Herein, we demonstrate the robustness of layer-by-layer (LbL)-assembled, pillared-paddlewheel-type MOF films toward conversion to new or modified MOFs via solvent-assisted linker exchange (SALE) and post-assembly linker metalation. Further, we show that LbL synthesis can afford MOFs that have proven inaccessible through other de novo strategies.

Metal–organic frameworks (MOFs) are hybrid materials composed of inorganic vertices connected to organic linkers. Due to the plethora of available linkers and vertices, MOFs can be easily tuned towards specific applications such as catalytic activity, chemical sensing, and light harvesting. Certain applications capitalizing on these behaviors require MOFs to be fabricated into thin films, ideally of well-defined and predetermined thickness and crystallographic orientation. Among the most versatile and useful approaches to MOF film synthesis is layer-by-layer (LbL) coordination, also called liquid-phase epitaxy (Scheme 1a). This approach successively and repetitively introduces solutions of each framework building block into contact with functionalized substrates and subsequently the growing MOF film. The advantage of LbL over other techniques is that MOF layer thicknesses can be controlled with molecular-scale precision. Notably, the composition of an added layer need not match that of preceding layers. Thus, complex, multifunctional crystalline MOF structures are, in principle, obtainable.

One of the current areas of focus of MOF research is the development of methods for obtaining frameworks that are inaccessible via conventional solvothermal methods, but that would be stable or meta-stable if they could indeed be made. Many desired, but conventionally inaccessible, MOFs are direct structural analogues of materials that, in contrast, are readily obtained via standard synthesis routes. For example, the widely studied compound ZIF-8 (or MAF-4) consisting of Zn(II) and 2-methylimidazolate in a sodalite topology, is easily obtained by solvothermal synthesis, whereas the methyl-free analogue, SALEM-2, is obtainable only indirectly. Defining an additional set of examples is the observation that traditional batch-solvothermal synthesis methods typically preclude the direct incorporation of free-base porphyrins as linkers in MOFs because the linkers spontaneously recruit metal ions present as building blocks for nodes.

A promising partial solution to the aforementioned problem is post-synthesis elaboration, subsequently renamed and generalized to post-synthesis modification (PSM), i.e. chemical alteration (atom, ion or functional group addition, subtraction, or transformation) of the framework without changing the parent topology. Indeed, the challenge of obtaining MOFs featuring metal-free porphyrin- or salen-based linkers has been met by first assembling metalated-linker versions of the compounds and then replacing nonstructural (i.e. linker-localized) metal ions with pairs of protons. A second PSM step permits new metal ions to

**Scheme 1** (a) Summary of the transformations performed on L2-MOF. (b) Representation of structural components used in the experiments.
be introduced, including catalytic metals that are incompatible with de novo MOF synthesis.\textsuperscript{14}

Closely related to PSM is the concept of MOF building-block replacement.\textsuperscript{15} One approach to building block replacement is solvent-assisted linker exchange (SALE).\textsuperscript{5,16} Implementation typically entails exposing MOF crystals to a solution of a candidate replacement linker in a carefully selected solvent. Notably, SALE occurs by ligand exchange within intact MOFs, rather than by dissolution and recrystallization. Consequently, the topology of the parent MOF is replicated in the daughter structure. Following the pioneering work of Choe and co-workers with a pillared paddlewheel parent MOF is replicated in the daughter structure. Following the occurrence by ligand exchange within intact MOFs, rather than by replacement linker in a carefully selected solvent. Notably, SALE typically entails exposing MOF crystals to a solution of a candidate solvent-assisted linker exchange (SALE).\textsuperscript{9,16} Implementation of Zn(II) ions in paddlewheel fashion, and (b) 4,4-bipyridine (bipy) pillar exchange, peaks attributable to bpy-H\textsuperscript{+} and dabco-H\textsuperscript{+}, respectively, pK\textsubscript{a} values are 4.9 and 9.8.

Typical conditions for film-based SALE consisted of several hours of exposure at 43 °C to a stirring solution of 2 mM of dabco. As noted above, the small absolute amount of material incorporated into or displaced from thin MOF films presents challenges for monitoring reaction progress. We found, however, that time-of-flight secondary ion mass spectrometry (TOF-SIMS) works well for this purpose. TOF-SIMS relies upon an ion beam (in our case \textsuperscript{69}Ga\textsuperscript{+} ion) to bombard a surface and eject surface/film components – generally as small, ionic fragments.\textsuperscript{15}

Fig. 1a shows a portion of the TOF-SIMS spectrum of an LbL-grown film of L2-MOF. The largest peaks appear at m/z 78 (A) and at m/z 65 (B) and are attributable, respectively, to pyridinium, bpy fragmentation product, and (with less certainty) 1,3-cyclopentadiene, a rearrangement product. Shown in Fig. 1b is a portion of the TOF-SIMS spectrum for a film following 13 hours of exposure to dabco. Consistent with conversion of L2-MOF to SALEF-1 via pillar exchange, peaks attributable to bpy fragmentation and rearrangement are absent. Instead, the spectrum is dominated by peaks assignable to N-methylene-methaniminium C and ethane D and consistent with fragmentation of dabco. Notably, for thinner films of L2-MOF, TOF-SIMS measurements show that less time is needed to complete their conversion to SALEF-1.

If LbL-grown films of L2-MOF are oriented as indicated in Scheme 1, complete exchange of bpy pillars for dabco pillars should decrease the film thickness. For a 45-cycle film (61 nm), the anticipated decrease is 15 nm. The experimentally observed

![Fig. 1 TOF-SIMS spectra of L2-MOF before and after SALE treatment. (a) Before SALE, (A) and (B) correspond to the presence of bpy pillar, but (b) after SALE, the nearly complete disappearance of A and B and appearance of mass peaks at C and D indicate nearly complete replacement of bpy by dabco (i.e., conversion of L2-MOF to SALEF-1). After 12 hours of magnesium(II) exposure, (c) UV-Vis spectra of 43.2 nm thick films of L2-MOF show collapse of four Q bands to two Q bands upon magnesiation. (d) XPS spectrum insets show regions where peaks for Zn 2p and Mg 2p appear in L2-MOF.](image)
The LbL-fabricated, thin-film material, L2-MOF, has proven to be sufficiently robust to participate, without detectable degradation, in both building-block replacement and PSM reactions. Thus, the dipyridyl pillars of the MOF can be readily and essentially completely replaced with dabco pillars via single-stage SALE from a 2 mM DMF solution of the replacement linker. Depending on film thickness, SALE equilibrium is achievable within 13 hours – with thinner films equilibrating more rapidly. TOF-SIMS measurements offer a convenient way of assessing SALE in samples such as LbL films that contain only tiny absolute amounts of materials. Complete post-assembly metalation of free-base-porphyrin-containing LbL films, proved possible, even with weakly coordinated Mg(n) ions. Additionally, using mild LbL conditions, we found that these weakly bound metal ions could be fully retained during film assembly – an outcome not achievable, in our experience, with MOF synthesis via conventional high-temperature solvothermal methods. Beyond the scope of our initial investigation, we believe that the ability of the known metal lability of magnesiated porphyrins should facilitate incorporation of other metal ions, including weakly bound ions, potentially displaying interesting redox, catalytic, or photophysical behavior. The findings effectively diversify the arsenal of techniques that can be deployed to obtain desired MOF films for sensing, catalysis, and energy conversion schemes.

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Notes and references


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