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Imparting Brønsted acidity into a zeolitic imidazole framework†

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In this work, we demonstrate the impartment of Brønsted acidity into a zeolitic imidazole framework, ZIF-90, via post-synthetically oxidizing the aldehyde group into carboxylate group to afford ZIF-90-COOH. The preservation crystallinity and porosity after post-synthetic oxidation was confirmed by powder X-ray diffraction studies and N₂ gas adsorption analysis respectively. The successful conversion of the aldehyde group into carboxylate group was verified by FT-IR studies, which resulted in remarkable enhancement of methylene blue uptake in the resultant ZIF-90-COOH due to the strong electrostatic interactions between cationic methylene blue and the anionic carboxylate group.

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Metal-organic frameworks (MOFs) comprise a structurally diverse family of three-dimensional porous crystalline materials facilitated by the combination of metal nodes coordinated by organic linkers.¹ Their permanent porosity, high surface area, well-defined pore sizes, and innate tunability allow for the design of these structures for various applications including gas storage,² catalysis,³ imaging and sensing,⁴ and energy storage.⁵ The broad and sundry applications of MOFs have extended to the exploitation of Brønsted acid moieties on or within the frameworks. Heterogenous catalysis has been heavily studied amongst MOF applications, with MOFs decorated with acidic protons showing excellent catalytic activity in Friedel-Craft alkylations,⁶ cellulose conversion,⁷ and more.⁸ In addition to their usage in catalysis, Brønsted acid moieties in MOFs have also shown potential in proton conduction applications. In comparison to many other solid state and porous materials, MOFs hold the advantage that they are robust coordination polymers with high flexibility and tunable reactivity, depending on the linkers.^{1,9} This not only gives way for more controlled conductivities, but also allows for the observation of proton-conducting pathways.¹⁰ One of the less explored methods of Brønsted acid inclusion in a MOF is the addition of acidic protons directly on the coordinating linkers of the construct.¹¹ The inclusion of polar and acidic groups within a MOF normally gives rise to Brønsted acidity and other measures related to acid strength. The mobility of the charge carriers present (*i.e.* carboxylates and phosphates) facilitate the Brønsted acidity and proton conductivity of the material.¹²

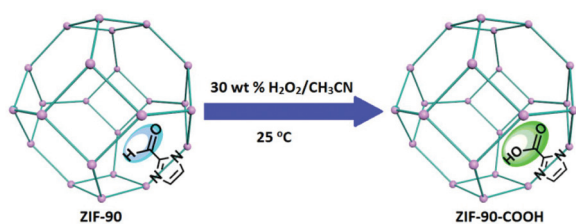
However, the embodiment of Brønsted acidity poses many challenges in the synthesis and design of MOFs. The incorporation of acidic protons can diminish structural stability or interfere with the formation of the framework, as Brønsted acid sites are typically the sites of metal coordination. Moreover, the characterization of solid acids proves arduous: the Brønsted acid sites are often sporadic and the acid-base equilibrium cannot be substantiated.¹³ Acid sites are generally introduced into the framework through encapsulation of the acid into the pores,¹⁴ ligating the acid onto metal sites,¹⁵ or covalently affixing the acid site onto the ligands of the framework.¹⁶ In this contribution, we report a different approach of post-synthetic oxidation to impart the Brønsted acidity into MOF as exemplified in the context of post-synthetically oxidizing the aldehyde group in a zeolitic imidazole framework (ZIF) into carboxylate group.

ZIFs, a subclass of MOFs, have shown both robust chemical and thermal stability, thereby making them good candidates for the post synthetic introduction of acid moieties under the predominantly harsh synthetic conditions required for grafting acidic protons on the framework.¹⁷ ZIF-90, a crystalline material with sodalite (sod) topology, is comprised of imidazole-2-carboxaldehyde and zinc(II) linkers and nodes, respectively. This construct was chosen for post-synthetic modification to augment Brønsted acidity present within the framework. Moreover, imidazole-2-carboxaldehyde is mono-substituted with an aldehyde functional group prior to ZIF-90 synthesis, making ZIF-90 an elementary ZIF ideal for a simple oxidation. Herein, we report a new framework, ZIF-90-COOH resulting from the post synthetic oxidation of ZIF-90 by hydrogen peroxide (Scheme 1).

ZIF-90 was synthesized *via* solvothermal methods¹⁸ and treated with hydrogen peroxide¹⁹ to generate a new framework, ZIF-90-COOH, decorated with -COOH groups. Due to the

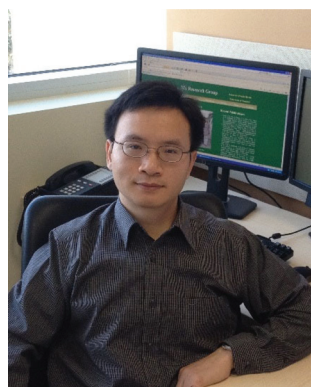
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Scheme 1 ZIF-90 was treated with 30 wt% H_2O_2 in acetonitrile for 72 hours at 25 °C to yield ZIF-90-COOH.

fragility of many MOFs and ZIFs, crystallinity must be ensured after post-synthetic modification, particularly because of the strong oxidizing nature of hydrogen peroxide. The phase purity of ZIF-90 was confirmed by powder X-ray diffraction (PXRD), and the resulting patterns are comparable to the calculated ones (Fig. 1a). Powder X-ray diffraction patterns were collected for the oxidized variant. The new construct, ZIF-90-COOH, show strong similarities to ZIF-90 while maintaining



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Shengqian Ma obtained his B.S. degree from Jilin University, China in 2003, and graduated from Miami University (Ohio) with a Ph.D. degree under the supervision of Hong-Cai Joe Zhou (currently at Texas A&M University) in 2008. After finishing two-year Director's Postdoctoral Fellowship at Argonne National Laboratory, he joined the Department of Chemistry at University of South Florida (USF) as an Assistant Professor in

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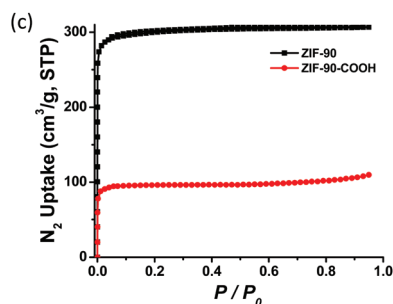
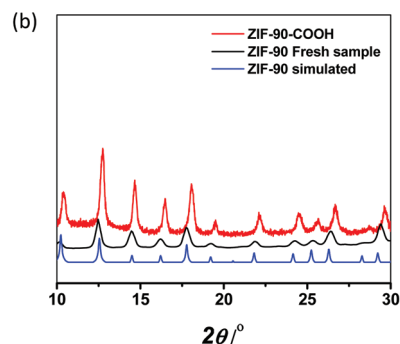
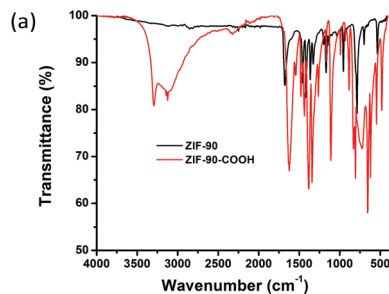


Fig. 1 (a) FT-IR spectra of ZIF-90 (black) and ZIF-90-COOH (red); (b) PXRD patterns of simulated ZIF-90 (blue), ZIF-90 fresh sample (black), and ZIF-90-COOH (red); (c) N_2 isotherms at 77 K of ZIF-90 (black) and ZIF-90-COOH (red).

crystallinity and structural integrity. To confirm the permanent porosity of ZIF-90-COOH, gas adsorption studies were carried out. N_2 isotherms at 77 K revealed that ZIF-90-COOH retains the microporous type-I adsorption behavior with a Brunauer-Emmett-Teller (BET) surface area of $376 \text{ m}^2 \text{ g}^{-1}$ (Langmuir surface area of $421 \text{ m}^2 \text{ g}^{-1}$), which is lower than that of the parent ZIF-90 with a BET surface area of $1166 \text{ m}^2 \text{ g}^{-1}$ (Langmuir surface area of $1302 \text{ m}^2 \text{ g}^{-1}$) (Fig. 1b). The observed reduction in surface area after post-synthetic oxidation should be presumably due to the conversion of the aldehyde groups to the more bulky carboxylate groups, which block the pores and reduce the pore volume. This is supported by the density functional theory (DFT) pore size distribution analysis, which shows that pore sizes of ZIF-90-COOH are predominantly distributed around 8.6 \AA as compared to 11.0 \AA for the parent ZIF-90 (Fig. S1†).

FT-IR was utilized to verify the carboxylic acid moiety in the new framework (Fig. 2a). A strong $\nu(\text{C}=\text{O})$ band was observed

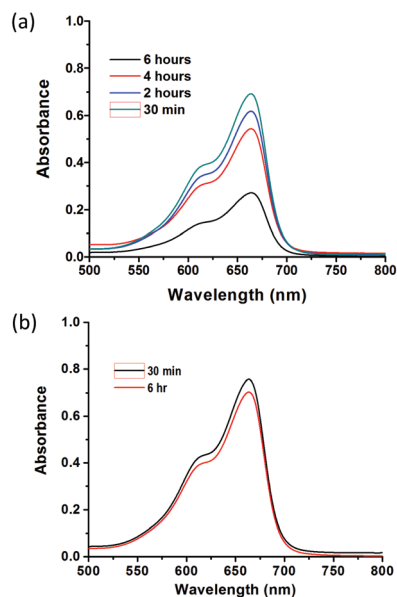


Fig. 2 (a) Aqueous methylene blue absorbancies of ZIF-90-COOH at 30 minutes (green), 2 hours (blue), 4 hours (red), and 6 hours (black); (b) aqueous methylene blue absorbancies of ZIF-90 at 30 min (black) and 6 hours (red).

at 1677 cm^{-1} in ZIF-90, indicating the carbonyl of the aldehyde. A similar $\nu(\text{C}=\text{O})$ of 1621 cm^{-1} in ZIF-90-COOH represents the retention of the carbonyl functionality in the new structure. A decrease in frequency from a standard ketone reference is attributed to the electron-donating properties of the imidazole constituents to which the carbonyls are attached. Furthermore, the hydroxyl group of the carboxylic acid was confirmed *via* the broad $\nu(\text{O}-\text{H})$ peak at 3293 cm^{-1} .

It has recently reported that MOFs containing carboxylic acid groups show remarkable methylene blue uptake from aqueous solutions due to the strong interactions between the dye and the framework.²⁰ As such, methylene blue adsorption was employed as a technique to further verify the presence of the carboxylic acid functionality. Methylene blue removal from aqueous solutions and the related surface interactions were studied for ZIF-90-COOH and control experiments were also conducted on the parent ZIF-90. ZIF-90-COOH was soaked in 20.0 mL of a 5 ppm aqueous methylene blue solution. The adsorption was observed by UV-VIS spectroscopy ($\lambda = 665\text{ nm}$) (Fig. 2a and b). Absorbancies were taken over time, resulting in a 64% decrease in concentration after 6 hours. For comparison, the same study was carried out with the parent ZIF-90, with larger pores but lacking the carboxylic acid functionality. After 6 hours, the concentration decreased only 8%. Adsorption capacity tests reveal methylene blue uptake of 43 mg g^{-1} for ZIF-90-COOH, which is about ten times higher than that for ZIF-90 (4 mg g^{-1}). Such dramatic boost of methylene blue uptake observed should be attributed to the strong interactions between methylene blue molecules and the carboxylate groups²⁰ within ZIF-90-COOH as evidenced by the FT-IR

studies (Fig. S2 and S3†). The symmetric and antisymmetric stretches of C–O on ZIF-90-COOH are characterized by the in phase and out of phase vibrational modes of $\nu_s(\text{COO})$ at 1393 cm^{-1} and $\nu_{as}(\text{COO})$ 1602 cm^{-1} . The electrostatic interactions between the cationic methylene blue and anionic carboxylate group give rise to a drift of the antisymmetric vibrational mode to a stronger band at 1623 cm^{-1} .

In summary, we have demonstrated the successful impartment of Brønsted acidity into a MOF *via* the post-synthetic oxidation of the aldehyde group in the zeolitic imidazole framework, ZIF-90, into carboxylate group to afford ZIF-90-COOH. The transformation from the aldehyde functionality to carboxylic acid leads to remarkable enhancement of methylene blue uptake in the resultant ZIF-90-COOH due to the strong electrostatic interactions between cationic methylene blue and the anionic carboxylate group. Moreover, the retained crystallinity and porosity of the resultant framework creates opportunity for further proton conduction studies, which will be carried out in our laboratory in the near future.

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