

## Postsynthetic Tuning of Metal–Organic Frameworks for Targeted Applications

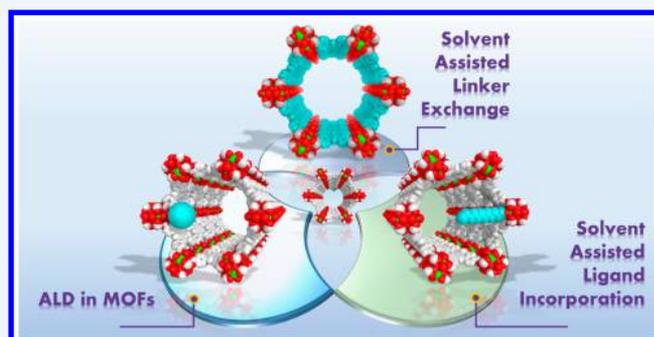
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**CONSPECTUS:** Metal–organic frameworks (MOFs) are periodic, hybrid, atomically well-defined porous materials that typically form by self-assembly and consist of inorganic nodes (metal ions or clusters) and multitopic organic linkers. MOFs as a whole offer many intriguing properties, including ultrahigh porosity, tunable chemical functionality, and low density. These properties point to numerous potential applications, including gas storage, chemical separations, catalysis, light harvesting, and chemical sensing, to name a few. Reticular chemistry, or the linking of molecular building blocks into predetermined network structures, has been employed to synthesize thousands of MOFs. Given the vast library of candidate nodes and linkers, the number of potentially synthetically accessible MOFs is enormous. Nevertheless, a powerful complementary approach to obtain specific structures with desired chemical functionality is to modify known MOFs after synthesis. This approach is particularly useful when incorporation of particular chemical functionalities via direct synthesis is challenging or impossible. The challenges may stem from limited stability or solubility of precursors, unwanted secondary reactivity of precursors, or incompatibility of functional groups with the conditions needed for direct synthesis. MOFs can be postsynthetically modified by replacing the metal nodes and/or organic linkers or via functionalization of the metal nodes and/or organic linkers.

Here we describe some of our efforts toward the development and application of postsynthetic strategies for imparting desired chemical functionalities in MOFs of known topology. The techniques include methods for functionalizing MOF nodes, i.e., solvent-assisted ligand incorporation (SALI) and atomic layer deposition in MOFs (AIM) as well as a method to replace structural linkers, termed solvent-assisted linker exchange (SALE), also known as postsynthetic exchange (PSE). For each functionalization strategy, we first describe its chemical basis along with the requirements for its successful implementation. We then present a small number of examples, with an emphasis on those that (a) convey the underlying concepts and/or (b) lead to functional structures (e.g., catalysts) that would be difficult or impossible to access via direct routes. The examples, however, are only illustrative, and a significant body of work exists from both our lab and others, especially for the SALE/PSE strategy. We refer readers to the papers cited and to the references therein. More exciting, in our view, will be new examples and new applications of the functionalization strategies—especially applications made possible by creatively combining the strategies. Underexplored (again, in our view) are implementations that impart electrical conductivity, enable increasingly selective chemical sensing, or facilitate cascade catalysis. It will be interesting to see where these strategies and others take this compelling field over the next few years.



### INTRODUCTION

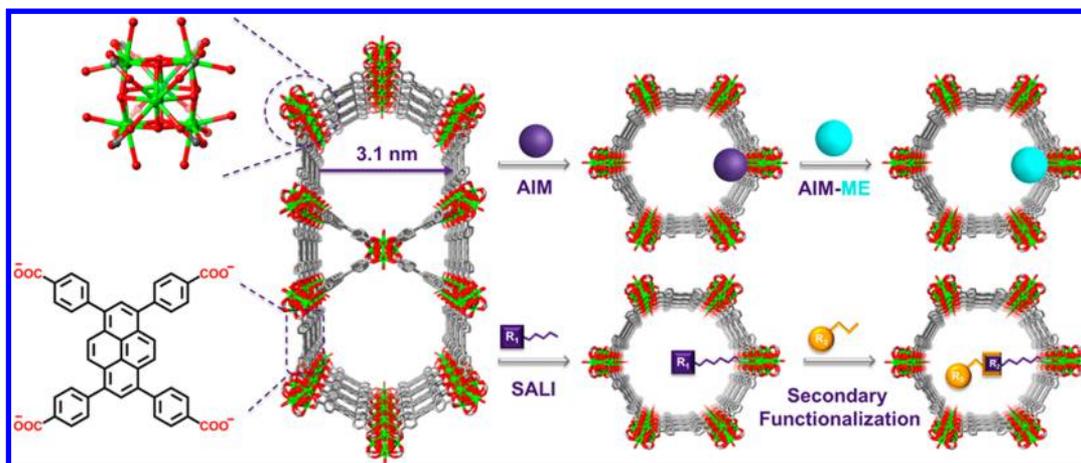
MOFs constitute one of the most widely studied classes of materials in contemporary chemistry.<sup>1–3</sup> Their modular structure and extraordinarily broad chemical and topological variety can be translated into property tunability. This in turn has motivated their investigation as materials for numerous potential applications, including gas storage and separation,<sup>4</sup> catalysis,<sup>5</sup> light-harvesting/solar-energy-conversion,<sup>6,7</sup> and chemical sensing.<sup>8</sup> With suitable attention to linker design and node composition, direct approaches to MOF synthesis—most notably, solvothermal methods—are effective for predictively modulating internal surface areas and cavity/pore

sizes and often also for incorporating desired chemical functionality.<sup>9–12</sup> Installing desired functionalities directly, however, is not always possible. To this end, postsynthetic modification (PSM) of MOFs has been instrumental in obtaining frameworks that feature desired functionalities.<sup>13</sup>

Our focus here is on three PSM strategies that are potentially transformational: (i) solvent-assisted ligand incorporation (SALI), which involves replacing labile, nonstructural inorganic ligands with functional organic ligands; (ii) atomic layer

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**Figure 1.** Schematic representation of AIM, AIM with metal exchange (AIM-ME), SALI, and secondary-functionalization-after-SALI processes in NU-1000. Color code (throughout): carbon (gray), oxygen (red), nitrogen (blue), zirconium (green), and zinc (yellow). For clarity, hydrogen atoms have been omitted.

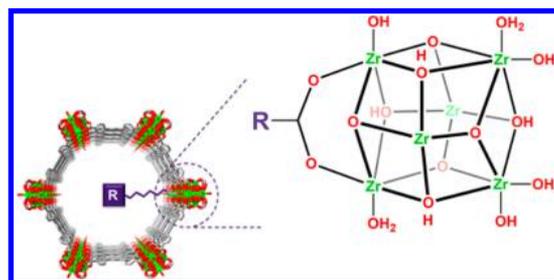
deposition in MOFs (AIM), which is effective for installing single metal complexes or metal-containing clusters on nodes as supports; and (iii) solvent-assisted linker exchange (SALE), which involves replacing structural ligands (linkers) with alternative linkers.

Our discussion of SALI and AIM revolves around the mesoporous Zr-based MOF NU-1000<sup>14</sup> as a platform but could in principle be based on related MOFs. NU-1000 is composed of  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(H_2O)_4(OH)_4$  nodes<sup>15</sup> and tetratopic 1,3,6,8-tetrakis(*p*-benzoate)pyrene (TBAPy<sup>4-</sup>) linkers<sup>16</sup> (Figure 1). Like other hexazirconium(IV) MOFs, NU-1000 is characterized by excellent chemical, thermal, and hydrothermal stability.<sup>17</sup> It presents large hexagonal channels (~31 Å in diameter) surrounded by ~12 Å triangular channels. The MOF node uses eight of 12 available sites to bind carboxylate-terminated linkers (and thus is termed “eight-connected”). This configuration leaves room on the node for eight singly coordinated nonstructural ligands (four aqua and four hydroxo ligands). These moieties are available for substitution (SALI) or for reaction with volatile organometallic complexes (AIM). Thus, these are node-centric PSM techniques, while SALE is linker-centric.

## ■ SOLVENT-ASSISTED LIGAND INCORPORATION (SALI)

Reversible incorporation of chemical functionality can be achieved through dative bonding of nonstructural ligands to unsaturated metal centers.<sup>18,19</sup> More tenacious ligand attachment can be achievable, however, by turning to chelation and ionic bonding. SALI capitalizes on both. Briefly, each node-based aqua/hydroxo pair can be displaced by a new ligand featuring a charge-compensating carboxylate, phosphonate, or similar group; thus, up to four new ligands can be installed on each node (Figure 2).<sup>20</sup> Notably, the conditions required for SALI are much milder than those for the synthesis of NU-1000, implying that even delicate functionalities can be incorporated.

Scheme 1 shows the ligands successfully SALI-ed to date. They include ligands presenting catechol, amine, hydroxyl, pyridine, and aromatic halide functionalities.<sup>21</sup> The ample width of NU-1000’s hexagonal channels, together with the material’s high chemical stability, allows for secondary PSM. Thus, ligands incorporated via SALI can be elaborated via condensation, quaternization, metalation, azide “click”, and catalyst activation



**Figure 2.** Molecular representation of an NU-1000 node after SALI.

reactions (Scheme 1). Secondary functionalization is one way to access functionalities that are incompatible with free oxyacid groups.

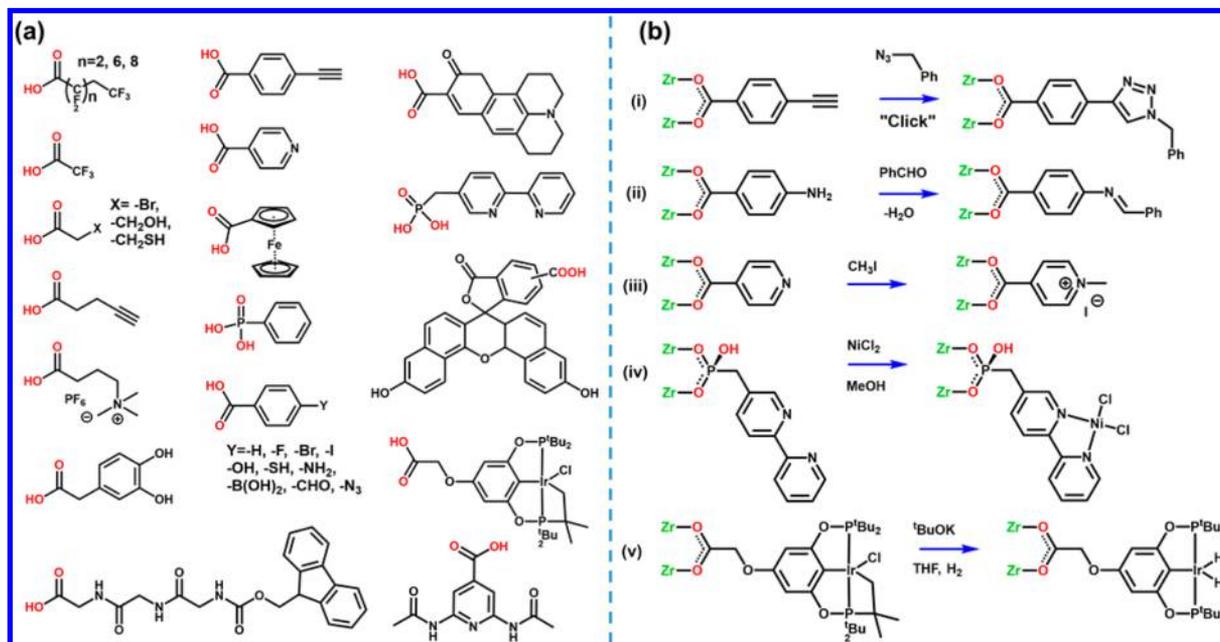
Scheme 1 includes four phosphonate-terminated ligands (shown in acid form).<sup>22</sup> We reasoned that the known higher affinity of phosphonates (vs carboxylates) for zirconia could be replicated in Zr-MOFs to strengthen ligand binding and boost chemical stability. Indeed, we found that SALI-installed phosphonates (but not carboxylates) are retained when the modified MOF is soaked, for example, in a 1:24 (v/v) mixture of 8 M HCl and DMF. Ligand persistence in aqueous base is also enhanced. Below we highlight a few lab-scale SALI-enabled MOF applications.

### Carbon Dioxide Capture

MOFs have been extensively studied as candidate solid adsorbents for CO<sub>2</sub> capture, especially from flue gas (mainly N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O) or dried flue gas.<sup>23</sup> Because of the hydrophobicity of perfluorinated organics and the known affinity of supercritical CO<sub>2</sub> for perfluoroalkanes, the notion of fluorinated linkers as building blocks for hydrophobic and CO<sub>2</sub>-philic MOF pores has attracted significant experimental attention.<sup>24,25</sup> A complementary idea is the introduction of nonstructural perfluoroalkanes within MOF channels.<sup>26</sup> We found that carboxylate-terminated perfluoroalkanes of varying length can be installed via SALI. The modified materials displayed increased isosteric heats of adsorption for CO<sub>2</sub> (up to double).

Also observed was enhanced stability toward repetitive filling and evacuation of pores with water.<sup>27</sup> NU-1000 and related MOFs are resistant to chemical degradation by water (i.e., hydrolysis). They are susceptible, however, to physical

**Scheme 1.** (a) Carboxylic and Phosphonic Acid-Terminated Ligands Incorporated via SALI within NU-1000; (b) Secondary Functionalization Reactions Involving SALI Derivatives of NU-1000: (i) “Click”, (ii) Imine Condensation, (iii) Methylation, (iv) Metalation, and (v) Catalyst Activation



degradation via capillary forces, as these forces must be overcome when solvent molecules (especially water) are removed from pores. Degradation is manifested as pore collapse, together with physical fracturing of linker–node bonds. With water, the forces are greatest when the MOF channels have a chemical affinity for water and when the water clusters residing in the MOF channels are large. The wide channels of NU-1000, together with its hydrogen-bonding-capable nodes, make it subject to stronger capillary forces than many MOFs. Fluoroalkane installation diminishes these forces both by eliminating hydrogen-bonding sites and by decreasing the water-accessible pore volume and therefore the water cluster size. Finally, installation also increases the hydrophobicity of the MOF with respect to liquid water, as evidenced by contact-angle measurements.

Another intriguing approach for capturing  $\text{CO}_2$  from gas mixtures is to decorate MOF pores with molecules that present charge distributions that are complementary to those of quadrupolar  $\text{O}=\text{C}=\text{O}$ . We observed that SALI-ing appropriately designed di- and tripeptides indeed does enhance the  $\text{CO}_2$  capturing ability of NU-1000.<sup>28</sup> We suggest that this molecular-recognition-type strategy can be productively extended to other targets.

### Catalysis

SALI can also be used to install molecular catalysts in MOFs. Beyond the obvious advantage of facilitating catalyst reuse (by rendering it a recoverable solid), the potential benefits are (i) catalyst isolation (thereby preventing, e.g., inactivation by dimerization) and (ii) facilitation of catalyst application to gas-phase chemical transformations.

Representative of what is possible is the catalytic performance of a pincer complex of iridium (Scheme 1) for condensed-phase hydrogenation of alkenes.<sup>29</sup> Relative to the solution-phase version of the catalyst, the SALI-immobilized version shows enhanced activity (up to 70-fold) and is longer-lived. Both outcomes are likely attributable to isolation of catalysts

from each other in the MOF environment. Often immobilization of molecular catalysts on solids is accompanied by decreases in catalytic activity—effects that can arise from decreased accessibility to the catalyst by molecular reactants or from unfavorable interactions between the catalyst and support material. That inactivation does not occur here may be a reflection of the ultrahigh porosity and low density of the MOF; if so, then preservation of molecular catalytic activity may prove to be a general finding.

A second example is the phosphonate-enabled immobilization of 2,2'-bipyridine followed by coordination of nickel(II). For ethylene dimerization (in inert solvent), this catalyst is about 10-fold more active than the homogeneous catalyst.<sup>30</sup> Notably, both SALI-ed complexes can also catalyze gas-phase reactions.

A third example is ferrocenecarboxylate. Its installation renders electrode-supported films of NU-1000 redox-conductive.<sup>31</sup>

### ■ ATOMIC LAYER DEPOSITION IN METAL–ORGANIC FRAMEWORKS (AIM)

Atomic layer deposition is a vapor-phase synthesis technique that has been widely used to fabricate ultrathin, pinhole-free films of metal oxides, sulfides, carbides, and nitrides from (i) volatile organometallic or inorganic complexes, (ii) reactive sources of main-group elements, such as steam,  $\text{H}_2\text{S}$ , and ammonia, and (iii) an initially hydroxylated substrate.<sup>32</sup> Conventional ALD is based on sequential surface reactions of two precursors, to which the substrate is exposed in successive steps. The precursors react with the evolving surface in a self-limiting fashion, viz., they react exclusively with complementary chemical species on the substrate and not with themselves. Repeating the steps leads to further film growth. One important consequence is that inorganic films can be grown with close to angstrom-level precision with respect to film thickness. A

second is that films can be grown in conformal fashion, even on high-area, high-porosity substrates.

The nodes of NU-1000 can be viewed as tiny pieces of hydroxylated zirconia, and therefore, they should be susceptible to reaction with ALD precursors (Figure 3). Instead of a

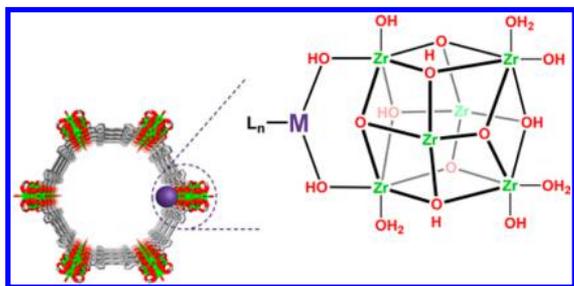


Figure 3. Simplified representation of an NU-1000 node after AIM.

continuous film, however, the product should be an array of uniformly sized and uniformly spaced node-supported clusters. The cluster size can be controlled on the basis of the number of AIM growth cycles.

More generally, a MOF will likely be suitable for elaboration via AIM if it (i) presents suitably reactive grafting sites, such as aqua or hydroxo ligands, (ii) has good thermal and chemical stability (ALD is typically done at 100 °C or higher), and (iii) features large enough pores and apertures to permit precursors to permeate the MOF quickly and completely.

#### Metal–Oxide AIM

For proof-of-concept AIM experiments, we chose highly reactive metal–alkyl complexes of Zn(II) and Al(III) (Figure 4).<sup>14,33</sup> Stepwise exposure of NU-1000 to either compound in

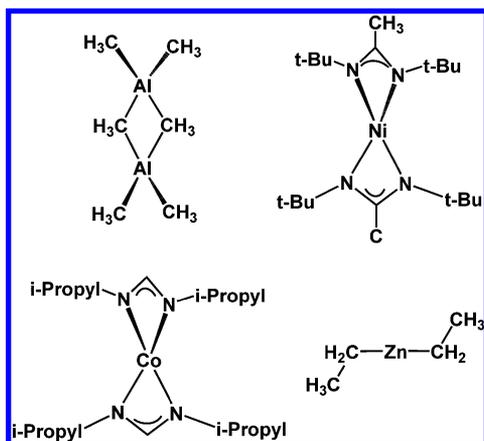


Figure 4. Chemical structures of some ALD precursors.

vapor form, followed by exposure to steam, yields the anticipated clusters. Initial studies further revealed that (i) the synthesis chemistry (AIM) is self-limiting, (ii) mixed-metal oxide/hydroxide clusters can be obtained by changing the identity of the ALD precursor in a second AIM cycle, (iii) the crystallinity and porosity of the MOF are retained, and (iv) apart from defect zones, the distribution of clusters is uniform. Metal nuclearities for single-AIM-cycle clusters range from ~4 for Zn(II) to ~8 for Al(III). The chemical basis for the differences is not yet understood.

A more detailed study with  $\text{In}(\text{CH}_3)_3$  as an AIM precursor showed that six In(III) ions were installed for each node.

Evidence that metal precursor binding is via reaction with aqua and hydroxo ligands is provided in part by the disappearance of node-based O–H stretches in the infrared spectrum and by X-ray pair distribution function measurements showing In–O bond lengths of 2.12 Å and In...Zr separations of 3.33 Å, distances that are consistent with DFT calculations.<sup>33</sup>

For many kinds of reactions, catalysts containing open-shell transition metals are desirable. We have discovered that bis(amidinate) complexes<sup>34</sup> are especially well suited for AIM of first-row transition metals. Using the precursors shown in Figure 4, tetranuclear cobalt(II)–oxo,hydroxo and nickel(II)–oxo,hydroxo clusters were installed in NU-1000. Because the MOF's crystallinity is preserved, differential electron density maps can be extracted from X-ray diffraction data collected before and after AIM.<sup>15</sup> To our surprise, the maps show that clusters are sited between pairs of nodes aligned along the *c* direction (the channel direction) of NU-1000, i.e., in pores within the walls of the MOF rather than within its channels. This intriguing observation extends to other cluster compositions.

The nickel-containing clusters show good catalytic activity for gas-phase hydrogenation of ethylene and for alkene oligomerization, e.g., turnover frequencies matching those of atomically dispersed nickel(II) on zirconia, a conventional support.<sup>35</sup> Notably, the AIM catalyst displays little loss of catalytic activity, even after 2 weeks of continuous use. In contrast, the conventionally supported catalyst deactivates completely within 6 h, likely because of sintering (active-site agglomeration). Postcatalysis characterization of the MOF-supported catalyst showed no detectable sintering—behavior that can be attributed to isolation of the nodes by the linkers and to the difficulty of transporting node-anchored clusters across linkers. The absence of appreciable sintering for Ni-AIM and related catalysts should greatly facilitate both mechanistic understanding and hypothesis-driven development of new catalysts.

An intriguing second example is the use of Co-AIM NU-1000, in electrode-supported form, for the four-electron conversion of aqueous  $\text{OH}^-$  to  $\text{O}_2$ , i.e., the oxidative half of a water-splitting cycle.<sup>36</sup> While the kinetic overpotential was greater than anticipated (~450 mV at 10 mA  $\text{cm}^{-2}$ ) and difficulties were encountered in electrochemically addressing the full complement of clusters, the initial findings offer a starting point for the development of new electrocatalytic clusters in the limit of single-metal-atom control of composition.

#### Metal–Sulfide AIM

Transition-metal/sulfur clusters are ubiquitous as cofactors for enzymes that catalyze reduction reactions (e.g., hydrogenases and nitrogenases). With this in mind, we first developed a vapor-phase route to node-supported cobalt(II) sulfide. Briefly, the synthesis relies upon AIM of bis(amidinate)cobalt(II) followed by  $\text{H}_2\text{S}$  at 130 °C—conditions that would destroy many MOFs<sup>37</sup> but leave the hexazirconium MOF undamaged.<sup>38</sup> As an initial test, we looked at the condensed-phase conversion of *m*-nitrophenol to *m*-aminophenol and found CoS-AIM to be catalytically competent.

Using similar principles, we installed clusters of nickel sulfide.<sup>39</sup> In the presence of a light-absorbing molecular dye, the clusters proved to be photocatalytic for the reduction of water to  $\text{H}_2$ , i.e., the other half of a water-splitting cycle.

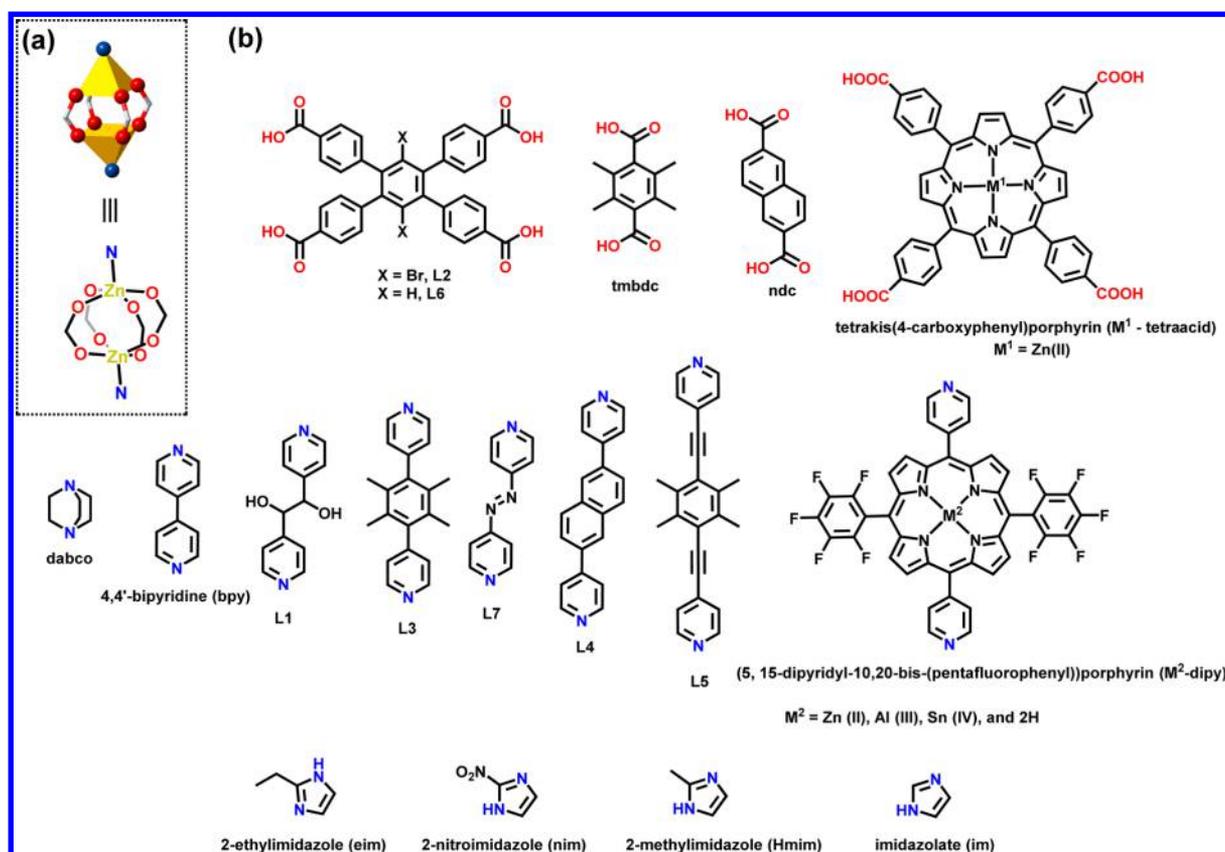


Figure 5. (a) Representative SBU for pillared-paddlewheel MOFs. (b) Organic linkers discussed in connection with SALE.

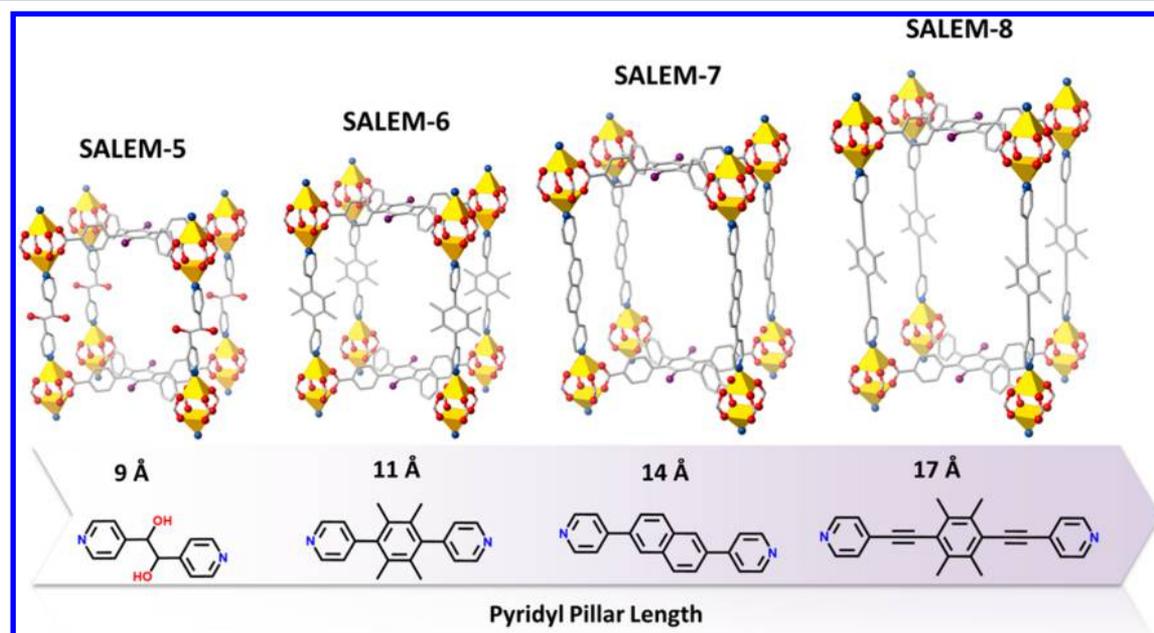


Figure 6. Increasing pore sizes in an isorecticular series of pillared-paddlewheel MOFs synthesized via SALE. The value in angstroms is the length of the dipyriddy linker used for SALE on the parent MOF SALEM-5.

### SOLVENT-ASSISTED LINKER EXCHANGE (SALE)

While SALI and AIM involve chemical modification of MOF metal nodes, SALE entails substitution of structural ligands, i.e., linkers.<sup>40</sup> SALE can be used to (i) synthesize new MOFs or introduce new chemical functionalities in MOFs (which may not be accessible de novo), (ii) control pore size/shape, (iii) control catenation, and (iv) access topologies that are unknown

for a particular linker/node combination. SALE is initiated by exposing a parent MOF to a concentrated solution of a new linker. The resulting daughter framework can contain the new linker at a concentration of anywhere from 1% to 100%. Importantly, the daughter MOF generally retains the topology of the parent framework. The first reported examples of SALE on 3D MOFs came from Burnett et al.<sup>41</sup> They focused on

pillared-paddlewheel MOFs (Figure 5a shows a typical pillared-paddlewheel secondary building unit (SBU)) and showed that a previously unobtainable MOF could be formed.

The SALE concept was soon extended to other classes of MOFs, including zeolitic imidazolate frameworks (ZIFs)<sup>42</sup> and, remarkably, high-stability Zr-based MOFs.<sup>43</sup> ZIFs, by definition, feature zeolite topologies. They consist of divalent single-metal-atom nodes tetrahedrally connected to imidazoles.<sup>44–46</sup> The first reported examples of ZIF-based SALE involved replacement of the ethylimidazolate linkers of CdIF-4 with 2-nitroimidazolate or 2-methylimidazolate to yield, respectively, CdIF-9 (known) or SALEM-1 (new).<sup>47</sup> In both cases, the *rho* topology of the parent MOF was retained. For the mixed-linker compound ZIF-69, SALE can be accomplished selectively: 5-(trifluoromethyl)benzimidazolate completely replaces the chlorobenzimidazolate linkers of ZIF-69 while leaving its nitroimidazolate linkers untouched.<sup>48</sup>

### Tuning the Porosity and Aperture Size

The ability to tune the porosity and aperture size of a MOF using SALE without changing the parent topology of the framework is very useful. The pillar ligands of SALEM-5 (L1, 9 Å) can be selectively exchanged with L3, L4, and L5 (11, 14, and 17 Å, respectively; Figure 6) to tune the pore size.<sup>49</sup> In the same study, we reported that linker basicity can be used as a proxy for relative dative bond strength and thus as a predictor of whether a given SALE reaction will occur. Briefly, linkers of higher basicity readily displace those of lower basicity, but not vice versa. As with most SALE reactions, the above-mentioned reactions take place via single-crystal-to-single-crystal transformation (see Figure 7) rather than by crystal dissolution and reprecipitation.

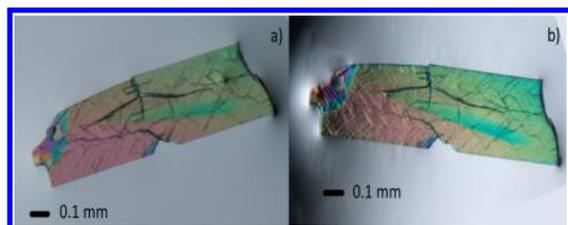


Figure 7. (a) A crystal of SALEM-5 and (b) the same crystal transformed to SALEM-6 after undergoing SALE with L3. Reproduced from ref 49. Copyright 2013 American Chemical Society.

Finally, SALE can be applied to ZIF-8 to make SALEM-2, the imidazolate (im) analogue (Figure 8). ZIF-8 is an extraordinarily stable ZIF with the *sod* topology composed of 2-methylimidazolate linkers that yield apertures with a width of  $\sim 3.8$  Å. SALEM-2, which is not attainable de novo, presents apertures with a width of  $\sim 6$  Å.<sup>42</sup> Solvent permeation studies

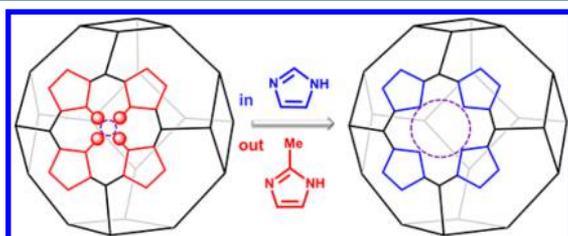


Figure 8. Aperture expansion in ZIF-8 via SALE.

revealed that SALEM-2 can admit guests that ZIF-8 size-excludes, such as cyclohexane and toluene.

### Catalysis

Robust porphyrinic MOFs (RPMs) consist of tetratopic tetrakis(4-carboxyphenyl)porphyrin linkers, ditopic dipyrityl-porphyrin pillars, and dinuclear transition-metal-ion nodes. Because they can present two different porphyrin-coordinating metal ions in a single framework, RPMs are potentially attractive for two-stage catalysis.<sup>50</sup> While a large number of metal–metal ( $M^1 M^2$ ) combinations can be obtained directly, some cannot. Moreover, attempts to incorporate free-base porphyrins have been unsuccessful (because of spontaneous metalation of the free base by ions needed for nodes). Free-base porphyrin linkers can, however, be incorporated via SALE and then metalated to give  $M^1 M^2$  combinations that are not otherwise accessible.<sup>51</sup> One example is ZnAl-RPM, a SALE-derived MOF that proved to be the most effective of a series of RPMs screened as Lewis acid catalysts for epoxide ring opening. Finally, returning to ZIF-8/SALEM-2, we found that replacing the 2-methylimidazolate linkers with imidazolate renders the material susceptible to reversible activation for Brønsted base-like catalysis.<sup>42</sup>

### Catenation Control

Although catenated frameworks are of interest for a few applications (e.g., selective guest capture), noncatenated frameworks offer higher surface areas and porosities. While methods exist for obtaining noncatenated MOFs, such as modulation of the synthesis conditions,<sup>52</sup> the use of templating agents,<sup>53</sup> and density separation of mixtures, they are not universally applicable.<sup>54</sup> SALE offers a promising alternative approach. Two early examples of its successful application are the synthesis of the noncatenated pillared-paddlewheel frameworks SALEM-3 and SALEM-4 (Figure 9). Neither is obtainable de novo, but both can be accessed by SALE-ing a noncatenated parent framework, DO-MOF.<sup>55</sup>

### Catalytic Composite Materials

The ability to obtain frameworks with the same topology and pore size but different aperture sizes is of interest for regio- and size-selective catalysis. An illustrative example is SALE of the composite material Pt@ZIF-8 (Pt nanoparticles encapsulated in ZIF-8) to give Pt@SALEM-2.<sup>56</sup> Both can catalyze *n*-hexene hydrogenation; however, for the larger-kinetic-diameter substrate *cis*-cyclohexene, only the expanded-aperture composite (Pt@SALEM-2) works.

## CONCLUSIONS AND OUTLOOK

The three strategies discussed all aim to introduce functionalities into MOFs, but they differ in important ways. For example, SALI and AIM take advantage of nonbridging, reactive, and labile ligands on MOF nodes. SALI allows for decoration of MOF pores with organic ligands and/or site-isolated complex catalysts. AIM enables the synthesis of metal oxide or sulfide clusters of well-defined nuclearity. SALE involves exchanging structural ligands, often for linkers that are incompatible with de novo synthetic techniques. SALE allows the physical and chemical properties of a framework to be altered without changing its topology.

SALI, AIM, and SALE have potential well beyond the applications outlined above. For example, SALI can be used to engender chemical sensing capabilities,<sup>57</sup> to boost light harvesting,<sup>58</sup> or even to create arrays of molecular machines.<sup>59</sup>

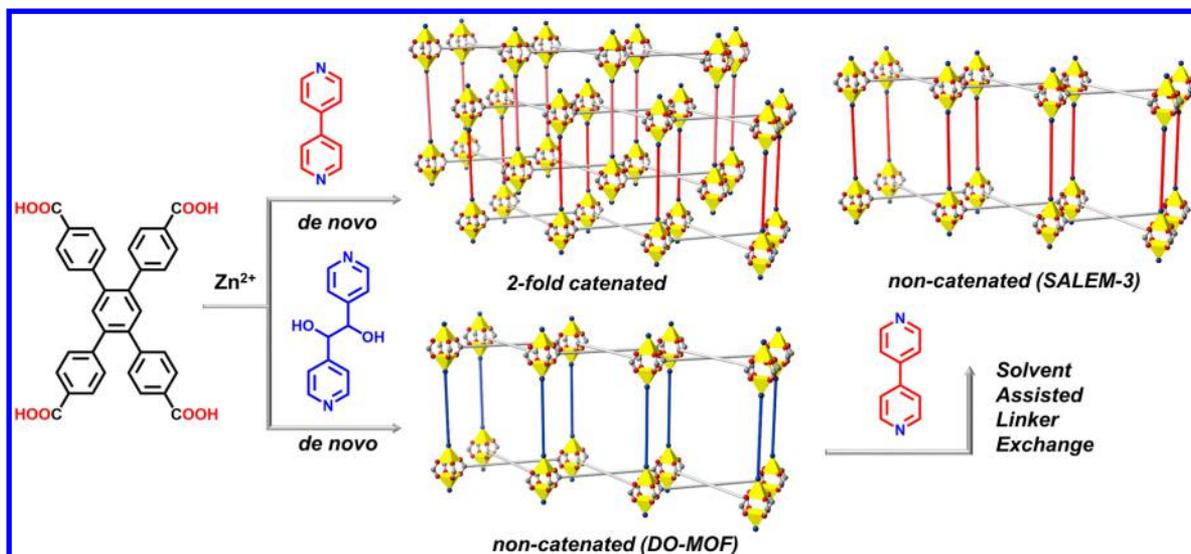


Figure 9. Schematic representation of MOFs synthesized via SALE that are otherwise not accessible de novo.

In view of the fact that automated AIM is a “keyboard-driven synthesis” with a breadth of ALD precursors available, this methodology offers many avenues for postsynthetic modification. Additionally, metal exchange can be performed following AIM (AIM-ME), which allows for the incorporation of metals that are challenging to install by AIM.<sup>60</sup> Yet to be significantly explored are synergetic mash-ups of AIM with SALI or SALE. Finally, in addition to the bulk MOF materials discussed, SALE can be performed on MOF thin films<sup>61,62</sup> or membranes<sup>63</sup> for practical future applications. We believe that all three techniques are important for the advancement of MOF chemistry in terms of both fundamental study and application of these captivating materials.

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### Notes

The authors declare no competing financial interest.

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**Dr. Timur Islamoglu** is a postdoctoral researcher in the Hupp and Farha group and works on the design and synthesis of MOFs as heterogeneous catalysts. He received his B.S. in Chemistry (2008) and Mathematics (2009, double major) from Dumlupinar University and his M.Sc. (2013) and Ph.D. (2016) in Chemistry from Virginia Commonwealth University under the supervision of Prof. Hani El-Kaderi.

**Dr. Subhadip Goswami** received his B.S. (2008, University of Calcutta) and M.S. (2010, IIT Kanpur) in India and his Ph.D. in Inorganic Chemistry from the University of Florida under the

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**Dr. Zhanyong Li** is a postdoctoral researcher in the Hupp and Farha group at Northwestern University. He earned his Ph.D. in Chemistry from Texas A&M University under the direction of Kim Dunbar. His current research focuses on the postsynthetic modification of MOFs for their application in gas-phase catalysis.

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## REFERENCES

- (1) Kitagawa, S.; Kitaura, R.; Noro, S.-I. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43* (18), 2334–2375.
- (2) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal–Organic Frameworks. *Science* **2013**, *341* (6149), 1230444.
- (3) Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal–Organic Framework Materials. *Acc. Chem. Res.* **2010**, *43* (8), 1166–1175.
- (4) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. Selective Gas Adsorption and Separation in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1477–1504.
- (5) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal–Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38* (5), 1450–1459.
- (6) So, M. C.; Wiederrecht, G. P.; Mondloch, J. E.; Hupp, J. T.; Farha, O. K. Metal–Organic Framework Materials for Light-Harvesting and Energy Transfer. *Chem. Commun.* **2015**, *51* (17), 3501–3510.
- (7) Williams, D. E.; Shustova, N. B. Metal–Organic Frameworks as a Versatile Tool to Study and Model Energy Transfer Processes. *Chem. - Eur. J.* **2015**, *21* (44), 15474–15479.
- (8) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal–Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112* (2), 1105–1125.
- (9) Farha, O. K.; Özgür Yazaydın, A.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. De Novo Synthesis of a Metal–Organic Framework Material Featuring Ultrahigh Surface Area and Gas Storage Capacities. *Nat. Chem.* **2010**, *2* (11), 944–948.
- (10) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydın, A. Ö.; Snurr, R. Q.; O’Keeffe, M.; Kim, J.; Yaghi, O. M. Ultrahigh Porosity in Metal–Organic Frameworks. *Science* **2010**, *329* (5990), 424–428.
- (11) Guillerm, V.; Kim, D.; Eubank, J. F.; Luebke, R.; Liu, X.; Adil, K.; Lah, M. S.; Eddaoudi, M. A Supermolecular Building Approach for the Design and Construction of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43* (16), 6141–6172.
- (12) Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G. Metal–Organic Frameworks as Platforms for Functional Materials. *Acc. Chem. Res.* **2016**, *49* (3), 483–493.
- (13) Wang, Z.; Cohen, S. M. Postsynthetic Modification of Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38* (5), 1315–1329.
- (14) Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework. *J. Am. Chem. Soc.* **2013**, *135* (28), 10294–10297.
- (15) Gallington, L. C.; Kim, I. S.; Liu, W.-G.; Yakovenko, A. A.; Platero-Prats, A. E.; Li, Z.; Wang, T. C.; Hupp, J. T.; Farha, O. K.; Truhlar, D. G.; Martinson, A. B. F.; Chapman, K. W. Regioselective Atomic Layer Deposition in Metal–Organic Frameworks Directed by Dispersion Interactions. *J. Am. Chem. Soc.* **2016**, *138* (41), 13513–13516.
- (16) Stylianou, K. C.; Heck, R.; Chong, S. Y.; Bacsá, J.; Jones, J. T. A.; Khimyak, Y. Z.; Bradshaw, D.; Rosseinsky, M. J. A Guest-Responsive Fluorescent 3d Microporous Metal–Organic Framework Derived from a Long-Lifetime Pyrene Core. *J. Am. Chem. Soc.* **2010**, *132* (12), 4119–4130.
- (17) Howarth, A. J.; Liu, Y.; Li, P.; Li, Z.; Wang, T. C.; Hupp, J. T.; Farha, O. K. Chemical, Thermal and Mechanical Stabilities of Metal–Organic Frameworks. *Nat. Rev. Mater.* **2016**, *1*, 15018.
- (18) Hwang, Y. K.; Hong, D.-Y.; Chang, J.-S.; Jhung, S. H.; Seo, Y.-K.; Kim, J.; Vimont, A.; Daturi, M.; Serre, C.; Férey, G. Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation. *Angew. Chem., Int. Ed.* **2008**, *47* (22), 4144–4148.
- (19) McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal–Organic Framework Mmen-Mg<sub>2</sub>(Dobpdc). *J. Am. Chem. Soc.* **2012**, *134* (16), 7056–7065.
- (20) DeCoste, J. B.; Demasky, T. J.; Katz, M. J.; Farha, O. K.; Hupp, J. T. A UiO-66 Analogue with Uncoordinated Carboxylic Acids for the Broad-Spectrum Removal of Toxic Chemicals. *New J. Chem.* **2015**, *39* (4), 2396–2399.
- (21) Deria, P.; Bury, W.; Hupp, J. T.; Farha, O. K. Versatile Functionalization of the NU-1000 Platform by Solvent-Assisted Ligand Incorporation. *Chem. Commun.* **2014**, *50* (16), 1965–1968.
- (22) Deria, P.; Bury, W.; Hod, I.; Kung, C.-W.; Karagiari, O.; Hupp, J. T.; Farha, O. K. MOF Functionalization via Solvent-Assisted Ligand Incorporation: Phosphonates vs Carboxylates. *Inorg. Chem.* **2015**, *54* (5), 2185–2192.
- (23) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 724–781.
- (24) Yang, C.; Kaipa, U.; Mather, Q. Z.; Wang, X.; Nesterov, V.; Venero, A. F.; Omary, M. A. Fluorous Metal–Organic Frameworks with Superior Adsorption and Hydrophobic Properties toward Oil Spill Cleanup and Hydrocarbon Storage. *J. Am. Chem. Soc.* **2011**, *133* (45), 18094–18097.
- (25) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous Materials with Optimal Adsorption Thermodynamics and Kinetics for CO<sub>2</sub> Separation. *Nature* **2013**, *495* (7439), 80–84.
- (26) Deria, P.; Mondloch, J. E.; Tylanakis, E.; Ghosh, P.; Bury, W.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. Perfluoroalkane Functionalization of NU-1000 via Solvent-Assisted Ligand Incorporation: Synthesis and CO<sub>2</sub> Adsorption Studies. *J. Am. Chem. Soc.* **2013**, *135* (45), 16801–16804.
- (27) Deria, P.; Chung, Y. G.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. Water Stabilization of Zr<sub>6</sub>-Based Metal–Organic Frameworks via Solvent-Assisted Ligand Incorporation. *Chem. Sci.* **2015**, *6* (9), 5172–5176.
- (28) Deria, P.; Li, S.; Zhang, H.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. A MOF Platform for Incorporation of Complementary Organic Motifs for CO<sub>2</sub> Binding. *Chem. Commun.* **2015**, *51* (62), 12478–12481.
- (29) Rimoldi, M.; Nakamura, A.; Vermeulen, N. A.; Henkelis, J. J.; Blackburn, A. K.; Hupp, J. T.; Stoddart, J. F.; Farha, O. K. A Metal–Organic Framework Immobilised Iridium Pincer Complex. *Chem. Sci.* **2016**, *7* (8), 4980–4984.
- (30) Madrahimov, S. T.; Gallagher, J. R.; Zhang, G.; Meinhart, Z.; Garibay, S. J.; Delferro, M.; Miller, J. T.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. Gas-Phase Dimerization of Ethylene under Mild Conditions Catalyzed by MOF Materials Containing (Bpy)Ni(II) Complexes. *ACS Catal.* **2015**, *5* (11), 6713–6718.
- (31) Hod, I.; Bury, W.; Gardner, D. M.; Deria, P.; Roznyatovskiy, V.; Wasielewski, M. R.; Farha, O. K.; Hupp, J. T. Bias-Switchable Permselectivity and Redox Catalytic Activity of a Ferrocene-Functionalized, Thin-Film Metal–Organic Framework Compound. *J. Phys. Chem. Lett.* **2015**, *6* (4), 586–591.
- (32) George, S. M. Atomic Layer Deposition: An Overview. *Chem. Rev.* **2010**, *110* (1), 111–131.
- (33) Kim, I. S.; Borycz, J.; Platero-Prats, A. E.; Tussupbayev, S.; Wang, T. C.; Farha, O. K.; Hupp, J. T.; Gagliardi, L.; Chapman, K. W.; Cramer, C. J.; Martinson, A. B. F. Targeted Single-Site MOF Node

Modification: Trivalent Metal Loading via Atomic Layer Deposition. *Chem. Mater.* **2015**, *27* (13), 4772–4778.

(34) Lim, B. S.; Rahtu, A.; Gordon, R. G. Atomic Layer Deposition of Transition Metals. *Nat. Mater.* **2003**, *2* (11), 749–754.

(35) Li, Z.; Schweitzer, N. M.; League, A. B.; Bernales, V.; Peters, A. W.; Getsoian, A.; Wang, T. C.; Miller, J. T.; Vjunov, A.; Fulton, J. L.; Lercher, J. A.; Cramer, C. J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K. Sintering-Resistant Single-Site Nickel Catalyst Supported by Metal–Organic Framework. *J. Am. Chem. Soc.* **2016**, *138* (6), 1977–1982.

(36) Kung, C. W.; Mondloch, J. E.; Wang, T. C.; Bury, W.; Hoffeditz, W.; Klahr, B. M.; Klet, R. C.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. Metal–Organic Framework Thin Films as Platforms for Atomic Layer Deposition of Cobalt Ions to Enable Electrocatalytic Water Oxidation. *ACS Appl. Mater. Interfaces* **2015**, *7* (51), 28223–28230.

(37) Hamon, L.; Serre, C.; Devic, T.; Loiseau, T.; Millange, F.; Ferey, G.; De Weireld, G. Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal–Organic Frameworks at Room Temperature. *J. Am. Chem. Soc.* **2009**, *131* (25), 8775–8777.

(38) Peters, A. W.; Li, Z.; Farha, O. K.; Hupp, J. T. Atomically Precise Growth of Catalytically Active Cobalt Sulfide on Flat Surfaces and within a Metal–Organic Framework via Atomic Layer Deposition. *ACS Nano* **2015**, *9* (8), 8484–8490.

(39) Peters, A. W.; Li, Z.; Farha, O. K.; Hupp, J. T. Toward Inexpensive Photocatalytic Hydrogen Evolution: A Nickel Sulfide Catalyst Supported on a High-Stability Metal–Organic Framework. *ACS Appl. Mater. Interfaces* **2016**, *8* (32), 20675–20681.

(40) Karagiari, O.; Bury, W.; Mondloch, J. E.; Hupp, J. T.; Farha, O. K. Solvent-Assisted Linker Exchange: An Alternative to the De Novo Synthesis of Unattainable Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2014**, *53* (18), 4530–4540.

(41) Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W. Stepwise Synthesis of Metal–Organic Frameworks: Replacement of Structural Organic Linkers. *J. Am. Chem. Soc.* **2011**, *133* (26), 9984–9987.

(42) Karagiari, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T. Opening Zif-8: A Catalytically Active Zeolitic Imidazolate Framework of Sodalite Topology with Unsubstituted Linkers. *J. Am. Chem. Soc.* **2012**, *134* (45), 18790–18796.

(43) Kim, M.; Cahill, J. F.; Su, Y.; Prather, K. A.; Cohen, S. M. Postsynthetic Ligand Exchange as a Route to Functionalization of 'Inert' Metal–Organic Frameworks. *Chem. Sci.* **2012**, *3* (1), 126–130.

(44) Tian, Y.-Q.; Cai, C.-X.; Ji, Y.; You, X.-Z.; Peng, S.-M.; Lee, G.-H. [Co<sub>5</sub>(Im)<sub>10</sub>·2 Mb]<sub>∞</sub>: A Metal–Organic Open-Framework with Zeolite-Like Topology. *Angew. Chem., Int. Ed.* **2002**, *41* (8), 1384–1386.

(45) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. Ligand-Directed Strategy for Zeolite-Type Metal–Organic Frameworks: Zinc(II) Imidazolates with Unusual Zeolitic Topologies. *Angew. Chem., Int. Ed.* **2006**, *45* (10), 1557–1559.

(46) Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R. D.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (27), 10186–10191.

(47) Karagiari, O.; Bury, W.; Sarjeant, A. A.; Stern, C. L.; Farha, O. K.; Hupp, J. T. Synthesis and Characterization of Isostructural Cadmium Zeolitic Imidazolate Frameworks via Solvent-Assisted Linker Exchange. *Chem. Sci.* **2012**, *3* (11), 3256–3260.

(48) Lalonde, M. B.; Mondloch, J. E.; Deria, P.; Sarjeant, A. A.; Al-Juaid, S. S.; Osman, O. I.; Farha, O. K.; Hupp, J. T. Selective Solvent-Assisted Linker Exchange (SALE) in a Series of Zeolitic Imidazolate Frameworks. *Inorg. Chem.* **2015**, *54* (15), 7142–7144.

(49) Karagiari, O.; Bury, W.; Tylanakis, E.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. K. Opening Metal–Organic Frameworks Vol. 2: Inserting Longer Pillars into Pillared-Paddlewheel Structures through Solvent-Assisted Linker Exchange. *Chem. Mater.* **2013**, *25* (17), 3499–3503.

(50) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. Active-Site-Accessible, Porphyrinic Metal–Organic Framework Materials. *J. Am. Chem. Soc.* **2011**, *133* (15), 5652–5655.

(51) Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. Solvent-Assisted Linker Exchange (SALE) and Post-Assembly Metallation in Porphyrinic Metal–Organic Framework Materials. *Chem. Sci.* **2013**, *4* (4), 1509–1513.

(52) Zhang, J.; Wojtas, L.; Larsen, R. W.; Eddaoudi, M.; Zaworotko, M. J. Temperature and Concentration Control over Interpenetration in a Metal–Organic Material. *J. Am. Chem. Soc.* **2009**, *131* (47), 17040–17041.

(53) Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T. Control over Catenation in Metal–Organic Frameworks via Rational Design of the Organic Building Block. *J. Am. Chem. Soc.* **2010**, *132* (3), 950–952.

(54) Farha, O. K.; Mulfort, K. L.; Thorsness, A. M.; Hupp, J. T. Separating Solids: Purification of Metal–Organic Framework Materials. *J. Am. Chem. Soc.* **2008**, *130* (27), 8598–8599.

(55) Bury, W.; Fairen-Jimenez, D.; Lalonde, M. B.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. Control over Catenation in Pillared Paddlewheel Metal–Organic Framework Materials via Solvent-Assisted Linker Exchange. *Chem. Mater.* **2013**, *25* (5), 739–744.

(56) Stephenson, C. J.; Hupp, J. T.; Farha, O. K. Postassembly Transformation of a Catalytically Active Composite Material, Pt@ZIF-8, via Solvent-Assisted Linker Exchange. *Inorg. Chem.* **2016**, *55* (4), 1361–1363.

(57) Moon, S.-Y.; Howarth, A. J.; Wang, T.; Vermeulen, N. A.; Hupp, J. T.; Farha, O. K. A Visually Detectable pH Responsive Zirconium Metal–Organic Framework. *Chem. Commun.* **2016**, *52* (16), 3438–3441.

(58) Howarth, A. J.; Buru, C. T.; Liu, Y.; Ploskonka, A. M.; Hartlieb, K. J.; McEntee, M.; Mahle, J. J.; Buchanan, J. H.; Durke, E. M.; Al-Juaid, S. S.; Stoddart, J. F.; DeCoste, J. B.; Hupp, J. T.; Farha, O. K. Postsynthetic Incorporation of a Singlet Oxygen Photosensitizer in a Metal–Organic Framework for Fast and Selective Oxidative Detoxification of Sulfur Mustard. *Chem. - Eur. J.* **2017**, *23* (1), 214–218.

(59) McGonigal, P. R.; Deria, P.; Hod, I.; Moghadam, P. Z.; Avestro, A.-J.; Horvitz, N. E.; Gibbs-Hall, I. C.; Blackburn, A. K.; Chen, D.; Botros, Y. Y.; Wasielewski, M. R.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K.; Stoddart, J. F. Electrochemically Addressable Trisradical Rotaxanes Organized within a Metal–Organic Framework. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (36), 11161–11168.

(60) Klet, R. C.; Wang, T. C.; Fernandez, L. E.; Truhlar, D. G.; Hupp, J. T.; Farha, O. K. Synthetic Access to Atomically Dispersed Metals in Metal–Organic Frameworks via a Combined Atomic-Layer-Deposition-in-MOF and Metal-Exchange Approach. *Chem. Mater.* **2016**, *28* (4), 1213–1219.

(61) So, M. C.; Beyzavi, M. H.; Sawhney, R.; Shekhah, O.; Eddaoudi, M.; Al-Juaid, S. S.; Hupp, J. T.; Farha, O. K. Post-Assembly Transformations of Porphyrin-Containing Metal–Organic Framework (MOF) Films Fabricated via Automated Layer-by-Layer Coordination. *Chem. Commun.* **2015**, *51* (1), 85–88.

(62) Goswami, S.; Ma, L.; Martinson, A. B.; Wasielewski, M. R.; Farha, O. K.; Hupp, J. T. Toward Metal–Organic Framework-Based Solar Cells: Enhancing Directional Exciton Transport by Collapsing Three-Dimensional Film Structures. *ACS Appl. Mater. Interfaces* **2016**, *8* (45), 30863–30870.

(63) Marti, A. M.; Van, M.; Balkus, K. J. Tuning the Crystal Size and Morphology of the Substituted Imidazole Material, SIM-1. *J. Porous Mater.* **2014**, *21* (6), 889–902.