

Electronic Supplementary Information

Imparting Brønsted Acidity into a Zeolitic Imidazole Framework

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General Methods

High purity reagents were purchased from Fisher Scientific and Alfa Aesar and used without further purification. ZIF-90 and ZIF-90-COOH were activated by submerging the crystals in neat methanol twice daily for 3 days, and were then activated under vacuum at 25 °C for 24 hours. Isotherms were collected on an ASAP 2020 Surface Area and Porosity System at 77K a liquid nitrogen bath. Methylene blue uptake was monitored on a JASCO V-670 spectrophotometer at 665 nm.

Synthesis of ZIF-90

ZIF-90 was synthesized solvothermally, modified from the description by Yaghi, *et al.*¹ Zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (0.027 g, 0.11 mmol) and imidazole-2-carboxyaldehyde (0.029 g, 0.30 mmol) were charged to a vial containing *N,N*-dimethylformamide (DMF, 15 mL) and heated in a programmable oven for 48 h at 85 °C. Yield (0.030 g, 54 %).

Synthesis of ZIF-90-COOH

ZIF-90 (30 mg, 0.12 mmol) was washed twice a daily with acetonitrile over a period of 3 days. The crystals were then immersed in 3 mL of acetonitrile. Hydrogen peroxide (30%, 50 μL , 0.49 mmol) was added to the reaction mixture. Yellow, opaque crystals were obtained after 48 h, and the solvent was further exchanged with acetonitrile twice daily over a period of 3 days, giving a yield of 0.02 g (61.5%).

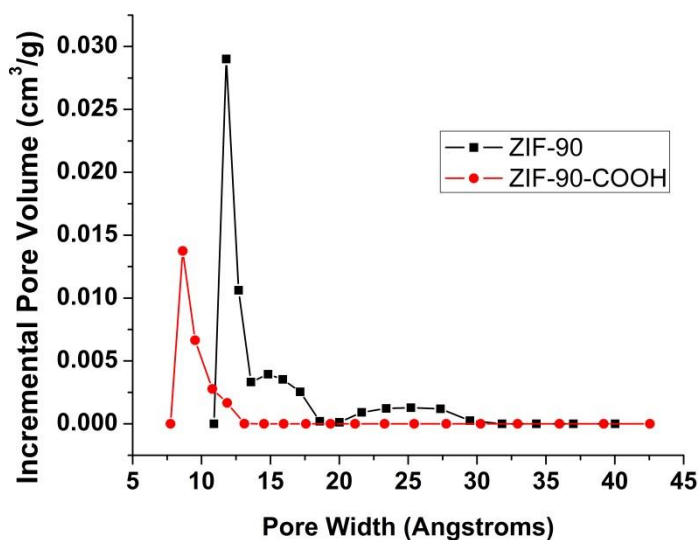


Fig. S1. Density functional theory (DFT) pore size distribution analysis for ZIF-90 (black) and ZIF-90-COOH (red) with N₂ at 77K.

Methylene blue Adsorption Tests

To determine the methylene blue uptake capacity, ZIF-90 and ZIF-90-COOH were activated and dried at 25 °C. The crystals (10 mg) were soaked in aqueous 20 mL methylene blue solutions ranging from 5 ppm to 100 ppm for 12 hours. The solutions were decanted and UV-Vis absorbencies were measured (at $\lambda = 665$ nm) and compared to the calibration curve. The adsorption capacities were calculated according to Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where Q_e (mg/g) is the adsorption capacity, C_0 (mg/L) was the initial concentration, C_e (mg/L) was the final concentration, m (g) was the mass of the framework used, and V (L) was the volume of the methylene blue solution.²

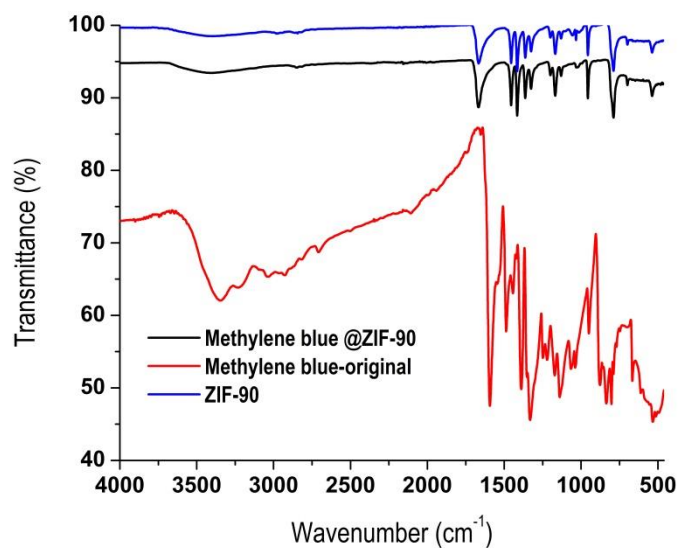


Fig. S2. Comparison of FTIR spectra of methylene blue (red), ZIF-90 (blue), and ZIF-90 with methylene blue (black).

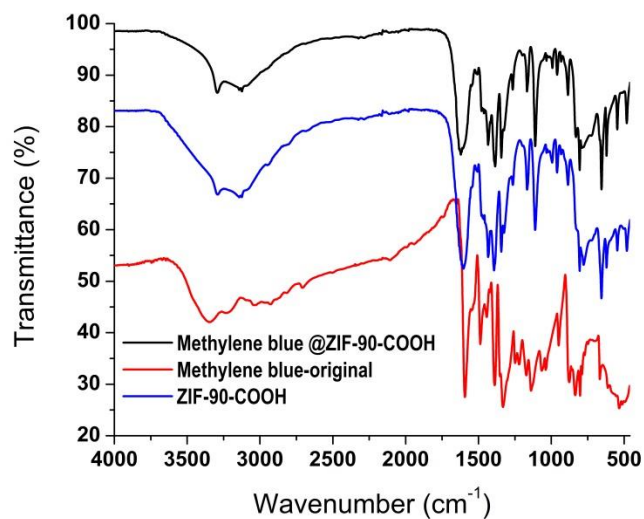


Fig. S3. Comparison of FT-IR spectra of methylene blue (red), ZIF-90-COOH (blue), and ZIF-90-COOH with methylene blue (black).

References

- 1 C. J. D. William Morris, Hiroyasu Furukawa, Rahul Banerjee, and Omar M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 12626.
- 2 J. Y. Qi Zhang, Jianfeng Cai, Ruijing Song, Yuanjing Cui, Yu Yang, and a. G. Q. Banglin Chen, *Chem. Commun.*, 2012, **50**, 14455.