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EDGE ARTICLE

Synthesis and characterization of isostructural cadmium zeolitic imidazolate frameworks *via* solvent-assisted linker exchange†Olga Karagiari, ^a Wojciech Bury, ^{ac} Amy A. Sarjeant, ^b Charlotte L. Stern, ^b Omar K. Farha ^{*,a} and Joseph T. Hupp ^{*,a}

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Herein, we present the first examples of solvent-assisted linker exchange (SALE) in zeolitic imidazolate frameworks (ZIFs). By exposing the ZIF **CdIF-4** to excess solutions of 2-nitroimidazole and 2-methylimidazole under solvothermal conditions, we were able to obtain a previously reported ZIF **CdIF-9** in high yield, as well as synthesize a new ZIF, Solvent-Assisted Linker-Exchanged Material-1 (**SALEM-1**). The parent and daughter ZIFs are isostructural (RHO zeolitic topology) and highly porous. Despite the high thermal and chemical stability of ZIFs, single crystal-to-single crystal linker exchange appears to be a suitable tool for the modification and functionalization of these materials. We anticipate that the addition of SALE to the arsenal of known synthetic techniques for ZIFs will significantly facilitate the quest to obtain interesting and useful ZIF compounds, including compounds that cannot be synthesized directly.

Introduction

Zeolitic imidazolate frameworks (ZIFs)^{1–4} are a subclass of metal azolate frameworks,⁵ which, in turn, are a subset of crystalline metal-organic framework (MOF) materials.^{6–10} ZIFs generally comprise tetrahedral di-positive metal ions (or supertetrahedra¹¹) as nodes and utilize deprotonated imidazole and/or its derivatives as linkers. Tri-positive metal ions can serve as nodes for a special class of metal azolate frameworks termed Z-MOFs;¹¹ furthermore, lithium–boron and copper–boron-based imidazolate frameworks (BIFs) have also been synthesized.¹² ZIFs (and Z-MOFs and BIFs) additionally are characterized by topologies corresponding to known aluminosilicate zeolite topologies (typically SOD, RHO, or GME). ZIFs are hybrid materials possessing the crystallinity, chemical and thermal stability, and porosity of their inorganic counterparts, zeolites, along with the mechanical stability¹³ and the chemical versatility and variety of organic linkers. Such coexistence of desirable properties makes ZIFs attractive candidates for materials applications involving

gas storage,^{14–17} gas separation,^{18–21} catalysis,^{22–25} and sensing.²⁶ In particular, the availability of imidazolate linkers with various functional groups provides ample room for the design of new ZIF structures tailored to exhibit chemical or steric properties suitable for the performance of a given task. ZIFs are typically synthesized solvothermally, although preparatory procedures for ZIFs involving mechanochemistry,²⁷ aqueous media at room temperature²⁸ and ionic liquids^{29,30} have been established.

The implementation of rigorous structure–property studies in ZIFs requires synthesis of isostructural ZIFs with varying functional groups on their imidazolate linkers. Early synthesis studies revealed that linker functional groups, especially alkyls, can sometimes serve as structure-directing agents; in other words, the zeolitic topology a ZIF assumes during its synthesis from inorganic metal precursors and imidazoles is often predetermined by the functional group on the linkers.² The linker-topology relationship has been more recently supported by DFT calculations that predict higher energies for nets within which initially present derivatized imidazoles have been hypothetically (*i.e.* computationally) replaced with unsubstituted imidazoles.³¹ Taking advantage of these findings, Banerjee *et al.* and Morris *et al.* successfully created two series of isostructural ZIFs: a GME series with mixed imidazolate linkers by utilizing 2-nitroimidazole as one of the linker precursors,³² and a RHO series by employing 4,5-substituted imidazolate linkers.³³ While the observed correlations between topologies obtained and types of imidazolate used are useful, they also are limiting; many potentially interesting ZIFs appear to be unobtainable *de novo*, as the employed imidazolate moieties thermodynamically favor the formation of a net other than the desired one. Thus, systematic investigations of isostructural series may be limited. Although

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exceptions to “linker-topology” rules exist, ZIFs possessing “forbidden” linker-topology combinations are usually isolated as minor components (only a few crystals) within a more thermodynamically stable phase.^{3,34,35}

The “linker-topology” problem could be overcome if, instead of the classical *de novo* ZIF synthetic methods, we could enlist an approach that enabled existing ZIF crystals to be treated like molecules – performing reactions directly on them to produce new materials, while retaining original topologies. Morris *et al.* experimented with this idea in a simplified way by performing reactions on the aldehyde moiety on a ZIF linker to introduce a new functional group.³⁶ A more invasive approach to composition alteration that allows production of new materials not related to their progenitors by the chemistry of their functional groups is the exchange of either the metal nodes or the organic linkers of a ZIF. Several examples of metal exchange (transmetalation) within MOFs are known.^{37–41} More recently, Choe *et al.*, Cohen *et al.*, and our own research group reported examples of obtaining desirable – and in some cases, otherwise unobtainable – MOF compounds *via* ligand exchange experiments.^{42–44} No linker exchanges, however, have been described yet for ZIFs, which are regarded as comparatively inert due to strong metal–linker bonds – a feature that provides ZIFs with their characteristic robustness.⁴⁵

Herein, we report two examples of a process that we term solvent-assisted linker exchange (SALE) in a cadmium-based ZIF, **CdIF-4**, originally synthesized by Tian *et al.*³⁵ SALE was documented, in part, by ¹H NMR of subsequently dissolved materials. Single crystal and powder X-ray diffraction (XRD) data confirmed the retention of the zeolite topology of the parent material. Additionally, the results are consistent (for the specific case examined) with linker-exchange *via* crystal-to-crystal transformation, rather than dissolution-reassembly. As a result of the linker exchange experiments, a new ZIF was obtained and a new method was established for the synthesis of an existing ZIF in higher purity and better yield (Fig. 1). We believe that SALE

constitutes a powerful tool for the development of new ZIFs with predictable topologies and desirable functional groups and that it will serve as a valuable addition to the arsenal of synthetic strategies for ZIFs.

Results and discussion

CdIF-4 is a cadmium-based ZIF of RHO topology possessing 2-ethylimidazolate (eim) linkers. The RHO topology endows its cage with comparatively large apertures (6.7 and 9.6 Å) and a 49% solvent-accessible volume (Table 1). As a result, **CdIF-4** is highly porous, with the Brunauer–Emmett–Teller (BET) surface area of 1658 m² g^{−1}. The synthesis of **CdIF-4** is extremely facile, giving 60% yield based on the amount of the cadmium starting material and excellent purity and crystallinity, so gram-scale amounts of the material are easily attainable. Unfortunately, the linker composition limits applications of **CdIF-4**, and the steric demands of the ethyl substituents limit its micropore volume to 0.764 cm³ g^{−1}.³⁵ It would therefore be desirable to have a synthetic procedure that would transfer the attractive aspects of **CdIF-4** (scalability, good crystal quality, RHO topology) to ZIFs featuring other linkers.

To explore this notion, SALE was attempted with **CdIF-4** with the aim of replacing eim with 2-nitroimidazolate (nim). A cadmium-based ZIF of RHO topology with nim linkers has been previously synthesized and is known as **CdIF-9**.³⁵ However, its synthesis *de novo* is not as efficient as that of **CdIF-4** (14% yield), the product is usually polycrystalline, and the majority of the starting material produces an amorphous phase. It has been found that the presence of the polarizing nitro group in ZIFs leads to an increased volumetric capacity of the material to store CO₂.³² Given the relatively high cost of 2-nitroimidazole (Hnim), a more effective route to **CdIF-9** would be desirable.

To perform the linker exchange, **CdIF-4** was immersed in a *N,N*-dimethylformamide (DMF) solution of Hnim and placed in an oven at 100 °C. After 24 h, the ¹H NMR spectrum of representative ZIF crystals (removed and dissolved) showed that 85% of the eim linkers had been replaced by nim; after 48 h, no signal from eim could be detected by NMR, indicating full linker exchange. The crystals maintained their original shapes and at no point during the reaction was the growth of new crystals on the vessel walls observed. After the reaction reached completion, the integrity of the parent RHO framework in the daughter ZIF **CdIF-9** was confirmed by PXRD (Fig. 2).

CdIF-9 possesses one of the highest reported surface areas among ZIFs.³⁵ We deemed it important, therefore, to determine whether the same high porosity is obtained when the compound is accessed *via* SALE. After residual eim and nim molecules were removed from the pores by Soxhlet extraction and the material was activated, its BET surface area was measured and found to be 1668 m² g^{−1} (Table 1). This value agrees well with the BET surface area of 1597 m² g^{−1} measured in our laboratory for the *de novo* synthesized **CdIF-9**.

Following the successful synthesis of **CdIF-9** by SALE, we decided to target the synthesis of a previously unreported ZIF – specifically, one that had proven inaccessible *via* conventional MOF assembly methods. Tian *et al.* reported the synthesis of three Cd(II) 2-methylimidazolate (mim) ZIFs – **CdIF-1**, **CdIF-2**, **CdIF-3** and **CdIF-5** with *sod*, *mer*, *yqt1* and *ict* nets, respectively. **CdIF-1** contains apertures of only modest width (6.2 Å), **CdIF-2**

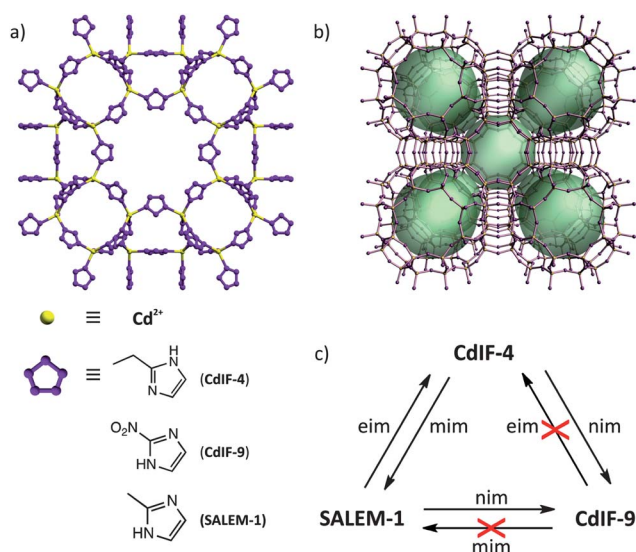


Fig. 1 (a) Schematic representation of the structure of **CdIF-4**, **CdIF-9** and **SALEM-1**; (b) a 3D representation of the RHO topology; (c) reaction scheme showing ligand exchange in the SALE experiments.

Table 1 Structural characteristic of **CdIF-4**, **CdIF-9** and **SALEM-1**

ZIF	Composition	Zeolite topology	Space group	Unit cell side length [Å]	Cd–N bond length [Å]	Solvent-accessible volume ^a [%]	BET surface area [m ² g ^{−1}]
CdIF-4	Cd(eim) ₂	RHO	<i>Im3m</i>	30.5886(5)	2.168(40), 2.189(4)	49.2	1632 ^b
CdIF-9	Cd(nim) ₂	RHO	<i>Im3m</i>	30.2375(4)	2.25(2), 2.233(6)	66.8	1668
SALEM-1	Cd(mim) ₂	RHO	<i>Im3m</i>	30.5539(5)	2.172(8), 2.126(2)	58.6	1385

^a Calculated by PLATON. ^b Reported for **CdIF-4** generated as a result of the eim–mim–eim ligand exchange.

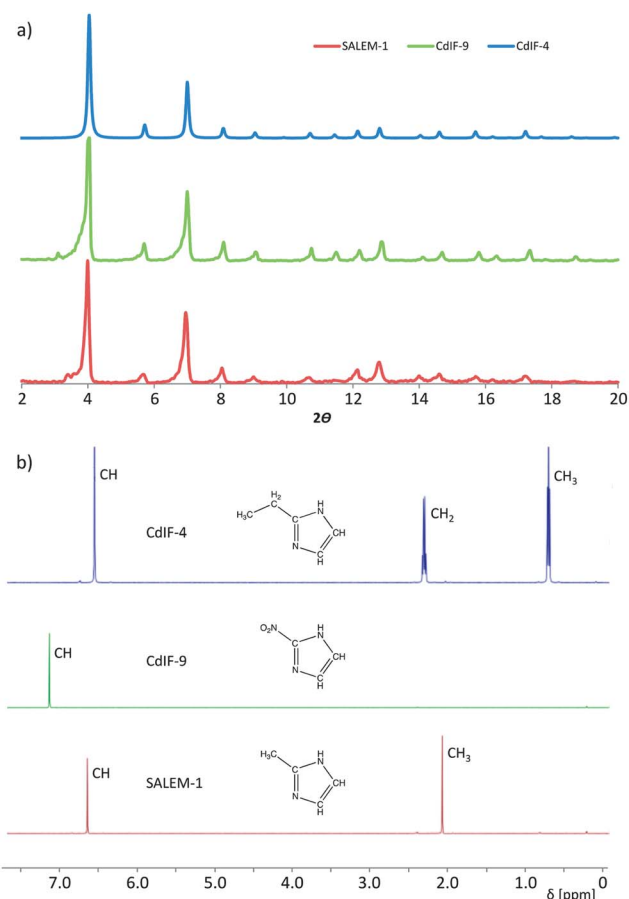


Fig. 2 (a) PXRD patterns and (b) ¹H NMR spectra of the parent **CdIF-4** and the ligand-exchange daughter materials **CdIF-9** and **SALEM-1** confirming ligand exchange and preservation of RHO topology. The ¹H NMR spectra were taken in D₂SO₄.

is reported to be unstable with respect to framework collapse during solvent evacuation, and **CdIF-3** and **CdIF-5** are nonporous.³⁵ We speculated that if the eim linkers of **CdIF-4** could be replaced with mim linkers, the result would be a Cd–mim ZIF of RHO topology, possessing a unit cell almost twice the size of that for **CdIF-1** and featuring a more open framework with apertures of *ca.* 9.6 Å diameter, like its nim and eim isomorphs.

To initiate the exchange, **CdIF-4** was placed in a DMF solution of 2-methylimidazole (Hmim). After 48 h of solvothermal reaction at 100 °C, ¹H NMR showed that 100% of the eim linkers had been replaced by mim. As anticipated, and as evidenced by PXRD data (Fig. 2), the new ZIF, Solvent-Assisted Linker-Exchanged Material-1 (**SALEM-1**), indeed is characterized by

RHO topology. It is also highly porous, with a BET surface area of 1385 m² g^{−1} (Table 1). To our knowledge, this is the first synthesis of a new ZIF *via* linker exchange.

Exploration of SALE reactions with **CdIF-4** shows that transformations to **CdIF-9** and **SALEM-1** with the preservation of RHO topology take place in a variety of solvents. When *N,N*-dimethylacetamide (DMA) and *n*-butanol (*n*-BuOH) are used as solvents, eim exchange with both nim and mim takes place at rates similar to those seen in DMF. The solvent appears to serve mainly as a medium for the reaction and as a base to deprotonate the imidazolate linkers; the pre-existing eim linkers in the **CdIF-4** framework apparently are the ones that direct the nim and the mim linkers to the desired positions in a true SALE fashion.

To gain additional insight into the mechanism of SALE, single-crystal studies were performed. Two crystals of **CdIF-4** were isolated, photographed and placed in solutions of Hnim and Hmim at 100 °C. They were photographed again after 60 h and it was discovered that the morphology and size of each crystal remained unchanged (Fig. 3). Single-crystal diffraction data collected on the linker-exchanged crystals confirmed that: (a) the materials are fully isostructural with **CdIF-4**, (b) all of the linkers have been exchanged, and (c) the size of the unit cell remains unchanged (Table 1). At least with **CdIF-4**, SALE appears to proceed *via* crystal-to-crystal transformation. This is

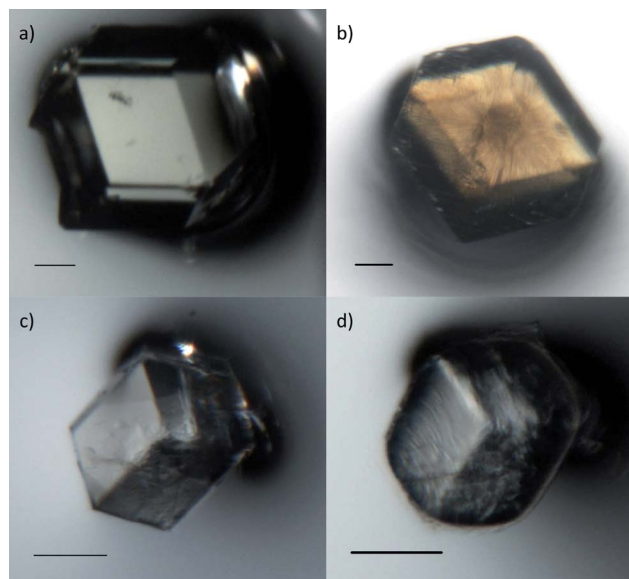


Fig. 3 (a) A crystal of **CdIF-4**; (b) the same crystal transformed to **CdIF-9** after 60 h in Hnim solution; (c) a second crystal of **CdIF-4**; (d) the same crystal transformed to **SALEM-1** after 60 h in Hmim solution. The bar corresponds to 0.1 mm.

highly advantageous in terms of reaction, as essentially every crystal is transformed into the new material and little attrition of the costly linkers takes place.

To begin assessing the scope of SALE, we investigated whether reverse or serial SALE can be accomplished with **CdIF-4** (Fig. 1c). ^1H NMR shows that the exchange from eim to mim is fully reversible. Exposure of **SALEM-1** to a DMF solution of excess 2-ethylimidazole (Heim) for 48 h at 100 °C leads to complete recovery of **CdIF-4** with preserved porosity (BET = 1632 m² g⁻¹, Table 1). Furthermore, upon obtaining **SALEM-1** through SALE, it is possible to transform it to **CdIF-9** by exposing it to a DMF solution of Hnim for 48 h at 100 °C. In contrast, transformation of **CdIF-9** to either **CdIF-4** or **SALEM-1** does not occur under the conditions we employed. When **CdIF-9** is exposed to solutions of Heim or Hmim in DMF, instead of formation of the desired daughter ZIF frameworks with the new linkers, the result is complete dissolution of the parent framework. This observation can be rationalized based on the relative stabilities of the Cd(eim)₂, Cd(mim)₂, and Cd(nim)₂ frameworks. The electron-withdrawing nature of the nitro substituent diminishes the Lewis basicity of the imidazolate nitrogens and yields weaker coordination bonds in Cd–nim than in either Cd–eim or Cd–mim, an assertion supported by the Cd–N bond-length data in Table 1.⁴⁶ Thus, when **CdIF-9** is placed in a DMF solution of excess Heim or Hmim, cadmium ions evidently are extracted from the framework, as soluble complexes, by the more strongly coordinating imidazolate derivatives. Consequently, single crystal-to-single crystal SALE does not take place. If our reasoning is correct, the findings suggest that ZIFs featuring electron-donating groups as linker substituents will prove to be the most suitable templates for SALE-based synthesis. Ongoing work in our lab is aimed at further testing this and related ideas.

Conclusions

SALE takes place readily with **CdIF-4** under solvothermal conditions. The technique can be used to optimize the yield and crystallinity of the previously reported compound **CdIF-9**, and to obtain **SALEM-1** – to our knowledge the first novel ZIF to be synthesized *via* linker exchange. Powder and single crystal XRD reveal complete preservation of the RHO zeolitic topology of the parent **CdIF-4** in the daughter structures **CdIF-9** and **SALEM-1**. BET measurements confirm the porosity of the materials obtained through SALE. The single-crystal SALE experiments serve as evidence that the integrity of individual crystals remains uncompromised during the reaction, *i.e.* in the cases examined, SALE appears to occur *via* single crystal-to-single crystal transformation rather than *via* dissolution and recrystallization. The fact that further SALE reactions take place in **CdIF-4** and **SALEM-1**, but not in **CdIF-9**, suggests that non-destructive linker exchange, with topology preservation, is most easily achieved when the initially present metal–nitrogen bonds of a framework are replaced by bonds of either weaker or similar strength – with stronger product bonding evidently favoring node extraction and solubilization, at least over the near term. Regardless, our studies clearly demonstrate that despite their renowned chemical and thermal stability, appropriately chosen ZIFs are readily amenable to transformation into other ZIFs *via* linker exchange. We anticipate that this new synthetic approach

will permit the synthesis of many new, previously unobtainable interesting materials characterized with high crystallinity and predetermined zeolitic topologies, and featuring linkers having functional groups that can be utilized for applications of choice.

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Experimental section

Materials

Cadmium(II) acetate dihydrate (Aldrich, 98%), *n*-butanol (Aldrich, ≥ 99.4%), *N,N*-dimethylformamide (Macron, 99.8%), *N,N*-dimethylacetamide (Aldrich, 99%), tetrahydrofuran (Aldrich, 99.9%), 2-ethylimidazole (Aldrich, 98%), 2-methylimidazole (Aldrich, 99%), 2-nitroimidazole (3B Scientific Corporation, 99%) and deuterated sulfuric acid (Cambridge, 96–98% solution in D₂O) were used as received.

Synthesis of CdIF-4

CdIF-4 was synthesized using a modified version of the procedure reported by Tian *et al.*³⁵ Cd(OAc)₂·2 H₂O (0.356 g, 1.33 mmol) and 2-ethylimidazole (0.547 g, 5.69 mmol) were placed in a crimp-top high pressure-resistant microwave vial and dissolved in *n*-butanol (20 mL) by sonication. The vial was capped and placed in an oven at 120 °C for 24 h. Colorless **CdIF-4** crystals were collected and washed with DMF. The crystals were stored in DMF until further use.

SALE procedure

2-Methylimidazole (Hmim) (25 mg, 0.30 mmol) or 2-nitroimidazole (Hnim) (25 mg, 0.22 mmol) was placed in an 8-dram vial and dissolved in DMF (10 mL), DMA or *n*-BuOH by sonication. 25 mg of unactivated **CdIF-4** crystals (0.083 mmol) were immersed in the resulting solution. The vial was capped and placed in an isothermal oven at 100 °C. After 24 h the solution was replaced with a fresh solution of the same concentration of Hnim or Hmim as the original. The progress of the linker exchange reaction was monitored by ^1H NMR and the reaction was stopped once ~100% linker exchange was achieved (48 h after initiation). The same procedure was followed for the reverse and serial SALE experiments. Elemental analysis for ZIF **SALEM-1**: calculated% (C₈H₁₀CdN₄, *M* = 274.60 g mol⁻¹): C, 34.99; H, 3.67; N, 20.40. Found%: C, 34.89; H, 3.50; N, 20.24. Elemental analysis for ZIF **CdIF-9** as obtained through SALE: calculated% (C₆H₄CdN₆O₄, *M* = 336.55 g mol⁻¹): C, 21.41; H, 1.20; N, 24.97. Found%: C, 21.69; H, 1.17; N, 24.42. (Prior to elemental analysis, the sample was subjected to Soxhlet extraction, as described below, and then heated for three hours at 100 °C under vacuum.)

Instrumentation

^1H NMR spectra were collected on a Bruker Avance III 500 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku ATXG diffractometer equipped with an 18 kW Cu rotating anode, MLO

monochromator, and a high-count rate scintillation detector (measurements made over a range of $2^\circ < 2\theta < 20^\circ$ in 0.05° step width with a 2 deg min^{-1} scanning speed). Elemental analysis was performed by Atlantic Microlab Inc. (Norcross, Georgia). Activation of the ZIFs prior to dinitrogen sorption measurements was done on a Micromeritics FlowPrep 060. N_2 isotherms were measured on a Micromeritics TriStar II 3020 at 77 K. Images of the single crystals were collected using a Nikon SMZ1500 stereozoom microscope equipped with a digital camera and video monitor for visualization of crystalline samples. The single crystal data were collected on a Bruker APEX2 V2.1-4 CCD diffractometer with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. This work made use of the J. B. Cohen X-Ray Diffraction Facility supported by the MRSEC program of the National Science Foundation (DMR-1121262) at the Materials Research Center of Northwestern University.

NMR of ZIF materials

Approximately 1 to 5 mg of each ZIF were placed in a 1.5-dram vial and dissolved in 1 mL of D_2SO_4 by sonication. Once a homogeneous solution was achieved, the sample was transferred to an NMR tube. The ^1H NMR spectra were obtained by locking the sample directly to D_2SO_4 .

Single crystal SALE experiment

Two **CdIF-4** crystals were removed from the bulk **CdIF-4** sample and placed in two separate vials containing 10 mg of 2-methylimidazole (0.12 mmol) or 2-nitroimidazole (0.088 mmol) dissolved in *n*-BuOH (5 mL). Images of the crystals were collected immediately after the initiation of the reaction and 60 h after the reaction had started.

Preparation of samples for dinitrogen sorption measurements

The ligand-exchanged ZIFs were subjected to Soxhlet extraction in tetrahydrofuran for 2 days in order to remove any excess linker molecules that might be trapped in the pores of the SALE products. After that, the ZIFs were activated on the FlowPrep instrument at 120°C for 24 h. Approximately 50–70 mg were used for the dinitrogen sorption measurements.

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