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From 2-methylimidazole to 1,2,3-triazole: A topological transformation of ZIF-8 and ZIF-67 by post-synthetic modification

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SUPPORTING INFORMATION

S1. Materials

1,2,3-Triazole (98% purity) was purchased from ABCR GmbH, Germany. 2-Methylimidazole (Hmim with 97% purity) and Zinc Nitrate Hexahydrate (Zn $(NO_3)_2$.6H2O, 99% purity – metal based) were purchased from Alfa Aesar. Cobalt (II) Nitrate Hexahydrate (Co $(NO_3)_2$.6H2O, reagent grade, 98% purity) was purchased from SigmaAldrich. Deuterium Oxide (D_2O, 99.9% purity), Sulfuric acid-D2 (96% solution in D_2O), and other solvents were purchased from Merck. All chemicals were used as received.

S2. General Methods and Instrumentation

^1H NMR spectra were recorded on a Bruker 400 spectrometer (1H, 400 MHz). For a typical measurement, approximately 10-20 mg ZIF was dissolved in 600 µL D_2SO_4/D_2O (10v/90v) stock solution, and ^1H NMR spectra were obtained by locking the sample D_2O. Powder X-ray diffraction (PXRD) patterns of all samples were acquired by using Panalytical Empyrean with Cu Kα source at a generator voltage of 40 kV and a tube current of 30 mA. The diffraction angle (2θ) range from 5° to 40° was scanned at a scan rate 0.013 min^{-1}. Thermal degradation of all samples was examined by Shimadzu DTG 60, under nitrogen atmosphere and at a heating rate of 10 °C min^{-1}. FT-IR spectra were recorded on a Thermo Nicolet 6700 with 4 cm^{-1} resolution between 400–4000 cm^{-1}. Gas adsorption/desorption isotherms were obtained by using Micromeritics Tristar II Plus Surface Area and Pore Size Analyzer. Samples were degassed at 100 ˚C overnight and degassed samples and sample tubes weighed before analysis. N_2 adsorption studies carried out under liquid nitrogen (77 K) and surface areas calculated using the Brunauer, Emmett and Teller (BET) method by considering consistency criteria. Horvath-Kawazoe method employed for micropore size distribution analysis. Low-pressure CH_4 uptakes measured at 273 K in an ice bath and at 298 K in a water bath.

S3. Synthesis of ZIF-8 and ZIF-67

ZIF-8 nanoparticles were synthesized using a reported procedure by Cravillon et al.[1] In a typical synthesis, 1.05 g (3.53 mmol) $Zn(NO_3)_2.6H_2O$ and 2.34 g (28.3mmol) 2-methlimidazole were dissolved in 50 ml methanol, separately. Then first solution was poured into second, and final solution was vigorously stirred at room temperature for 1 h. (The molar ratio of $Zn(NO_3)_2.6H_2O$:Hmim:MeOH is approximately 1:8:700.) The obtained white ZIF-8 NPs were collected by centrifuging and washing with methanol. Finally, ZIF-8 was dried in a vacuum oven at 80 °C for 24 h.

ZIF-67 nanoparticles were synthesized using a reported procedure by Qian et al.[2] In a typical synthesis, 0.45 g (1 mmol) Co $(NO_3)_2$.6H2O and5.5 g (58 mmol) 2-methylimidazole was dissolved in 3 ml and 20 ml deionized water, respectively. And then those two solutions were mixed and vigorously stirred at room temperature for 6 h. (The molar ratio of $Co(NO_3)_2 .6H_2O$: Hmim: DI is approximately 1:58:1100). The obtained purple ZIF-67 NPs were collected by centrifuging and with washing water and methanol. Finally, ZIF-67 NPs was dried in a vacuum oven at 80 °C for 24 h.

S4. Synthesis of ZIF-8-TZ and ZIF-67-TZ

Approximately 150 mg as-synthesized ZIF-8 were dispersed in 30 ml methanol and 300 mg 1,2,3-Triazole was dissolved in 10 ml methanol. And then second solution was poured into first and the resulting mixing was hold at room temperature. The experiment was optimized with respect to process time of maximum exchange point observed.

ZIF-67-TZ was synthesized according to the same procedure as in ZIF-8-TZ.

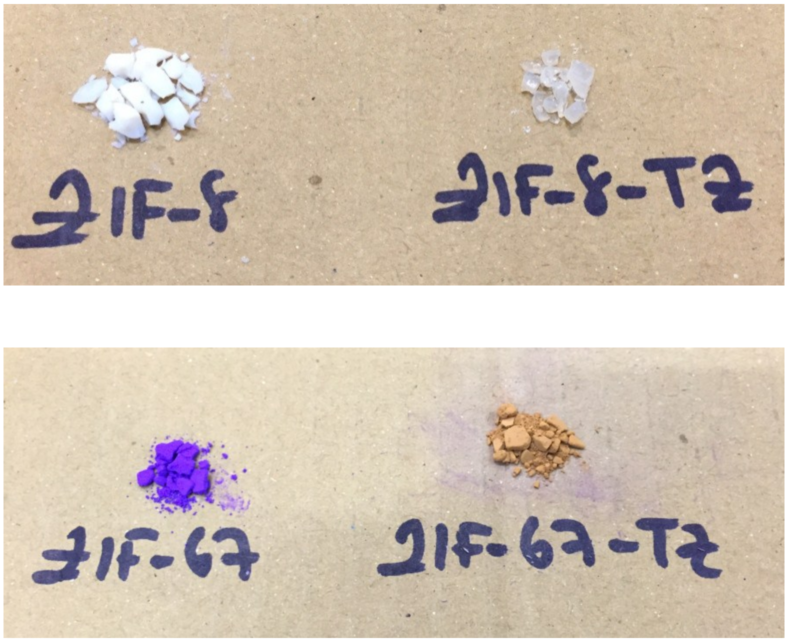

Figure S1. Digital images of ZIF-8, ZIF-8-TZ, ZIF-67 and ZIF-67-TZ.

S5. PXRD Data for ZIF-8-TZ and ZIF-67-TZ

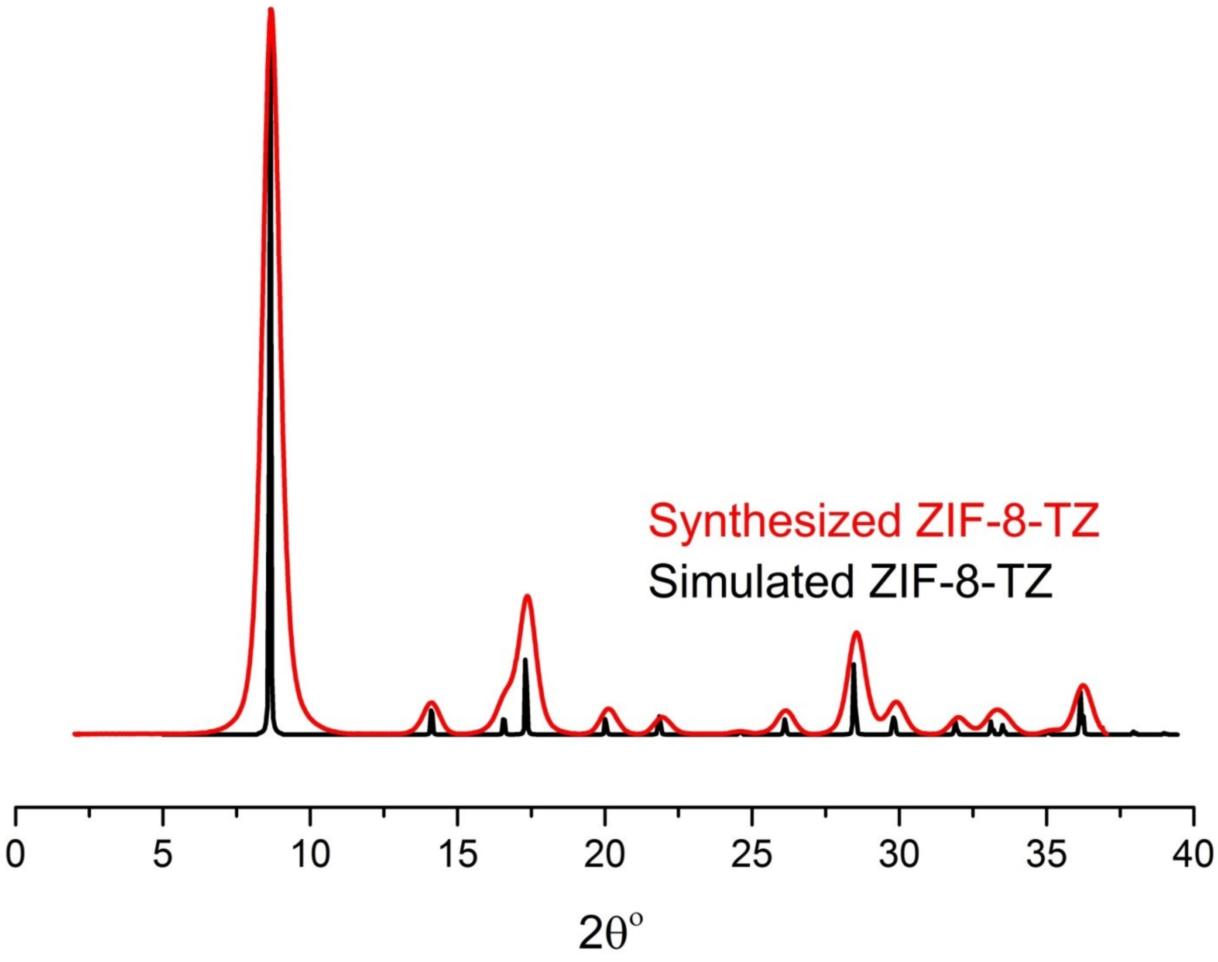

Figure S2. Simulated and experimentally obtained PXRD patterns for ZIF-8-TZ

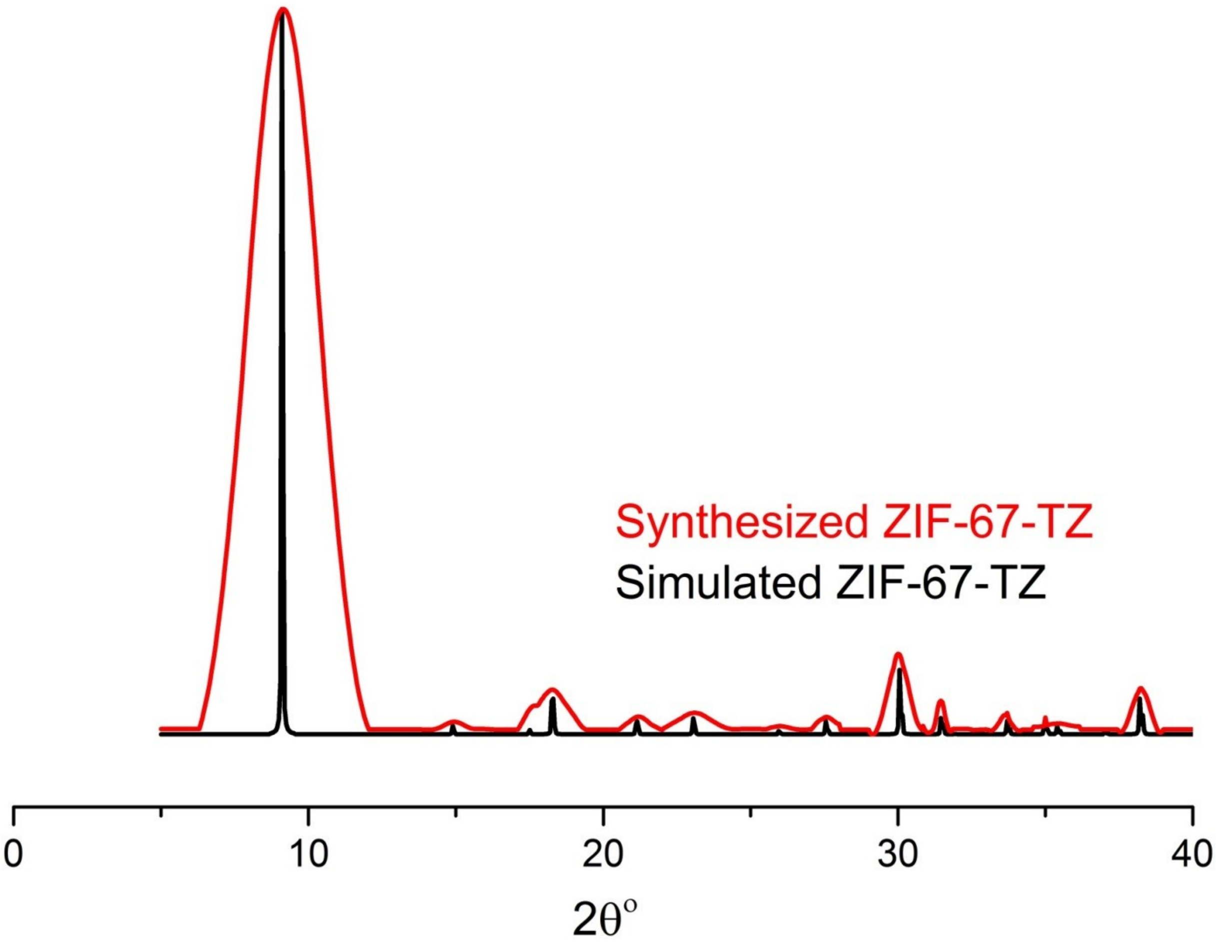

Figure S3. Simulated and experimentally obtained PXRD patterns for ZIF-67-TZ

S6. NMR Data for ZIF-8-TZ and ZIF-67-TZ

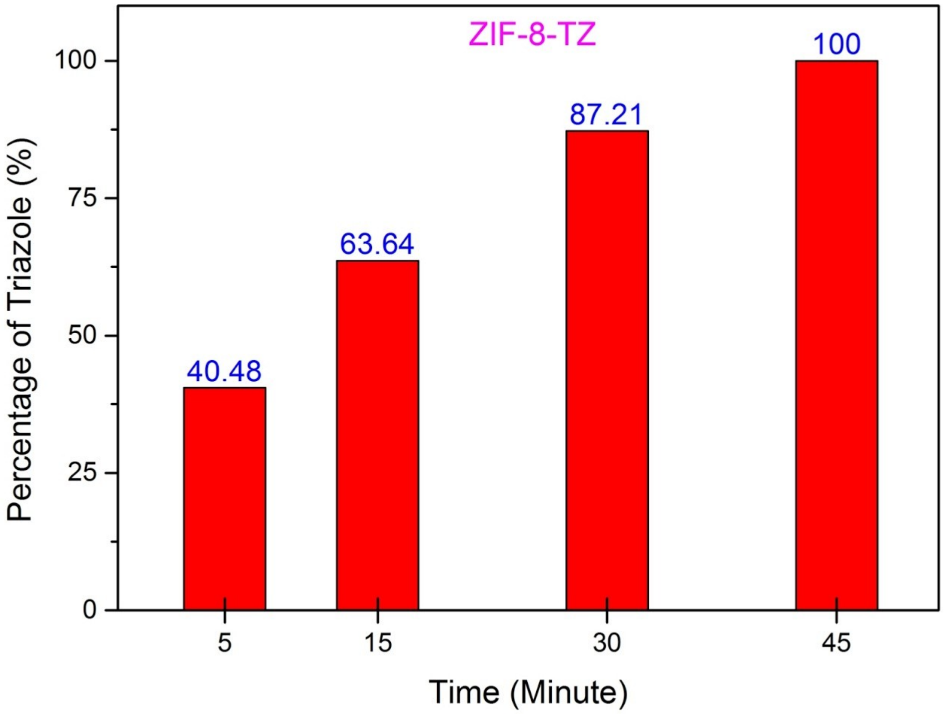

Figure S4. BLR evolution for ZIF-8-TZ at RT. (Concentration of ZIF-8/1,2,3 Triazole (mg/mg): (150:300))

(The evolution time does not include the centrifugation process.)

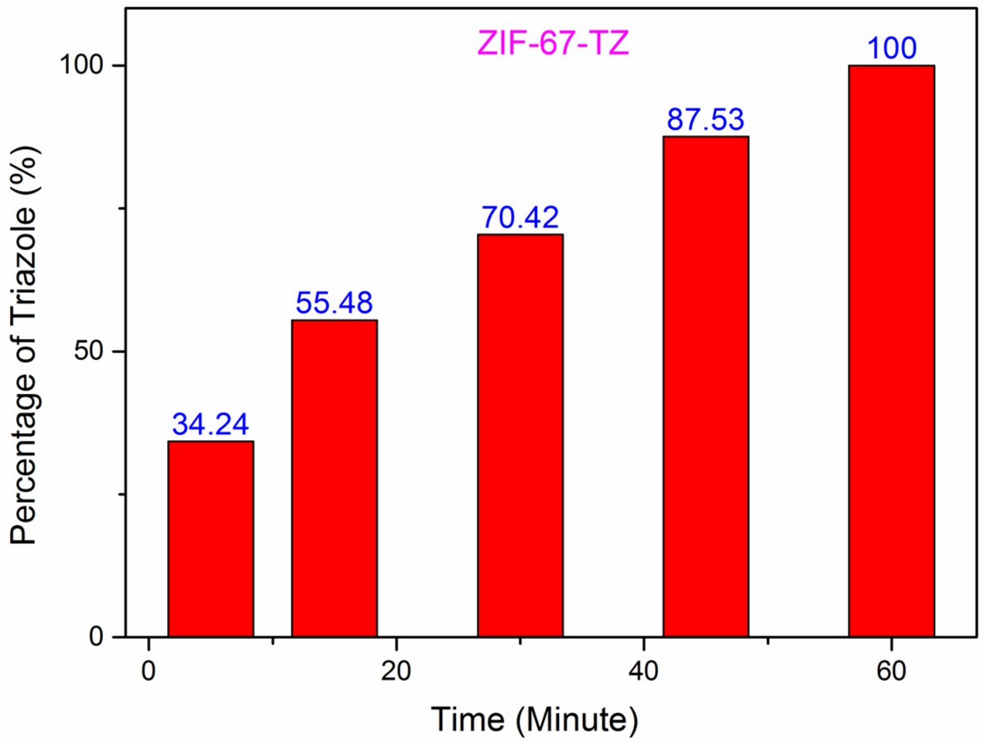

Figure S5. BLR evolution for ZIF-67-TZ at RT. (Concentration of ZIF-8/1,2,3 Triazole (mg/mg): (150:300))

(The evolution time does not include the centrifugation process.)

Concentration of ZIF-8/1,2,3 Triazole (mg/mg)	The required time(min) for full conversion in ZIF-8-TZ	The required time(min) for full conversion in ZIF-67-TZ
150/300	45	60
150/150	75	105

Table S1. The required time for full conversion to concentration of ZIF/1,2,3-Triazole for ZIF-8-TZ and ZIF-67-TZ

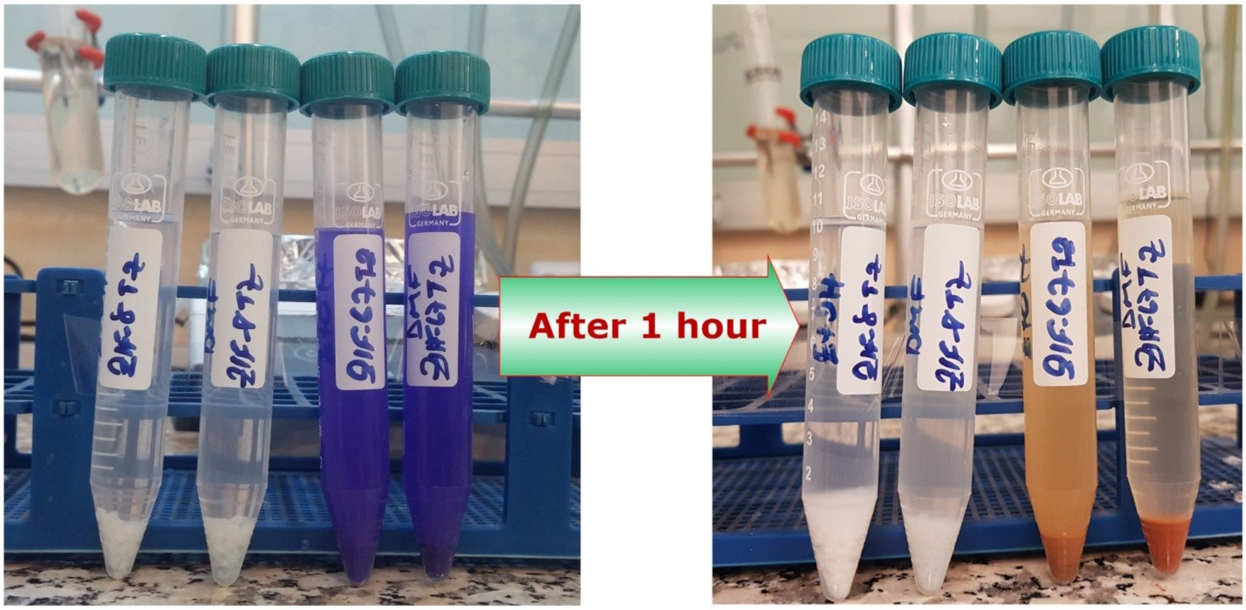

Figure S6. BLR evolution in EtOH and DMF for ZIF-8 and ZIF-67

S7. BET Measurements

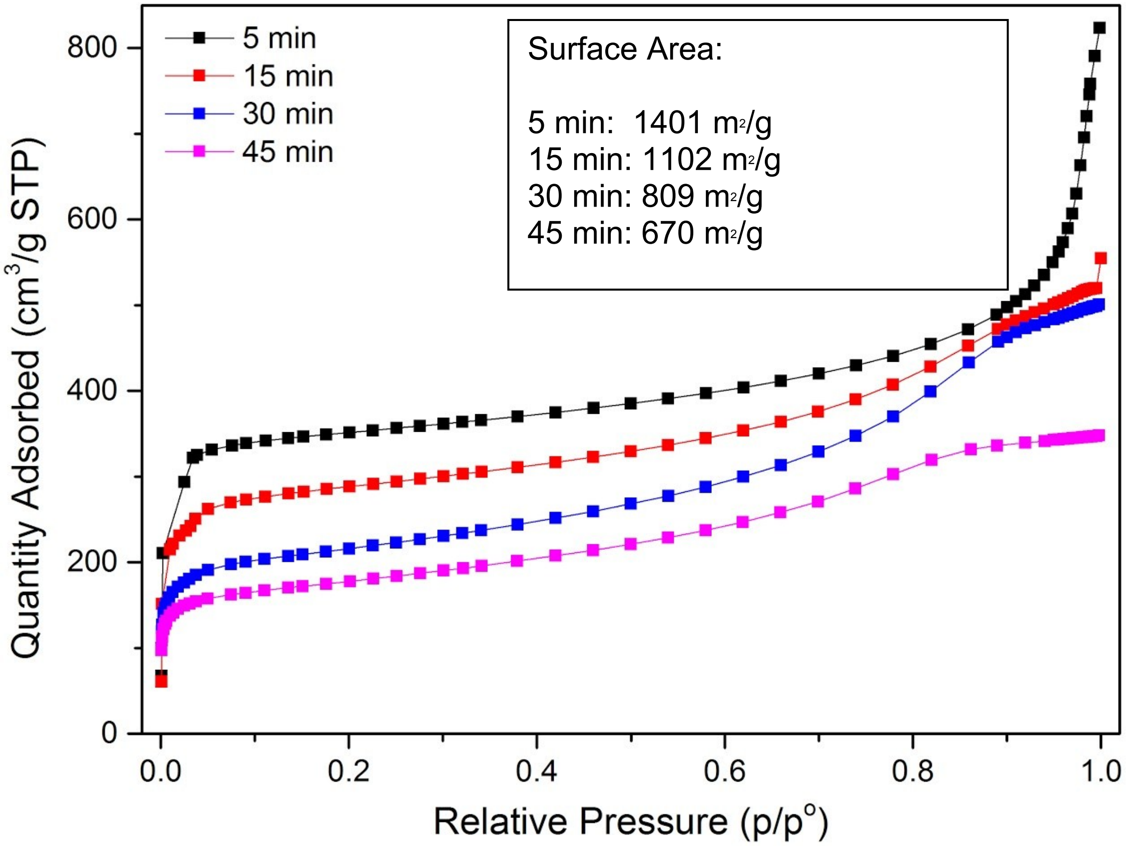

Figure S7. BET surface area evolution in ZIF-8 during BLR process

S8. FT-IR Data for ZIF-8, ZIF-67, ZIF-8-TZ and ZIF-67-TZ

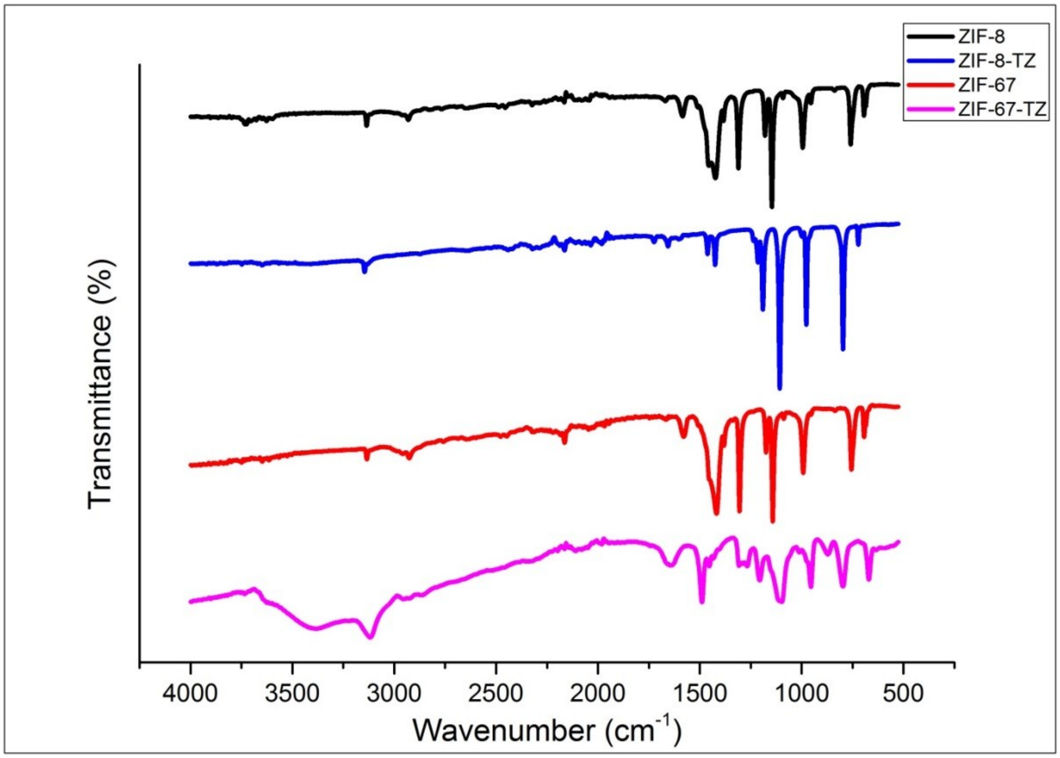

Figure S8. FT-IR spectra for ZIF-8, ZIF-67, ZIF-8-TZ, ZIF-67-TZ

S9. TGA Data for ZIF-8, ZIF-67, ZIF-8-TZ and ZIF-67-TZ

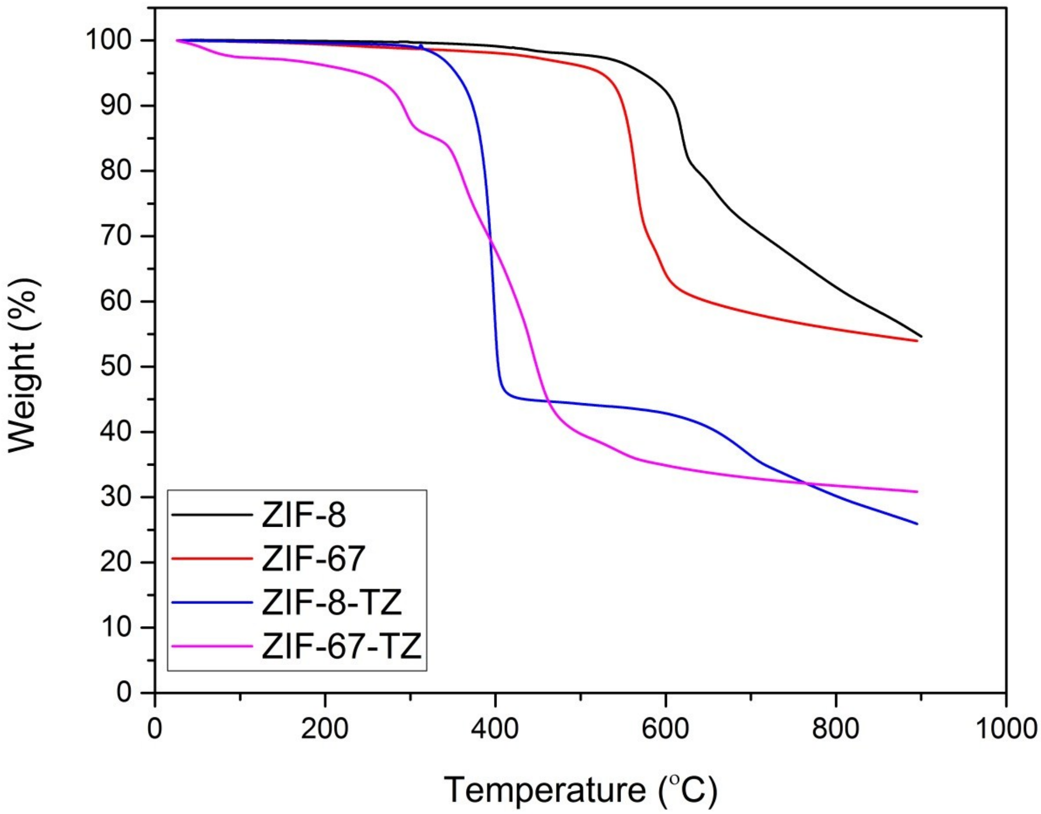

Figure S9. TGA thermograms for ZIF-8, ZIF-67, ZIF-8-TZ, ZIF-67-TZ

S10. Density Functional Theory Calculations

Periodic DFT calculations were performed with the CASTEP 16.1[3] package to optimize the atomic positions of the ZIF-8-TZ and ZIF-67-TZ. In order to save computing time primitive unit cells were used which were converted back to the cubic unit cell after the optimization. Calculations were performed with the PBE[4] exchange-correlation functional using ultrasoft pseudopotentials with a 440 eV cutoff.

S11. References

1. J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chemistry of Materials*, 2009, **21**, 1410-1412.
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3. J. Clark Stewart, D. Segall Matthew, J. Pickard Chris, J. Hasnip Phil, I. J. Probert Matt, K. Refson and C. Payne Mike, *Journal*, 2005, **220**, 567.
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