

Solvent-assisted linker exchange (SALE) and post-assembly metallation in porphyrinic metal–organic framework materials†

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Using recently reported robust porphyrinic metal–organic framework (RPM) materials, we have examined the systematic exchange of pillaring linkers/struts as a means of accessing new versions of these materials. Dipyrindyl-porphyrin Zn(II) (Zn-dipy) struts were successfully replaced by M²-dipy (M² = 2H(+), Al(III), Sn(IV)), forming crystalline solid solutions of **Zn(Zn_{1-x}M_x)-RPM** in variable ratios. In addition, post-synthetic metallation was demonstrated using **Zn2H-RPM**, again with retention of crystallinity. We examined catalytic activity for an epoxide ring-opening reaction with a series of **ZnM²-RPMs**. The catalytic activity depends strongly on the identity of the metal ion present in the dipyrindyl-porphyrin unit.

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Introduction

Metal–organic frameworks (MOFs) are hybrid solids possessing an infinite lattice constructed from organic linkers and metal-ion or -cluster based nodes.^{1–3} MOFs displaying nanoscale porosity and high internal surface areas have generated considerable excitement because of their potential for a wide range of applications including gas storage and release,^{4–6} gas separation,^{6,7} chemical sensing,⁸ and chemical catalysis.^{9–12} One of the extraordinary features of MOFs is the extent to which one can engender desired functional behavior by choosing appropriate linker molecules. In particular, catalysis has emerged as a promising application of MOFs – in part because of the potential for integrating the well defined, single-site activity of homogeneous catalysts with the shape-, size-, chemo-, and enantioselectivity that can be designed into micropores.^{10,13,14}

MOFs containing active-site-accessible metalloporphyrins are attractive targets^{15–27} both because of their chromophoric properties and because many metalloporphyrins are functional as chemical catalysts. Recently we reported on the synthesis and catalytic application of a series of porphyrin based MOFs

termed robust porphyrinic metal–organic framework (RPM) materials. As shown in Scheme 1, they are constructed from two types of porphyrin molecules: tetrakis(4-carboxyphenyl)porphyrin (M¹-tetraacid) and (5,15-dipyrindyl-10,20-bis-(pentafluorophenyl))porphyrin (M²-dipy), as shown in Scheme 1.²⁸ Because the compounds contain two types of porphyrins, whose metal centers need not match, they are candidates for applications requiring multi-functional performance – for example, two-stage chemical catalysis or broadened spectral coverage (*i.e.* light harvesting).

To date we have synthesized **M¹M²-RPMs** with the following combinations of metal ions: ZnZn, ZnMn, AlZn, FeZn, FeMn, and PdZn. Nevertheless, the variety of metal ions that can be introduced by conventional solvothermal methods is surprisingly limited. For instance, our attempts to incorporate cobalt failed because of poor solubility of Co-dipy, while attempts to utilize Sn-dipy as a building block afforded only amorphous solids. Additionally, incorporation of free-base porphyrins [M = 2H(+)] has been problematic under MOF synthesis conditions, because the porphyrins spontaneously metallate (with zinc).

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† Electronic supplementary information (ESI) available: Synthetic procedures, ICP-OES data, ¹H NMR of SALE products, additional PXRD data, and SEM image and EDS spectrum of cut **ZnSn-RPM** crystal. See DOI: 10.1039/c2sc21516k



Scheme 1 Synthesis of **M¹M²-RPM** materials from M¹-tetraacid, M²-dipy and Zn(NO₃)₂·6H₂O. Crystallography derived stick representations of the unit cells of **RPM** (yellow = Zn, red = O, green = F, blue = N, gray = C). Hydrogen atoms and disordered solvent molecules have been omitted for clarity.

With one recent and important exception, there is no report of a microporous MOF containing a coordination-site-accessible, free-base porphyrin. (The exception is work by Morris and Yaghi on a MOF featuring weakly porphyrin-coordinated zirconium ions that can be removed without degrading the framework.²⁹) MOFs featuring free-base-porphyrin linkers would enable us to introduce a wide variety of metal ions, *via* mild post-assembly chemistry. Here we report on the use of solvent-assisted linker exchange (SALE)^{30,31} of a representative RPM (the ZnZn compound) in order to introduce new, functional metalloporphyrin species into MOF structures.

Prior to our study, Choe and co-workers reported pillar linker exchange (replacement) in MOFs.³² They demonstrated the replacement of lengthy *N,N'*-di-4-pyridylnaphtthalenetetracarboxydiimine linkers with 4,4'-bipyridine in pillared-paddlewheel compounds. Although they did not describe the case of isostructural MOF inter-conversion, their results encouraged us to try linker exchange. Additionally, Lee and co-workers from our lab showed that a similar approach could be used to convert a 3D pillared-paddlewheel MOF to a 2D layered material.²³ Karagiari and co-workers demonstrated SALE with Cd(II)-based zeolitic imidazolate frameworks, obtaining otherwise synthetically inaccessible materials *via* this approach, as well as with ZIF-8.³⁰ Also pertinent are recent demonstration by Cohen and co-workers of linker exchange with UiO-66 and its derivatives, as well as a MIL compound and a ZIF compound.³³

Results and discussion

As illustrated in Scheme 2, exchange of Zn-dipy for M-dipy (M = 2H, Al(III),³⁴ Sn(IV)), starting from ZnZn-RPM, was examined under conditions similar to those for synthesis of RPM materials (Scheme 1). For Al-dipy and Sn-dipy as replacement linkers, the extent of incorporation (*i.e.* exchange) was determined by inductively-coupled-plasma optical-emission-spectroscopy (ICP-OES), and for 2H-dipy by ¹H-NMR – in each case after fully dissolving the sample. The analyses revealed that Zn-dipy linkers were partly replaced by other M-dipy linkers to form Zn(Zn_{1-x}M_x)-RPM compounds ($x = 0.43, 0.51$ and 0.47 for M = 2H(+), Al(III) and Sn(IV), respectively). Fig. 1 shows powder X-ray diffraction (PXRD) patterns of the three pillar-exchanged

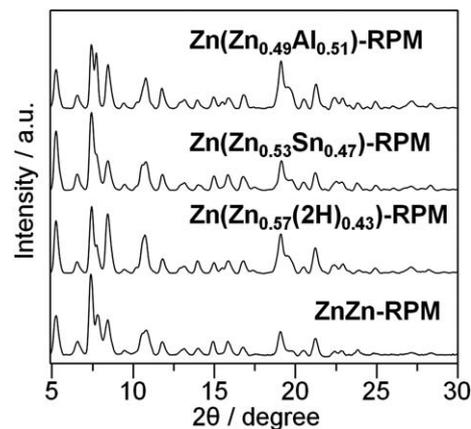
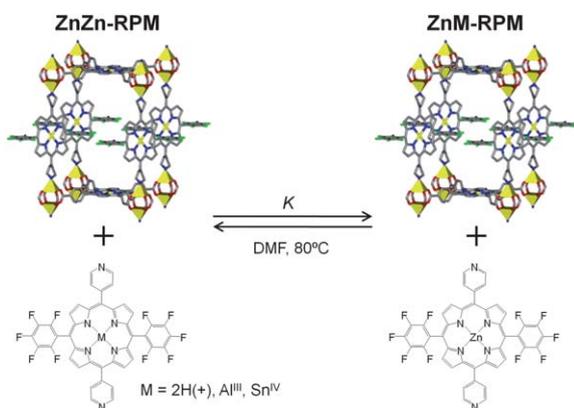


Fig. 1 PXRD patterns of partly linker-exchanged samples together with that of ZnZn-RPM.

samples. The measurements demonstrate that crystallinity is retained and that the basic RPM structure is unchanged by SALE.

Next we examined the rate of pillar linker exchange. Fig. 2 shows the time evolution of exchange reactions with mechanically ground (typical crystal length = ~ 0.01 mm) and as-synthesized (typical crystal length = ~ 0.1 mm) ZnZn-RPM samples. In both experiments, we added 2.3 equivalents of 2H-dipy ligand to ZnZn-RPM in DMF and heated to 80 °C. SALE with the ground sample reached equilibrium at *ca.* 65% conversion after 24 h. This percentage is in agreement with that expected from the ratio of 2H-dipy and Zn-dipy in the system (7 : 3), if the value of the equilibrium constant (K) of Scheme 2 is approximately 1. For the as-synthesized sample, the SALE reaction was much slower and, even after 96 h, did not reach equilibrium. The crystal size dependence clearly indicates that diffusion of linker molecules through the pores of the MOF is the rate-determining step for the exchange reaction. We also examined the time evolution of linker exchange of Al- and Sn-dipy with ZnZn-RPM. As detailed in the ESI,[†] similar results were obtained. Notably, neither Zn2H-RPM nor ZnSn-RPM proved accessible by conventional direct solvothermal synthesis.



Scheme 2 Pillar-based SALE reactions.

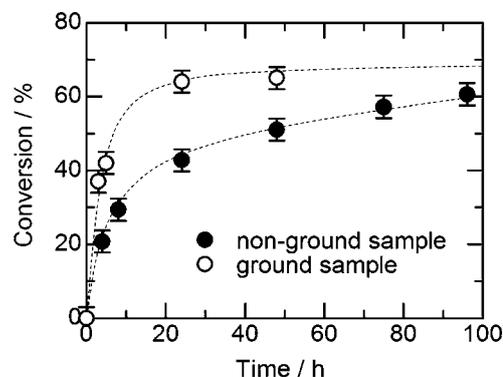


Fig. 2 Time evolution of linker exchange. Experimental conditions: ZnZn-RPM 30 mg (0.016 mmol) and 2H-dipy 30 mg (0.038 mmol) are dissolved in 5 ml DMF and heated at 80 °C. Conversion % was evaluated from integration ratio of ¹H-NMR spectra. Dotted lines show guides to the eye. See ESI[†] for detail.

Next, we examined the spatial distribution of metals in the partly exchanged crystals. Panels (a) and (b) of Fig. 3 show a scanning electron microscope (SEM) image and the spatial distribution of tin on the surface (ab plane) of a partly pillar-exchanged crystal, respectively. The distribution of tin was evaluated *via* energy dispersive X-ray spectroscopy. As can be seen, the tin concentration is comparatively high at and near the crystal edge, and much lower at its center. In contrast, a flat distribution of tin was observed along the *c*-axis direction of the cut crystal (see ESI†). These results indicate that pillar linker exchange progresses along the *ab*-plane. (These observations also provide support for a single-crystal-to-single-crystal SALE mechanism, as opposed to SALE involving dissolution and recrystallization. For an example of the latter, see the report by Karagiari, *et al.* on cadmium-containing ZIFs.³⁰)

The anisotropic behavior can be readily understood from the crystal structure of **ZnZn-RPM**. Panels (c) and (d) of Fig. 3 show space-filling representation of the crystal structure. Pore apertures in the *a* and *b* plane (*i.e.*, in the direction of the *c*-axis) are too small to permit porphyrin linkers to enter (or exit), while entry (or exit) along the direction of the *a*-axis (or equivalently, the *b*-axis) is sterically feasible. (Although at first glance panel (d) seems to show insufficient room for linker entry from the *a* direction, uniaxial rotations of the existing RPM pillars would make entry possible.)

We next turned to **Zn2H-RPM** and its post-synthesis metalation. Nearly pure **Zn2H-RPM** (>95% conversion) was obtained by repeating the aforementioned pillar (linker) exchange procedure three times. On the basis of PXRD measurements (Fig. 4), samples exposed to divalent Co ions retained crystallinity, while those exposed to divalent Mg, Cr, Mn, or Cu did not retain crystallinity.

ICP-OES results indicated that in the cobalt case, Co exchange occurred not only in the dipyr linker, but also on the

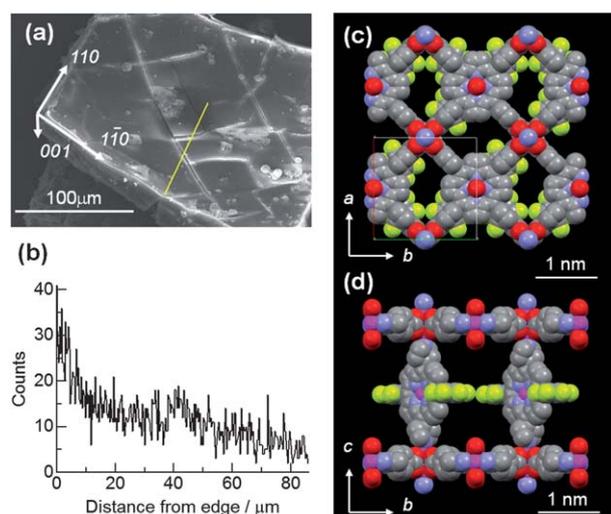


Fig. 3 (a) SEM image and (b) tin concentration distribution profile of a partly exchanged crystal (on the yellow line of panel (a)). Space-filling representations of the crystal structure of **ZnZn-RPM** projected along the (c) *c*- and (d) *a*-axes. Pink = Zn, gray = C, blue = N, yellow = F, red = O.

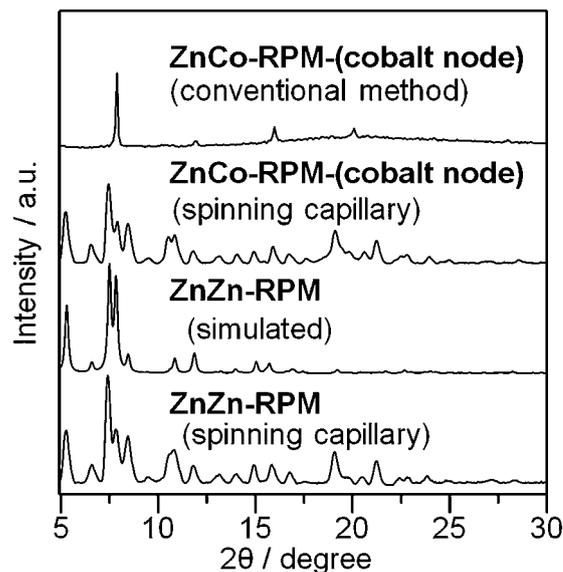


Fig. 4 PXRD patterns **ZnCo-RPM**-(cobalt node), and **ZnZn-RPM**.

paddlewheel corner. In the Ni case, crystallinity was retained (see Fig. S6†) and only the paddlewheel corner ions (*i.e.* node) exchanged with Ni^{2+} .

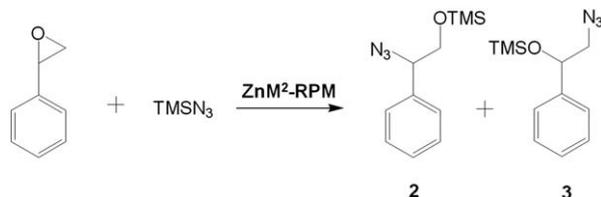
With a variety of **ZnM²-RPMs** in hand, including three that could be obtained only *via* SALE, we turned to chemical catalysis as a means of testing/illustrating differences in functional behavior. Specifically, we examined the ring-opening of styrene epoxide with trimethylsilylazide (TMSN_3), a reaction known to be catalyzed by Lewis acids, with stronger acids being more effective catalysts.

The results are summarized in Table 1. In the presence of 0.8 mol% **ZnZn-RPM**, the ring opening reaction (Scheme 3) afforded product 2 in only 2% NMR yield. This result indicates that neither the $[\text{Zn}_2(\text{O}_2\text{CR})_4]$ paddle-wheel units nor the Zn-porphyrin moieties appreciably contribute to the catalytic reaction. **Zn2H-** and **ZnSn-RPM** also barely showed catalytic activity for the ring-opening reaction. Presumably pre-existing axial ligands on Sn(IV) prevent the tin ion from interacting with the epoxide. In contrast, porphyrinic Al(III) in **ZnAl-RPM** proved significantly catalytic, consistent with its comparatively strong Lewis acidity (*e.g.*, relative to Zn(II)).

Table 1 Summary of ring-opening reaction data for candidate RPM catalysts^a

M^2	Conversion ^b (%)	2/3 ^b
Zn^{II}	2	—
2H	<1	—
Sn^{IV}	2	—
Al^{III}	60	73/27
Co^c	6	80/20

^a Styrene oxide 15 mg (0.13 mmol), TMSN_3 22 mg (0.19 mmol), **ZnM²-RPM** 2 mg (0.001 mmol), CDCl_3 5 ml, 20 °C, 18 h. ^b Product ratio (Scheme 3) as determined by ^1H NMR. ^c Although introduced as Co(II), in porphyrin coordination environments cobalt is often air-oxidized to Co(III).



Scheme 3 Ring opening reaction with TMSN₃.

Conclusions

Solvent-assisted linker exchange is a useful strategy for introducing free-base porphyrins and new metallo-porphyrins into RPM materials, where the exchanging linkers are dipyrrolyl-porphyrin pillars. Depending on RPM crystallite size, SALE equilibrium is achievable within one to several days – with smaller crystallites equilibrating more rapidly. The exchange process is spatially anisotropic, occurring *via* channels directed along the *a* or *b* axes, but not *via* the small channels directed along the *c* axis. We find that linker exchange can be driven to completion (or nearly so) by repetitively introducing exchangeable linkers. Among the new materials that can be prepared *via* SALE are ZnAl-RPM, ZnSn-RPM, Zn2H-RPM, ZnCo-RPM-(cobalt node), and Zn2H-RPM-(nickel node). The first of these was found to be competent as a catalyst for epoxide ring-opening by trimethylsilylazide. The last two were accessed *via* linker-metallation and/or node-metal-exchange, starting from SALE-prepared Zn2H-RPM. Notably, most, if not all, of the new RPMs are difficult, or perhaps impossible, to prepare *via* direct solvothermal methods, underscoring the utility of SALE. More generally, SALE shows considerable promise as a strategy for synthesizing otherwise inaccessible metal-organic framework materials.

Experimental section

Materials

meso-Tetra(4-carboxyphenyl)porphine (Frontier Scientific), trimethylsilylazide (Aldrich, 99.5%), and *N,N*-dimethylformamide (Macron, 99.8%) were used as received.

Typical SALE procedure

ZnZn-RPM (15 mg) crystals were soaked in 2 ml of *N,N*-dimethylformamide (DMF) and then, M-dipy (15 mg) was added and heated for 24 h at 80 °C. Product crystals were isolated by filtration.

Metallation of Zn2H-RPM

To a suspension of **Zn2H-RPM** (5 mg) in DMF was added excess of chloride or acetate salt of metals (M = Mg, Cr, Mn, Co, Ni or Cu). The solution was heated at 80 °C for 24 h. Solvent was decanted and replaced with fresh DMF. The decant-replace process was repeated about 10 times over several days to remove unreacted metal salt completely.

Instrumentation

ICP-OES measurements were conducted on a Varian ICP-OES spectrometer that is equipped to cover the spectral range from 175 to 785 nm. Samples (1–2 mg) were digested in 3 : 1 v/v conc. H₂SO₄ : H₂O₂ (30 wt% in H₂O) and heated at 120 °C until the solution became clear and colorless and no further vapor was produced. An aliquot of this acidic solution was diluted to 1 vol % with deionized H₂O. PXRD patterns for capillary-encapsulated samples were obtained at room temperature with a Bruker MX I μ S microsource (CuK α radiation) and ApexII CCD detector. Samples were mounted in spinning capillaries^{28,35} with supernatant liquid; capillaries were sealed with wax and placed on goniometer heads for mounting on the diffractometer. The PXRD data were collected with an area detector as rotation frames over 180° in ϕ at 2θ values of 12°, 24°, and 36° and exposed for 10 minutes for each frame.

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Notes and references

- 1 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191–214.
- 2 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704.
- 3 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276–288.
- 4 M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2011, **112**, 782–835.
- 5 R. Zou, A. I. Abdel-Fattah, H. Xu, Y. Zhao and D. D. Hickmott, *CrystEngComm*, 2010, **12**, 1337–1353.
- 6 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
- 7 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2011, **112**, 869–932.
- 8 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2011, **112**, 1105–1125.
- 9 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459.
- 10 L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248–1256.
- 11 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606–4655.
- 12 M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2011, **112**, 1196–1231.
- 13 S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun.*, 2006, 2563–2565.
- 14 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151–1152.
- 15 M. H. Alkordi, Y. Liu, R. W. Larsen, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 12639–12641.

- 16 Z. Zhang, L. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **134**, 928–933.
- 17 Z. Zhang, L. Zhang, L. Wojtas, P. Nugent, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2011, **134**, 924–927.
- 18 E.-Y. Choi, P. M. Barron, R. W. Novotny, H.-T. Son, C. Hu and W. Choe, *Inorg. Chem.*, 2008, **48**, 426–428.
- 19 E.-Y. Choi, P. M. Barron, R. W. Novotny, C. Hu, Y.-U. K. Kwon and W. Choe, *CrystEngComm*, 2008, **10**, 824–826.
- 20 E.-Y. Choi, C. A. Wray, C. Hu and W. Choe, *CrystEngComm*, 2009, **11**, 553–555.
- 21 P. M. Barron, C. A. Wray, C. Hu, Z. Guo and W. Choe, *Inorg. Chem.*, 2010, **49**, 10217–10219.
- 22 A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2009, **131**, 4204–4205.
- 23 C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 15858–15861.
- 24 K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. Nakagaki, D. W. Smithenry and S. R. Wilson, *Acc. Chem. Res.*, 2005, **38**, 283–291.
- 25 A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angew. Chem., Int. Ed.*, 2012, **51**, 7440–7444.
- 26 A. Fateeva, S. Devautour-Vinot, N. Heymans, T. Devic, J.-M. Grenèche, S. Wuttke, S. Miller, A. Lago, C. Serre, G. De Weireld, G. Maurin, A. Vimont and G. Férey, *Chem. Mater.*, 2011, **23**, 4641–4651.
- 27 D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2012, **51**, 10307–10310.
- 28 O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 5652–5655.
- 29 W. Morris, C. J. Doonan and O. M. Yaghi, *Inorg. Chem.*, 2011, **50**, 6853–6855.
- 30 O. Karagiari, W. Bury, A. A. Sarjeant, C. L. Stern, O. K. Farha and J. T. Hupp, *Chem. Sci.*, 2012, **3**, 3256–3260.
- 31 The term SALE seems preferable to “post-synthesis modification” [PSM] as the linker-exchange process is, a continuation of the materials synthesis process, rather than an elaboration of a largely completed materials synthesis process.
- 32 B. J. Burnett, P. M. Barron, C. Hu and W. Choe, *J. Am. Chem. Soc.*, 2011, **133**, 9984–9987.
- 33 M. Kim, J. F. Cahill, Y. Su, K. A. Prather and S. M. Cohen, *Chem. Sci.*, 2012, **3**, 126–130.
- 34 We found that we could also synthesize **ZnAl-RPM** via conventional methods.
- 35 A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 13252–13255.