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Selective Solvent-Assisted Linker Exchange (SALE) in a Series of Zeolitic Imidazolate Frameworks

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Supporting Information

ABSTRACT: Solvent-assisted linker exchange (SALE) has recently emerged as an attractive strategy for the synthesis of metal−organic frameworks (MOFs) that are unobtainable via traditional synthetic pathways. Herein we present the first example of selective SALE in which only the benzimiadazolate-containing linkers in a series of mixed-linker zeolitic imidazolate frameworks (ZIF-69, -78, and -76) are replaced. The resultant materials (SALEM-10, SALEM-10b, and SALEM-11, respectively) are isostructural to the parent framework and in each case contain trifluoromethyl moieties. We therefore evaluated each of these materials for their hydrophobicity in condensed and gas phases. We expect that selective SALE will significantly facilitate the design of improved, and potentially complex, MOF materials with new and unusual properties.

Metal−organic frameworks (MOFs) are porous crystalline materials composed of organic linkers and metal-based nodes.[1−3] By using a building-block-like approach with appropriate metals and organic linkers, MOFs can be tailored for a wide variety of potential applications.[3] MOFs are typically synthesized under solvothermal conditions (i.e., de novo conditions), and this approach has led to over 20000 variants.[3] However, the de novo synthesis of MOFs can be challenging; it can lead to, for example, an undesired number of topologies, catenated networks, and a lack of desired functionality within the framework.[4] High-throughput screening along with postsynthesis modification have been utilized to overcome some of these difficulties,[5−7] yet more general synthetic strategies are still needed.

Recently, solvent-assisted linker exchange (SALE) has emerged as an attractive alternative to the de novo synthesis of MOFs.[4,8] SALE involves the placement of template MOF crystals in an excess solution of a secondary linker. Following a SALE reaction, the daughter framework retains the original MOF topology, but linkers from the reaction solution will have replaced the original MOF linkers. Along with the incorporation of the desired linkers in MOFs that are inaccessible de novo,[9−13] SALE can also impart new properties onto the framework. For example, SALE has been used to introduce catalytically active moieties,[14,15] gain control over catenation,[16] demonstrate ring-closing metathesis,[17] enhance proton conductivity[18] as well as photochemical H_2 production,[19] and incorporate free carboxylic acid groups by functionalizing defect sites.[20]

While SALE has proven to be a powerful tool for imparting functionality within MOFs, it has been limited to the exchange of MOFs that contain organic linkers with only one type of coordination bond to the metal-based nodes. (One notable exception is pillar-paddlewheel-type MOFs, which have two different functional groups attaching the organic linkers to the metal nodes. However, SALE has been limited to exchange at the dipyridyl struts and does not occur at the carboxylate-terminated linkers.[9]) A new and highly attractive concept would be selective SALE, in which only one linker is replaced in a MOF containing at least two different linkers but with the same coordination chemistry (see Figure 1, for example).

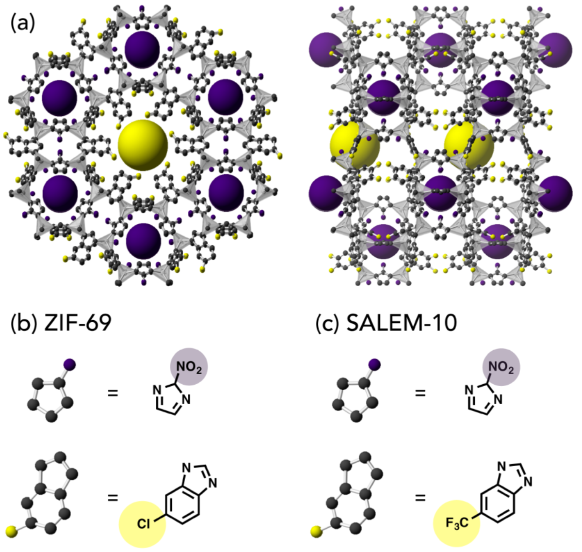

Figure 1. (a) Illustration of the MOF ZIF-69. SALE occurs selectively at the benzimidazolate linkers that line the pores indicated with yellow spheres but not the 2-nitroimidazolate linkers highlighted with the purple spheres (b and c).

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Selective SALE has the potential to (i) greatly broaden the variety of accessible frameworks accessible via SALE, by giving additional control over the incorporation of linkers into a specific topology, (ii) create complex pore environments (e.g., containing linkers with multiple functionalization) that could provide opportunities for uncovering new and unusual properties, and (iii) allow functional groups that are incompatible under de novo synthetic conditions to be found in close proximity to each other. To date, selective SALE has not been demonstrated in a MOF with two linkers that have identical coordination chemistry at the metal nodes.

Herein we demonstrate the first examples of selective SALE by using a series of zeolitic imidazolate frameworks (ZIFs),[5] namely, ZIF-69, ZIF-78, and ZIF-76. Each of these ZIFs contains two types of linkers, but in each case, both linkers are connected to the metal node via imidazolate-terminated coordination bonds, and thus they are attractive candidates for selective SALE. The resultant materials are termed solvent-assisted linker exchange material-10 (SALEM-10), SALEM-10b, and SALEM-11, respectively. In our prototype system (the conversion of ZIF-69 to SALEM-10), both materials have been characterized by ^{1}H NMR, powder X-ray diffraction (PXRD), N_2 gas adsorption, single-crystal X-ray diffraction, condensed-phase contact-angle measurements, and water vapor adsorption measurements.

To start, selective SALE was carried out with ZIF-69, which exhibits gme topology and is composed of a 1:1 ratio of 2-nitroimidazolate (nim) and 5-chlorobenzimidazolate (cbim) linkers coordinated to tetrahedral zinc nodes (Figure 1a). ZIF-69 and other gme ZIFs are attractive candidates for selective SALE because nim has shown resistance to SALE in single-linker ZIFs, such as CdIF-4.[10] Hence, we hypothesized that nim in ZIF-69 would remain in place, while cbim would be susceptible to replacement via SALE. When selecting a candidate linker for selective SALE, we opted for 5-(trifluoromethyl)benzimidazole. The goal of incorporating fluorinated functional groups was to demonstrate selective SALE and to increase the hydrophobicity of the framework.

SALE was performed by submerging 30 mg of ZIF-69 in 10 mL of a 2 M solution of 5-(trifluoromethyl)benzimidazole in *n*-butanol at 120 °C for 3 days. ^{1}H NMR indicated that 95% of cbim was replaced by 5-(trifluoromethyl)benzimidazolate (fbim; Figure 2). If SALE occurs selectively at the cbim linker, the ratio between the total benzimidazolate and nim linkers should remain unchanged. This was confirmed by examining the ^{1}H NMR spectrum of SALEM-10 (Figure 2). The ratio between the total amount of benzimidazole (i.e., the remaining parent cbim and fbim) and imidazole remains constant. The selective nature of the SALE reaction was corroborated by single-crystal X-ray diffraction (Figure 1a), which reveals that fbim selectively replaced the cbim linker. [See the Supporting Information (SI) for additional details.] Finally, the bulk phase purity and permanent porosity of SALEM-10 were confirmed by PXRD (Figure S3 in the SI) and N_2 adsorption measurements (Figure S6 in the SI).

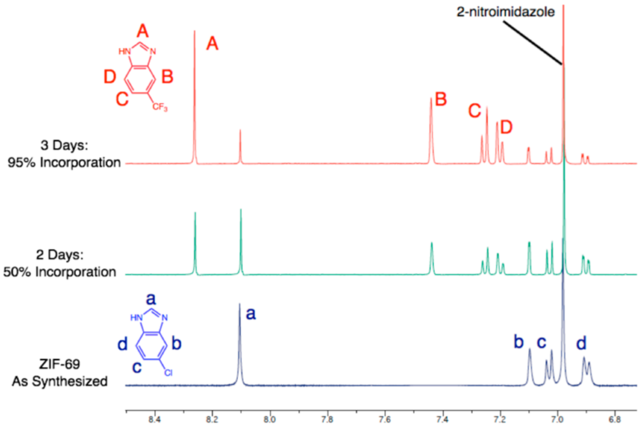

Figure 2. Reaction progress followed by ^{1}H NMR for conversion of ZIF-69 into SALEM-10.

To further probe the selectivity of the SALE process, we pursued analogous experiments with two other ZIFs: ZIF-78,[21] a gme topology ZIF analogous to ZIF-69 but containing 5-nitrobenzimidazolate (nbim) linkers instead of cbim linkers, and ZIF-76, an lta topology ZIF composed of imidazole and cbim. The ^{1}H NMR results for the SALE reactions are summarized in Table 1. In addition to replacing 95% of cbim in ZIF-69, 5-(trifluoromethyl)benzimidazole replaced 90% of nbim in ZIF-78 and 90% of cbim in ZIF-76. The resulting daughter ZIFs are named SALEM-10b and SALEM-11, respectively. PXRD and N_2 adsorption analyses confirmed the bulk phase topology and permanent porosity of SALEM-10b and SALEM-11. (See the SI for additional details.) Notably, attempts to synthesize SALEM-10 and -11 de novo were unsuccessful; see the SI.

Table 1. MOFs, Their Linkers, pK_a Values, and Percentage of Linker Exchange

MOF	linkers	pK_a values[a]	% linker exchange[b]
ZIF-69	nim and cbim	−1.73 and 5.74	
SALEM-10	nim and fbim	−1.73 and 5.74	95
ZIF-78	nim and nbim	−1.73 and 5.03	
SALEM-10b	nim and fbim	−1.73 and 5.74	90
ZIF-76	im and cbim	6.97 and 5.74	
SALEM-11	im and fbim	6.97 and 5.74	90

[a] For the protonated N3. [b] Determined by ^{1}H NMR.

Insight into selective SALE can be gained by examining the pK_a values for the nitrogen atoms of imidazole and imidazolium versions of the molecules deployed as linkers. Table 1 lists pK_a values for N3 in each linker precursor, and an identical trend can be observed for the N1, the details of which are given in the SI. As we previously noted,[22] the linker basicity (as reflected in the pK_a values of the corresponding acids) can be used as a proxy for the relative Zn−L bond strength, and it is clear that thermodynamic factors are playing a large role in governing the selective nature of the SALE reaction. For example, 5-(trifluoromethyl)-benzimidazole (5.74) selectively replaces cbim (5.74). However, Zn−L bond strengths alone cannot explain all of the observed data; on the basis of pK_a values, one would expect 5-(trifluoromethyl)benzimidazole (5.74) to also replace nim (−1.73) in ZIF-69, yet this is not observed experimentally. At this point in time, we cannot unequivocally determine whether this is due to steric and/or kinetic effects.

Fluoroalkane-containing linkers within MOFs have received attention because they are often hydrophobic. For example, Yang et al. presented a series of fluorous MOFs with notable hydrophobicity for the adsorption of aromatic and aliphatic components of oil.[23] Comparing the results of water contact-angle measurements of the ZIFs and the fluorinated SALEM materials reveals significantly larger contact angles for the SALEMs (Figure S9 in the SI). Recognizing that contact-angle measurements report exclusively on interactions of the *exterior* surfaces of materials with *liquid*-phase water, we also measured the water vapor uptake of ZIF-69 and SALEM-10. In contrast to the contact-angle measurements, vapor sorption measurements showed no enhancement of the hydrophobicity for SALEM-10 relative to ZIF-69 (Figure 3). The contrast between these two results can likely be attributed to the cohesive forces between water molecules, resulting in higher surface tension in the contact-angle measurements. This discrepancy in hydrophobicity measurements will influence how hydrophobicity is quantified on the surface and in the pores of future materials.

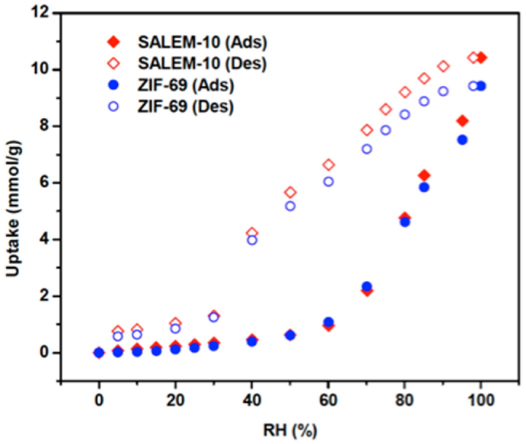

Figure 3. Water vapor adsorption isotherms for ZIF-69 (blue) and SALEM-10 (red).

In conclusion, we have presented the first examples of selective SALE within MOFs. The structure and permanent porosity of the examined ZIFs are retained in SALEM-10, -10b, and -11, as demonstrated by PXRD and N_2 adsorption. The selective nature of the SALE reaction was confirmed by ^{1}H NMR and in our prototypical example (SALEM-10) by single-crystal X-ray analysis. While the selective nature of the SALE process is largely governed by the pK_a values of the linkers, steric and/or kinetic factors must also play a key role. We look forward to exploring new materials with potentially unique properties prepared by selective SALE.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, experimental details, NMR, PXRD, TGA, BET surface area, single-crystal X-ray parameters, and contact-angle measurements. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01231.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191−214.

(2) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695−704.

(3) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.

(4) Karagiaridi, O.; Bury, W.; Mondloch, J. E.; Hupp, J. T.; Farha, O. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 4530−4540.

(5) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. *Science* **2008**, *319*, 939−943.

(6) Sumida, K.; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L.; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. *Chem. Sci.* **2010**, *1*, 184−191.

(7) Cohen, S. M. *Chem. Rev.* **2012**, *112*, 970−1000.

(8) Deria, P.; Mondloch, J. E.; Karagiaridi, O.; Bury, W.; Hupp, J. T.; Farha, O. K. *Chem. Soc. Rev.* **2014**, *43*, 5896−5912.

(9) Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W. *J. Am. Chem. Soc.* **2011**, *133*, 9984−9987.

(10) Karagiaridi, O.; Bury, W.; Sarjeant, A. A.; Stern, C. L.; Farha, O. K.; Hupp, J. T. *Chem. Sci.* **2012**, *3*, 3256−3260.

(11) Kim, M.; Cahill, J. F.; Fei, H.; Prather, K. A.; Cohen, S. M. *J. Am. Chem. Soc.* **2012**, *134*, 18082−18088.

(12) Kim, M.; Cahill, J. F.; Su, Y.; Prather, K. A.; Cohen, S. M. *Chem. Sci.* **2012**, *3*, 126−130.

(13) Lee, C.-Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858−15861.

(14) Karagiaridi, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 18790−18796.

(15) Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. *Chem. Sci.* **2013**, *4*, 1509−1513.

(16) Bury, W.; Fairen-Jimenez, D.; Lalonde, M. B.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *Chem. Mater.* **2013**, *25*, 739−744.

(17) VermeUlen, N. A.; Karagiaridi, O.; Sarjeant, A. A.; Stern, C. L.; Hupp, J. T.; Farha, O. K.; Stoddart, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 14916−14919.

(18) Kim, S.; Dawson, K. W.; Gelfand, B. S.; Taylor, J. M.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2013**, *135*, 963−966.

(19) Pullen, S.; Fei, H.; Orthaber, A.; Cohen, S. M.; Ott, S. *J. Am. Chem. Soc.* **2013**, *135*, 16997−17003.

(20) Karagiaridi, O.; Vermeulen, N. A.; Klet, R. C.; Wang, T. C.; Moghadam, P. Z.; Al-Juaid, S. S.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. *Inorg. Chem.* **2015**, *54*, 1785−1790.

(21) Banerjee, R.; Furukawa, H.; Britt, D.; Knobler, C.; O'Keeffe, M.; Yaghi, O. *J. Am. Chem. Soc.* **2009**, *131*, 3875−3877.

(22) Karagiaridi, O.; Bury, W.; Tylianakis, E.; Sarjeant, A. A.; Hupp, J. T.; Farha, O. K. *Chem. Mater.* **2013**, *25*, 3499−3503.

(23) Yang, C.; Kaipa, U.; Mather, Q. Z.; Wang, X.; Nesterov, V.; Venero, A. F.; Omary, M. A. *J. Am. Chem. Soc.* **2011**, *133*, 18094−18097.