Opening Metal–Organic Frameworks Vol. 2: Inserting Longer Pillars into Pillared-Paddlewheel Structures through Solvent-Assisted Linker Exchange

Olga Karagiardi,†,⊥ Wojciech Bury,†,‡,⊥ Emmanuel Tylianakis,§,∥ Amy A. Sarjeant,† Joseph T. Hupp,*† and Omar K. Farha*†

†Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States
‡Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
§Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States
∥Materials Science and Technology Department, University of Crete, P.O. Box 2208, 71409 Heraklion, Crete, Greece

Supporting Information

ABSTRACT: Solvent-assisted linker exchange (SALE) was performed on a pillared-paddlewheel metal–organic framework (MOF), SALEM-5, to achieve incorporation of longer linkers into the material. The 9-Å meso-1,2-di(4-pyridyl)-1,2-ethanediol pillar of SALEM-5 was successfully replaced by 11-, 14-, and 17-Å pillars to generate daughter MOFs SALEM-6, SALEM-7, and SALEM-8. The daughter frameworks possess more open cages, as was demonstrated by structural modeling from the powder X-ray diffraction patterns, and larger solvent accessible space, as was demonstrated by thermogravimetric analysis. Finally, a study was performed to examine the effect of pK_a of monoprotonated dipyridyl pillars (as an indicator of the Zn–L bond strength) on the outcome of SALE.

KEYWORDS: metal–organic frameworks, solvent-assisted linker exchange, pK_a

INTRODUCTION

Metal–organic frameworks (MOFs) constitute a highly investigated class of hybrid materials that have attracted an unprecedented amount of research effort over the past decade. Their highly porous1,2 and modular nature endows them with a vista of attractive properties, and their potential has been examined in many different areas such as gas storage,3,4 catalysis,5 sensing,6 separations,7 removal of hazardous materials,8 and light harvesting.9–13

One of the greatest challenges in MOF research lies in devising a sufficiently diverse set of synthetic pathways to enable desired new MOF structures to be routinely obtained experimentally. Several factors can make this surprisingly difficult, even when the desired new MOFs constitute analogues of known materials. First, the traditional solvothermal synthesis of MOFs may preclude the incorporation of certain linkers de novo (e.g., free-base porphyrins).14 Second, precursors for nodes and other metal sites (typically, labile metal complexes) are free to react with mult-topic linkers, thereby making the incorporation of coordinatively unsaturated metals difficult. Finally, there is limited control over the topological arrangement of the metal nodes and the linkers; de novo assembly may favor the production of low-energy structures, which are not always the desired products.15 Numerous procedures have been devised to circumvent these obstacles, including templating,16 use of porogens,17 prefabrication of structural building blocks,18 stepwise synthesis,14 and postsynthesis modification of either the ligand or the metal node.19

A recently discovered and very promising method that can be applied toward the solution of the aforementioned problems is solvent-assisted linker exchange (SALE).20–23,45 Appealingly facile in its implementation, SALE involves exposing parent MOF crystals to a concentrated solution of linkers of choice in a carefully selected solvent. A successful outcome is a daughter MOF structure that possesses the topology of the parent combined with the linkers from the reaction solution. Even though Robson predicted SALE as early as in 1990,24 the actual conceptualization of the process was slow to develop. Kitagawa and co-workers followed by Chen and co-workers performed a series of experiments in 2004 that involved linking 2D paddlewheel layers with bipyridyl pillars to obtain 3D
Zhou’s group was perhaps the first to perform SALE in molecular metal–organic polyhedra, in which they replaced the existing pillars with monodentate and bidentate ligands.27,28 However, the first SALE in MOFs was implemented in 2011 by Choe and co-workers. They replaced \( N,N' \)-di-4-pyridylphthalalenetetracarboxydiimide linkers in a pillared-paddlewheel porphyrin MOF with 4,4′-bipyridyl moieties.29

Shortly afterward, Cohen and co-workers achieved solid-to-solid and solution-to-solid replacement of benzene-dicarboxylate derivatives in the notoriously robust UiO-66 structure.30 Since then, there has been a rapid increase of interest in the exploitation of SALE, and this method has been applied toward resolving a variety of challenges in MOF synthesis, such as modification of chemically “inert” structures,20,31 bulk preparation of comparatively high-energy polymorphs,21 opening of apertures,22 and synthesis of catalytically active materials.22,32 This is not surprising, as the composition of these materials suggests facile replacement of the relatively weakly bound pillars.

Pillared-paddlewheel MOFs have been utilized as model systems in many reports regarding SALE.22,23,29,32 This is not surprising, as the composition of these materials suggests facile replacement of the relatively weakly bound pillars. Nevertheless, a perceived limitation of SALE for pillared-paddlewheel MOFs is the challenge associated with replacing existing pillars with ones of greater length, with retention of the parent topology.

In the present work, we have successfully used SALE to incorporate a variety of longer linkers into a pillared-paddlewheel structure. The parent material Solvent-Assisted Linker Exchanged Material-5 (SALEM-5, Scheme 1) features meso-1,2-di(4-pyridyl)-1,2-ethanediol (L1) pillars that are approximately 9 Å long. The monoprotonated conjugate-acid of L1 is moderately acidic (\( \text{pK}_a \approx 4.68 \)). We hypothesized that the relatively low \( \text{pK}_a \) of the acid would render the corresponding pillar fairly susceptible to linker exchange.33 The pillars connect layers of 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (L2), a tetra-carboxylate specifically designed by our group to inhibit catenation by preventing access of building blocks through the \( xy \)-plane of the crystal structure.34 The utilization of L2 thus ensures the lack of catenation in the parent and daughter SALE materials. Here, we examine two concepts: (i) the incorporation of longer (11 Å, 14 Å, and 17 Å) pillars into SALEM-5 and (ii) the effect of the \( \text{pK}_a \) of the conjugate acid of the pillar as a predictor of the outcome of SALE.

**RESULTS AND DISCUSSION**

SALEM-5, as its name reveals, is in itself a material produced through SALE. Even though the bromine-free analogue of SALEM-5 (DOMOF) is known,35 attempts to access the brominated analogue via direct (de novo) synthesis invariably yielded 2D sheets of zinc clusters linked by L2. As a result, we resorted to performing SALE of L1 into a pillared-paddlewheel material previously synthesized by us that features L0 pillars and L2-based sheets (Scheme 1).34 This SALE reaction proved facile, yielding SALEM-5 overnight.

In our attempts to incorporate longer linkers into the SALEM-5 framework, we initially selected a daughter linker that was only slightly longer than the 9-Å parent. Our choice was the 11-Å pillar L3. The presence of four nonstructural methyl groups endows L3 with good solubility in solvents used for SALE (e.g., \( \text{N,N-dimethylformamide} \)) and facilitates the monitoring of its insertion by \( ^1\text{H} \) NMR. To our pleasant surprise, after 24 h of SALE at 100 °C using 4 equiv. of L3, \( ^1\text{H} \) NMR showed 100% replacement of the parent L1 pillars by the daughter linker (Figure S3, Supporting Information). The crystallinity of the new structure, SALEM-6, was examined by powder X-ray diffraction (PXRD) in the presence of solvent in a spinning capillary, in order to avoid preferential orientation and preserve the integrity of the material.14,36 The position of the first peak at \( 2\theta = 4.76° \) suggests that SALEM-6 possesses a larger unit cell than SALEM-5, which yields a first reflection peak at \( 2\theta = 5.60° \) (Figure 1, vide infra).

Inspired by the success of SALEM-6, we wondered whether we could insert an even longer pillar into SALEM-5. The 14-Å long pillar L4 was selected. Daily monitoring of the SALE reaction by \( ^1\text{H} \) NMR indicated a steady increase in the content of L4; the progress of the reaction was expedited by replacing the solution with fresh batches when the rate of linker replacement plateaued. By day four, the replacement of L1 by L4 exceeded 90% (Figures S4 and S6, Supporting Information). Paralleling data obtained for SALEM-6, the PXRD pattern for the L4-SALE product SALEM-7 indicated an even smaller angle for the first reflection peak (\( 2\theta = 4.20° \)) and therefore an even larger unit cell.

Finally, to investigate the limits of SALE, we experimented with the replacement of L1 by the pillar L5, which possesses a structure analogous to that of L3, but at 17 Å, it is almost twice as long as the parent pillar. The SALE reaction proceeded at a very slow rate, presumably due to the great strain associated with the incorporation of such a large pillar.59 Indeed, two weeks were required for the reaction to approach completion.
The structures of SALEM-5, SALEM-6, SALEM-7, and SALEM-8 were constructed in silico and optimized using the lattice parameters obtained from the experimental PXRD patterns (Table 1). The experimental PXRD patterns of the SALE materials and their respective simulated patterns are compared in Figure 1, and it can be seen that they are in excellent agreement. Based on the simulated PXRD patterns, we were able to index the unit cells. Since the 2D sheets formed as additional support for the incorporation of longer linkers in SALEM-5 through SALE. So, despite the notorious difficulty associated with the activation of this family of pillared-paddlewheel MOFs, such measurements were performed on SALEM-5 and SALEM-7. Density functional theory (DFT) pore size distribution reveals the presence of a pore with the width of 8.6 Å in SALEM-5; SALEM-7, on the other hand, features an 11.8 Å pore. The increase in pore width following the SALE of L1 in SALEM-5 by L4 is consistent with the fact that the pillars L1 and L4 differ in length by 4.5 Å (Figure S20, Supporting Information).

It is evident from the results that incorporation of longer pillars into pillared-paddlewheel structures through SALE is feasible. Moreover, we observed that the utilization of a longer incoming linker does not necessarily lead to increased times for the SALE reaction to be completed. For example, we previously observed that the exchange of the DOMOF L1 pillar for 4,4′-bipyridine (L6, approximately 7 Å long; see Table 1) took place overnight—just as rapidly as the replacement of the same parent linker by L3, even though the latter is 2 Å longer than

Table 1. Length and pKₐ Values of the Relevant Linkers Used in the Pillared-Paddlewheel Structures, and Lattice Parameters of the Simulated Structures of SALEM-5, SALEM-6, SALEM-7, and SALEM-8

<table>
<thead>
<tr>
<th>pillar</th>
<th>length [Å]</th>
<th>pKₐ</th>
<th>MOP structure</th>
<th>unit cell dimensions [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>8.795</td>
<td>4.68</td>
<td>SALEM-5</td>
<td>a = 11.4700</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 15.7553</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 15.7553</td>
</tr>
<tr>
<td>L3</td>
<td>11.440</td>
<td>4.86</td>
<td>SALEM-6</td>
<td>a = 11.4439</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 15.5304</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 18.5173</td>
</tr>
<tr>
<td>L4</td>
<td>13.527</td>
<td>4.75</td>
<td>SALEM-7</td>
<td>a = 11.7407</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 15.9200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 20.6200</td>
</tr>
<tr>
<td>L5</td>
<td>16.511</td>
<td>4.21</td>
<td>SALEM-8</td>
<td>a = 11.4439</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 15.5304</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 23.5000</td>
</tr>
<tr>
<td>L6</td>
<td>7.079</td>
<td>4.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L7</td>
<td>9.080</td>
<td>3.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the parent linker. At the same time, the SALE reaction leading to the replacement of the \( L_1 \) linker by 4,4′-azobis(pyridine) (L7), a linker of roughly the same length as \( L_1 \), needed about three days to come to completion.\(^\text{23} \) These observations made us ask whether, along with the linker length, the \( pK_a \) of the conjugate acid of the incoming linker is a predictor of the rate of SALE. Linkers with higher conjugate acid \( pK_a \) values form stronger bonds with the zinc centers and lead to more energetically favored structures.

We wanted to examine whether the Zn–L bond strength plays a role in engendering preferential incorporation of a pillar when the parent MOF crystals are exposed to an equimolar mixture of candidate replacement pillars. Thus, we performed a series of mixed linker experiments, in which we exposed \( \text{SALEM-5} \) crystals to pairs of different pillars (Scheme 2). We deliberately selected a pair of pillars with a small difference in conjugate acid \( pK_a \) and a pair in which there was a marked difference. At the same time, the selected pillars differed in length, so that we could study whether it is the linker length or the strength of the Zn–L bond that determines the linker distribution over the course of the SALE reaction.

In the first experiment, we exposed \( \text{SALEM-5} \) crystals to an equimolar mixture of \( L_6 \) and \( L_7 \) under SALE conditions. \( L_6 \) is shorter than \( L_7 \) but also has a higher conjugate acid \( pK_a \) (Table 1). From the onset of the reaction, monitoring by \( ^1\text{H} \) NMR performed on digested crystals indicated preferential incorporation of \( L_6 \) into the crystals. \( L_6 \) was eventually able to replace almost all the parent \( L_1 \) pillars, whereas \( L_7 \) exhibited minimal incorporation, presumably due to its steric demands and lower affinity for the metal centers.

In a second experiment, \( \text{SALEM-5} \) crystals were exposed to an equimolar mixture of \( L_3 \) and \( L_6 \). These linkers have a smaller difference in basicity than \( L_6 \) and \( L_7 \) but differ appreciably in length (Table 1). To our surprise, the result of this reaction was quite rapid replacement of almost all \( L_1 \) pillars with \( L_3 \). Even though \( L_6 \) is almost 3 Å shorter than \( L_3 \) and is expected to encounter a lower kinetic barrier as it diffuses into \( \text{SALEM-5} \), the stronger interaction of \( L_3 \) with Zn(II) (as implied by the higher \( pK_a \) of \( L_3 \)) appears to be the critical factor in the outcome of the reaction, as the incorporation of \( L_6 \) did not exceed 11%.

The structural consequences of the comparatively greater affinity of the basic ligand \( L_3 \) for the zinc clusters in the pillared-paddlewheel structure on SALE are remarkable. Having observed extended reaction times with the SALE of the longer (and more acidic) linkers \( L_4 \) and \( L_5 \), we hypothesized that the rate of these reactions could be increased if a parent with a longer pillar than \( \text{SALEM-5} \) were used. To test the hypothesis, we examined competitive SALE of \( L_4 \) and \( L_5 \) on \( \text{SALEM-6} \) and compared the progresses of these two reactions to those of the respective SALE experiments on \( \text{SALEM-5} \). Although we expected that the longer linkers would react more rapidly with the more open compound, \( \text{SALEM-6} \), the results of our experiment were quite surprising (Figures S15–S16, Supporting Information). \( L_4 \) replaced \( L_1 \) in \( \text{SALEM-5} \) at a rate similar to that for \( L_3 \) exchange into \( \text{SALEM-6} \); \( L_5 \) actually had a higher SALE rate into \( \text{SALEM-5} \) than into \( \text{SALEM-6} \). Although \( \text{SALEM-6} \) offers a larger window for the longer linkers to enter, once inside the structure, it seems that they have to battle against the tight metal binding of the basic \( L_3 \), which poses a greater thermodynamic challenge than the relatively acidic \( L_1 \). Therefore, merely opening the cage does not necessarily guarantee more facile SALE, and the energetic factors governing SALE, such as \( pK_a \), have to be taken into consideration.\(^\text{44} \)

**CONCLUSION**

In conclusion, we have demonstrated that the utilization of SALE for the insertion of longer pillars into a pillared-paddlewheel system is feasible and can proceed at reasonable rates. The morphology of the crystals is not detectably altered during the reaction. Finally, linker basicity (as a surrogate for relative Zn-L bond strength) plays an important role in the incorporation of the incoming linkers, with more basic linkers preferentially exchanging into pillared-paddlewheel structures.

**ASSOCIATED CONTENT**

* Supporting Information

Experimental details for the synthesis of \( L_3 \), \( L_4 \), and \( L_5 \) and the SALE procedures; \(^1\text{H} \) NMR, thermogravimetric analysis, and powder X-ray diffraction data; plots of the rates of SALE in mixed linker experiments and variable linker length experiments; details pertaining to the modeling procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

*Corresponding Author

E-mail: j-hupp@northwestern.edu; o-farha@northwestern.edu.

**Author Contributions**

All authors have given approval to the final version of the manuscript. These authors contributed equally.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the Basic Energy Sciences Office of the U.S. Dept. of Energy (Grant No. DE-FG2-08ER15967), the Foundation for Polish Science through the “Kolumb” Program (W.B.) and the Global Climate and Energy Project (E.T.) for the financial support of this project.

---

**Scheme 2. Summary of the Mixed Linker Reactions Performed on \( \text{SALEM-5} \)**

---

**Table 1. Linker lengths and \( pK_a \) values**

<table>
<thead>
<tr>
<th>Linker</th>
<th>Length (Å)</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_1 )</td>
<td>11.5</td>
<td>3.2</td>
</tr>
<tr>
<td>( L_3 )</td>
<td>13.5</td>
<td>2.8</td>
</tr>
<tr>
<td>( L_4 )</td>
<td>15.5</td>
<td>2.4</td>
</tr>
<tr>
<td>( L_5 )</td>
<td>17.5</td>
<td>2.0</td>
</tr>
<tr>
<td>( L_6 )</td>
<td>9.5</td>
<td>4.0</td>
</tr>
<tr>
<td>( L_7 )</td>
<td>11.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

---

dx.doi.org/10.1021/cm401724v | Chem. Mater. 2013, 25, 3499–3503
REFERENCES


(21) Burnett, B. J.; Choe, W. CrystEngComm 2012, 14, 6129.

(22) Burnett, B. J.; Choe, W. CrystEngComm 2012, 14, 6129.

(23) Li pillars are more weakly bound to the zinc cluster, as will be elaborated further in the text.


(27) The length of the pillars was estimated by measuring their length in relevant crystallographic information files (CIFs) featuring their structures.


(29) We speculate that the success of SALE of L5 does not pertain to the rate of the diffusion of L5 through the MOF channel, but rather has to do with the dependence of the strength of the Zn–N coordinate bond on the angle at which L5 approaches the zinc cluster. Having a length twice that of the parent Li pillar, L5 faces a significant challenge to orient itself at a proper angle to the zinc cluster and has to rely on the presence of defects, which presumably impedes the rate of incorporation into the framework. The presence of the bromine substituents of L2 exacerbates this problem.

(30) An inherent side effect of SALE involves development of cracks within the crystals.


(34) In other words, the competitive linker insertion experiments that we performed indicate the favorable formation of the thermodynamic product rather than of the kinetic product.
