co(NO_3)_2$ or $Ni(NO_3)_2$ (0.2 M), respectively. During three days, the color of the immersed crystals gradually changed to purple and light-green, respectively. Then the crystals were filtered and washed with sufficient DMF to get crystals of **2** and **3**. The final cation-

captured crystals were kept in fresh DMF for convenient observation and removing surface adsorption.

Single-crystal X-ray crystallography was carried out on a Bruker Kappa APEX II CCD diffraction system. Supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] Recent reviews: a) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4670-4679; b) R. E. Morris, P. S. Wheatley, *Angew. Chem. Int. Ed.* **2008**, *47*, 4966-4981; c) S. Ma, H.-C. Zhou, *Chem. Comm.* **2010**, *46*, 44-53; d) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724-781; e) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* **2012**, *41*, 2308-2322.
- [2] a) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.*, **2009**, *38*, 1477-1504; b) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869-932.
- [3] a) K. S. Min, M. P. Suh, *J. Am. Chem. Soc.* **2000**, *122*, 6834-6840; b) H. Fei, D. L. Rogow, S. R. J. Oliver, *J. Am. Chem. Soc.*, **2010**, *132*, 7202-7209.
- [4] M. Kurmoo, *Chem. Soc. Rev.*, **2009**, *38*, 1353-1379.
- [5] a) J.Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450-1459; b) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248-1256; c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196-1231.
- [6] C. Wang, T. Zhang, W. Lin, *Chem. Rev.* **2012**, *112*, 1084-1104.
- [7] Recent reviews: a) K. Uemura, R. Matsuda, S. Kitagawa, *J. Solid State Chem.* **2005**, *178*, 2420-2429; b) A. J. Fletcher, K. M. Thomas, M. J. Rosseinsky, *J. Solid State Chem.* **2005**, *178*, 2491-2510; c) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273-282; d) S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695-704.
- [8] For example, see: a) K. Biradha, M. Fujita, *Angew. Chem. Int. Ed.* **2002**, *41*, 3392-3395; b) T. Pretsche, K. W. Chapman, G. J. Halder, C. J. Kepert, *Chem. Commun.* **2006**, 1857-1859; c) D. Liu, Z.-G. Ren, H.-X. Li, J.-P. Lang, N.-Y. Li, B. F. Abrahams, *Angew. Chem. Int. Ed.* **2010**, *49*, 4767-4770; d) J. Sun, F. Dai, W. Yuan, W. Bi, X. Zhao, W. Sun, D. Sun, *Angew. Chem. Int. Ed.* **2011**, *50*, 7061-7064; e) J. M. Falkowski, C. Wang, S. Liu, W. Lin, *Angew. Chem. Int. Ed.* **2011**, *50*, 8674-8678.
- [9] a) E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, C. J. Kepert, *J. Am. Chem. Soc.* **2002**, *124*, 9574-9581; b) K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 14063-14070. c) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem. Int. Ed.* **2004**, *43*, 5033-5036; d) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 13519-13521; e) D. Tanaka, *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 3914-3918.
- [10] a) J. P. Zhang, X. M. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 6010-6017; b) Horcajada, P. *et al. J. Am. Chem. Soc.* **2008**, *130*, 6774-6780; c) S. Shimomura, *et al. Nat. Chem.* **2010**, *2*, 633-637; d) N. Yanai, *et al. Nat. Mater.* **2011**, *10*, 787-793; e) J. Seo, C. Bonneau, R. Matsuda, M. Takata, S. Kitagawa, *J.*

- Am. Chem. Soc.*, **2011**, *133*, 9005–9013. f) J. Park, D. Yuan, K.T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99–102.
- [11] a) X. N. Cheng, W. X. Zhang, X. M. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 15738–15739; b) W. Kaneko, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 13706–13712.
- [12] a) Q. L. Chu, D. C. Swenson, L. R. MacGillivray, *Angew. Chem.* **2005**, *117*, 3635–3638; *Angew. Chem. Int. Ed.* **2005**, *44*, 3569–3572; b) R. Medishetty, L. L. Koh, G. K. Kole, J. J. Vittal, *Angew. Chem. Int. Ed.* **2011**, *46*, 10949–10952.
- [13] a) C. Mellot-Draznieks, C. Serre, S. Surble, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 16273–16278; b) C. Serre; C. Mellot-Draznieks, S. Surble, N. Audebrand, Y. Filinchuk, G. Férey, *Science* **2007**, *315*, 1828–1831.
- [14] T. K. Maji, R. Matsuda, S. Kitagawa, *Nature Mater.* **2007**, *6*, 142–148.
- [15] a) S. Das, H. Kim, K. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 3814–3815; b) M. Plabst, L. B. McCusker, T. Bein, *J. Am. Chem. Soc.* **2009**, *131*, 18112–18118.
- [16] a) C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Loueer, G. Férey, *J. Am. Chem. Soc.* **2002**, *124*, 13519–13526; b) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373–1382.
- [17] a) H. Kim and M. P. Suh, *Inorg. Chem.*, **2005**, *44*, 810–812; b) P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 16842–16843; c) L. L. Liang, J. Zhang, S.-B. Ren, G.-W. Ge, Y.-Z. Li, H.-B. Du, X.-Z. You, *CrystEngComm*, **2010**, *12*, 2008–2010; d) J. Tian, R. K. Motkuri, P. K. Thallapally, *Cryst. Growth Des.* **2010**, *10*, 3843–3846. a) Z.-G. Guo, R. Cao, X. Wang, H. Li, W. Yuan, G. Wang, H. Wu, J. Li, *J. Am. Chem. Soc.* **2009**, *131*, 6894–6895; b) M. R. Kishan, J. Tian, P. K. Thallapally, C. A. Fernandez, S. J. Dalgarno, J. E. Warren, B. P. McGrail, J. L. Atwood, *Chem. Commun.* **2010**, *46*, 538–540; c) T.-F. Liu, J. Lü, Z.-G. Guo, D. M. Proserpio, R. Cao, *Cryst. Growth Des.* **2010**, *10*, 1489–1491; d) T.-F. Liu, J. Lü, X. Lin, R. Cao, *Chem. Commun.*, **2010**, *46*, 8439–8441; e) L.-L. Liang, S.-B. Ren, J. Zhang, Y.-Z. Li, H.-B. Du, X.-Z. You, *Dalton Trans.* **2010**, *39*, 7723–7726.
- [19] T.-F. Liu, J. Lü, C. Tian, M. Cao, Z. Lin, R. Cao, *Inorg. Chem.* **2011**, *50*, 2264–2271.
- [20] L. E. Kreno, K. Leong, O. M. Farha, M. Allendorf, R. P. V. Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105–1125.