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Inter-conversion between zeolitic imidazolate frameworks: a dissolution–recrystallization process†

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Post-synthetic ligand exchange (PSE) approach has been widely used for the incorporation of functional moieties into metal–organic frameworks (MOFs) to achieve desired properties. It allows the replication of MOF superstructures with desired linker functionality through the conversion of preformed superstructures. However, this replication might turn to be unsuccessful if the conversion is a dissolution–recrystallization process. In this work, we report the inter-conversion of a variety of zeolitic imidazolate frameworks (ZIFs) following the PSE procedure using dimethylformamide as the solvent instead of alcoholic solvents. A dissolution–recrystallization process is demonstrated by the studies on the conversion of ZIF thin films and metal nanoparticle loaded ZIFs.

Introduction

Metal–organic frameworks (MOFs, also named as porous coordination polymers (PCPs)) are porous crystalline materials built from metal (or inorganic clusters) centers bridged by organic linkers through coordination bonds.¹ Owing to their various functional properties (*e.g.*, high porosity and well-defined pore network), MOFs have attracted great interests in a large number of applications ranging from life sciences to industry applications.^{2–5} The assembly of functional linkers into the framework with the desired topology has been limited by the solvothermal synthetic conditions.^{6,7} To address this challenge, one of the promising strategies is to perform post-synthetic ligand exchange (PSE, also named as “solvent-assisted linker exchange”, SALE).^{8,9} The procedure of PSE involves exposing the parent MOF to a concentrated solution of the daughter linker to achieve the incorporation of the desired linker into the daughter MOF while maintaining the topology of the parent MOF. This novel method has shown great advantages in the pore functionalization (*e.g.*, volume, surface functionality and aperture size), the introduction of active sites (*e.g.*, defects, catalytically sites and proton-conducting sites), and the control over catenation.^{9–21}

The underlying scheme of the PSE method is *via* the diffusion of the daughter linker into the parent MOF pores and subsequently linker exchange within the intact MOF.^{9–12} Obtaining insights into the PSE process may facilitate this type of control and consequently open the applicability of this novel approach for other important applications. For instance, through the careful management of the linker diffusion during the PSE process, core–shell architectures or well-mixed structures can be realized, leading to different application perspectives.^{22–28} It has been proposed that the pK_a value of the conjugate acid can be used as a predictor of the exchange rate that more basic linker preferentially exchanges into the structures.^{11,29} In addition, Morabito *et al.* demonstrated linker exchange reactions proceed *via* a competition between dissociative and associative exchange mechanisms, thus enabling the guest encapsulation due to the formation of short-live “open” states of the pores upon linker dissociation.³⁰ Apart from the linker exchange in the liquid phase, vapor-phase linker exchange has been recently demonstrated,^{31,32} offering an alternative route to adjust pore structures, sorption properties and other physicochemical characteristics.

Shaping MOFs into superstructures (*e.g.*, hollow spheres, nanosheets and thin films) can enhance their performances in a variety of applications and may open novel research orientations.^{33,34} Following the linker exchange mechanism, one could expect that the replication of MOF superstructures with desired linker functionality may become feasible through the straightforward transformation of the preformed MOF superstructures.^{28,34–37} However, this replication might turn to be unsuccessful if the transformation is a dissolution–recrystallization process. Thus, it is essential to verify the underlying mechanism of the conversion process is a linker exchange or a dissolution–recrystallization process. In this work, we

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achieved the inter-conversions of a variety of zeolitic imidazolate frameworks (ZIFs, a subclass of MOFs) following the PSE procedure (Fig. 1). Previous reports on the PSE of ZIFs were mostly performed in *n*-butanol, which resulted in the linker exchange process, demonstrated by a single-crystal-to-single-crystal transformation.^{10,22} When using dimethylformamide (DMF) instead of *n*-butanol as the solvent, reversible linker incorporation was also achieved together with topology transformations (Fig. 1). Therefore, a dissolution–recrystallization process is proposed for the inter-conversions in DMF, which is demonstrated by the studies on the fabrication of MOF superstructures (*e.g.*, thin films and nanoparticles or dye molecules loaded ZIFs) under the transformation conditions.

Results and discussion

Inter-conversion of ZIF powders

As illustrated in Fig. 1, following the PSE procedure, parent ZIFs can be converted to daughter ZIFs with or without topology transformations. Specifically, ZIF-7 (ref. 38 and 39) ($\text{Zn}(\text{blm})_2$, blm = benzimidazole) and ZIF-8 (ref. 39 and 40) ($\text{Zn}(\text{mlm})_2$, mIm = 2-methylimidazole) are crystallized in trigonal and cubic space group, respectively. Both are of zeolitic sodalite-type (SOD) topology (4^26^4), which contains a large cavity connected *via* hexagonal small pore windows. These two ZIFs can be reversibly converted to each other by the reaction of the parent ZIF with the corresponding daughter linker. The ZIF inter-conversion occurred not only on single-linker ZIFs, but also on mixed-linker ZIFs. ZIF-76 (ref. 41) ($\text{Zn}(\text{Im})_x(\text{cbIm})_{2-x}$, Im = imidazole, cbIm = 5-chlorobenzimidazole), with a zeolitic LTA topology ($4^{12}6^88^6$) containing two types of cages (α and β cages),

was also inter-convertible with ZIF-8. The powder X-ray diffraction (PXRD) patterns and the liquid-phase ^1H nuclear magnetic resonance (NMR) spectra of the parent and daughter ZIFs demonstrate these reversible conversions with the possibility of $\sim 100\%$ conversion (Fig. 2a, b and ESI Section 2†). Apart from the reversible transformations, irreversible conversions also occurred. ZIF-71 (ref. 41) ($\text{Zn}(\text{dcIm})_2$, dcIm = 4,5-

Fig. 2 PXRD patterns ((a) and (c)) and liquid-phase ^1H NMR spectra ((b) and (d)) of parent ZIFs and daughter ZIFs. (a and b) Demonstrate the inter-conversions illustrated in Fig. 1a. (c and d) Demonstrate the conversions illustrated in Fig. 1b. The ^1H NMR spectra were recorded on the digested powder samples.

Fig. 1 Schematic illustration of (a) reversible and (b) irreversible conversion of ZIFs by exposing parent ZIFs into the solutions of daughter linkers. The scheme represents the ZIF inter-conversions with or without topology transformations. The three-letter abbreviations refer to ZIF topologies.

dichloroimidazole) is of zeolitic RHO topology ($4^{12}6^88^6$) with large cages interconnected through double-eight-membered rings (D8R). It can be converted to a series of ZIFs with other topologies (SOD or LTA; Fig. S10†). However, all of the obtained daughter ZIFs cannot be converted back to ZIF-71. Instead, a ZIF ($\text{Zn}(\text{dcIm})_2$, named as ZIF-8_dcIm) isostructural to ZIF-8 was formed (Fig. 2c and d).

According to the unconventional topology transformations ($\text{SOD} \leftrightarrow \text{LTA}$ and $\text{RHO} \rightarrow \text{SOD}$) of ZIFs following the PSE procedure, the simplistic linker exchange mechanism cannot be applied. Hence, the mechanistic process of this ZIF inter-conversion is proposed to occur *via* the gradual dissolution of the parent ZIFs and the simultaneous recrystallization to form the daughter ZIFs. Taking the conversion of ZIF-71 (RHO) to ZIF-8 (SOD) as an example, at the first step, the cleavage of tetrahedral Zn -dcIm coordination bonds occurred by the dissociative protons deprotonated from the concentrated daughter mIm linkers. Thus, the framework of ZIF-71 was gradually dissolved, giving rise to the existence of free Zn^{2+} cations in the solution. Simultaneously, the free Zn^{2+} cations preferred to coordinate with the mIm linkers, and consequently recrystallized to ZIF-8 crystallites. Because of the continuous process of gradual dissolution and recrystallization in the solution, the complete conversion can be achieved. Different from previous reports on the linker exchange of ZIFs using *n*-butanol as the solvent,^{10,22} employing DMF here resulted in a dissolution-recrystallization process. It has been studied that ZIFs can undergo dissolution in acidic conditions, which involves the insertion of water or acidic molecules into the Zn -N bonds and the subsequent dissociation of the protonated imidazole linkers away from the framework.⁴² As DMF is more basic than *n*-butanol, it is easier to be protonated by the imidazole linkers. Thus, it is proposed that the protonated DMF performs an acidic attack on the Zn -imidazole coordination bonds, inducing the dissolution of the ZIFs.

Inter-conversion of ZIF thin films

To gain further insights into the inter-conversion processes, we performed the studies on the transformations of ZIF thin films deposited on quartz crystal microbalance (QCM) sensors. QCM technique is a gravimetric sensing method that can detect the film mass in nanogram scale,^{43–45} enabling the monitoring of mass changes of MOF films before and after the conversion. The XRD patterns confirmed the successful transformation of ZIF films except for the conversion of ZIF-8 film by dcIm linker (Fig. S19†). ZIF-8 film obtained from the transformation of the ZIF-71 film showed similar morphology as the starting film (Fig. 3a and b). However, after exposing ZIF-8 film in dcIm solution for 1 day, the surface was nearly blank with a small number of particles (Fig. 3c and d), showing the significant dissolution in dcIm solution. The dissolution can also be confirmed by the mass changes determined by the QCM data (Table 1). Interestingly, the ZIF-8 powder sample was able to be converted by dcIm to form ZIF-8_dcIm crystallites, whereas its thin-film form cannot undergo the conversion. This significant difference

Fig. 3 SEM images of parent and daughter ZIF thin films deposited on QCM sensors. (a) ZIF-71; (b) ZIF-71 + mIm; (c) ZIF-8; (d) ZIF-8 + dcIm; (e) ZIF-8 + bIm and (f) ZIF-8 + Ica.

can be attributed to the occurrence of the recrystallization in the solution. In the thin-film form of ZIF-8, the cleavage of Zn -mIm bonds resulted in the dissolution of components in the solution. Consequently, ZIF-8_dcIm recrystallized in the synthetic solution rather than on the surface. The etching effect can also be observed in the case of conversion of ZIF-8 by 2-imidazolecarboxaldehyde (Ica, the linker for ZIF-90;⁴⁶ Fig. 3f). After reacting with different daughter linkers, ZIF-8 film underwent different extent of etching effect from nearly complete dissolution to partial dissolution following the order: $\text{dcIm} > \text{Ica} > \text{bIm}$. This difference can be attributed to different dissolution rates, resulting from the acidity difference of the imidazolate linkers. The daughter linkers with lower $\text{p}K_{\text{a}}$ value (*i.e.*, dcIm and Ica) would promote the cleavage of Zn -imidazolate bonds, leading to the fast dissolution of parent ZIFs and recrystallization in the solution (Table 1). In contrast, the bond cleavage induced by the daughter linker with higher $\text{p}K_{\text{a}}$ value (*i.e.*, mIm and bIm) was less favorable. Therefore, the dissolution rate was relatively slower, resulting in the recrystallization of daughter ZIF film on the substrates rather than in the solution. Even though no significant morphological changes were observed in the conversions of ZIF-71 and ZIF-8 films by mIm and bIm linkers, respectively (Fig. 3), the experimental mass ratios between daughter and parent ZIF films were much lower than the corresponding theoretical ones (Table 1). Thus, it is evident that the ZIF thin films were partially dissolved in the daughter linker solutions, supporting the dissolution-recrystallization mechanism.

Table 1 pK_a values of daughter linkers and mass changes of ZIF thin films on QCM sensors before and after the conversion

Mass of parent ZIF film (ng)	Mass of daughter ZIF film (ng)	pK_a values of daughter linkers as acids ⁴⁷	Theoretical mass ratio ^a (%)	Experimental mass ratio (%)
ZIF-71 (3643)	ZIF-8 (1974)	13.92 (mIm)	67.8	54.2
ZIF-8 (8487)	ZIF-8_dcIm (175)	9.57 (dcIm)	147.6	2.1
ZIF-8 (8120)	ZIF-90 (4287)	10.23 (Ica)	112.3	52.8
ZIF-8 (7472)	ZIF-7 (7315)	12.25 (bIm)	132.6	97.9

^a The theoretical mass ratio between daughter and parent ZIF films was calculated according to the formula of each MOF.

Inter-conversion of bulk ZIF composites

Encapsulation of guest active species (*e.g.*, metal nanoparticles (NPs), metalloporphyrin, polyoxometalate) into MOFs to form MOF composites has potentials in various important applications such as heterogeneous catalysis, sensing and biomedicine.^{42,48–51} It has been shown that the location of metal NPs inside or outside the MOF crystal (refer to NPs@MOF and NPs-on-MOF, respectively) plays a significant role in the shape-selective catalysis.⁵² In this work, we investigated whether or not the inter-conversion of ZIFs is able to be used for the localized formation of ZIF composites, for instance, the synthesis of NP@ZIF-B *via* the transformation of preformed NP@ZIF-A. After the conversion of Au@ZIF-8 in the mixed-linker solution (cbIm and Im), the Au NPs stabilized at the external surface of the daughter ZIF-76 crystallites (Fig. 4). In addition, the well-shaped ZIF-8 crystals turned to be poorly

shaped ZIF-76 crystallites. These observations can further confirm the proposed dissolution–recrystallization mechanism for these ZIF inter-conversions.

Although the dissolution–recrystallization process does not facilitate the localized conversion of MOF composites, it can be employed for the encapsulation of large molecules that exceed the size of MOF pore opening. As a proof-of-concept study, we performed the encapsulation of large metalloporphyrin molecules (zinc tetraphenylporphyrin, ZnTPP) into ZIF-76 through the conversion of ZIF-8 in the presence of ZnTPP (Fig. 5). Due to the relatively small cage size (11.6 Å) of ZIF-8,⁴⁰ ZnTPP cannot be incorporated into its cages. The presence of large α cage in ZIF-76 may enable the encapsulation of ZnTPP molecules. However, due to the limitation of the small cage windows, ZnTPP cannot be encapsulated into ZIF-76 cavities through the post-insertion method. Exposing ZIF-8 to the solution of cbIm and Im resulted

Fig. 4 (a) Schematic illustration of the conversion of NPs@ZIF A to NPs-on-ZIF B. After the conversion process, ZIF A can be converted to ZIF B, whereas the NPs localize at the outer surface of ZIF B. (b) PXRD patterns of Au@ZIF-8, calculated ZIF-76 and Au@ZIF-8 converted by the mixed-linker solution of cbIm and Im. (c) BRTEM image of as-synthesized Au@ZIF-8. (d) BRTEM image of Au-on-ZIF-76 obtained by the conversion of Au@ZIF-8.

Fig. 5 (a) Schematic illustration of the encapsulation of ZnTPP into ZIF-76 via the conversion of ZIF-8 to ZIF-76 in the presence of ZnTPP. (b) Molecular structure of ZnTPP. (c) Optical images of ZIF-76 (light yellow) and ZnTPP@ZIF-76 (dark red). (d) UV-Vis diffuse reflectance spectra of solid-state ZnTPP and ZnTPP@ZIF-76.

in the existence of ZnTPP, Zn^{2+} , and the mixed linkers in the solution. During the recrystallization process, the ZnTPP can be encapsulated into the α cage of ZIF-76. The PXRD patterns (Fig. S22†) confirmed the structural transformation from ZIF-8 to ZIF-76. After the conversion, the samples were extensively washed with DMF and no ZnTPP can be detected in the residual DMF by UV-Vis spectroscopy, excluding the molecules adsorbed on the external surfaces. As shown in Fig. 3d, the UV-Vis spectrum of ZnTPP@ZIF-76 matched the spectrum of pure ZnTPP complex. The loading amount of ZnTPP in ZIF-76 quantified by ^1H NMR of the acid-digested sample is 2.2 wt% (Fig. S23†). The obtained ZnTPP@ZIF-76 remained the microporosity with Brunauer–Emmett–Teller surface area of $786\text{ m}^2\text{ g}^{-1}$ (Fig. S24†), which was lower than the surface area of guest-free ZIF-76 because of the occupation of ZnTPP in the α cages. This method also showed its feasibility for the encapsulation of 9-chloroanthracene-10-carbaldehyde into the cavities of ZIF-8 via the conversion of ZIF-7 (Fig. S25–S27†). This encapsulation method provides an alternative way to incorporate large active species into MOF cavities when the *de novo* encapsulation method fails because of the poor compatibility of active species with the condition used for MOF synthesis.

Conclusions

In summary, we achieved the inter-conversions of a variety of ZIFs following the PSE procedure. Different from previous

report on the linker exchange of ZIFs in alcoholic solution, the inter-conversion of ZIFs in the DMF solution follows the dissolution–recrystallization process. The dissolution of parent ZIFs can be ascribed to the acidic attack from the protonated DMF. Simultaneously, the free cations prefer to coordinate with highly concentrated daughter linkers, and consequently recrystallize to daughter ZIFs. The different transformation behaviors between powder and thin-film forms can be attributed to the occurrence of recrystallization in the solution rather than on the substrate surface. This study is important for the further utilization of the PSE procedure, especially in the transformations of MOF superstructures (*e.g.*, thin films, nanocrystals, composites). Furthermore, taking advantage of the inter-conversion process, a synthetic method has been developed for the encapsulation of large molecules that exceed the size of MOF pore opening. It provides an alternative post-synthetic route to incorporate large active species (*e.g.*, metalloporphyrin, polyoxometalate, and biomolecules) into the MOF cavities, towards the applications in catalysis, chemical sensing, and biomedicine.

Experimental section

General methods

Powder X-ray diffraction (PXRD) data of ZIF powders were recorded by the X'Pert PRO PANalytical equipment. The powder samples were dropped onto a zero background silicon

wafer. The samples were measured in Bragg–Brentano geometry (with automatic divergence slits, position-sensitive detector, continuous mode, room temperature, Cu-K α radiation, Ni filter, the typical range of $2\theta = 5\text{--}50^\circ$, at a step of 0.0197° , with accumulation time 200 s per step). ZIF thin films were also measured by the X'Pert PRO PANalytical equipment (the typical range of $2\theta = 3\text{--}20^\circ$, at a step of 0.0197° , with accumulation time 550 s per step). Scanning electron microscope (SEM) images were recorded on a LEO1530 Gemini FESEM or FEI ESEM Dual Beam™ Quanta 3D FEG microscope to investigate the morphology of MOF thin films. The bright-field transmission electron microscopy (BRTEM) measurements were performed on a Tecnai G2F20 and Philips CM20 microscopes with an acceleration voltage of 200 kV. Liquid-phase ^1H NMR spectra were measured on a Bruker Avance DPX-200 spectrometer at room temperature in DCl/D $_2\text{O}$ /DMSO- d_6 for the digested dried ZIF samples. Typically, *ca.* 2 mg dried MOF powder was added into the NMR tube. Subsequently, a few drops of DCl (37 wt% in D $_2\text{O}$) and 500 μL DMSO- d_6 were added to digest the powders. UV-Vis diffuse reflectance spectra of powder samples were recorded by Perkin-Elmer Lambda 650 UV-Vis spectrophotometer using BaSO $_4$ as a reference. The spectra were converted into the absorption spectra using the Kubelka–Munk function. For liquid solution, UV-Vis absorption spectra were measured by the same instrument using pure DMF solvent as a reference.

Inter-conversion of ZIF powders

The parent MOF powders were synthesized and activated according to previously reported procedures (details given in ESI Section 2†).^{45,53} Generally, the conversion of ZIF powders was performed by immersing a certain amount of activated ZIF powders into 5 mL concentrated (5 times higher than parent linker) daughter imidazolate linker DMF solutions at 60 °C. After every 24 hours, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original. The progress of the conversion reaction was monitored by liquid-phase ^1H NMR, and the reaction was stopped once $\sim 100\%$ conversion was achieved. For instance, in the case of the transformation of ZIF-8 to other ZIFs, 30 mg activated ZIF-8 (*ca.* 0.2 mmol equiv. of mIm for ZIF-8) was immersed into 5 mL DMF solution of 1 mmol other imidazolate linkers (bIm:120 mg, dcIm: 140 mg, Ica: 96 mg, mixture of cbIm and Im: 75 mg and 34 mg, respectively). The mixture was ultrasonicated for 10 min to get a uniform suspension of ZIF-8 in the solution. Afterwards, the suspension was kept in a convection oven at 60 °C. After each 24 hours reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers as the original until $\sim 100\%$ conversion was achieved.

Inter-conversion of MOF thin films

ZIF-8 and ZIF-71 films were deposited on SiO $_2$ coated QCM sensors according to the previously reported procedure.⁴⁵ Similar to the conversion of ZIF powders, the fabricated ZIF films were immersed in 5 mL concentrated daughter linker solutions (the same concentration as the powder case) at 60 °C for 1 day. Quantitative mass study of ZIF films deposited on QCM sensors

was obtained from the frequency changes (before and after deposition of MOF films) according to the Sauerbrey equation (eqn (1)),⁵⁴ where ΔM is the mass change on the QCM device; F_0 is the fundamental frequency of blank QCM substrate; A is the surface area of the sensor (0.2 cm 2); μ is Shear stress of quartz ($2.947 \times 10^{10} \text{ kg (m} \times \text{s}^2)^{-1}$); ρ is the density of quartz (2648 kg m $^{-3}$); ΔF is the frequency change. Prior to the record of the frequency, it is important to remove solvent molecules from the pores of ZIF films. The activation process was performed in two steps: MOF films were soaked in absolute CH $_2\text{Cl}_2$ for 1 day at room temperature and subsequently dried in a He stream under 80 °C for 2 hours. The frequency could reach equilibrium in 2 hours activation at 80 °C, indicating the complete removal of guest molecules. After the conversion, the frequencies of daughter ZIF films was recorded following the same procedure.

$$\Delta M = -\frac{A\sqrt{\mu \times \rho}}{2F_0^2} \Delta F \quad (1)$$

Inter-conversion of bulk MOF composites

Au@ZIF-8 was synthesized following the reported procedure.⁵⁵ 30 mg Au@ZIF-8 (Au $\approx$ 3 wt%, *ca.* 0.2 mmol equiv. of mIm for ZIF-8) was immersed into 5 mL DMF solution of cbIm (75 mg, 0.5 mmol) and Im (34 mg, 0.5 mmol) mixture. The mixture was then ultrasonicated for 1 h to get uniform suspension of ZIF-8 in the solution. Subsequently, the suspension was kept in an oven at 60 °C for 1 day. In the case of encapsulation of ZnTPP in ZIF-76 through the conversion of ZIF-8, 30 mg ZIF-8 (*ca.* 0.2 mmol equiv. of mIm for ZIF-8) was immersed into 5 mL DMF solution of ZnTPP (25 mg, 0.04 mmol), cbIm (75 mg, 0.5 mmol) and Im (34 mg, 0.5 mmol) mixture. The mixture was then ultrasonicated for 1 h to get a uniform suspension of ZIF-8 in the reaction solution. Subsequently, the suspension was kept in an oven at 60 °C for 1 day. After each day's reaction, the solution was replaced with a fresh solution of the same concentration of imidazolate linkers together with ZnTPP as the original until $\sim 100\%$ conversion was achieved. The obtained powder material was washed thoroughly with DMF by 6 repetitions of sonication–centrifuge cycles.

Conflicts of interest

The authors declare no conflict of interest.

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