Electronic Supplementary Information

Highly Selective Sorption of Small Hydrocarbons and Photocatalytic Properties of Three Metal-Organic Frameworks based on Tris(4-(1H-imidazol-1-yl)phenyl)amine Ligand

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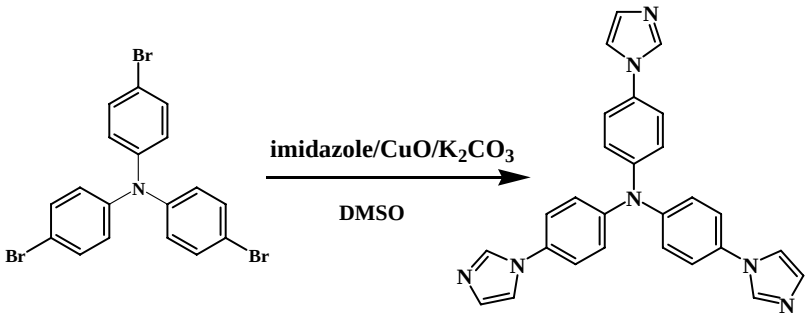
General methods

Commercially available reagents were purchased used without further purification. tri(4-pyridylphenyl)amine(Tipa) were syntheized via ullmann reaction by procedures reported earlier.[1]



A mixture of tris-(4-bromophenyl)amine (2.41 g, 5 mmol)], imidazole (1.36 g, 20 mmol), potassium carbonate (5.52 g, 40 mmol) and CuO (0.16 g, 2 mmol) were heated while stirring in 20 mL of DMSO at 150 ºC for 48h. The resulting slurry was cooled to room temperature, and solids were removed by filtration. DMSO of the filtrate was removed by distillation under reduced pressure. Methylene chloride was added to the remaining filtrate, and the mixture was then washed with water and dried over sodium sulfate. The methylene choride was then removed. The tri(4-imidazolylphenyl)amine was crystallized in methanol and water, and light pale solid was obtained.

Powder X-ray Diffraction Studies

X-ray powder diffraction (XPD) patterns of 1-3 were collected on a MiniFlex-II diffractometer with a step size of 1.0°.

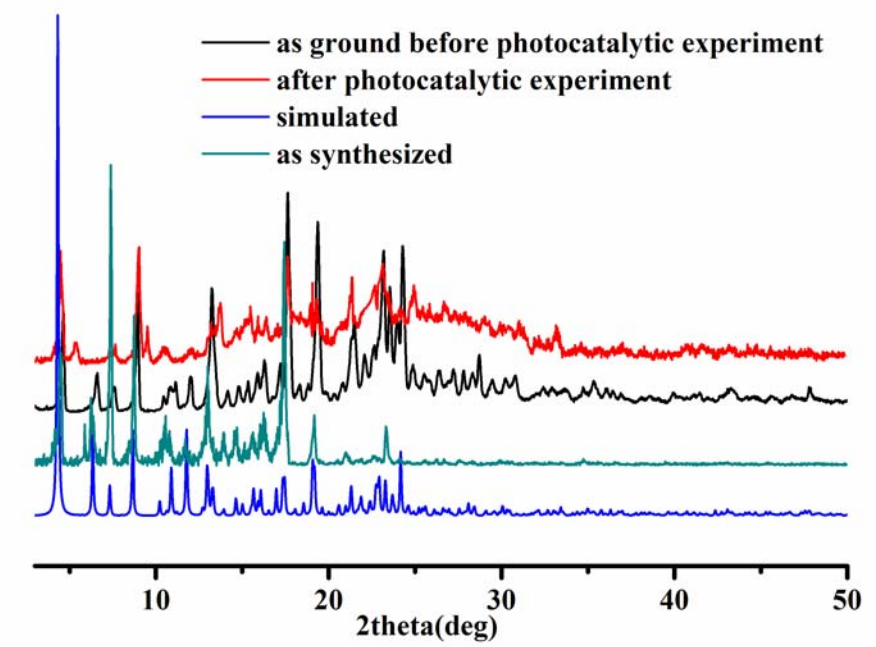


Figure S1. For **1**: Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination, the as-synthesized product and the crystal powder after photocatalytic experiment.

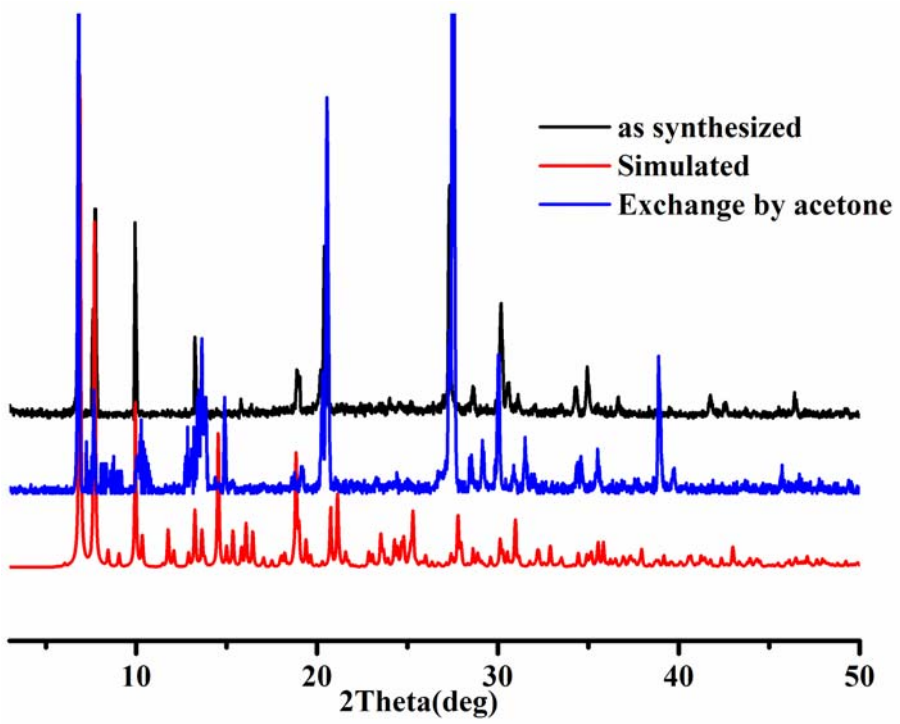


Figure S2. For **2**: Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product.

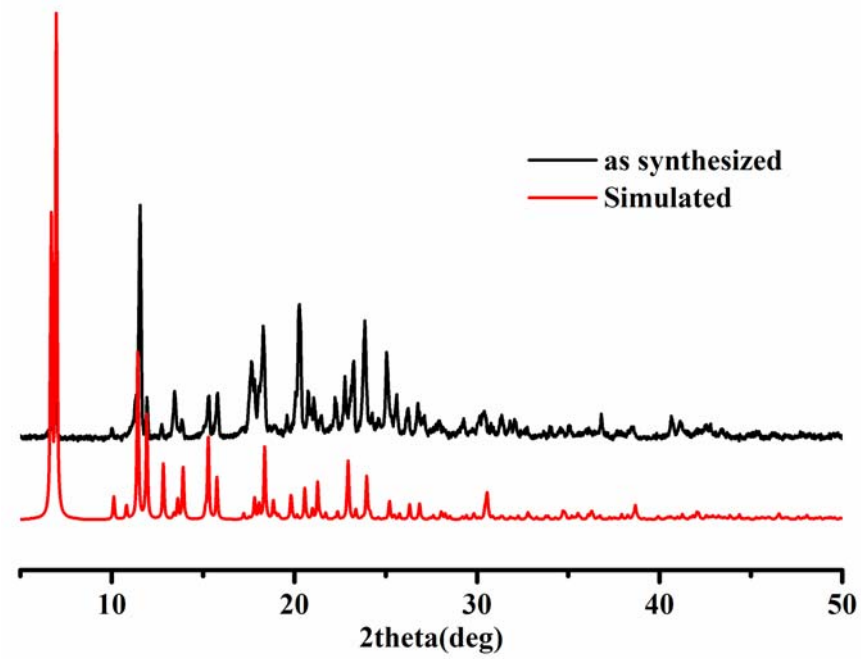


Figure S3 For **3**: Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product.

Themogravimetric Analysis of MOFs

Thermal Gravimetric Analysis (TGA) was carried out using a NETSCHZ STA-449C simultaneous TG-DSC thermoanalyzer, under a constant stream of dry nitrogen gas (flow rate 20 mL min^{-1}) over the temperature range of 30 to 600 °C and at a heating rate of 10 °C min^{-1}.

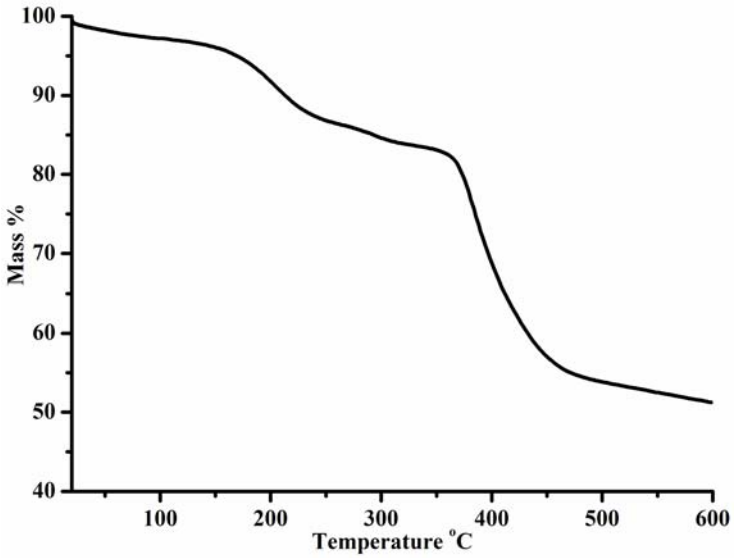


Figure S4 TGA curves of compound **1** under N_2 atmosphere.

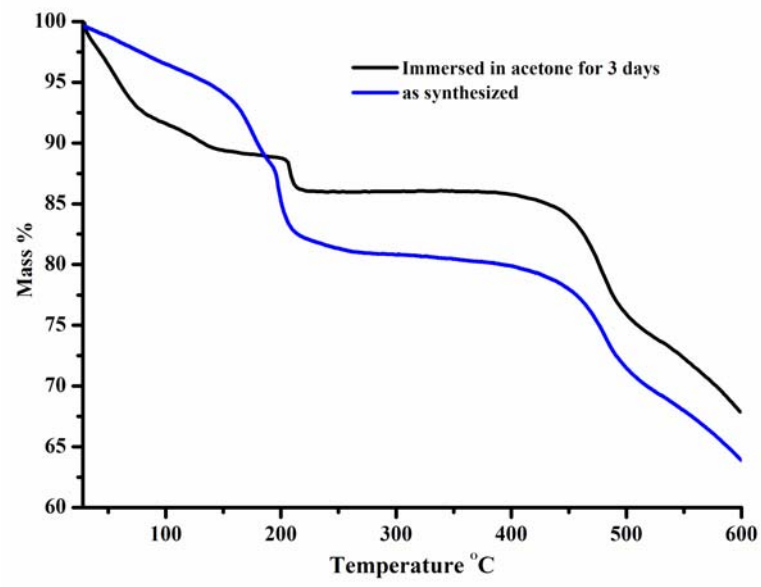


Figure S5 TGA curves of compound **2** under N_2 atmosphere.

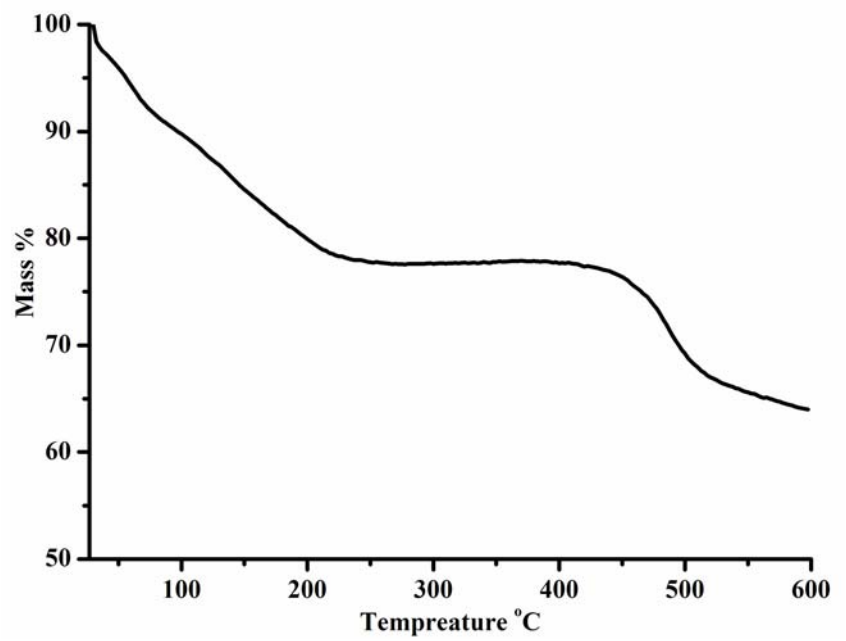


Figure S6 TGA curves of compound **3** under N_2 atmosphere.

Isotherm Models. In order to evaluate the adsorption equilibrium selectivity and predict adsorption of gas mixture from pure component isotherms, the Henry's law linear isotherm equation and the Langmuir model were used to correlate the C2H2 and C2H4 adsorption on **2**. The Henry's isotherm equation is

$$q = KP$$

where q is the adsorbed amount per unit weight of adsorbent($cm^3\ g^{-1}$), P is the adsorbate gas pressure at equilibrium (torr), and K is the Henry's law constant ($cm^3\ g^{-1}\ torr^{-1}$).

The Langmuir isotherm is formulated as

$$q = \frac{q_m bP}{1 + bP}$$

where q_m ($cm^3\ g^{-1}$) and b ($torr^{-1}$) are the Langmuir isotherm equation parameters. The values of qm and b were determined can be determined from the slope and intercept of a linear Langmuir plot of (*1/q*) versus (*1/P*).

Adsorption Equilibrium Selectivity. In order to evaluate the efficacy of an adsorbent for gas separation and purification such as removal/separation of C2H2 from ethylene by adsorption, it is necessary to know the adsorbent selectivity. The adsorption equilibrium selectivity α_{12} between components 1 and 2 is defined as

$$\alpha_{12} = \frac{X_1}{X_2} * \frac{Y_2}{Y_1} = \frac{K_1}{K_2} = \frac{q_{m1} b_1}{q_{m2} b_2}$$

where component 1 is the stronger adsorbate and 2 is the weaker adsorbate. X_1 and X_2 are the molar fractions of components 1 and 2 on the adsorbent surface (or in the adsorbed phase), Y_1 and Y_2 are the molar fractions of components 1 and 2 in the gas phase. qm1 and qm2 and b_1 and b_2 are the Langmuir equation constants for

components 1 and 2. K_1 and K_2 are the Henry's constants for components 1 and 2.

1 (a) Wu, H.; Liu, H.-Y.; Liu, B.; Yang, J.; Liu, Y.-Y.; Ma, J.-F.; Liu, Y.-Y. and Bai. H.-Y. *CrystEngComm* **2011**, *13*, 3402–3407. (b) Wu, H.; Liu, H.-Y.; Liu, Y.-Y.; Yang, J.; Liu, B. and Ma, J. F. *Chem. Commun.* **2011**, *47*, 1818-1820.