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

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Abstract: Zeolitic imidazolate frameworks (ZIFs) are a sub-class of metal-organic frameworks (MOFs). Although generally stable, ZIFs can undergo post-synthetic linker exchange (PSLE) in solution under mild conditions. Here we present a novel, solvent-free approach to post-synthetic linker exchange through exposure to linker vapor.

ZIFs are comprised of divalent metal cations coordinated by imidazolate linkers.[1,2] 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. Examples of other Zn(II)-based sod ZIFs with different linkers are ZIF-7 (benzimidazolate), ZIF-71-sod (4,5-dichloro imidazolate), ZIF-65 (2-nitro imidazolate) and ZIF-90 (2-carboxaldehyde imidazolate).[3–7] While these materials are similar in unit cell and pore dimensions, their chemical properties differ due to the different imidazolate linkers. PSLE enables mixed-linker ZIFs and, in some cases, materials not accessible through direct synthesis.[8] This solution-based approach requires large solvent volumes and the linker incorporation preference can be hard to rationalize due to solvent effects. Interestingly, several ZIF materials can be synthesized through vapor-based and other solvent-free methodologies.[9–12] Here we present a novel, solvent-free approach to post-synthetic linker exchange in ZIF-8 through exposure to linker vapor.

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 S1). As CHO-HIm is prone to side-reactions,[13–15] VPLE trials (24 h) were performed at different temperatures. Reaction at 353 and 373 K resulted in a yellow ZIF powder, similar to what is obtained through direct synthesis or PSLE with CHO-HIm in solution.[16,17]. X-ray diffraction (XRD) confirms that the sod topology is maintained after VPLE. ¹H NMR analysis of the acid-digested samples revealed the incorporation of intact CHO-HIm (Figure S6). At 393 K, the sample turned brown (Figure S7) and XRD and electron microscopy reveal signs of degradation together with a drop in BET surface area from 1306 to 638 m²g⁻¹(Figures S8-10), similar to PSLE in MeOH.[16] For further VPLE experiments, 353 K was used.

Figure 1. Schematic representation of the VPLE process.

VPLE was monitored as a function of time for ZIF-8 crystals ranging in size from < 100 nm to > 100 μm . For each time point, the linker ratio was analyzed by ^1H -NMR (Figure S11). A clear dependence of the linker exchange kinetics on the particle size would indicate diffusion limitations during the exchange process. In contrast to this intuitive expectation, crystals of different sizes show similar exchange kinetics and end up with an identical fraction of CHO-Im in the framework (84 ± 6 %; Figure 2). FTIR analysis (Figure S11) confirms the progressive decrease of mIm bands (e.g., at 991 cm^{-1}), accompanied by increasing signals characteristic of CHO-Im incorporation (e.g., at 1667 cm^{-1}). This size-independence is in contrast with the mass transport limitations reported for linker exchange in solution. [16] In that case, after 24 h of exchange, the CHO-Im linker fraction was 70 % for nanocrystals compared to only 26 % for micron-sized crystals.

Figure 2. VPLe as a function of time. Parent ZIF-8 crystals of different sizes were used: 90 nm (blue squares), 15 μm (green squares), and 150 μm (orange squares). For reference, the reported CHO-Im fractions after 24 h of PSLE in solution in 90 nm (blue triangles) and 150 μm (orange triangles) ZIF-8 crystals are included.^[16] Error bars correspond to the standard deviation of three experimental points.

VPLe consists of the following steps: (i) adsorption of the incoming linker, (ii) exchange of protons between adsorbed CHO-HIm 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 XRD, through reversible changes in the low-angle diffraction peaks of ZIF-8 upon exposure to CHO-HIm vapor (Figure S13). When the framework mIm linker is protonated, the bond to the Zn(II) cations is weakened and the HmIm molecule is volatilized. Since the **sod** topology and particle size distribution are maintained before and after VPLe (Figure S14), the Zn(II) cations likely have no or limited mobility – as expected in the absence of a liquid phase. In other words, VPLe occurs in a single-crystal to single-crystal manner, since MOF dissolution-recrystallization cannot occur in the absence of a solvent.

After 72 h of VPLe, the BET surface area decreases slightly, from $1430\text{ m}^2\text{g}^{-1}$ to $1340 \pm 20\text{ m}^2\text{g}^{-1}$, averaged over the different particle sizes. This slight decrease is expected based on the BET surface area of pure ZIF-90 ($1291\text{ m}^2\text{g}^{-1}$). The incorporation of CHO-Im leads to higher N_2 uptake in the low-pressure range ($< 0.1\text{ P/P}_0$; Figure S15). Similarly, the MeOH uptake gradually transitions from the ZIF-8 to the ZIF-90 isotherm (Figure S16). VPLe works equally well for ZIF-8 films deposited on quartz crystal microbalance (QCM) substrates (Figures S17-18). The gravimetric MeOH isotherms recorded for the resulting ZIF layers follow a similar trend as the VPLe ZIF powders (Figure S19).

Figure 3. The linker scope of VPLE. Top: pKa values of different imidazoles. Molecules tested in this work are represented by blue squares, others by red circles. The melting temperature of each imidazole, an estimator of vapor pressure, is represented by grey bars. Bottom: summary of successful VPLE modifications.

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 coordinate the Zn(II) cations while maintaining the **sod** 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 suggests a range of incoming linker candidates (Figure 3), of which 4,5-dichloroimidazole (4,5-dCl-Im), benzimidazole (bzIm) and 2-nitroimidazole (NO₂-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 % NO₂-Im).^[18–21] For each linker, VPLE was performed below the melting point and the thermal stability limit (Table S2). All linkers were successfully incorporated in ZIF-8 after 72 h, although to different extents: 68% for NO₂-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 less. Nevertheless, only the **sod** topology was observed, thus supporting the notion of a single-crystal to single-crystal transformation (Figures S20–21). As a negative control, VPLE was attempted with 2-ethylimidazole (Helm). As expected based on the lower acidity of this linker, no exchange was observed.

The absence of adsorbed or proton-shuttling solvent molecules results in a different structure-energy landscape during VPLE compared to linker exchange in solution.^[22,23] For instance, exposure of ZIF-8 to vapor of unsubstituted imidazole (HIm) results in a transformation to the mixed-linker MOF ZIF-61 with a denser **zni** topology.^[24] Although the same exchange retains the **sod** topology when performed in *n*-butanol,^[8] in the absence of solvent the **zni** topology of ZIF-61 represents the lowest-energy structure for the Zn(Im)(mIm) composition (Figure S22).

Figure 4. VPLE as a function of 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 was 90 nm ZIF-8 and incoming linker was CHO-Im. Error bars correspond to standard deviation of three experimental points.

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, CHO-Im 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 aids VPLE, compared to dry argon and nitrogen.^[25] The catalyzing effect of moisture was confirmed by 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 uptakes at such a low relative humidity (Figure S23), the 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.^[26]

The distribution of the CHO-Im linker in large 150 μm ZIF-8 crystals after VPLE was investigated. Solid-state ^1H NMR spin-diffusion measurements were performed for VPLE samples with a ZIF-8₄₉-90₅₁ composition (ZIF_{VPLE}). These measurements were benchmarked against a mixed-linker ZIF material obtained through direct solvothermal synthesis and with a nearly identical composition, ZIF-8₅₂-90₄₈ (ZIF_{DS}). For mixed-linker ZIFs prepared by direct synthesis, the homogenous distribution of the mIm and CHO-Im linkers was previously confirmed through similar NMR experiments.^[27] The signal highlighted in Figure 5a corresponds to the polarization transfer between the aldehyde and methyl group of CHO-Im and mIm, respectively. This result confirms the close proximity of both linkers in ZIF_{DS}. In contrast, the absence of this signal in ZIF_{VPLE} (Figure 5b) indicates the formation of segregated domains. This observation is in accordance with the spectrum of 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 (Figures S24-25).^[27]

Figure 5. Linker distribution in 150 μm mixed-linker ZIF crystals obtained through direct synthesis and VPLe. 2D NOESY spectra for directly synthesized ZIF-8₅₂-90₄₈ (a) and ZIF-8₄₉-90₅₁ obtained after 48 h of VPLe (b). The position of the -CHO/-CH₃ cross-peak is indicated with a red dashed circle. SRS mapping of the carbonyl signal at a focal plane in the middle of the large crystals: ZIF-8₆₂-90₃₈ after 24 h of VPLe (c); ZIF-8₄₉-90₅₁ after 48 h of VPLe (d). The scale bar is 20 μm . Signal intensity increases from blue to red.

To further understand the linker segregation in ZIF_{VPLe}, the same crystals were imaged using stimulated Raman scattering (SRS). This technique allows to probe vibrational modes at a selected depth within the crystals. SRS microscopy confirms the increasing intensity of the carbonyl band at 1690 cm^{-1} with increasing CHO-Im incorporation (Figure S26). Visualizing the CHO-Im distribution based on this vibration band reveals a higher concentration in the crystal core, throughout the VPLe process (Figure 5c-d). These results are in contrast to the linker distribution after solution-based linker exchange. In that case, NMR experiments also show non-perfect mixing, but with a higher CHO-Im concentration in the shell due to diffusion limitations.^[16] 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. In the presence of sodium formate, ZIF-8 initially grows via a nanoparticle aggregation, before transitioning to a linker-particle attachment.^[28] We hypothesize that this growth mode results in defects in the core of the large crystals, and that linker exchange initially occurs at these defect sites, as suggested by theoretical calculations for ZIFs^[29,30] and experimentally observed in other MOFs.^[31] The resulting local changes in pore polarity and hydrogen bonding capability likely favor the adsorption and incorporation of further CHO-Im molecules. Such autocatalytic behaviour 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.^[26] Additionally, the ability of incorporated CHO-Im linkers to act as both H-bond donors and acceptors might facilitate linker exchange at adjacent sites.^[32] These effects are thought to be responsible for the observed CHO-Im domain formation in large ZIF-8 crystals after VPLe.

In conclusion, VPLe is a novel method for solvent-free linker exchange in MOFs. The method was demonstrated for ZIF-8 with a range of imidazoles and the criteria governing the process were established. Since VPLe was demonstrated for thin films as well, we foresee its combination with the chemical vapor deposition of MOFs,^[9] to form a vapor-only processing toolbox for the microfabrication of chemical sensors.^[33]

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