Electronic Supplementary Information Motorized Janus Metal Organic Framework Crystals

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Experimental

Materials and Methods. All starting materials and reagents were purchased from commercial sources and used as received. Dimethylformamide, polyvinylpyrrolidone (average Mw ~ 40,000), poly (methyl methacrylate) (average Mw ~120,000) and 2-methylimidazole were purchased from Sigma Aldrich. $Zn(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ were purchased from Alfa Aesar. Acetic acid was purchased from Merck Millipore. Inductively coupled plasma mass spectrometry (ICP-MS) was done using an Agilent 7700 Series ICP-MS.

Synthesis of $[Zn(MeIm)_2]_n$ (ZIF-8) crystals. $Zn(NO_3)_2.6H_2O$ (240 mg), 2-methylimidazole (130 mg), polyvinylpyrrolidone (90 mg) and acetic acid (0.1 mL) were added to 40 mL of DMF in a glass bottle. The bottle was capped and placed in an oven at 120 ºC. ZIF-8 crystals with a truncated rhombic dodecahedron habit (about 300-500 μm diameter) were observed after about 3 days. The solvent was decanted and the crystals were washed and stored in ethanol.

Synthesis of $[Co(MeIm)_2]_n$ (ZIF-67) crystals. $Co(NO_3)_2.6H_2O$ (230 mg), 2-methylimidazole (130 mg), polyvinylpyrrolidone (90 mg) and acetic acid (0.1 mL) were added to 40 mL of DMF in a glass bottle. The bottle was capped and placed in an oven at 120 ºC. ZIF-67 crystals with a range of habits (rhombic dodecahedrons and truncated rhombic dodecahedrons, 200-500 μm diameter) were observed after about one week. The solvent was decanted and the crystals were washed and stored in ethanol.

Embedding ZIF-8 crystals in polymer films. ZIF-8 crystals were floated on a water surface and a 10% w/w solution of PMMA in ethyl acetate was layered on top of the water. The ethyl acetate was allowed to evaporate at room temperature in a fume hood and the dried polymer film with embedded ZIF-8 crystals was removed from the water surface after about 24 hours.

Synthesis of Janus ZIF-8/ZIF-67 crystals. $Co(NO_3)_2.6H_2O$ (540 mg), 2-methylimidazole (530 mg) and polyvinylpyrrolidone (90 mg) were dissolved in H_2O (40 mL). The polymer films with embedded ZIF-8 were immersed in the solution and placed in an oven at 80 ºC for 24 hours. The films were then removed from the solution and rinsed with water. The polymer was redissolved in ethyl acetate or acetone. The Janus crystals were collected and rinsed with ethyl acetate and ethanol.

X-Ray Fluorescence Elemental (XRF) Mapping

XRF mapping was performed using a Bruker M4 Tornado Micro X-ray Fluorescence mapping system. The instrument was equipped with a micro-focused Rh source (50 kV, 30 W) and a silicon drift detector. Crystals were placed in a polystyrene petri dish and XRF spectra obtained under vacuum.

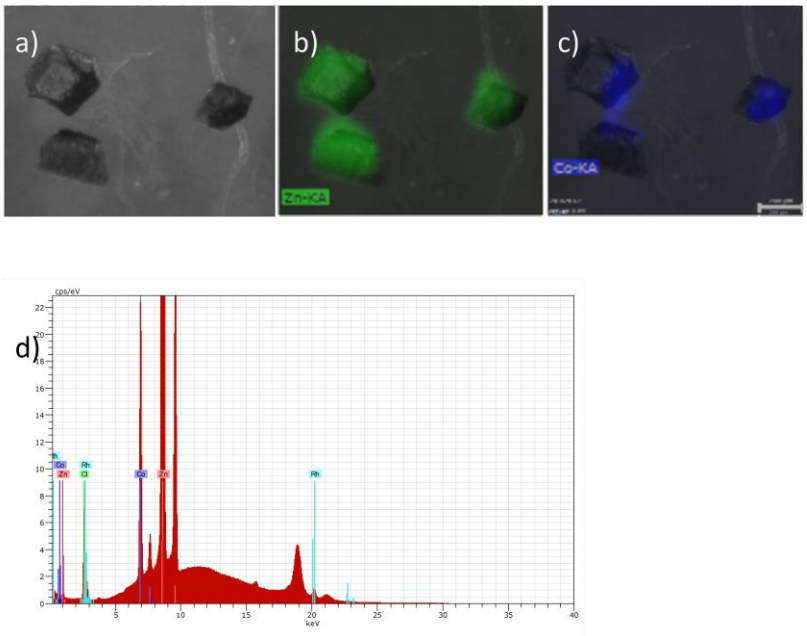

Figure S1: a) Video map, b) Zn map, c) Co map and d) XRF spectra of Janus ZIF-8/ZIF-67 particles

Scanning Electron Microscopy & Energy-dispersive X-ray spectroscopy

Scanning electron Microscopy (SEM) analysis was performed with a JEOL JSM 5600 scanning electron microscope (tungsten source), equipped with an Oxford Link ISIS with an accelerating voltage of 10 to 15 kV. Prior to SEM analysis, samples were sputtered with gold using a JEOL JFC-1200 Fine Coater.

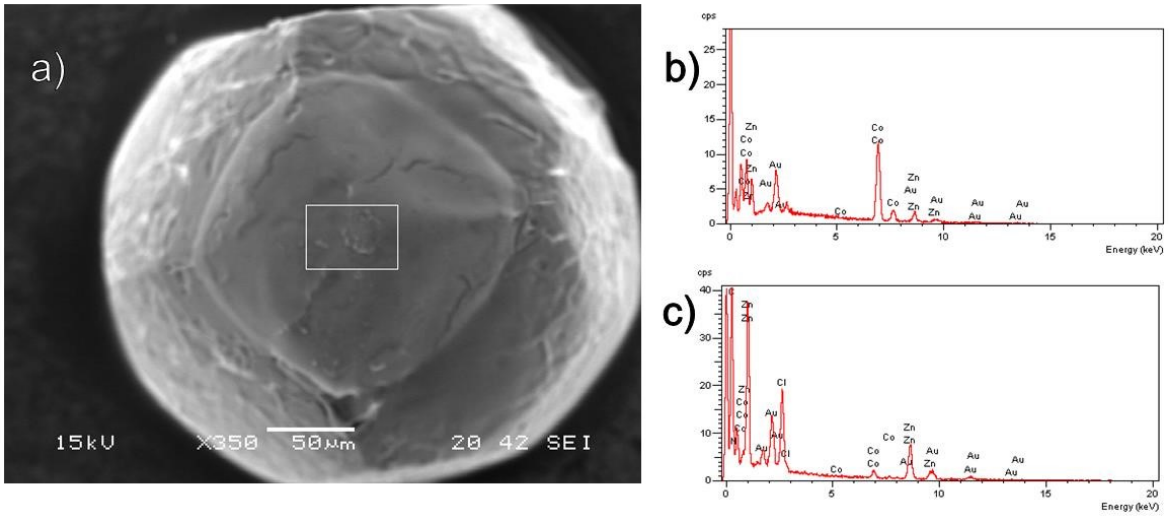

Figure S2: a) SEM image of Janus ZIF-8/ZIF-67 crystal and EDS spectra of b) ZIF-67 region and c) ZIF-8 region.

X-ray Diffraction (XRD)

Single crystal XRD measurements were done on a Bruker APEX II diffractometer by using graphite -monochromated Mo Kα (λ = 0.71073 Å) irradiation.

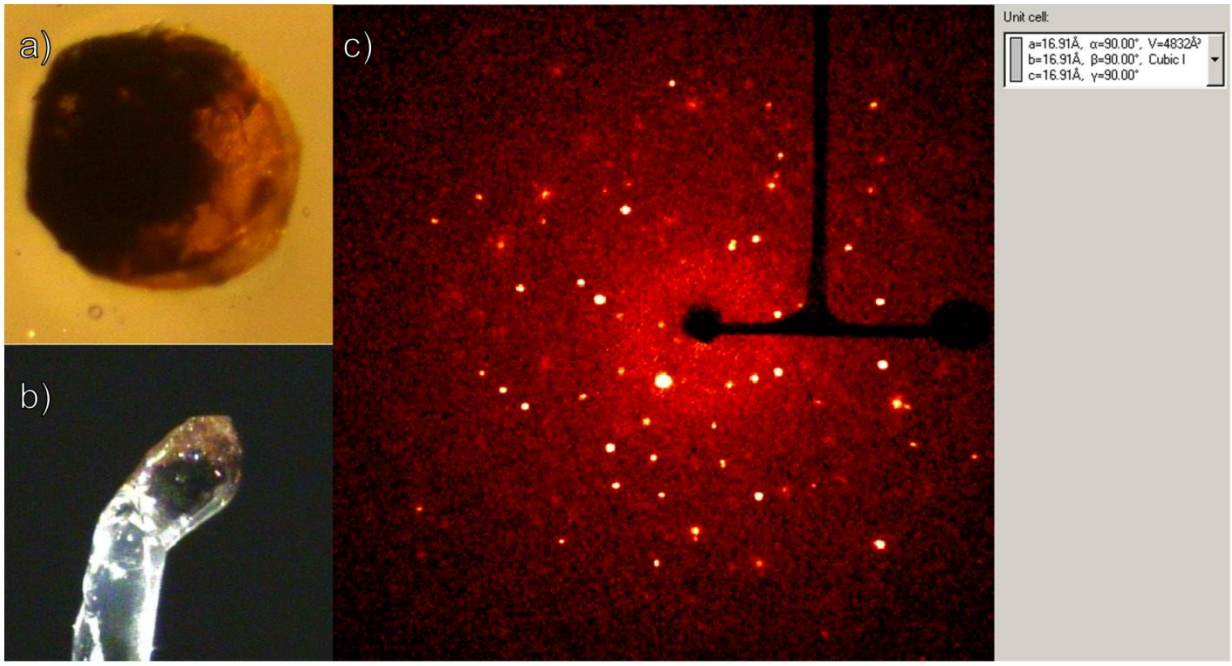

Figure S3. a) Optical microscope image of ZIF-8/ZIF-67 Janus crystal, b) image of crystal mounted on glass fibre during data collection, c) CCD detector images of the reflections of ZIF-8/ZIF-67. The cell parameters of crystal measured matched cell parameters of ZIF-8.[2]

Powder XRD measurements were recorded with a Bruker D8 General Area Detector Diffraction System micro-diffractometer equipped with a VANTEC-2000 area detector with Φ rotation method. The X-ray generated from a sealed Cu tube was monochromated by a graphite crystal and collimated by a 0.5 mm MONOCAP (λ Cu-Kα = 1.54178 Å). The tube voltage and current were 40 kV and 40 mA respectively.

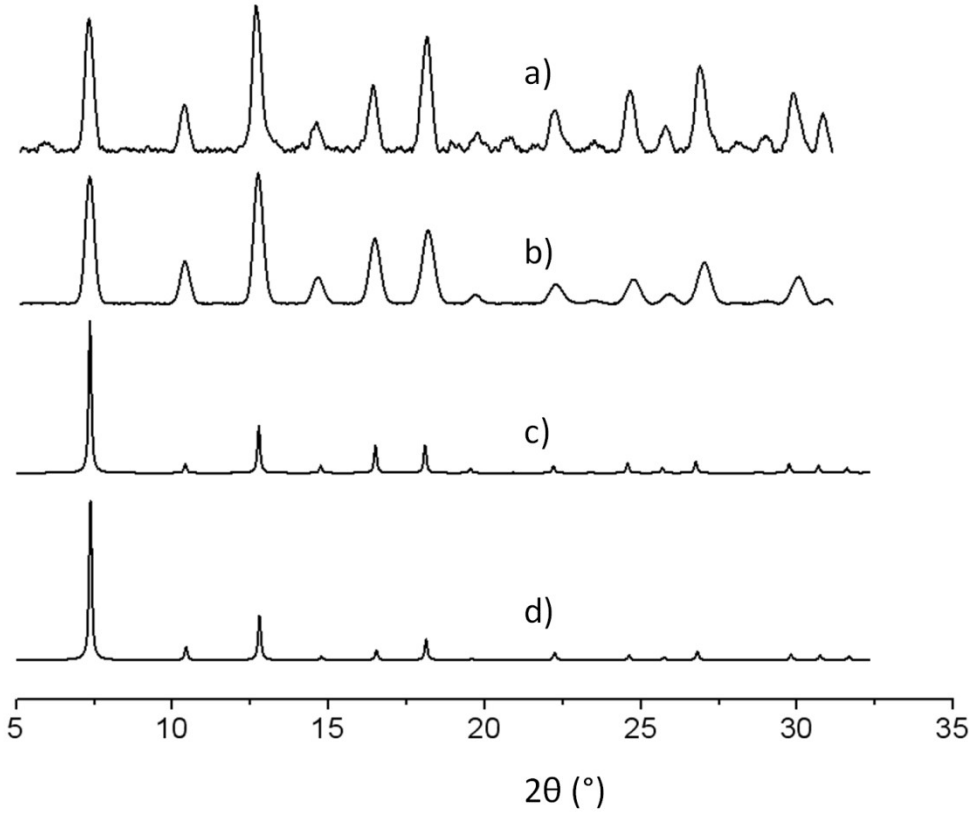

Figure S4. Powder diffraction patterns of a) ZIF-67 powder deposited on polymer films, b) ground up Janus MOF crystals, c) calculated ZIF-8 powder diffraction pattern, [2] d) calculated ZIF-67 powder diffraction pattern.[1]

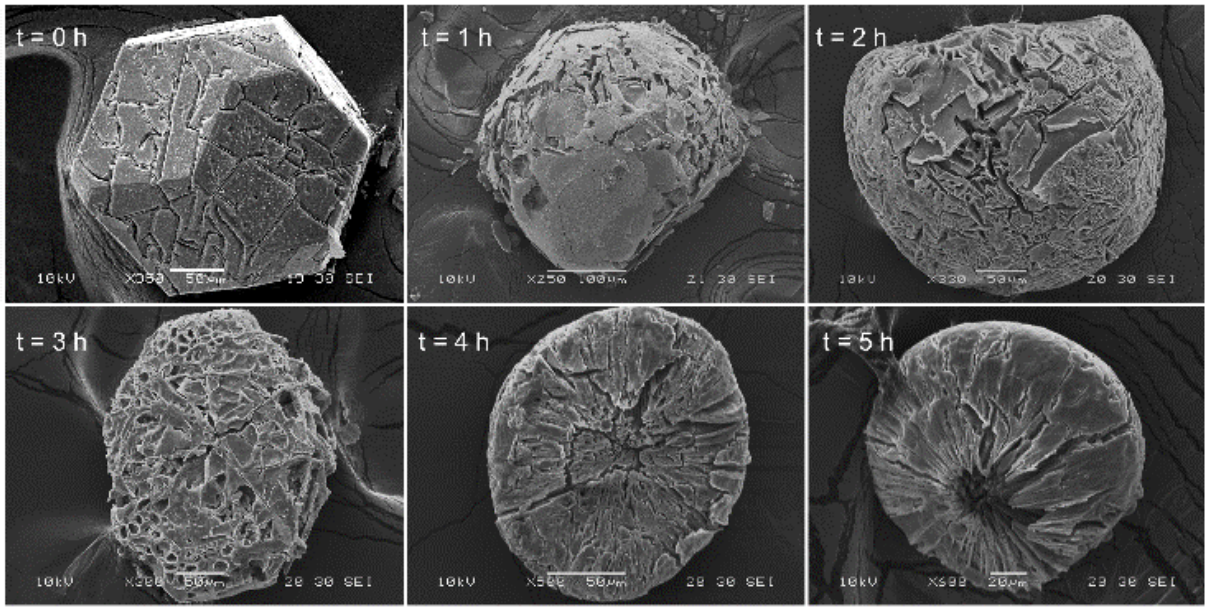

Figure S5. SEM images of representative Janus ZIF-8/ZIF-67 crystals after they have been immersed in 5% H_2O_2 over a 5 hour period.

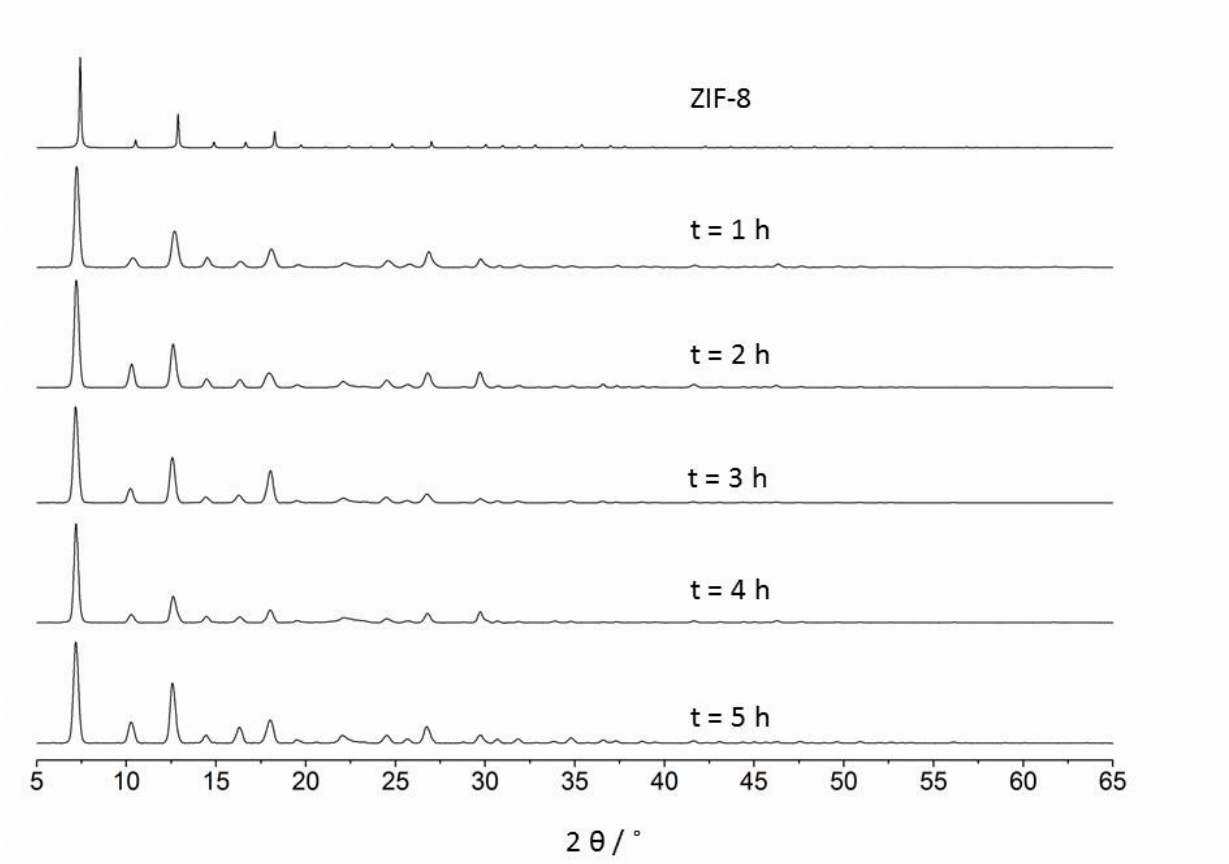

Figure S6: X-ray diffraction patterns of Janus ZIF-8 / ZIF-67 particles that had been placed in 5% H_2O_2 for t = 1 – 5 hours. The bulk crystallinity of the Janus particles appears unchanged over the 5 hour period.

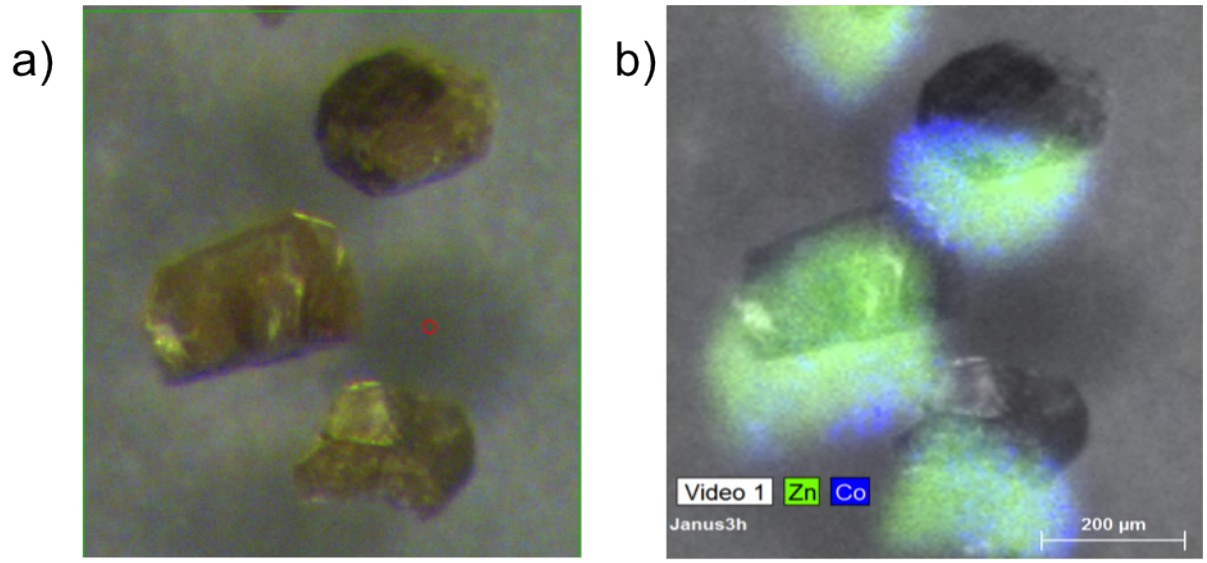

Figure S7: a) Video capture and b) XRF elemental mapping of Janus crystals after soaking in 5% H_2O_2 for 1 hour.

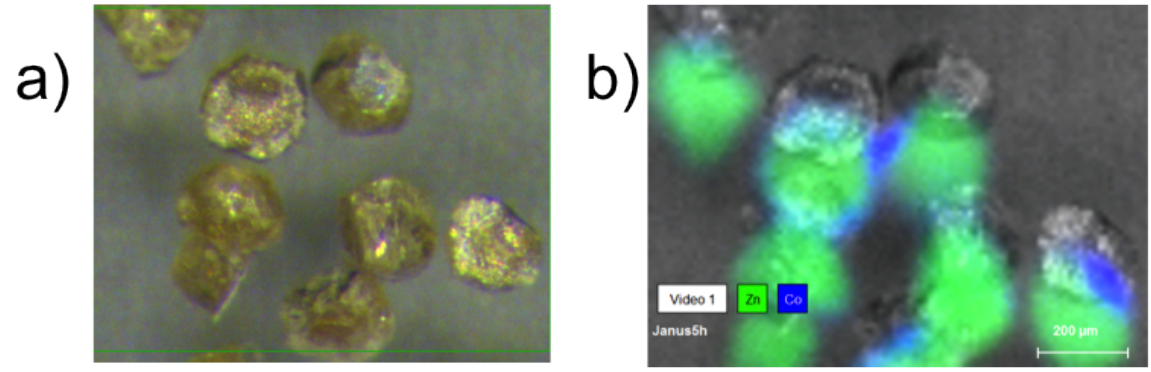

Figure S8: a) Video capture and b) XRF elemental mapping of Janus crystals after soaking in 5% H_2O_2 for 5 hours.

Infrared spectra:

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a Perkin Elmer Spectrometer. MOF crystals were ground with KBr and pelletized for FTIR analysis.

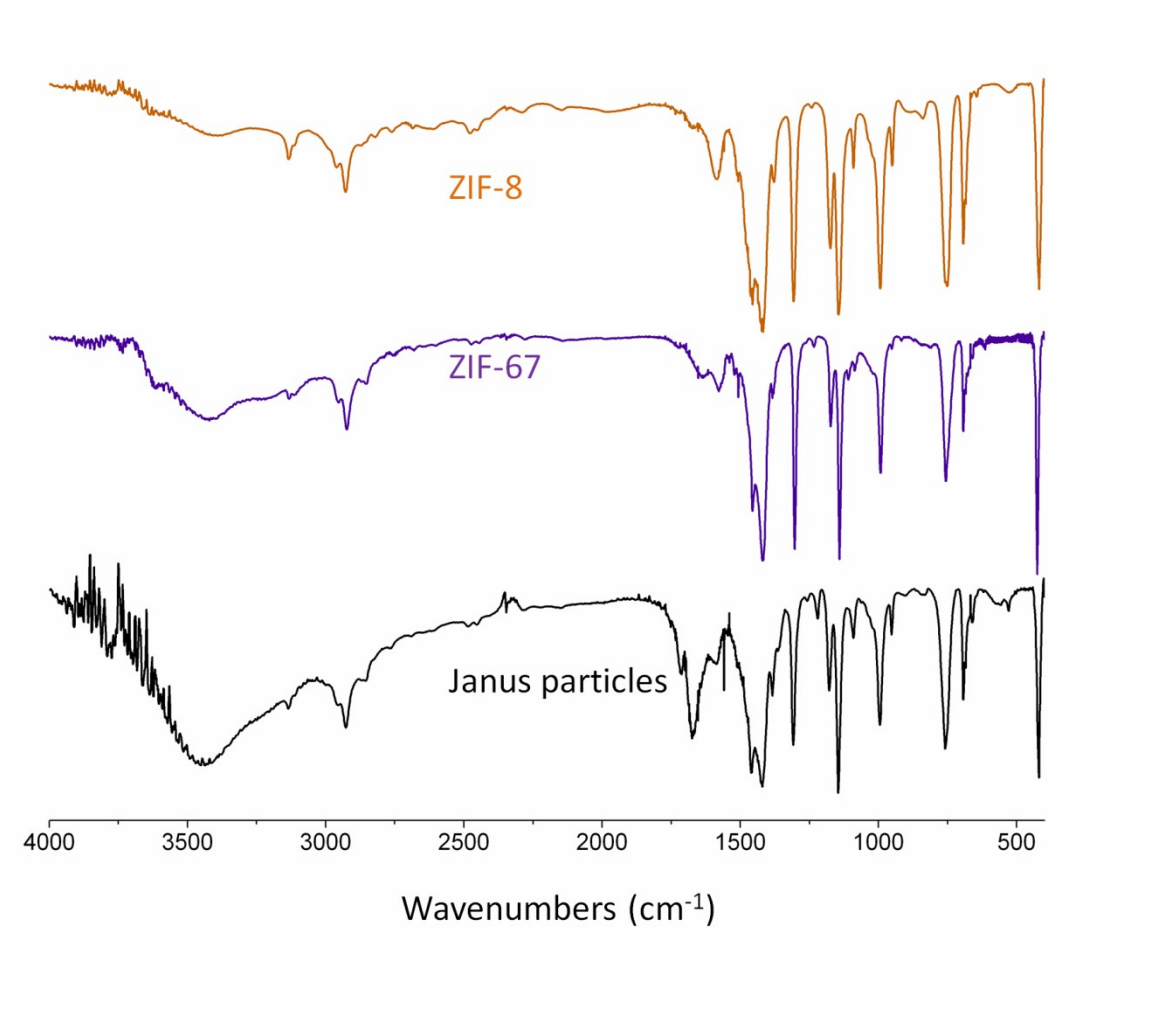

Figure S9: Infrared transmission spectra of ZIF-8, ZIF-67 and Janus ZIF-8/ZIF-67 particles.

References:

[1] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* 2008, *319*, 939.

[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, *Proc. Natl. Acad. Sci. U.S.A.,* 2006, *103*, 10186.