Resin-assisted solvothermal synthesis of metal–organic frameworks†

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Transition metal-exchanged polymer resin beads have been used as a heterogeneous controlled-release source of metal cations in high yielding, phase pure solvothermal syntheses of novel transition metal–organic frameworks.

The synthesis of metal–organic frameworks (MOFs) has attracted significant interest due to their structural diversity and vast range of potentially useful applications.[1–3] Typically MOFs are synthesized using room temperature crystallizations or *via* hydro(solvo)thermal conditions. Syntheses can take days or weeks and the phase purity of the resulting network solids has always been a major consideration.[4–6] Synthetic chemists are continuously seeking new synthetic approaches that will deliver cleaner syntheses and greater yields. Recently, microwave-assisted solvothermal synthesis methods have been introduced to dramatically reduce the reaction times for the preparation of known coordination polymers.[7,8] Traditionally these approaches all involve homogeneous nucleation of MOFs but more recently heterogeneous nucleation on ordered self-assembled monolayers has been used to grow orientated thin films of Cu and Fe-containing MOFs.[9,10]

In this communication we report on the use of a heterogeneous cation-exchangeable polymer resin to direct the bulk synthesis of MOFs. Through a combination of both surface interactions with the organic macromolecule and the slow cation release characteristics of the resin we hope to influence the nucleation and growth of metal–organic frameworks so that we gain more control of the growth and purity of the products of these reactions. In this paper we have investigated the use of a transition metal-exchanged sulfonated styrene–divinylbenzene resin beads. Sulfonated styrene–divinylbenzene resin beads are commercially available as either the H^+ or Na^+ form. We have found that the Na^+ cations in this resin are readily exchangeable for a range of transition metal ions by treatment with a concentrated solution of the appropriate metal salt for 1 day.‡ A suspension of the exchanged resin beads does not release any metal cations into solution until the denaturalisation temperature, which is typically *ca.* 120 °C. These exchanged resin beads were then used in place of a typical metal salt precursor in a range of solvothermal syntheses. We hoped that the metal cations would be slowly released from the surface of the resin beads as the resin beads approached the denaturalisation temperature, which would create a limited number of crystal nucleation sites and also provide a metal cation concentration gradient near the surface of the beads which may have a positive benefit on the crystallization and growth kinetics.

We find that the introduction of the resin beads has a dramatic effect on the outcome of many solvothermal reactions. Here we report three syntheses of novel MOFs that we have been unable to prepare using conventional metal nitrate precursors.

Commercially available sulfonated styrene–divinylbenzene cation-exchange resin beads as the Na^+ form were firstly converted into the Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+} ion-exchanged form by treatment with the corresponding metal salts. Heating either the Fe^{2+} or Co^{2+}-exchanged styrene–divinylbenzene beads with 2,6-naphthalenedicarboxylic acid (2,6-NDC), tetramethylammonium chloride and *N*,*N*-dimethylformamide (DMF) at 180 °C for 1 day leads to the phase pure synthesis of Fe(2,6-NDC), **1**, and $Co_3(NHMe_2)_2(DMF)_2(2,6\text{-NDC})_3$, **2**, respectively. Estimates of the metal loadings in the resin gives yields in the range 70–80%. The resin is denatured at the reaction temperature and appears in the reaction product as a black solid. However, the denatured resin and the desired MOF products have different densities and so they can be conveniently separated using flotation methods. Thus when the solids obtained from the syntheses of **1** and **2** are added to chloroform (d = 1.48 g cm^{-3}) (Fig. 1), the denatured resin

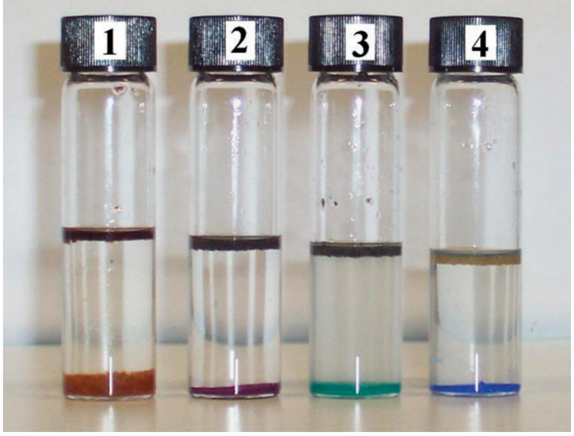

Fig. 1 Photographs of the separation of the denatured sulfonated styrene–divinylbenzene polymer resin beads from the MOF products using floatation. Chloroform is used for the separation of **1** and **2** (left to right) and dichloromethane for **3** and **4**.

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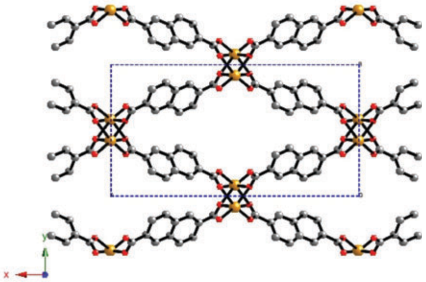

Fig. 2 Ball-and-stick representation for **1**. Fe: orange; oxygen: red; carbon: grey; hydrogen omitted for clarity.

floats to the top leaving the more dense **1** ($d_{\mathrm{calc}} = 1.61\ \mathrm{g\ cm^{-3}}$) and **2** ($d_{\mathrm{calc}} = 1.55\ \mathrm{g\ cm^{-3}}$) to settle to the bottom.

Single crystal X-ray analysis§ revealed that compound **1** is constructed from only one crystallographically unique Fe^{2+} cation and one $C_{12}H_6O_4^{2-}$ (2,6-NDC) anion (Fig. 2). Each Fe^{2+} ion is coordinated to six bridging carboxylate oxygen atoms. The octahedral geometry of Fe^{2+} ion is significantly distorted. The Fe–O bonds lengths are grouped in pairs (Fe–O 2.059(2), 2.148(2), 2.202(2) Å). The Fe–O octahedra share edges to form zigzag chains parallel to the *c*-axis. The zigzag chains are connected by bridging NDC ligands to give parallelogram shaped channels. Using van der Waals radii for the atoms we estimate that a sphere of diameter 5 Å could be accommodated within these channels.

Fig. 3 shows the crystal structure of compound **2** which consists of linear trimeric Co_3 clusters. The coordination around the central Co is a regular octahedron formed by six carboxylate oxygen atoms from six different 2,6-NDC ligands. The centrosymmetrically related terminal Co^{2+} ions are co-ordinated by four carboxylate oxygen atoms, one DMF molecule and one dimethylamine ligand. The dimethylamine ligand is derived by partial decomposition of the added DMF. The linear trimeric Co^{2+} building units are crosslinked *via* the 2,6-NDC ligands to give a 3D network as is similar to the reported $Co_3(2,6\text{-NDC})_3(DMF)_4$ MOF.[4]

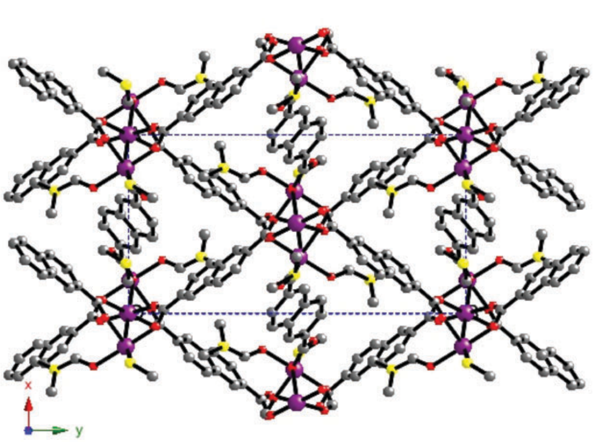

Fig. 3 Ball-and-stick representation for **2**. Co: purple; oxygen: red; carbon: grey; nitrogen: yellow; hydrogen omitted for clarity.

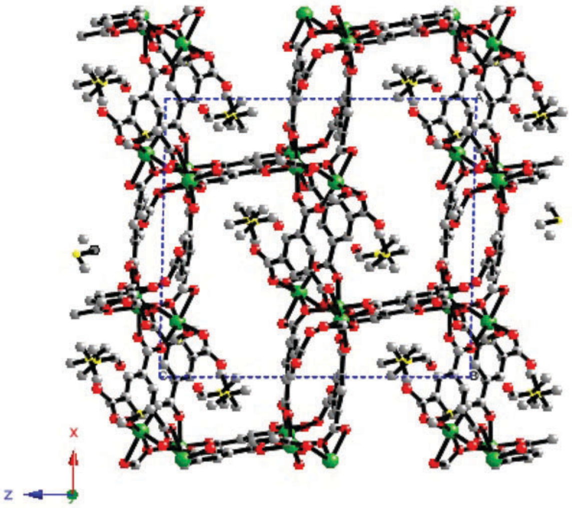

Fig. 4 Ball-and-stick representation for **3**. Ni: green; oxygen: red; carbon: grey; nitrogen: yellow; hydrogen omitted for clarity.

Heating the Ni^{2+}-exchanged styrene–divinylbenzene beads with 1,3,5-benzenetricarboxylic acid (1,3,5-BTC), ethanol and DMF at 180 °C for 1 day followed by cooling to room temperature gave phase pure $Ni_3(NMe_4)_1(1,3,5\text{-BTC})_3(DMF)_2$; **3** in 61% yield. The structure of compound **3** consists of three crystallographically independent nickel atoms, all in distorted octahedral geometry as shown in Fig. 4. The central Ni^{2+} ion is coordinated by six bridging carboxylates from six different 1,3,5-BTC ligands. One terminal Ni^{2+} ion is chelated by one carboxylate group from one 1,3,5-BTC and its coordination sphere is further completed by four bis-bridging carboxylates from four different 1,3,5-BTC ligands. The other terminal Ni^{2+} ion is also chelated by one carboxylate group from one 1,3,5-BTC. Its coordination sphere is further completed by one DMF molecule and three bis-bridging carboxylate groups. Each of the 1,3,5-BTC ligands in the *yz* plane connect three trimeric nickel centres to form a 2D layered structure. A double wall structure is observed in the *xy* plane by parallel stacking of the 1,3,5-BTC ligands.

Heating the Cu^{2+}-exchanged styrene–divinylbenzene beads with 2,6-benzenedicarboxylic acid (1,4-BDC), in a mixture of thf, methanol, water and pyridine to 180 °C for 1 day followed by slow cooling to room temperature gave bulk phase pure $Cu(1,4\text{-BDC})(py)_2(H_2O)$; **4** in 54% yield. Bright blue crystals of **4** were obtained by flotation of the reaction mixture; dichloromethane ($d = 1.33\ \mathrm{g\ cm^{-3}}$) was used for **4** ($d_{\mathrm{calc}} = 1.38\ \mathrm{g\ cm^{-3}}$) (Fig. 1). Compound **4** has been previously reported by Wang *et al.*, by heating a mixture of 4-cyanobenzoic acid, CuO, pyrimidine and H_2O under hydrothermal conditions for 5 days.[11] The authors report no yield nor phase purity for their synthesis. Comparison of the two X-ray structures suggests that the crystal quality of our material is higher.

In summary, we present the first resin-assisted solvothermal syntheses of a series of novel MOFs. This approach should now offer another synthetic option for the high yield, phase pure synthesis of novel MOFs. The use of a resin as a novel metal resource may also provide a route to higher quality materials with better phase purity.

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Notes and references

‡ Synthesis and data. The resin beads were purchased in Na^+ form (DOWEX MARATHON® C), composed of styrene–divinylbenzene. They were then converted into either the Fe^{2+}, Co^{2+} or Ni^{2+} exchanged form by addition of the appropriate saturated metal chloride solution in 5 cycles (3 h per cycle). Crystals of **1** and **2** were prepared in a solvothermal reaction of Fe^{2+} or Co^{2+} resin beads (0.3 g), 2,6-naphthalenedicarboxylic acid (2,6-NDC; 0.2 g), tetramethylammonium chloride (0.05 g) and *N*,*N*-dimethylformamide; (DMF; 6 ml). For **3**, Ni^{2+} resin beads (0.3 g), 1,3,5-benzenetricarboxylic acid (1,3,5-BTC; 0.2 g), tetramethylammonium chloride (0.05 g), DMF (5 ml) and ethanol (1 ml) were reacted. The reactant mixture was then heated in a 25 ml Teflon lined autoclave at 180 °C for 1 day followed by slow cooling to room temperature at a rate of 0.5 °C min^{-1}. Orange crystals of Fe(2,6-NDC), **1**, were obtained in 83% yield based on Fe^{2+} resin. Obs.% (calc.%): C 53.24 (53.37), H 2.29 (2.22), N 0.18 (0). Pink purple crystals of $Co_3(NHMe_2)_2(DMF)_2(2,6\text{-}NDC)_3$; **2** were obtained in 71% yield based on Co^{2+} resin. Obs.% (calc.%): C 52.27 (52.33), H 4.32 (4.39), N 5.28 (5.31). Green crystals of $Ni_3(NMe_4)_1(1,3,5\text{-}BTC)_3(DMF)_2$, **3**, were obtained in 61% yield based on Ni^{2+} resin. Obs.% (calc.%): C 44.11 (43.62), H 4.61 (3.46), N 4.72 (4.13). All of the yields shown above were estimated from the maximum uptake of the resin beads (0.0024 eq g^{-1} in Na^+ form resin). The powder XRD and TGA data of bulk samples of **1–3** were identical to the single crystal structure solutions as shown in the ESI.†

§ Crystallography. For **1–3** the sample was mounted in perfluorinated polyether oil on a hair and quench cooled to 150 K using an Oxford Cryosystems Cryostream 600 series open flow N_2 cooling device.[12] Data were collected using a Nonius Kappa-CCD area detector diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell parameters and intensity data were processed using the DENZO-SMN package and reflection intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laué equivalent reflections.[13] The structures were solved by direct methods[14] and refined by full-matrix least squares on F^2 using the CRYSTALS suite.[15] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were positioned geometrically and refined using a riding model. In the case of **1** and **3**, the difference map indicated the presence of diffuse electron density believed to be disordered solvent which was modelled using SQUEEZE.[16] In the case of **3**, the disordered component appears to consist primarily of tetramethyl ammonium ions. This is evident from the need for the material to charge balance, but also from the structure visible in the difference map for the void region. From this it is evident that there are at least two NMe_4^+ ions present and concerted efforts were made to refine this model. However, refinement was extremely unstable without severe restraints and constrained thermal parameters. Addition of two disordered NMe_4^+ moieties to the model reduced R_1 by about 1% from *ca.* 8.5% to 7.5%. Removal of the four components of the disorder and modelling with SQUEEZE reduced R_1 by a further 1% suggesting that the disorder model was not accommodating the entirety of the problem. In addition to the improvement to the statistical indicators modelling the disorder in this way improved the stability of the refinement such that no restraints or constraints were required. Since it didn't completely fit the data, it was evident that there was something unaccounted for in the multi-component disorder model, possibly additional solvent (supported by the number of electrons "removed" by SQUEEZE). For this reason, the second, SQUEEZE-model was used. The obs.% (calc.%) elemental analysis for **3** in the first model $Ni_3(NC_4H_{12})_3(C_9H_3O_6)_3(NC_3H_7O)_2$, is C 44.11 (46.42), H 4.61 (6.11), N 4.72 (6.01).

Single crystal diffraction data for **1** (brown, 0.02 × 0.02 × 0.22 mm): $FeC_{12}H_6O_4$ M_r = 270.02; monoclinic, *C*2/*c*; *a* = 21.1466(8) Å, *b* = 11.1836(4) Å, *c* = 4.7297(2) Å, *β* = 92.888(2)°, *V* = 1117.13(7) $Å^3$; *T* = 150 K; *Z* = 4; *μ* = 1.347 mm^{-1}; D_{calc} = 1.605 g cm^{-3}. Reflections collected = 9067; independent reflections = 1260 (R_{int} = 0.069); *R* values [$I > 2\sigma(I)$, 1015 reflections]: R_1 = 0.0367, wR_2 = 0.0891. *Single crystal diffraction data for* **2** (purple, 0.13 × 0.20 × 0.25 mm): $Co_3(NC_2H_7)_2(NC_3H_7O)_2(C_{12}H_6O_4)_3$, M_r = 1055.69; monoclinic, $P2_1/n$; *a* = 11.3972(2) Å, *b* = 18.9914(4) Å, *c* = 11.8255(2) Å, *β* = 118.0382(7)°, *V* = 2259.20(7) $Å^3$; *T* = 150 K; *Z* = 2; *μ* = 1.162 mm^{-1}; D_{calc} = 1.552 g cm^{-3}. Reflections collected = 42 896; independent reflections = 5142 (R_{int} = 0.092); *R* values [$I > 2\sigma(I)$, 3232 reflections]: R_1 = 0.0396, wR_2 = 0.0933. *Single crystal diffraction data for* **3** (pale-green, 0.18 × 0.05 × 0.03 mm): $Ni_3(NC_4H_{12})_1(C_9H_3O_6)_3(NC_3H_7O)_2$, M_r = 1017.82; monoclinic, $P12_1/n1$; *a* = 17.8669(6) Å, *b* = 14.1157(6) Å, *c* = 19.8394(7) Å, *β* = 91.256(3)°, *V* = 5002.4(3) $Å^3$; *T* = 150 K; *Z* = 4; *μ* = 1.189 mm^{-1}; D_{calc} = 1.351 g cm^{-3}. Reflections collected = 16 260; independent reflections = 9586 (R_{int} = 0.150); *R* values [$I > 2\sigma(I)$, 4709 reflections]: R_1 = 0.0651, wR_2 = 0.1521.

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