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Supplementary information

Zeolitic imidazolate frameworks as heterogeneous catalysts for a one-pot P–C bond formation reaction via Knoevenagel condensation and phospha-Michael addition

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Experimental procedure

Synthesis of ZIF-7: ZIF-7 was synthesized using the previously-reported method.[1] Benzimidazole (0.25 g) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 0.75 g) were dissolved in dimethylformamide (DMF, 75 mL). The resulting solution was subjected to solvothermal conditions in a Teflon-lined stainless-steel autoclave at 400 K for 48 h under autogenous pressure. The generated precipitate was collected by filtration, washed repeatedly with methanol and dried at room temperature in air.

Synthesis of ZIF-9: ZIF-9 was synthesized using the previously-reported method.[2] Benzimidazole (0.60 g) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 2.1 g) were dissolved in DMF (180 mL), which was then distributed into 20 mL vials and capped tightly. The solution was subjected to temperature at 413 K for 48 h in an oven (heat up rate was 5 K min^{-1}). After that, the mother liquor was removed by decantation from the resulting mixture, and chloroform (20 mL) was added into the vials. Finally, purple crystals were collected from the upper chloroform layer and dried at 353 K overnight.

Synthesis of ZIF-67: ZIF-67 was synthesized using the previously-reported method.[3] 2-methylimidazole (5.5 g) dissolved in deionized water (20 mL) and $Co(NO_3)_2 \cdot 6H_2O$ (0.45 g) dissolved in deionized water (3 mL) were mixed and stirred at room temperature for 6 h. The generated precipitate was collected by centrifugation, washed repeatedly with deionized water and methanol and then dried at 353 K for 24 h.

Synthesis of IRMOF-3: IRMOF-3 was synthesized using the previously-reported method.[4] 2-aminobenzene-

1,4-dicarboxylic acid (0.040 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 g) were dissolved in DMF (10 mL). The resulting mixture was heated at 378 K for 48 h. The generated precipitate was collected by filtration, washed repeatedly with methanol and dried at room temperature in air.

Synthesis of HKUST-1: HKUST-1 was synthesized using the previously-reported method.[5] 1,3,5-Benzenetricarboxylic acid (0.126 g) suspended in deionized water (6 mL) was added into a solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.070 g) dissolved in deionized water (6 mL) were vigorously stirred at room temperature for 1 h. The generated precipitate was collected by centrifugation, washed repeatedly with ethanol and then dried at 373 K under vacuum overnight. SEM

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[2] K.S. Park, Z. Ni, A.P. Cote, J.Y. Choi, R. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe and O.M. Yaghi, *PNAS*, 2006, **27**, 10186.

[3] J. Qian, F. Sun and L. Qin, *Mat. Lett.*, 2012, **82**, 220.

[4] H. Yim, E. Kang and J. Kim, *Bull. Korean Chem. Soc.*, 2010, **31**, 1041.

[5] J. Huo, M. Brightwell, S.E. Hankari, A. Garai and D.Bradshaw, *J. Mater. Chem. A*, 2013, **1**, 15220.

General method: Standard θ–2θ X-ray diffraction (XRD) data were recorded on a Shimadzu X-ray diffractmeter XRD-6100 using Cu Kα radiation (λ = 1.5406 Å). Nitrogen adsorption-desorption isotherms were collected by using a BEL-SORP mini (BEL Japan, Inc.) at 77 K. The BET area was determined by using a BET-method-based calculation on N_2 adsorption isotherm data. Fourier transform infrared (FT-IR) spectroscopy was performed with a resolution of 4 cm^{-1} in transmission mode in air using a JASCO FT-IR 660 Plus apparatus. The self-supporting pellet of the sample was loaded in a specially constructed IR cell, which was equipped with CaF2 windows. Thermal gravimetric analysis (TGA) data were obtained by using a Shimadzu DTG-60 with a heating rate of 10 K min^{-1} under nitrogen atmosphere. Scanning electron microscope (SEM) images were collected with Ir conductive coating using a Philips XL-30 FESEM.

Knoevenagel condensation reaction: The reaction was carried out in liquid phase in a 35 mL glass reactor. A solution of benzaldehyde (1 mmol), malononitrile (3 mmol) and 1, 4 dioxane (4 mL) was stirred at 323 K with 50 mg of the catalyst in powder form. The progression of the reaction was monitored by gas chromatography (Shimadzu GC-14B with a flame ionization detector) equipped with an InertCap®1 capillary column and ^{1}H-NMR spectroscopy (JEOL ECX-400 spectrometer operating at 400 MHz) with 1, 2-Diphenylethane as an internal standard.

Phospha-Michael addition reaction: The reaction was carried out in liquid phase in a 35 mL glass reactor. A solution of benzylidenmalononitrile (1 mmol), diethyl phosphite (3 mmol) and 1, 4-dioxane (4 mL) was stirred at 323 K with 50 mg of the catalyst in powder form. The progression of the reaction was monitored by using gas chromatography and ^{1}H-NMR spectroscopy (see above).

One-pot Knoevenagel condensation and phospha-Michael addition reaction: The reactions were carried out in liquid phase in a 35 ml glass reactor. A solution of benzaldehyde (1 mmol), malononitrile (3 mmol), diethyl phosphite (3 mmol) and 1, 4 dioxane (4 mL) was stirred at 323 K with 50 mg of the catalyst in powder form. The progression of the reaction was monitored by using gas chromatography and ^{1}H-NMR spectroscopy (see above). Reusability of the catalyst was studied as follows. After the first run, the catalyst was separated from the reaction mixture by filtration after cooling to room temperarue, washed three times with methanol, dried at 333 K in air and reused for the next run. The above procedure was repeated three times.

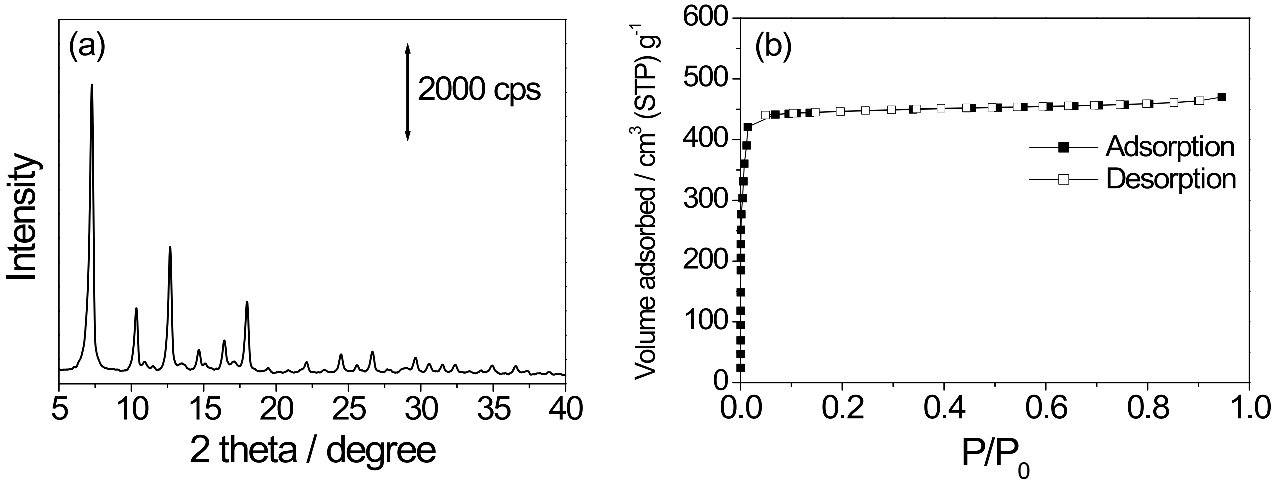

Figure S1. (a) XRD pattern and (b) N_2 adsorption–desorption isotherm of ZIF-8.

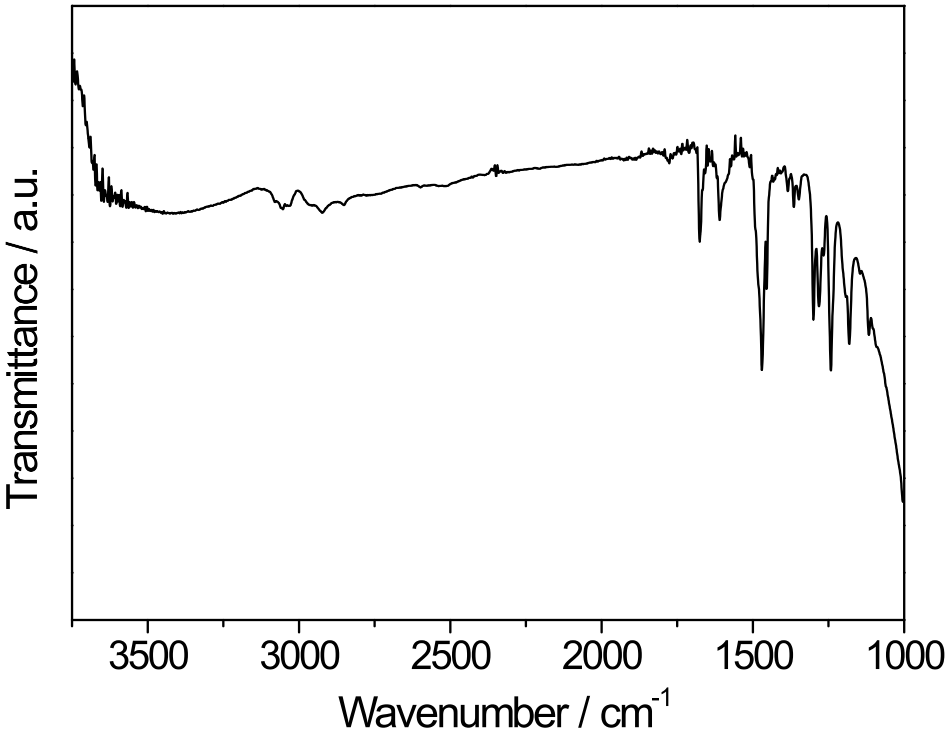

Figure S2. FT-IR spectrum of ZIF-8.

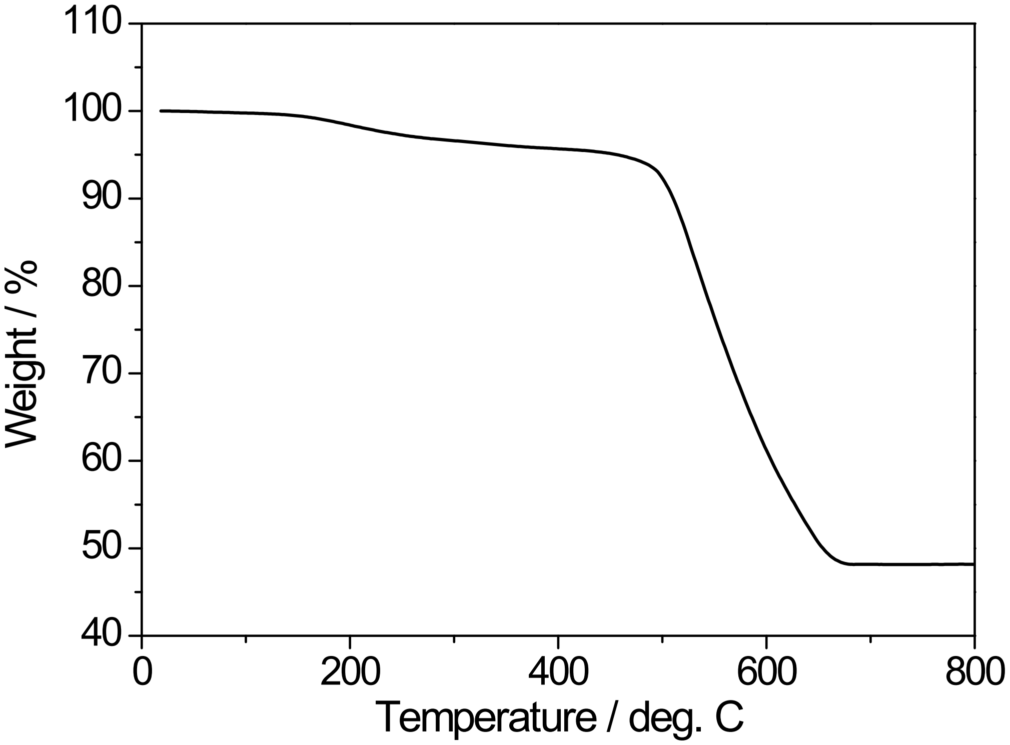

Figure S3. TGA analysis of ZIF-8.

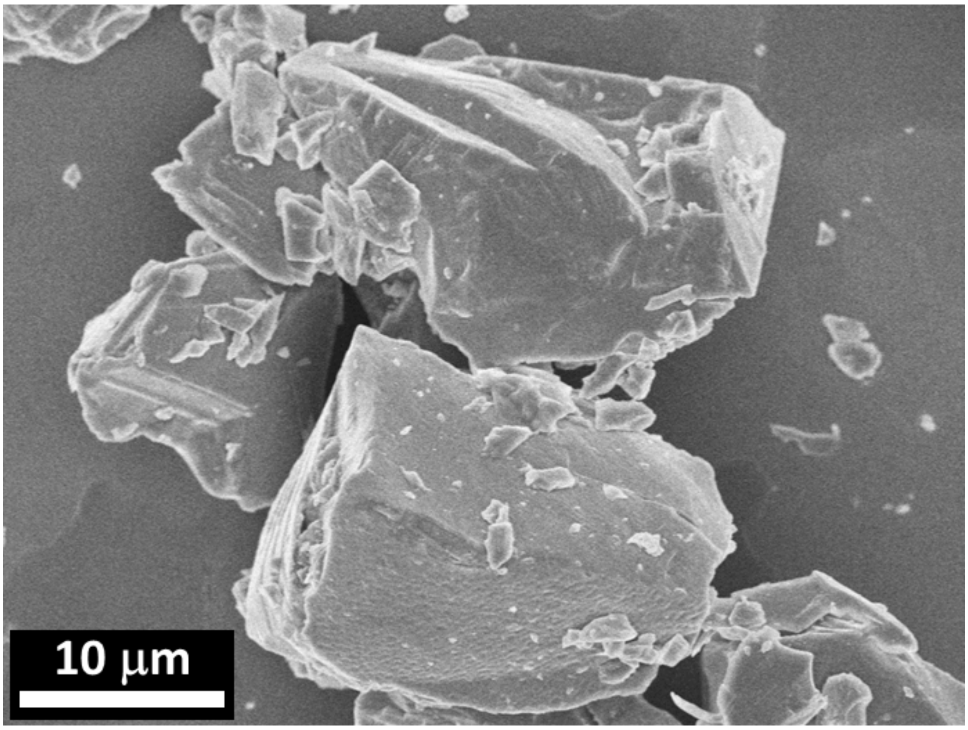

Figure S4. SEM image of ZIF-8.

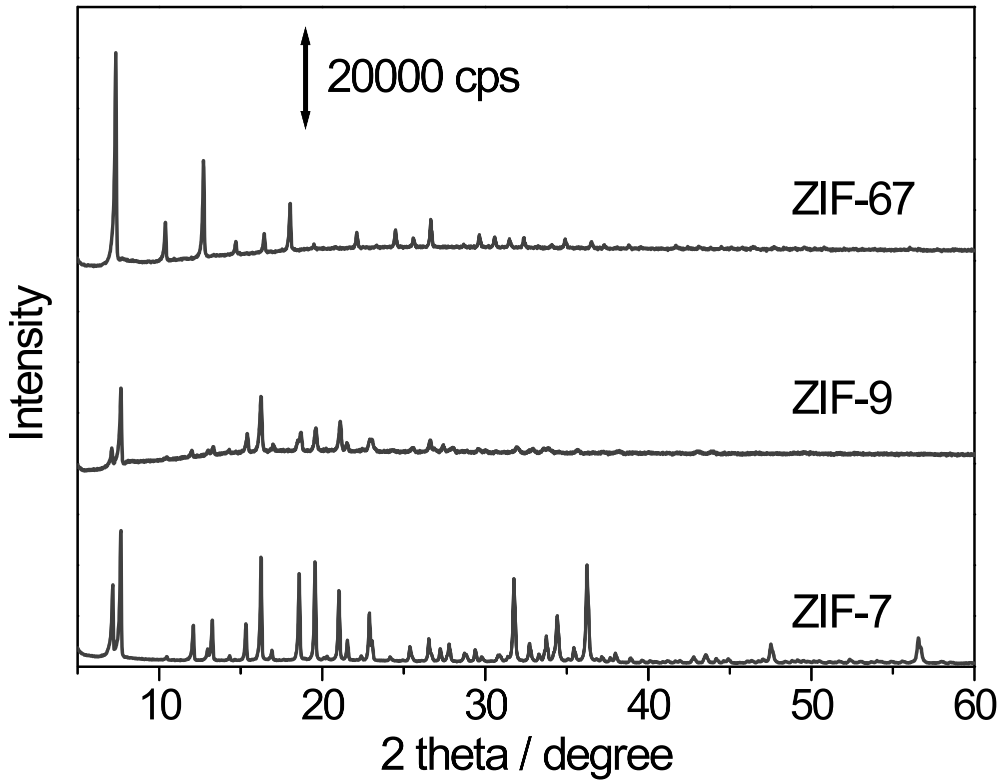

Figure S5. XRD patterns of ZIF-7, ZIF-9 and ZIF-67.

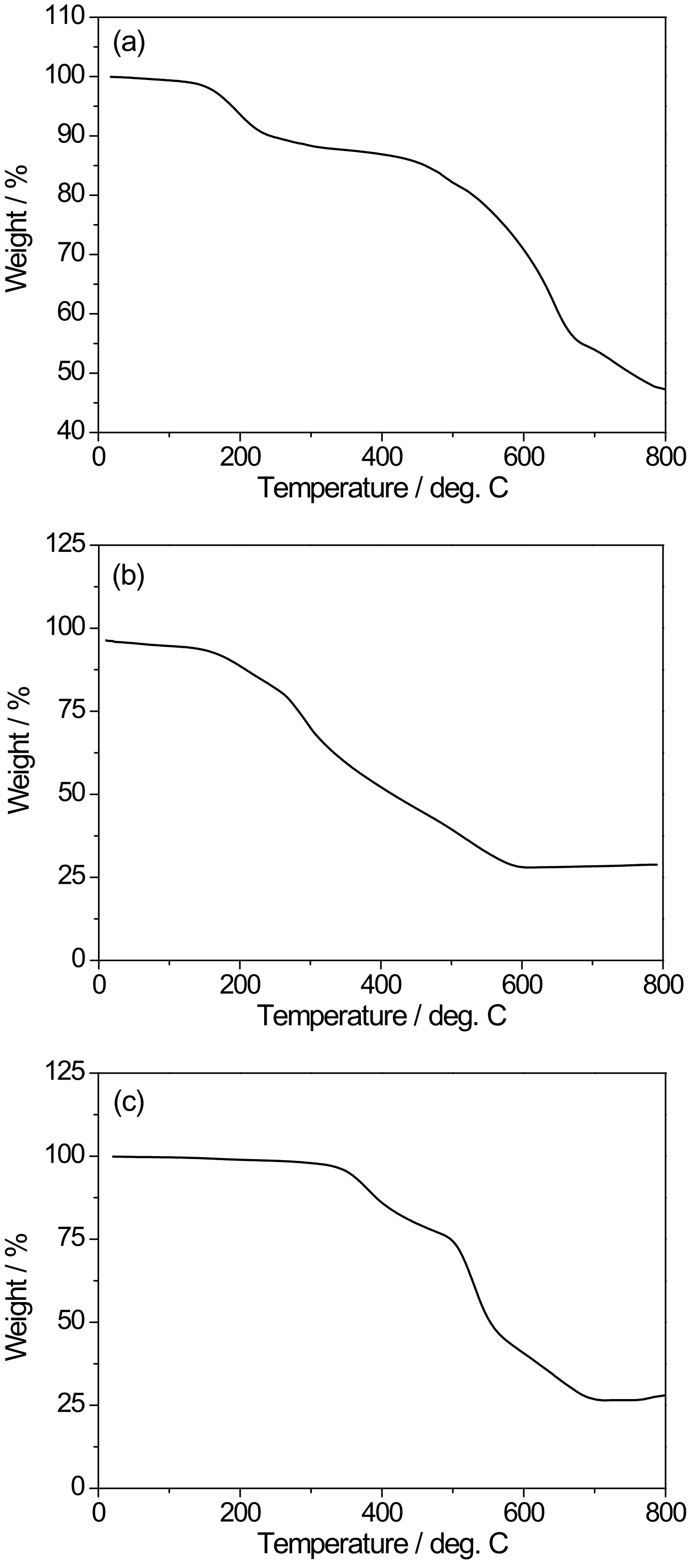

Figure S6. TGA analyses of (a) ZIF-7, (b) ZIF-9 and (c) ZIF-67.

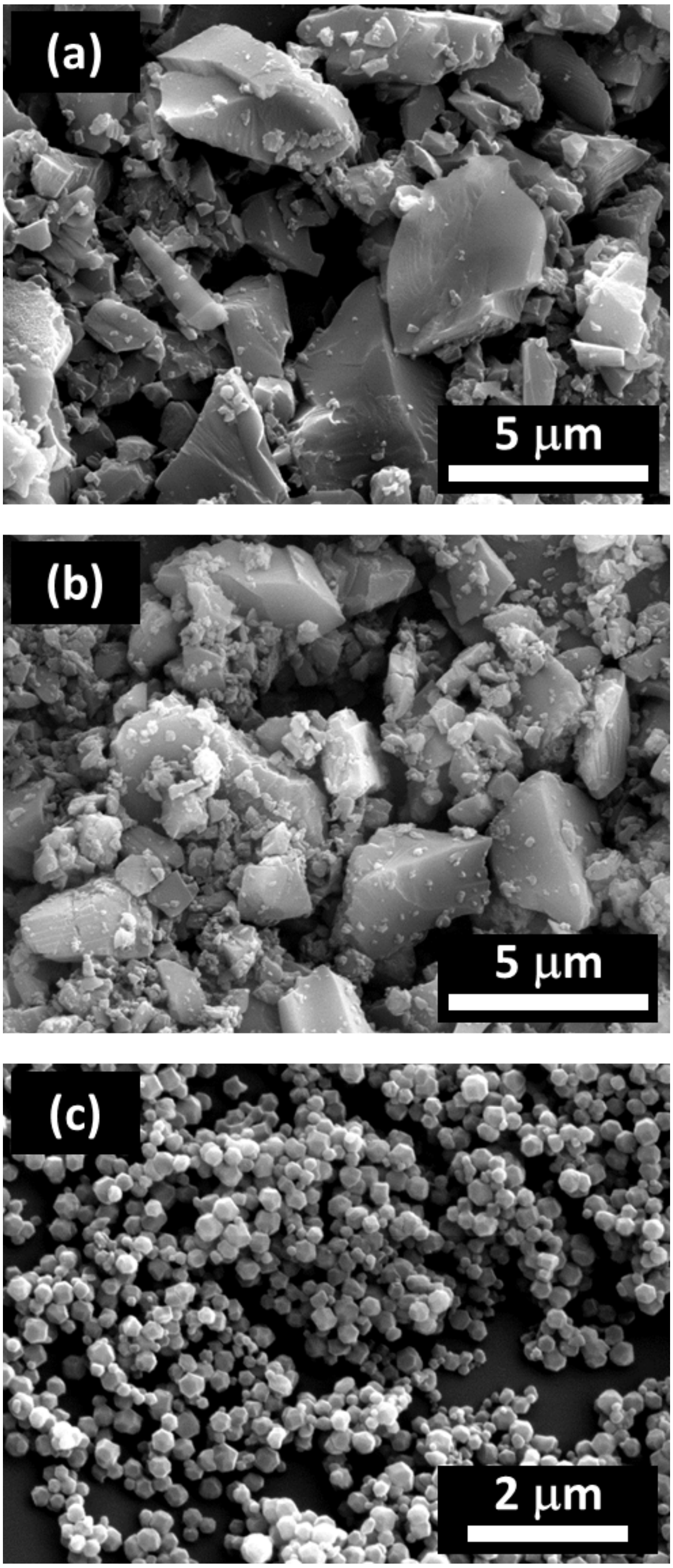

Figure S7. SEM images of (a) ZIF-7, (b) ZIF-9 and (c) ZIF-67.