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Supporting Information

Flexible MOF-Aminoclay Nanocomposites Showing Tunable Stepwise/Gated Sorption for C_2H_2, CO_2 and Separation for CO_2/N_2 and CO_2/CH_4

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Materials

All the reagents and solvents employed are commercially available and used as supplied without further purification. $Cu(NO_3)_2{\cdot}2.5H_2O$, 2,3-pyridine dicarboxylic acid, 1,3-bis(4-pyridyl)-propane, 2,5-dihydroxybenzoic acid and 4,4'-bipyridine were obtained from the Aldrich Chemical Co.

Synthesis

Aminoclay: Aminoclay (AC) was prepared following typical reaction conditions reported by Mann and co-workers.[1] 3-aminopropyltriethoxysilane (1.3 mL, 5.85 mmol) was added dropwise to an ethanolic solution of $MgCl_2$ (0.84 g, 3.62 mmol) in ethanol (20 g). The white slurry obtained was stirred overnight and the precipitate was isolated by centrifugation and then was washed with ethanol (50 mL) and dried at 40 °C. PXRD pattern (Figure S1) of the dried compound shows typical reflection corresponding to the d_{001} interlayer spacing of 1.6 nm originating from the bilayer arrangement of propylamine groups.

Bulk F-MOF1: 0.25 mmol of 2,3-pyridine dicarboxylic acid was taken in 10 mL H_2O and pH of the solution was adjusted to 9 by adding 0.1 (M) KOH solution. 0.25 mmol of 1,3-bis(4-pyridyl)-propane was dissolved in 10 mL MeOH and this solution was added to the above solution of 2,3-pyridine dicarboxylic acid and was stirred for ten minutes to prepare the ligand solution. $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.25 mmol) was dissolved in 15 mL water and the ligand solution was dropwise added to the Cu(II) solution. The resulting blue turbid solution was stirred for 6 h and then filtered. The blue solid residue was washed several times with 1:1 H_2O: MeOH solution and was dried to obtain phase pure **F-MOF1** (Figure S2). Yield, 56%, relative to Cu(II). Anal. calc. for $C_{20}H_{27}N_3O_9Cu$: C, 46.46; H, 5.26; N,8.13. Found: C, 46.44; H, 5.22; N, 8.34. Selected

IR data (KBr, cm^{-1}); 3406 br, 1653s, 1616s, 1585s, 1430w, 1351s, 1271w, 1116m, 835m, 526w.

Bulk F-MOF2: 0.8 mmol of 4,4'-bipyridine was dissolved in 10 mL EtOH and a solution of 2,5-dihydroxybenzoic acid (3.2 mmol in 10 mL EtOH) was added to the above solution. The mixture was stirred for ten minutes to prepare the ligand solution. $Cu(NO_3)_2 \cdot 2.5H_2O$ (0.8 mmol) was dissolved in 5 mL water and the ligand solution was slowly added to the Cu(II) solution. The resulting green turbid solution was stirred for 12 h and then filtered. The green solid residue was washed several times with 1:1 H_2O: EtOH solution and was dried to obtain phase pure **F-MOF2** (Figure S3). Yield, 49%, relative to Cu(II). Anal. calc. for $C_{24}H_{14}N_2O_{10}Cu$: C, 52.04; H, 2.55; N,5.06. Found: C, 52.16; H, 2.46; N, 5.04. Selected IR data (KBr, cm^{-1}); 2795m, 1496s, 1385w, 1282w, 1242m, 816s, 650w, 550w.

Reference:

1. A. J. Patil, E. Muthusamy and S. Mann, *Angew. Chem. Int. Ed.*, 2004, **43**, 4928.

Physical Measurements

Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Discover instrument using Cu–Kα radiation. Energy-dispersive X-ray (EDX) analyses were carried out using field emission scanning electron microscope. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) measurements were recorded on Perkin Elmer Optima 7000dv ICP-AES instrument. The scanning electron microscopy images were obtained using a Nova Nanosem 600 FEI field emission scanning electron microscope (FESEM). The samples were prepared by dispersing the sample in MeOH and then dropping 5 μL of the solution onto a small piece of silicon wafer and drying into air. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-3010 transmission electron microscope operating at 200 kV. The samples were prepared in the same way as described above, but the drop cast was made onto a carbon-coated TEM grid. Adsorption isotherms were recorded with the desolvated samples using QUANTACHROME QUADRASORB-SI analyser and AUTOSORB IQ2 instrument. High-pressure CO_2 adsorption isotherm measurements at 298 K and 273 K were carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. The hydrogen used for the high pressure measurements is of scientific/research grade with 99.999% purity. To prepare the desolvated samples, approximately 150 mg of sample was degassed under

10^{-1} pa vacuum for about 8 hours prior to the measurements. The **F-MOF1** and its composites were activated at 80 °C while **F-MOF2** and its composites were activated at 100 °C.

Breakthrough column experiments

Breakthrough experiments were performed using a column (packed with about 200 mg of desolvated samples) of 1 cm long length and 0.3 cm diameter. The sample was first activated (at 100 °C under 10^{-1} pa vacuum for about 8 hours) prior to loading in column. After loading the sample was again activated with the He flow for 30 minutes. CO_2/N_2 (V/V: 0.15:0.85) and CO_2/CH_4 (V/V: 0.5:0.5) streams were passed from the corresponding gas cylinders containing the gas mixtures through the column with He. The flow was continuous and the flow rate was regulated by mass flow controller (MFC). The rate of the flow (He: binary gas mixture = 90: 10) was fixed at 1 mL/min. The gas stream at the outlet of the column was analyzed on-line with a GC.

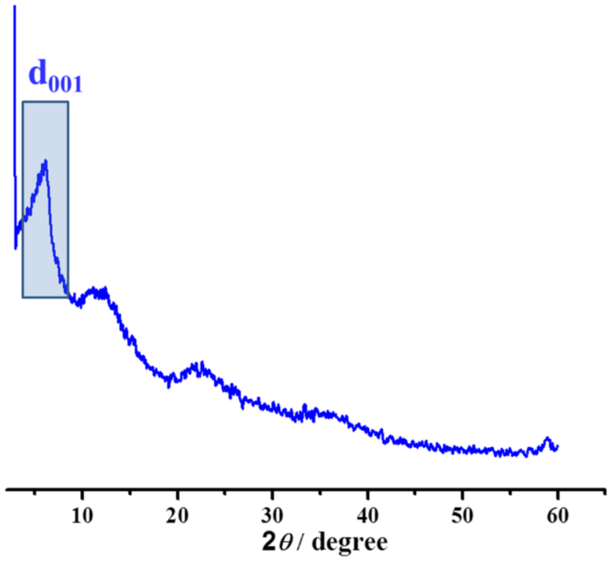

Figure S1. PXRD pattern of aminoclay. The d_{001} peak is highlighted.

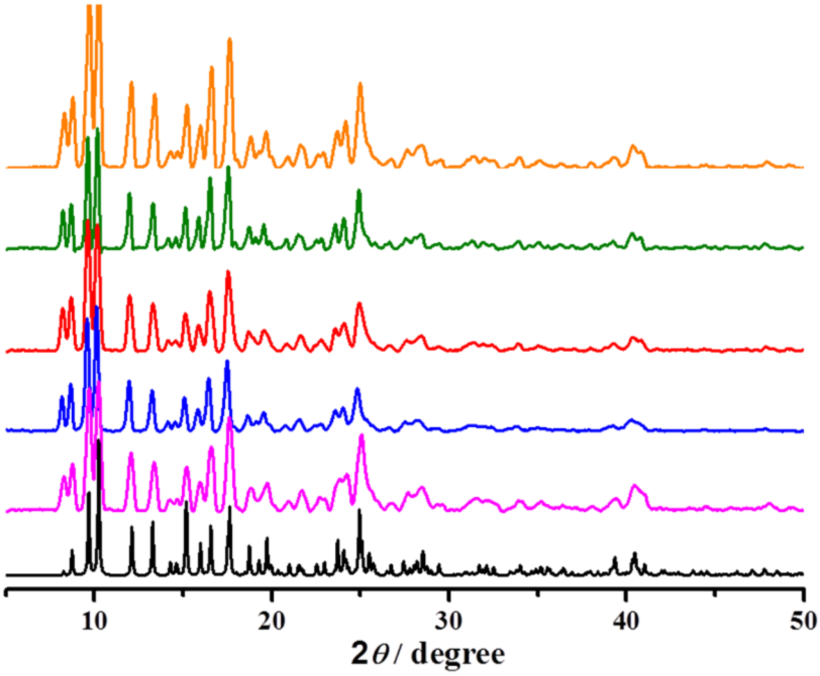

Figure S2. PXRD pattern of simulated (black) and experimental plots of **F-MOF1** (pink) and **F-MOF1@AC-1** (blue), **F-MOF1@AC-2** (red), **F-MOF1@AC-3** (green) and **F-MOF1@AC-4** (orange).

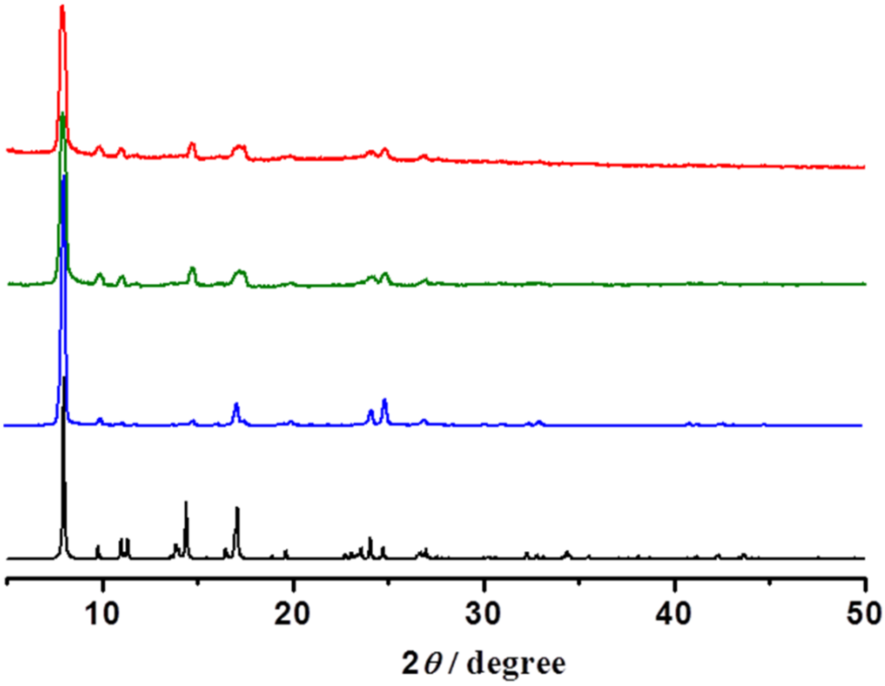

Figure S3. PXRD pattern of simulated (black) and experimental plots of **F-MOF2** (blue) and **F-MOF2@AC-1** (green) and **F-MOF2@AC-2** (red).

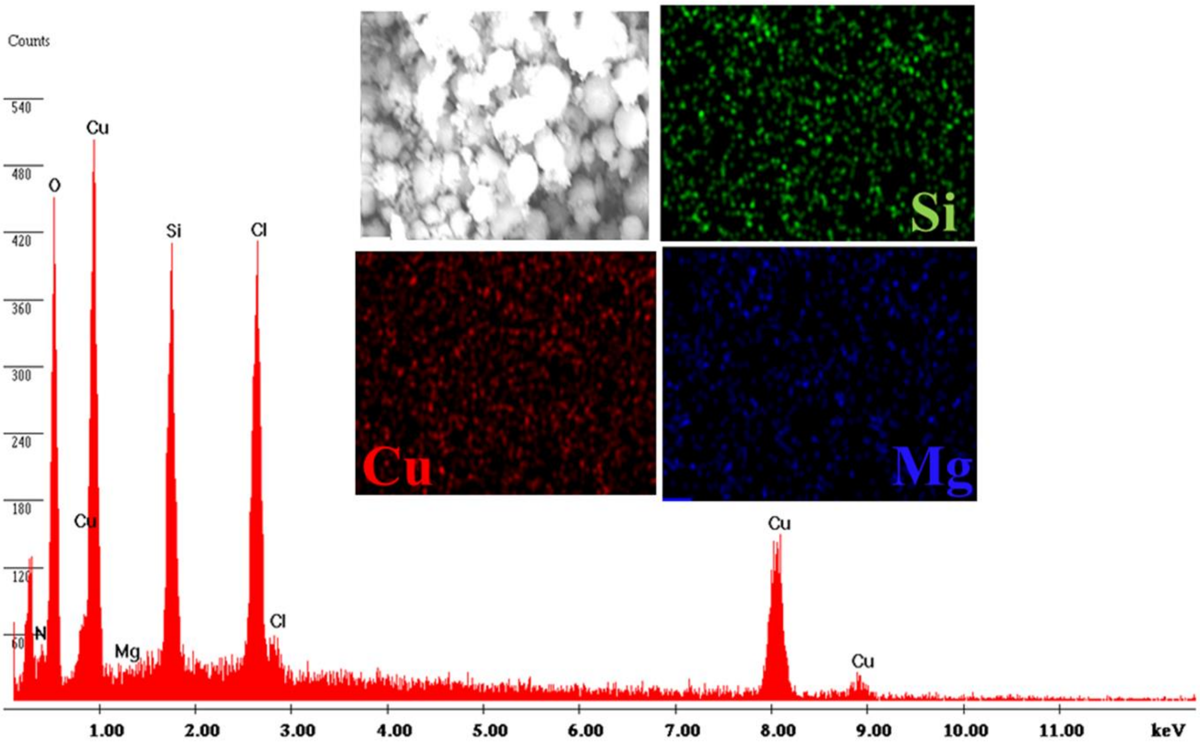

Figure S4. Element mapping of **F-MOF@AC-1** showing phase purity with homogeneous distribution of the elements (Si, Mg and Cu) throughout the sample. The EDX spectrum shows the presence of Cu (from **F-MOF1** component) and Si, Mg (from AC).

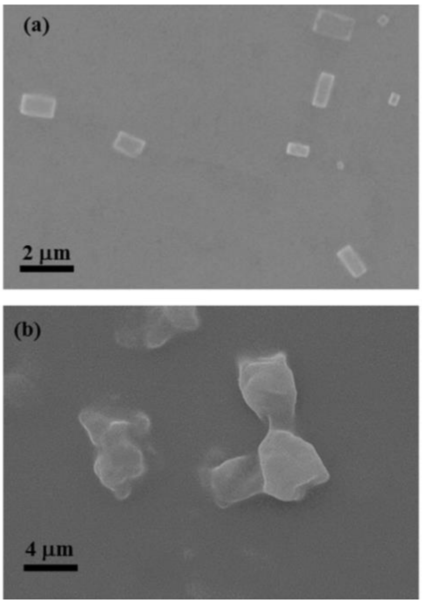

Figure S5. SEM images of (a) as-synthesized bulk **F-MOF1** and (b) AC.

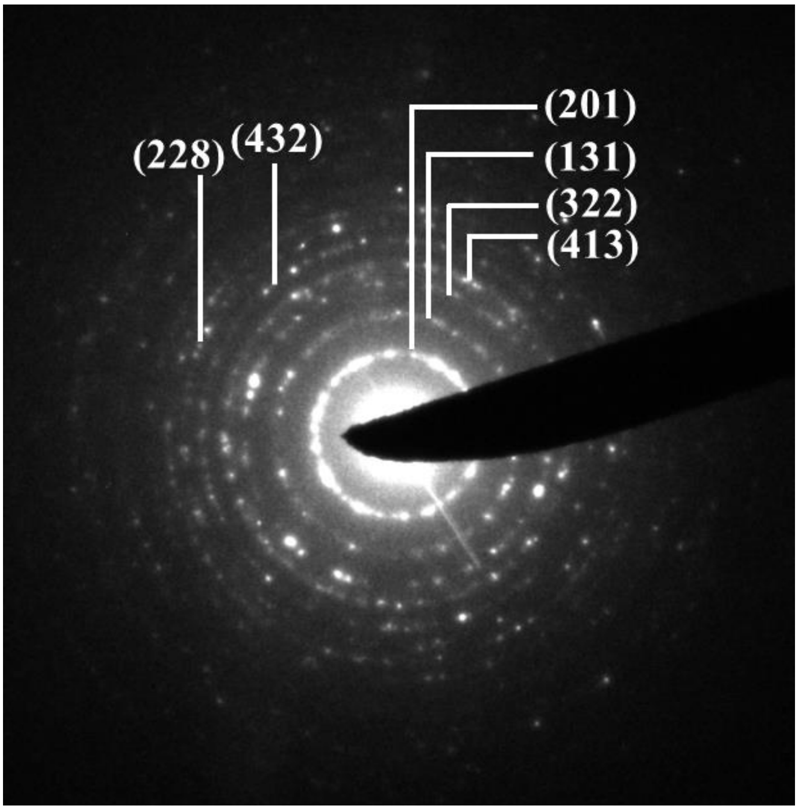

Figure S6. Selected area electron diffraction pattern of **F-MOF1@AC-1**. The d-spacing values were calculated from the spacing between the rings. The corresponding (hkl) values corroborate well with that for F-MOF1.

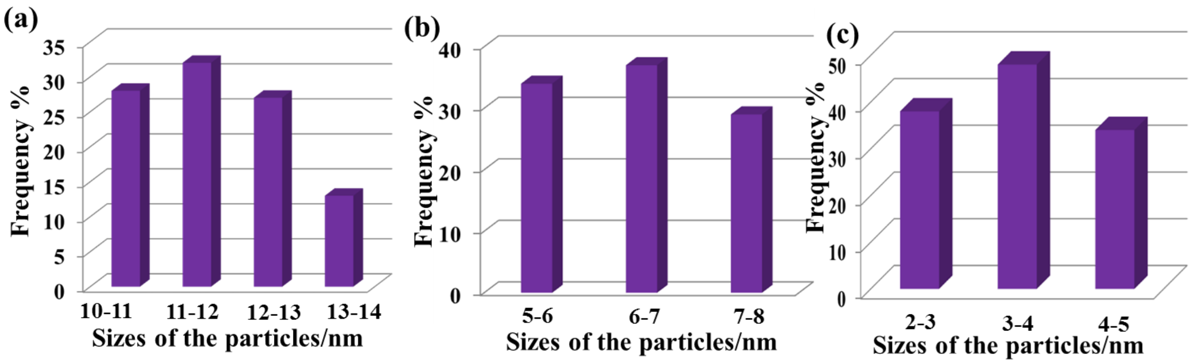

Figure S7. The size distribution histogram plots of (a) **F-MOF1@AC-1**, (b) **F-MOF1@AC-2** and (c) **F-MOF1@AC-3**.

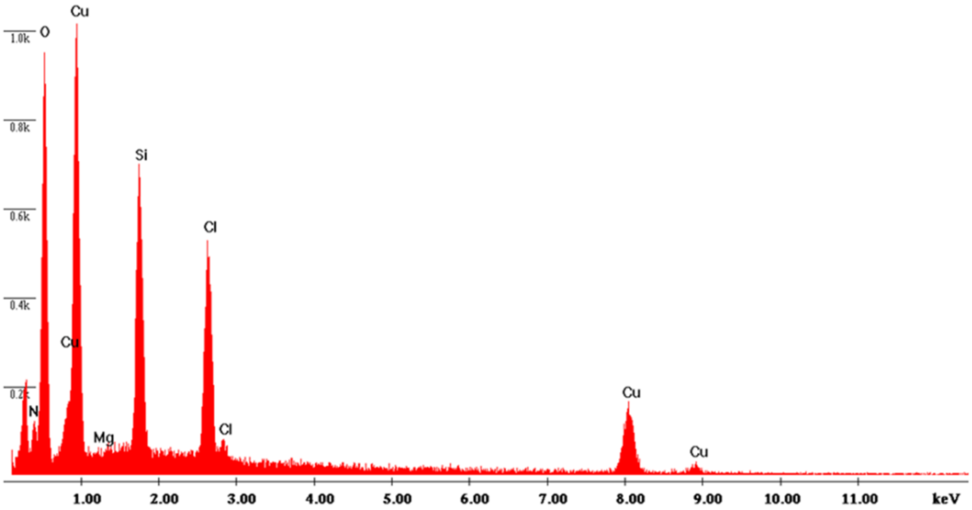

Figure S8. The EDX spectrum of Cu@AC solid showing shows the presence of Si, Mg (from AC) and Cu.

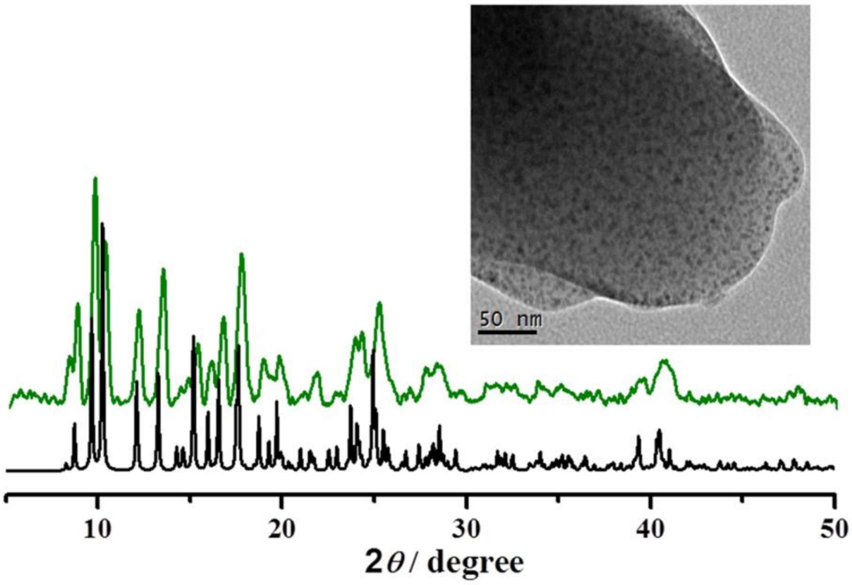

Figure S9. PXRD patterns of simulated **F-MOF1** (black) and the solid (green) obtained from the reaction of Cu@AC and the ligand solution. Inset shows the TEM image.

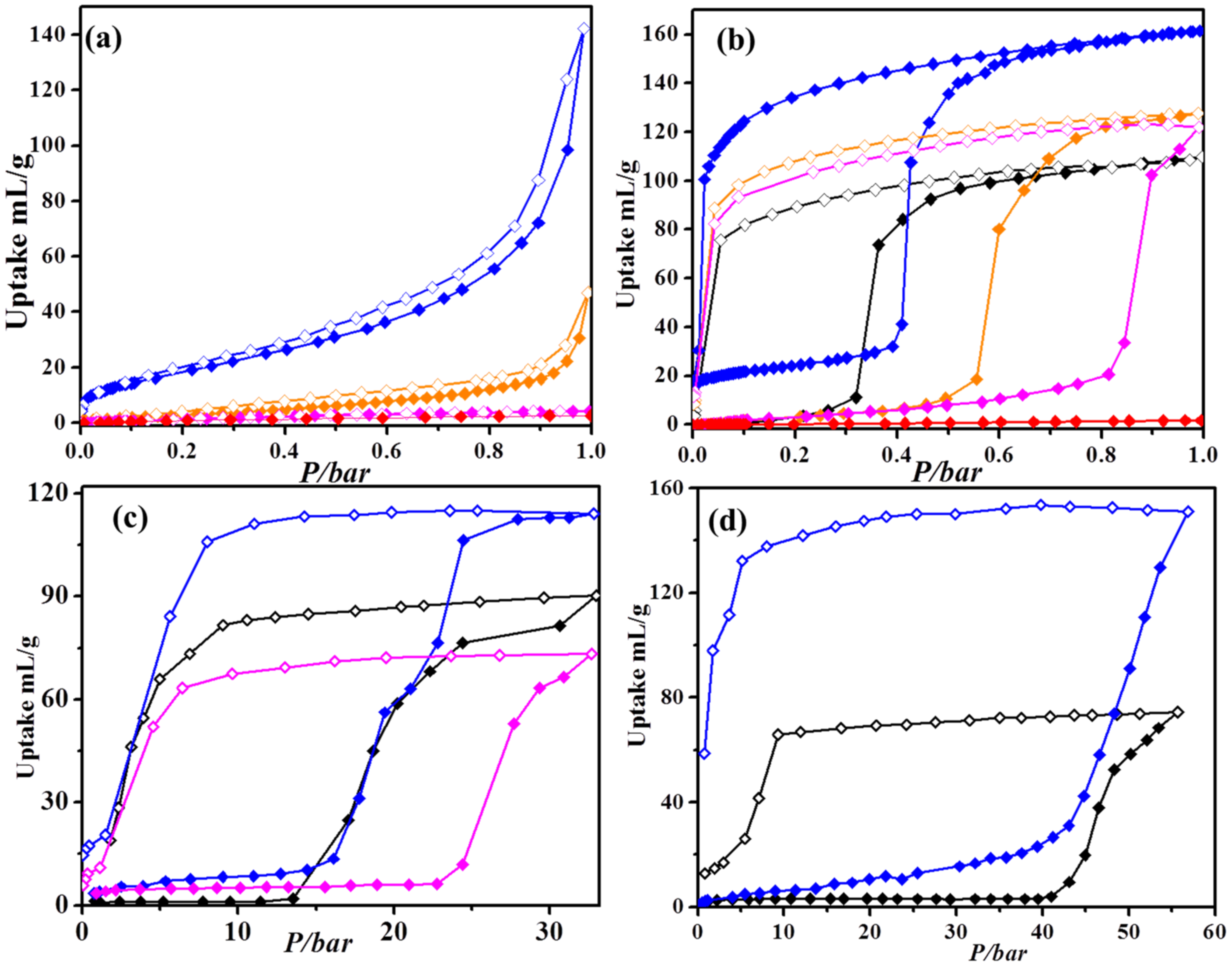

Figure S10. (a) N$_2$ adsorption isotherms at 77 K. (b) CO$_2$ adsorption isotherms at 195 K. High pressure CO$_2$ adsorption isotherms at (c) 273 K and (d) 298 K. Color code: **F-MOF1**: black, AC: red, **F-MOF1@AC-1**: blue, **F-MOF1@AC-2**: orange, **F-MOF1@AC**: magenta. (Open and closed symbol denotes adsorption and desorption respectively). The isotherms for composites represent uptake per gram of the FMOF-1.

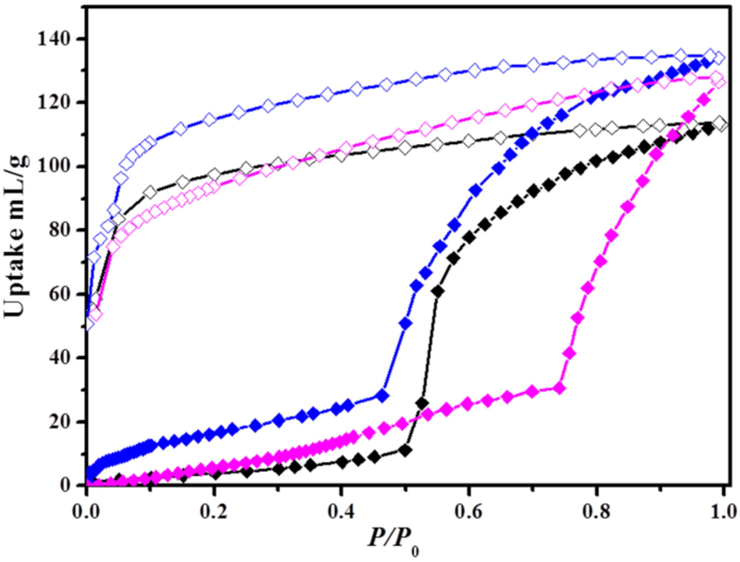

Figure S11. C_2H_2 adsorption isotherms at 195 K. Open and closed symbol denotes adsorption and desorption respectively. Color code: activated **F-MOF1** (black), **F-MOF1@AC-1** (blue), and **F-MOF1@AC-3** (pink). The isotherms for composites represent uptake per gram of the F-MOF1.

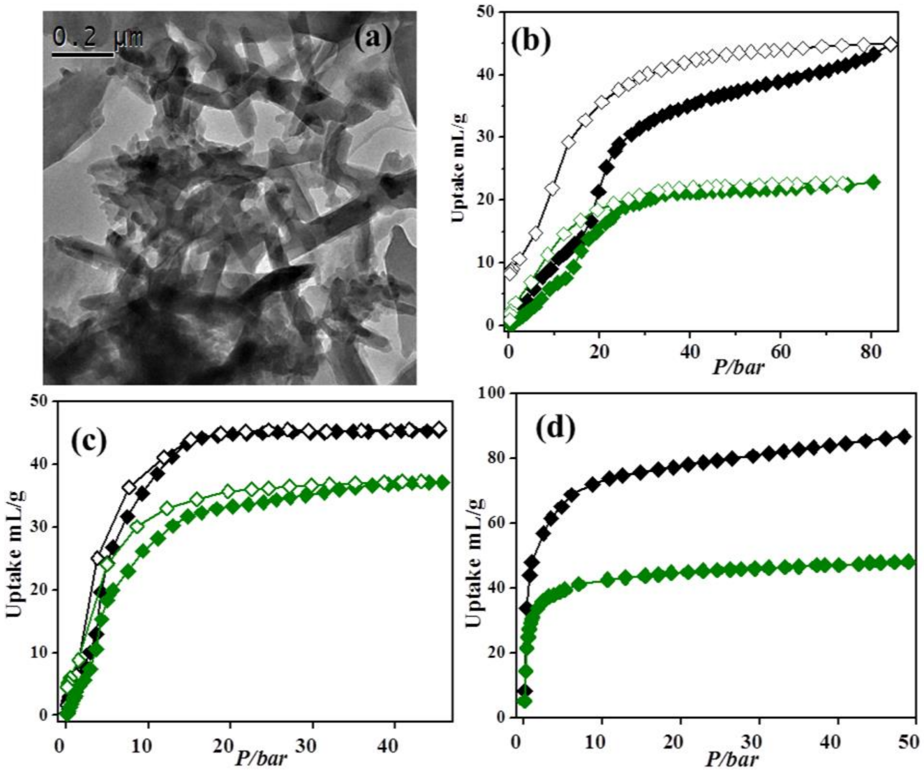

Figure S12. (a) TEM images of **F-MOF2@AC-2.** High-pressure isotherms at 298 K for (b) N_2 (c) CH_4 and (d) CO_2 adsorption. Color code of activated samples: **F-MOF2** (black) and **F-MOF2@AC-2** (green). Open and closed symbol denotes adsorption and desorption respectively. The isotherms for composites represent uptake per gram of the respective composite.

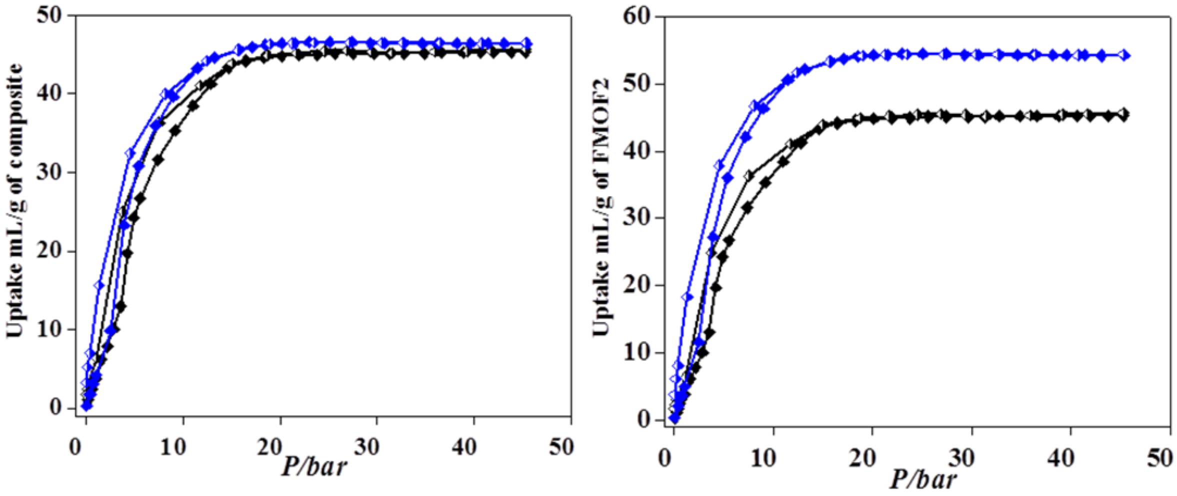

Figure S13. High-pressure CH_4 adsorption isotherms at 298 K. Color code: activated **F-MOF2** (black) and **F-MOF2@AC-1** (blue). Left and right: The isotherms for the composite represent uptake per gram of the composite and F-MOF2, respectively.