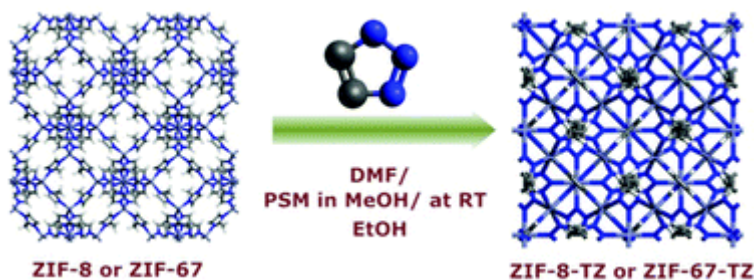# Abstract

Bridging ligand replacement in zeolitic imidazolate frameworks, ZIF-8 and ZIF-67, by 1,2,3-triazole was investigated. A complete substitution of 2-methylimidazole by 1,2,3-triazole resulted in a topological transformation of the parent framework from a sodalite (SOD) network to a diamond (DIA) network.
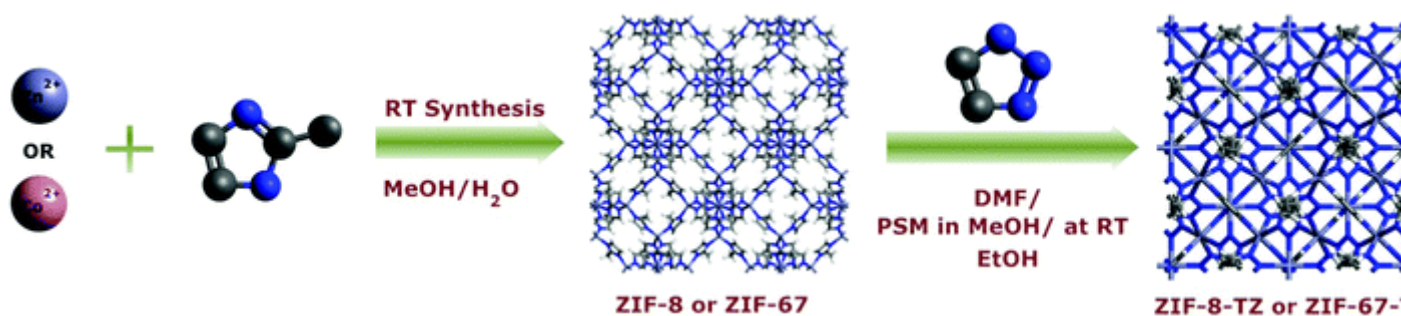
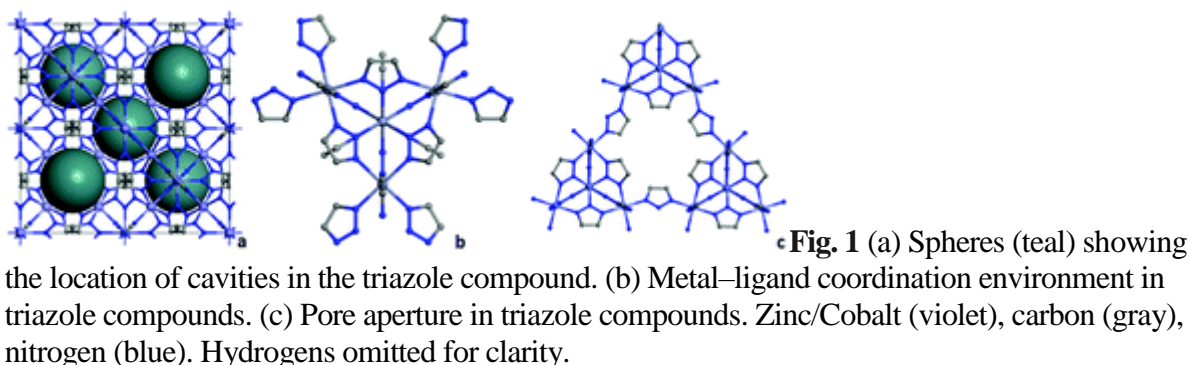- This article is part of the themed collection: Most downloaded articles of 2017: Organic and Biological Chemistry

Over the last two decades metal–organic frameworks (MOFs) have attracted enormous attention due to their diverse structural topologies[1] and chemical functionalities.[2] These properties gave MOFs their potential for a wide range of applications including, but not limited to gas storage,[3–6] separations,[7,8] catalysis,[9,10] electrochemical[11–14] and biological applications.[15,16] Zeolitic imidazolate frameworks (ZIFs), a sub-class of MOFs, are isomorphous with zeolites, and they usually exhibit exceptional chemical and thermal stability. ZIFs are composed of tetrahedral inorganic building units, wherein every divalent metal cation M^{2+} (M = Co and Zn) coordinates to four imidazolate based anion linkers ($Im^- = C_3H_3N_2^-$) to form neutral porous framework structures ($M(Im)_2$) with zeolitic topologies.[17–22]

Triazole based-ligands are considered as multifaceted building units in organometallic chemistry due to the simplicity of their synthesis and the three nitrogen atoms available for coordination.[23] However, there has been only a few studies in the literature on 1,2,3-triazole-based MOFs.[24–26] This is because the steric demand has an undesirable effect on metal–triazole bonds due to the vicinal arrangement of the nitrogen atoms in the 1,2,3-triazole ring.[26] To this end, Gandara *et al.* reported six porous isostructural metal–triazolates based on 1,2,3-triazole, denoted as MET-(Mg, Mn, Fe, Co, Cu, Zn).[24] Ruan *et al.* synthesized 1,2,3-triazole and benzotriazole metal organic frameworks from nano-sized Cu_{20} and Cu_{30}.[25] Zhou *et al.* studied two coordination polymers which consist of 1,2,3-triazole, cadmium and copper.[26]

Post-synthetic modification (PSM) is a versatile modification method which can be used for the functionalization of preassembled MOFs or the formation of novel MOFs which are not attainable by *de novo* synthesis.[27–29] Several examples of PSM in MOFs have been demonstrated, either for the purpose of functionalization of existing MOFs or for the syntheses of new ones.[30–33] In all these reports ligands in the solvent medium replaced the bridging ligands in the MOFs; however, the topology of the parent framework remained unchanged. Herein, we report the first examples of the simultaneous non-assisted replacement of ligands and the conversion of topology in MOFs by applying the PSM approach where the 2-methylimidazole bridging ligands in ZIF-8 and ZIF-67 were completely replaced with 1,2,3-triazole (Scheme 1) and the formation of two MOFs with diamond network (Fig. 1).

Scheme 1 Graphical summary of the synthesis of ZIF-8 and ZIF-67 and PSM route on these MOFs.

Fig. 1 (a) Spheres (teal) showing the location of cavities in the triazole compound. (b) Metal–ligand coordination environment in triazole compounds. (c) Pore aperture in triazole compounds. Zinc/Cobalt (violet), carbon (gray), nitrogen (blue). Hydrogens omitted for clarity.

In a typical PSM reaction, when the number of coordination sites of the inserted and the replaced ligands are same, and when both ligands have similar pK_a values, the topology of the parent framework is conserved.[27,29,34,35] On the other hand, introducing new ligands with more/less coordinative units may result in catalytically active sites and/or defect sites in the daughter structure. Therefore, in order to add potential active sites (*i.e.* catalytic sites or guest binding sites) for our PSM processes, ZIF-8 and ZIF-67 were chosen as parent frameworks and 1,2,3-triazole as daughter ligand. ZIF-8 and ZIF-67 are isostructural frameworks and are formed by the coordination of 2-methylimidazolate (mIM) anions with zinc and cobalt cations, respectively. Both frameworks feature the sodalite (SOD) topology. We hypothesized that a partial exchange of 2-methylimidazolate by 1,2,3-triazole would result in additional active sites due to the presence of a third nitrogen atom in the 1,2,3-triazole linker. The resultant frameworks were named ZIF-8-TZ (**1**) and ZIF-67-TZ (**2**). For both systems, the conversion was characterized by ^{1}H NMR, powder X-ray diffraction (PXRD), N_2 gas adsorption, methane uptake, pore size and pore distribution, thermal gravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) measurements.

   1 and **2** were obtained by submerging crystals of ZIF-8 and ZIF-67, respectively, in a methanol solution of 1*H*-1,2,3-triazole at room temperature. ^{1}H NMR showed that HmIM linkers in both ZIF-8 and ZIF-67 disappeared after PSM and the crystallinity of **1** and **2** was confirmed by PXRD (Fig. 2). Their PXRD spectra demonstrate patterns noticeably different from the starting frameworks. Since we were unable to obtain suitable crystals of **1** and **2** for single-crystal X-ray diffraction, we checked the triazole based ZIFs reported in the literature in order to elucidate the structures of **1** and **2**. Two triazole based ZIFs, Co–triazolate and Zn–triazolate (**MET-4** and **MET-6**), synthesized by Gandara, *et al.*[24] showed similar PXRD patterns. However, these researchers were also unable to obtain suitable crystals to solve the structures of **MET-4** and **MET-6**. Nevertheless, they were able to get the unit cell dimensions of **MET-4** and **MET-6** and an approximate representation of the structures using charge-flipping method; however, crystallographic coordinates of the framework atoms were still not determined. At this point we turned to computational methods to confirm the structures of **1** and **2**. Zhou *et al.* reported the

crystallographic structure of Cd–triazolate.[26] Anticipating that this structure is the isomorph of Co and Zn–triazolates reported by Gandara *et al.*,[24] we computationally generated two structures by scaling the unit cell dimensions and positions of the framework atoms of the Cd–triazolate to match the unit cell dimensions of **MET-4** and **MET-6** and by replacing the Cd atoms with Co and Zn atoms, respectively. We then optimized the structures by performing periodic density functional theory (DFT) calculations using CASTEP 16.1[36] (see the ESI†for details of the simulations). As can be seen in Fig. 2a and c, the simulated PXRD patterns of the DFT optimized structures give a perfect match with PXRD patterns obtained from experimental structures (Fig. S2 and S3, ESI†).
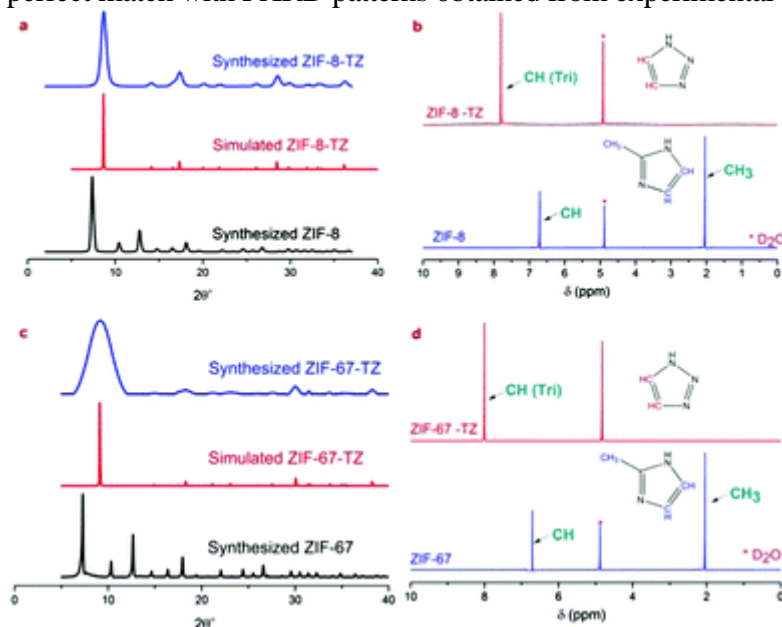

Fig. 2 (a) PXRD patterns of simulated ZIF-8, simulated and synthesized ZIF-8-TZ. (b) ^{1}H NMR spectra of ZIF-8 and ZIF-8-TZ. (c) PXRD patterns of simulated ZIF-67, simulated and synthesized ZIF-67-TZ. (d) ^{1}H NMR spectra of ZIF-67 and ZIF-67-TZ.

Further characterization also supports that **1**/**2** and **MET-6**/**MET-4** are one and the same, respectively. The colours of the parent frameworks were entirely changed at the end of PSM process (Fig. S1, ESI†). Thermogravimetric analysis (TGA) measurements show that although **1** and **2** are stable up to 250 °C they are less thermally stable than ZIF-8 and ZIF-67 (Fig. S9, ESI†). FTIR spectra show that the bands in the spectral region of 1300–1500 cm^{-1} assigned to the HmIM ring stretching, are observed in the spectra of ZIF-8 and ZIF-67, but are absent from the spectra of **1** and **2** (Fig. S8, ESI†).

Porosity measurements demonstrate that both **1** and **2** adsorb considerable amounts of N_2 in the micropore region; the Brunauer–Emmet–Teller (BET) surface areas for **1** and **2** are 710 and 720 m^2 g^{-1}, respectively (Fig. 3). The calculated pore volume for both daughter frameworks is about 0.28 cm^3 g^{-1} (Table 1). These values are in good agreement with those reported for **MET-6** and **MET-4**. Although the surface areas of the daughter frameworks are lower than their parent counterparts, their methane uptakes at 1 bar and ambient (and near ambient) temperatures considerably exceed those for the parent compounds (Table 1 and Fig. 4). This is most likely due to reduced pore size with additional nitrogen sites which enables strong interactions between linkers and methane.[37]
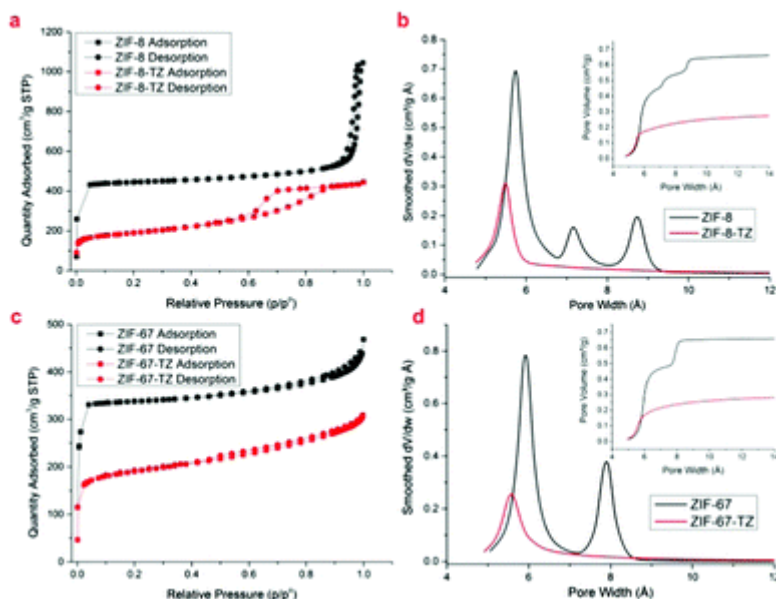
Fig. 3 (a) N_2 adsorption/desorption isotherms of ZIF-8 and ZIF-8-TZ. (b) Pore size distribution and pore volume of ZIF-8 and ZIF-8-TZ. (c) N_2 adsorption/desorption isotherms of ZIF-67 and ZIF-67-TZ. (d) Pore size distribution and pore volume of ZIF-8 and ZIF-8-TZ.

Table 1 Experimental BET surface areas, pore volumes and CH_4 uptakes values for ZIF-8, ZIF-8-TZ (**1**), ZIF-67 and ZIF-67-TZ (**2**)

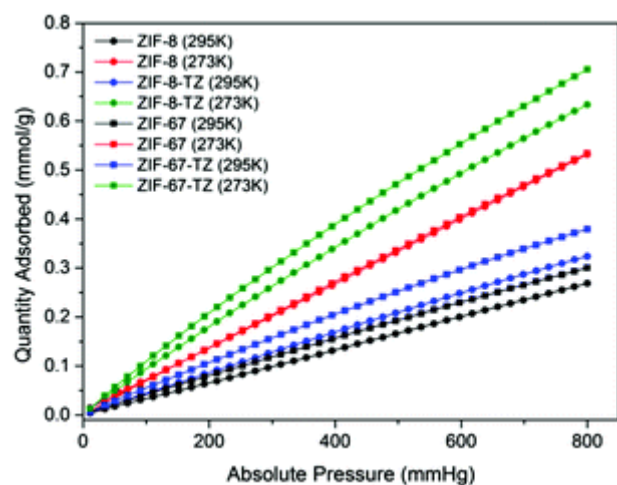|	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	CH_4 uptake (mmol g^{-1}) (295 K)	CH_4 uptake (mmol g^{-1}) (273 K)
ZIF-8	1703	0.64	0.255	0.505
ZIF-8-TZ	706	0.28–0.26	0.309	0.607
ZIF-67	1468	0.64	0.290	0.508
ZIF-67-TZ	721	0.28–0.27	0.363	0.676

Fig. 4 CH_4 adsorption isotherms at 273 and 295 K.

Furthermore, we investigated the effect of the type of solvent and the concentration of ligand on the PSM process. Evolution of the reactions was observed with ^{1}H NMR. Reaction evolutions were

performed in different solvents (EtOH and DMF) showed no apparent effect of solvent on the conversion rate and time (Fig. S6, ESI†). However, as expected, higher concentrations of 1,2,3-triazole are more favourable for ligand replacement (Table S1, ESI†). Additionally, in contrast to typical slower post-synthetic ligand exchange processes, in our experiments 1,2,3-triazole completely replaced HmIM in about one hour (Fig. S4 and S5, ESI†).

During a PSM-or a post synthetic ligand exchange-bonds are broken and formed dynamically. Especially, in the course of PSM experiments which involve N-heterocyclic ligands, pK_a difference in the "N–H" bonds broken and formed can be a measure for the equilibrium constant of the exchange reaction, and a lower pK_a for the daughter ligand is typically required. In comparison with HmIM (pK_a (N–H) = 14.4), 1H-1,2,3-triazole has a significantly lower pK_a (N–H) of 9.3 which promotes the ligand exchange reaction. In addition, the coordination number of each metal center (Zn^{2+} and Co^{2+}) increase from 4 to 6 during this exchange reaction, which is another important thermodynamic contributor to the PSM process. Therefore, we speculate that the observed spontaneous conversions of ZIF-8 and ZIF-67 to **1** and **2**, respectively, have strong thermodynamic contributions.

In conclusion, in this study, we demonstrated the topological transformation from SOD to DIA *via* PSM within ZIFs. The structural and topological transformations within ZIFs have been characterized by PXRD, ^{1}H NMR, N_2sorption measurement as well as modelling. Due to large difference between the pK_a values of the incoming and outgoing ligands, the conversion occurs rapidly, irrespective of solvent type and at room temperature. Our findings suggest that this approach can be useful for exploring novel MOFs and in our future research we intend to concentrate on these studies.

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