## Vapor-phase linker exchange of the metal-organic framework ZIF-8: a solvent-free approach to postsynthetic modification

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Zeolitic imidazolate frameworks (ZIFs) are a sub-class of metal-organic frameworks (MOFs). Because of their high porosity and chemical modularity, ZIFs have shown promise in fields such as sensing,<sup>1</sup> gas storage,<sup>2</sup> and separation.<sup>3</sup> ZIFs are comprised of divalent metal cations tetrahedrally coordinated by imidazolate linkers, resulting in porous three-dimensional zeolite topologies.<sup>4,5</sup> ZIF-8 is arguably the most well-studied member of the ZIF family. It consists of Zn(II) and 2-methyl imidazolate (mIm) connected in a sodalite (SOD) topology, with cages of 11.4 Å in diameter interconnected by 3.4 Å diameter windows. Other Zn(II)-based SOD ZIFs with different linkers are increasingly investigated.<sup>6–10</sup> Examples include ZIF-7 (benzimidazolate), ZIF-71-SOD (4,5-dichloro imidazolate), ZIF-65 (2-nitro imidazolate) or ZIF-90 (2-carboxaldehyde imidazolate). While these SOD ZIF materials are similar in unit cell and pore dimensions, their properties differ widely due to the different linker in the framework.

Although generally considered stable materials, ZIFs can undergo post-synthetic linker exchange (PSLE) in solution under mild conditions.<sup>11,12</sup> Since the parent topology is maintained throughout the exchange process, PSE expands the chemical versatility of ZIFs to mixed-linker materials and in some cases to materials not accessible through direct synthesis.<sup>13</sup> Nevertheless, the solution-based approach requires large solvent volumes and the linker incorporation preference can be hard to rationalize due to solvent effects. On the other hand, several ZIF materials can be synthesized through vapor-based and other solvent-free methodologies.<sup>14-17</sup> Here we present a novel, solvent-free approach to post-synthetic linker exchange in ZIF-8 through exposure to linker vapor. As in the solvent-based approach, this vapor-phase linker exchange (VPLE) method retains the parent SOD topology and proceeds in a single-crystal to single-crystal manner. The scope of linkers that can be incorporated through VPLE was studied and criteria for the selection of further candidates were formulated. In large crystals, the incoming linker was found to form domains instead of distributing homogeneously, similar as for solution-based linker exchange. In contrast to the latter approach, VPLE yields a higher concentration of the incoming linker in the crystal core instead of the shell.

### **Results and Discussion**



Figure 1 – Schematic representation of the VPLE process.

Initial VPLE tests were performed by exposing ZIF-8 to 2-carboxaldehyde imidazole (CHO-HIm) vapor (Figure 1). 2-Methyl imidazole (HmIm) and CHO-HIm have similar dimensions, small enough to allow diffusion through the ZIF pore network (Table S2). As CHO-Im is prone to side-reactions due to the reactive nature of the aldehyde group,<sup>18–20</sup> VPLE trials (24 h) were performed at 353, 373 and 393 K. Reaction at the lower temperatures resulted in a color change from white to yellow, similar to ZIFs obtained through direct synthesis or linker exchange using CHO-HIm solutions.<sup>21,22</sup> The sample treated at 393 K turned brown (Figure S1). Nevertheless, <sup>1</sup>H NMR analysis of the acid-digested samples revealed the incorporation of intact CHO-Im in all ZIF-8 samples, without the detection of decomposition products (Figure S2). For a fixed VPLE duration, the extent of CHO-Im incorporation increased with the reaction temperature, from 47 to 63%. PXRD analysis of the mixed-linker ZIFs confirms that the SOD topology is maintained after VPLE at 353 and 373 K. At 393 K, PXRD and SEM micrographs reveal signs of degradation together with a drop in BET surface area from 1306 m<sup>2</sup>g<sup>-1</sup> to 638 m<sup>2</sup>g<sup>-1</sup>(Figures S3-5), similar to what was reported by Nair and collaborators for linker exchange of ZIF-8 with CHO-HIm in MeOH.<sup>21</sup> For further experiments, 353 K was selected for VPLE.

VPLE was monitored as a function of time for ZIF-8 crystals ranging in size from < 100 nm to > 100  $\mu$ m. For each time point, a separate experiment was performed and the linker ratio in acid-digested samples was analyzed by <sup>1</sup>H-NMR (Figure S6). A clear dependence of the linker exchange kinetics on the particle size would indicate the diffusion-limited nature of the exchange process. Surprisingly, the differently sized crystals show similar exchange kinetics and end up with an identical fraction of CHO-Im incorporated in the framework (84 ± 6 %; Figure 2). FTIR analysis of samples at each time point confirms the progressive decrease of mIm bands (e.g., at 991 cm<sup>-1</sup>), accompanied by increasing signals characteristic of CHO-Im incorporation (e.g., at 1667 cm<sup>-1</sup>). The observed size-independence of VPLE kinetics is in contrast with the mass transport limitations reported by Nair and coworkers for linker exchange in solution. <sup>21</sup> In their case, after 24 h of exchange, the CHO-Im linker fraction was 70 % for nanocrystals compared to only 26 % for micron-sized crystals.

The VPLE process requires the following steps: (i) adsorption of the incoming linker, (ii) exchange of protons between the adsorbed CHO-HIm molecules and the mIm linkers in the ZIF-8 framework, and (iii) removal of protonated HmIm. The size-independence of the VPLE kinetics suggests that the phenomena

related to mass transport in the ZIF-8 pores are not rate-determining, *i.e.*, linker adsorption, diffusion, and desorption. Adsorption of the incoming linker is evidenced by PXRD, through reversible changes in the low-angle diffraction peaks upon exposure of the parent ZIF-8 material to CHO-HIm vapor (Figure S7). When the framework mIm linker is protonated, the bond with the Zn(II) cations is weakened and HmIm is volatilized. Given that the sodalite ZIF structure is maintained (Figure S8) and the particle size distribution is similar before and after linker exchange, the framework Zn(II) cations likely have no or limited mobility – as would be expected in the absence of a liquid phase. In other words, VPLE occurs in a single-crystal to single-crystal manner, since MOF dissolution-recrystalliztion cannot occur in the absence of a solvent.



Figure 2 – Evolution of the ZIF composition as a function of VPLE time. Parent ZIF-8 crystals of different sizes were used: 90 nm (blue squares), 15  $\mu$ m (green squares), and 15  $\mu$ m (orange squares). For reference, the previously reported CHO-Im fraction incorporated after 24 h of solution-based linker exchange in 90 nm (blue triangles) and 150  $\mu$ m (orange triangles) ZIF-8 crystals is included.<sup>21</sup> Error bars correspond to standard deviation of three experimental points.

After after 72 h of VPLE, the BET surface area decreases slightly, from 1430 m<sup>2</sup>g<sup>-1</sup> for the parent ZIF-8 to 1340  $\pm$  20 m<sup>2</sup>g<sup>-1</sup>, averaged over the different particle sizes. This slight decrease is expected based on the BET surface area of pure ZIF-90 (1291 m<sup>2</sup>g<sup>-1</sup>). A larger fraction of incorporated CHO-Im leads to higher N<sub>2</sub> uptake in the low-pressure range (< 0.1 P/P<sub>0</sub>; Figure S9). Similarly, MeOH isotherms show a gradual transition from the ZIF-8 to the ZIF-90 profile, with an uptake at P/P<sub>0</sub>< 0.1 that increases with the CHO-Im content (Figure S10). VPLE works equally well for ZIF-8 films deposited on quartz crystal microbalance (QCM) substrates (Figures S11 and S12). The gravimetric MeOH adsorption isotherms recorded for the resulting mixed-linker ZIF layers follow a similar trend as VPLE ZIF powders (Figure S13).



Figure 3– Versatility of the VPLE process. Top: pK<sub>a</sub> values of different imidazoles. The molecules included in this work are represented by blue squares, others by red circles. The melting temperature of each imidazole, a rough estimate of its vapor pressure, is represented by grey bars. Bottom: summary of successful VPLE trials.

VPLE requires (i) that the incoming linker protonates the framework linker, (ii) that the protonated forms of both linkers are sufficiently volatile, and (iii) that the incoming linker can form a framework of the same topology. Since vapor pressure data is not readily available for other imidazole linkers of interest, their melting point was used instead as a rough estimator. Combining the pKa, melting point and topology criteria reveals a range of incoming linker candidates (Figure 3), of which 4,5-dichloro imidazole (dCl-Im), benzimidazole (bzIm) and 2-nitro imidazole (NO<sub>2</sub>-Im) were selected for VPLE tests. The SOD ZIFs formed by these linkers are referred to as ZIF-71-SOD (100 % dCl-Im), ZIF-7 (100 % bzIm), and ZIF-65-Zn (100 % NO<sub>2</sub>-Im).<sup>23-26</sup> For each linker, the VPLE temperature was adjusted to stay below the melting point and the thermal stability limit (Table S2). Starting from ZIF-8, all linkers were successfully incorporated after 72 h of VPLE, although to a different extent: 68% for NO<sub>2</sub>-Im, 44% for bzIm, and 37% for dCl-Im. More bulky linkers and linkers that can form ZIF topologies other than SOD seem to be incorporated to a lower extent. Nevertheless, only the SOD topology was observed, thus supporting the idea of VPLE as a single-crystal to single-crystal transformation (Figures S14 and S15). As a negative control experiment, VPLE was attempted with 2-ethylimidazole (eIm). As would be expected based on the lower acidity of this linker, no exchange was observed.



Figure 4 - Evolution of the ZIF composition as a function of VPLE time under different reaction atmospheres: nitrogen (green), argon (light blue), ambient air (brown), vacuum (red) and vacuum with 5% relative humidity (dark blue). The parent material and incoming linker for these tests were 90 nm ZIF-8 crystallites and CHO-Im, respectively.

To understand the influence of the atmosphere on VPLE of CHO-Im in ZIF-8, trials were performed under argon, nitrogen, and air (Figure 4). After 24 h, the extent of linker incorporation under argon and nitrogen reached 30 %, compared to 47 % under vacuum. Likely, the vacuum conditions enhance the vaporization rate and gas phase diffusion of the incoming linker through an increased mean free path length. Tests with ambient air in the reaction vessel led to VPLE rates similar as under vacuum. We hypothesized that moisture in the ambient air could improve VPLE compared to argon and nitrogen atmospheres. The catalyzing effect of moisture was confirmed by deliberately adding water vapor after evacuating the reaction vessel, to achieve 5 % relative humidity at 298 K. VPLE under these conditions led to the incorporation of 63 % CHO-Im after 24 h. Since neither ZIF-8 nor ZIF-90 have significant water uptake at these low concentrations (Figure S16), the observed effect is likely due to co-adsorption of water with the incoming linker. We hypothesize that, similar as for acid gases in ZIFs, the incoming linker and water form a more reactive complex.<sup>27</sup>



Figure 5 – Linker distribution in 150  $\mu$ m mixed-linker ZIF crystals obtained through direct synthesis and VPLE. Top and middle: 2D NOESY spectra for directly synthesized ZIF-8<sub>52</sub>-90<sub>48</sub> (top) and ZIF-8<sub>49</sub>-90<sub>51</sub> obtained after 48 h of VPLE (middle). The position of the -CHO/-CH<sub>3</sub> cross-peak is indicated with a red dashed circle. Bottom: SRS mapping of the carbonyl signal at a focal plane in the middle of the large crystals: ZIF-8<sub>62</sub>-90<sub>38</sub> after 24 h of VPLE; ZIF-8<sub>49</sub>-90<sub>51</sub> after 48 h of VPLE. The scale bar is 20  $\mu$ m and the signal intensity increases from blue to red.

The distribution of the CHO-Im linker in large 150  $\mu$ m ZIF-8 crystals subjected to VPLE was investigated. Solid-state <sup>1</sup>H NMR spin-diffusion measurements were performed for VPLE samples with a ZIF-8<sub>49</sub>-90<sub>51</sub> composition (ZIF<sub>VPLE</sub>). These measurements were benchmarked against a mixed-linker ZIF material obtained through direct solvothermal synthesis and with a nearly identical composition, ZIF-8<sub>52</sub>-90<sub>48</sub> (ZIF<sub>DS</sub>). For mixed-linker ZIFs prepared by direct synthesis, the homogenous distribution of the mIm and CHO-Im linkers was previously confirmed through similar solid-state NMR experiments.<sup>28</sup> The signal highlighted in the 2D spectra (Figure 5 – top) corresponds to polarization transfer between the protons of the aldehyde and methyl group of CHO-Im and mIm, respectively. This result confirms the close proximity of both linkers in ZIF<sub>DS</sub>. In contrast, the absence of this signal for ZIF<sub>VPLE</sub> (Figure 5 - middle) indicates the formation of segregated domains. This observation is in accordance with the absence of this signal for physical mixtures of ZIF-8 and ZIF-90 crystals, *i.e.* when both domains are completely segregated, and is further supported by the spin diffusion curves (Figure S17 and S18).<sup>28</sup>

To further understand the linker segregation in ZIF<sub>VPLE</sub>, the same crystals were imaged using stimulated Raman scattering (SRS). This technique allows to selectively probe vibrational modes at a given focal plane within the crystals. SRS microscopy confirms the increasing intensity of the carbonyl band at 1690 cm<sup>-1</sup> with increasing CHO-Im incorporation (Figure S19). Visualizing the CHO-Im distribution based on this vibration band reveals a higher concentration in the crystal core, throughout the VPLE process (Figure 5 – bottom). These results are in contrast to the linker distribution after solution-based linker exchange. In that case, SS-NMR experiments also show non-perfect mixing, but a higher CHO-Im concentration is observed in the crystal shell due to diffusion limitations.<sup>21</sup> Since VPLE is not diffusion-limited (vide supra), other factors must determine the linker distribution. The large ZIF-8 crystals are synthesized in the presence of sodium formate as a modulator. It has previously been observed that in the presence of sodium formate, ZIF-8 initially grows via a nanoparticle aggregation, before transitioning to a linkerparticle attachment.<sup>29</sup> We hypothesize that this growth mode results in defects in the core of the large crystals, and that linker exchange initially occurs at such sites, as suggested by theoretical calculations for ZIFs<sup>30,31</sup> and experimentally observed in other MOFs.<sup>32</sup> The resulting local changes in pore polarity and hydrogen bonding capability likely favor the adsorption of further CHO-HIm molecules and their incorporation in the crystal lattice. Such autocatalytic behavior has been observed for Zn-N bond cleavage in ZIFs upon exposure to humid acid gases, and was explained by a simultaneously increasing water uptake and defectivity.<sup>27</sup> Additionially, the ability of incorporated CHO-Im linkers to act as both H-bond donors and acceptors might facilitate linker exchange at adjacent sites.<sup>33</sup> These effects are thought to be responsible for the observed CHO-Im domain formation in ZIF-8 after VLE.

## Conclusion

VLE is a novel method for solvent-free post-synthetic linker exchange in MOFs. The method was demonstrated for ZIF-8 with a range of imidazole linkers and the criteria governing the process were established, *i.e.* pK<sub>a</sub> and vapor pressure. For large parent ZIF-8 crystals, the linker distribution after VLE was demonstrated to be not well-mixed, with the formation of a CHO-Im-rich core. Since VLE was demonstrated for thin films as well, we foresee its combination with the chemical vapor deposition of MOFs,<sup>14</sup> to form a vapor-only processing toolbox for the microfabrication of chemical sensors.<sup>34</sup>

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