

Supporting Information

In situ Growth of Self-assembled ZIF-8-Aminoclay Nanocomposites with Enhanced Surface Area and CO₂ Uptake

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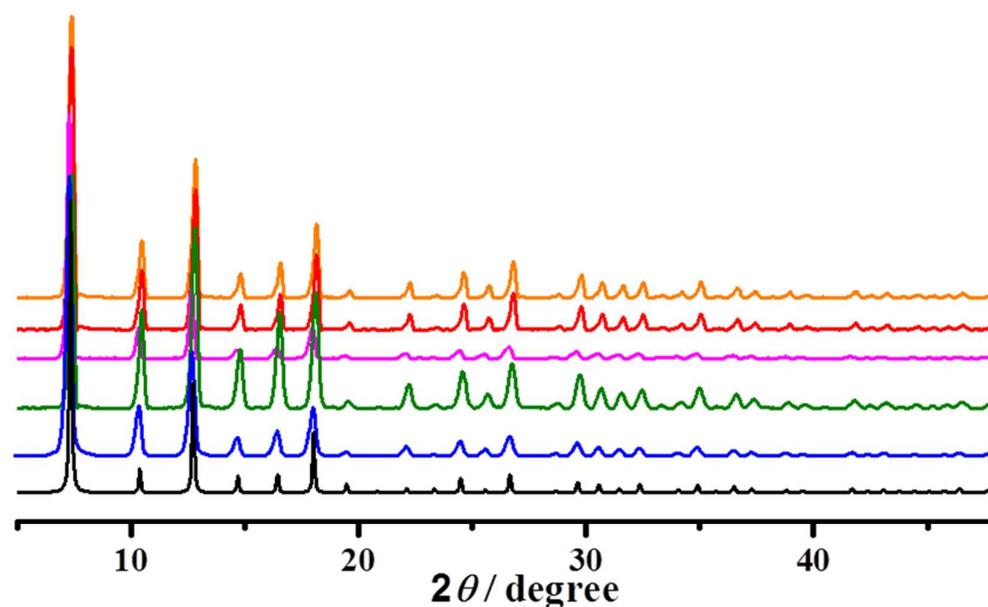


Figure S1. PXRD patterns of simulated plot (black) of ZIF-8, and experimental plots of ZIF-8 NP (blue), ZIF-8@AC-1 (green), ZIF-8@AC-2 (pink), ZIF-8@AC-3 (red) and ZIF-8@AC-4 (orange).

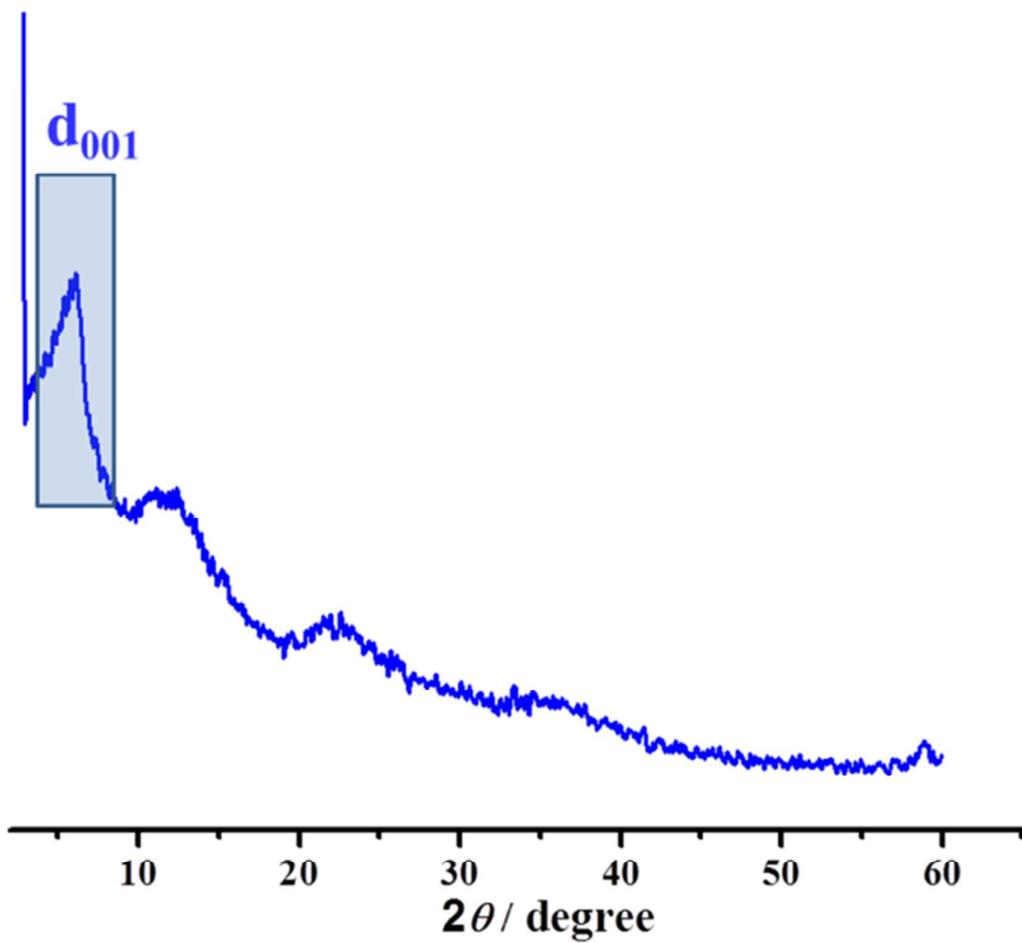


Figure S2. PXRD pattern of AC. The d_{001} peak is highlighted.

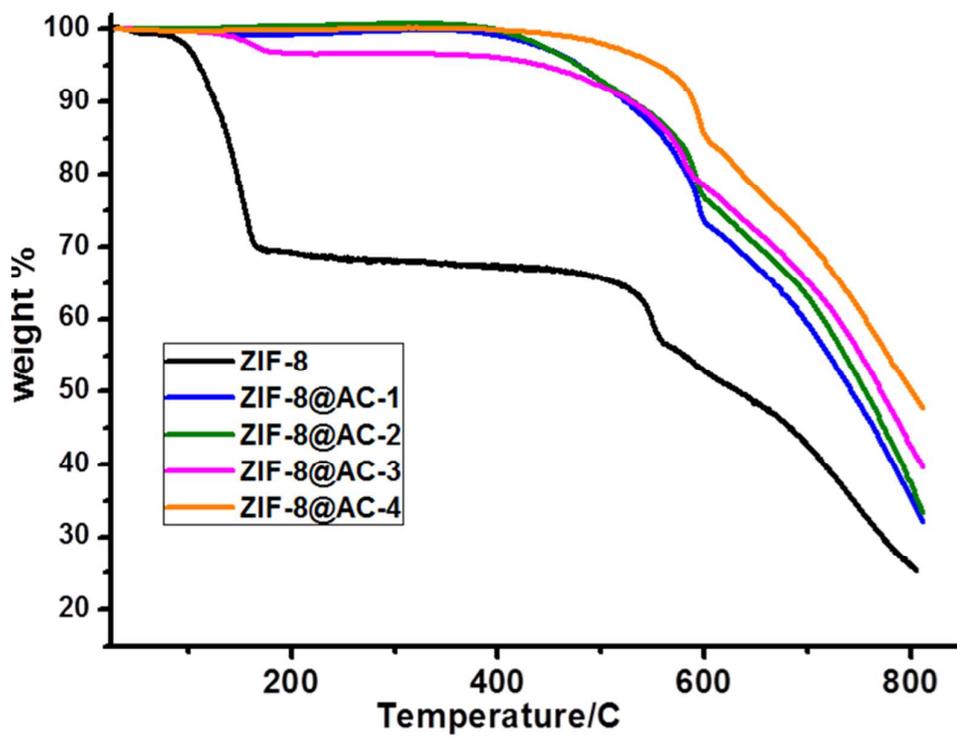


Figure S3. TGA profiles of pristine ZIF-8, ZIF-8@AC-1, ZIF-8@AC-2, ZIF-8@AC-3 and ZIF-8@AC-4.

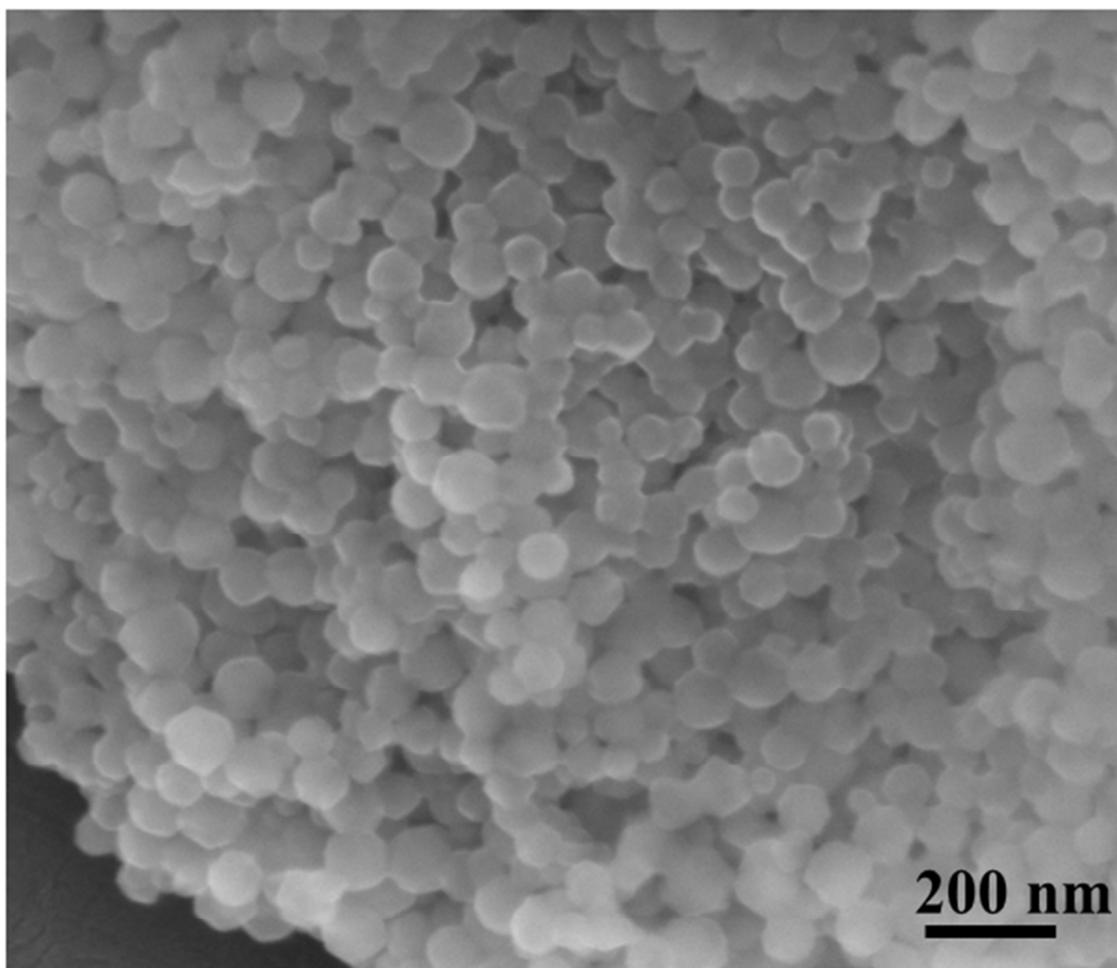
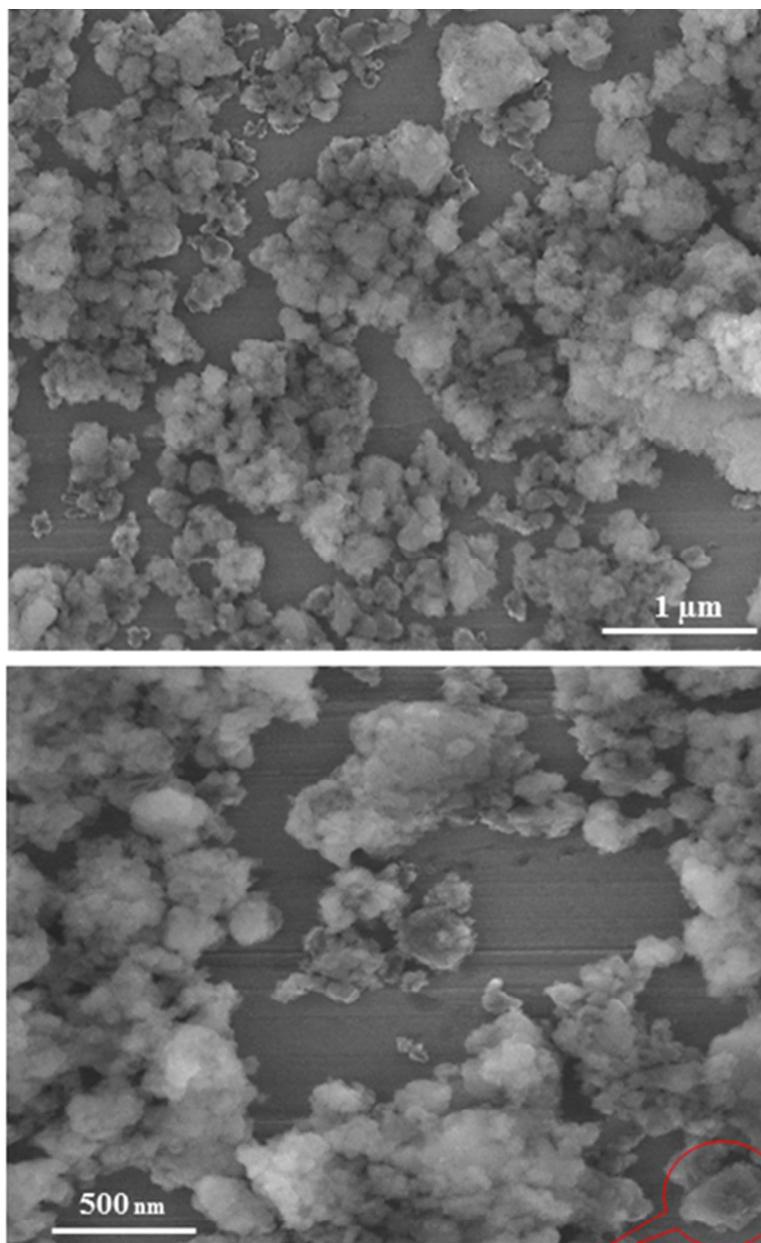


Figure S4. SEM image of the pristine nanosized ZIF-8.



Layered sheets of AC

Figure S5. FESEM image of the pristine aminoclay. A layered sheet-like structure has been highlighted.

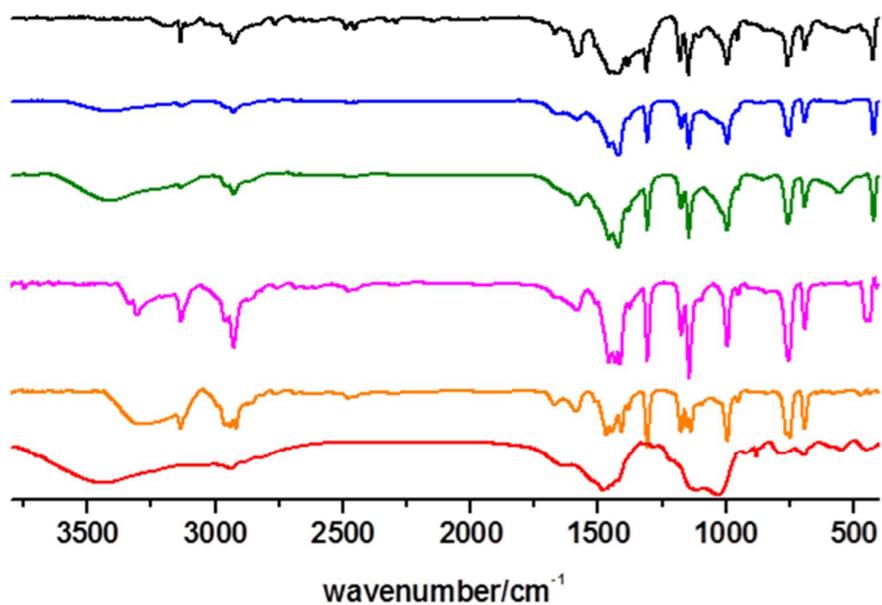


Figure S6. IR spectra of ZIF-8 (black), AC (red), ZIF-8@AC-1 (blue), ZIF-8@AC-2 (green), ZIF-8@AC-3 (magenta) and ZIF-8@AC-4 (orange).

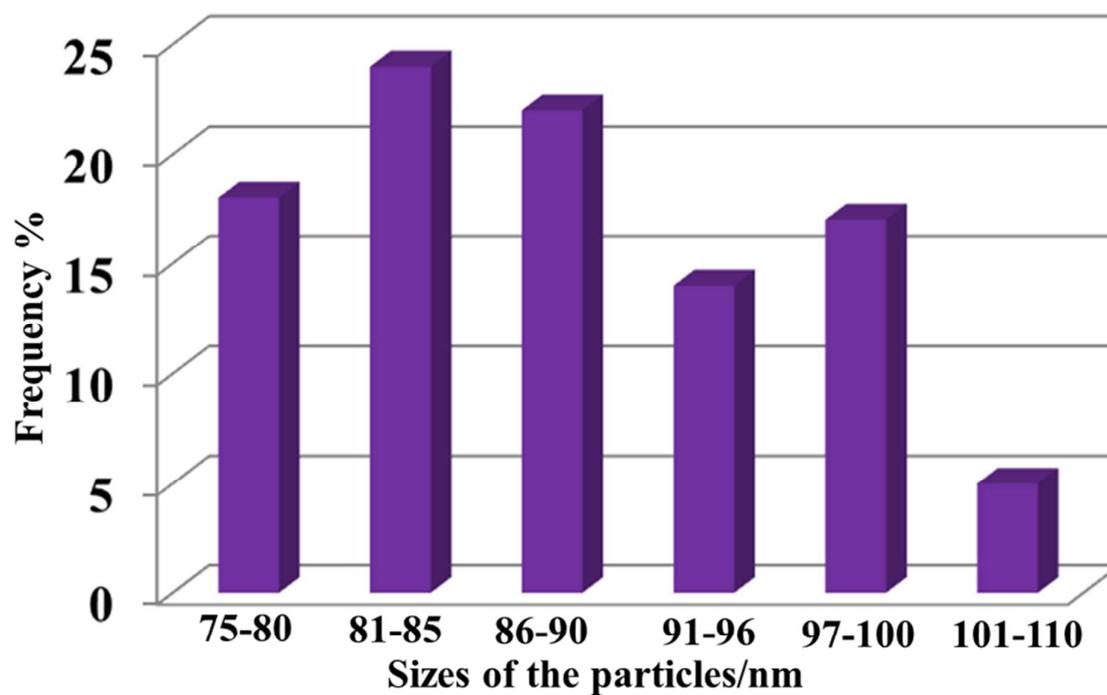


Figure S7. The size distribution histogram plots of ZIF-8@AC-1.

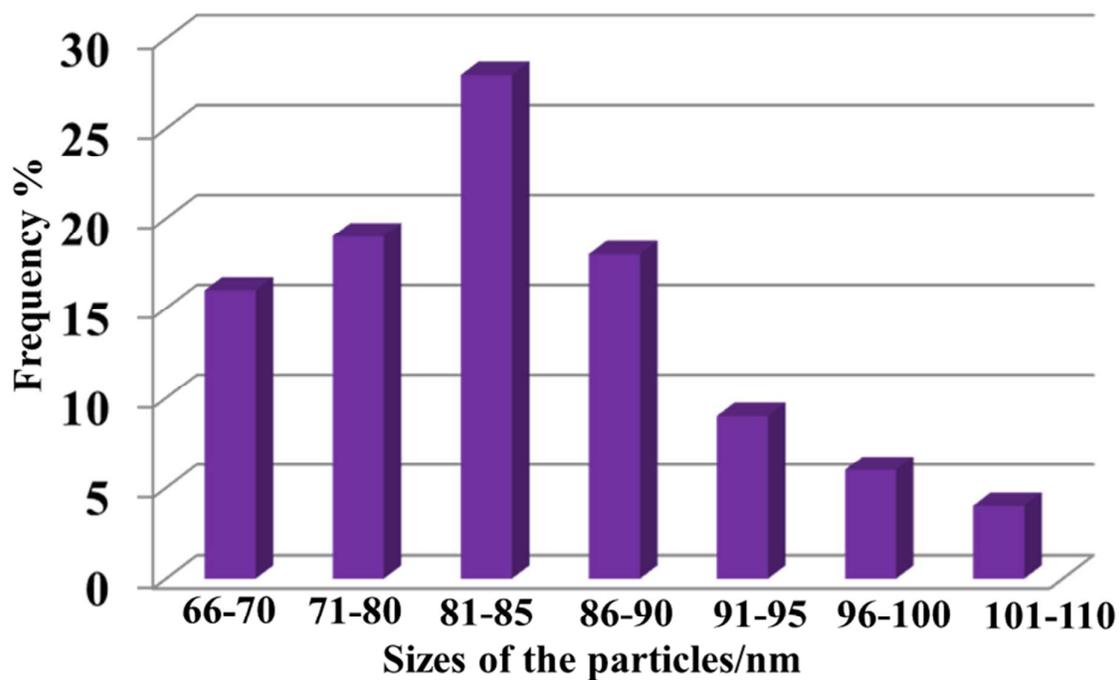


Figure S8. The size distribution histogram plots of ZIF-8@AC-2.

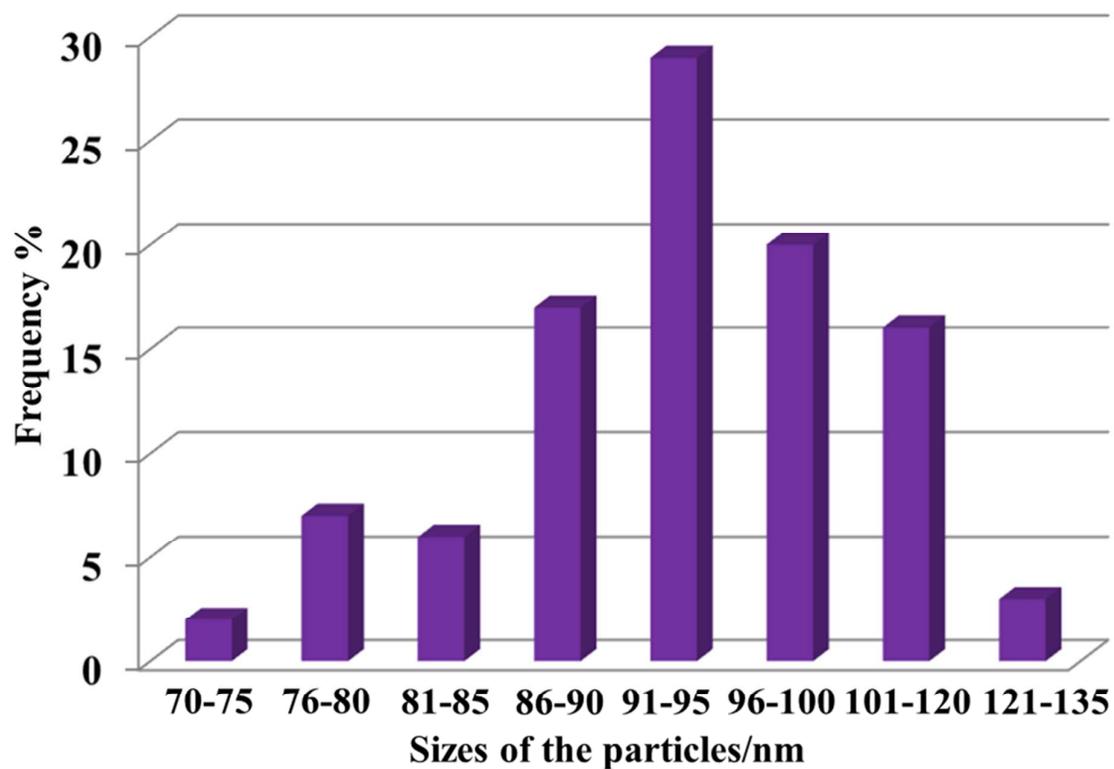


Figure S9. The size distribution histogram plots of ZIF-8@AC-3.

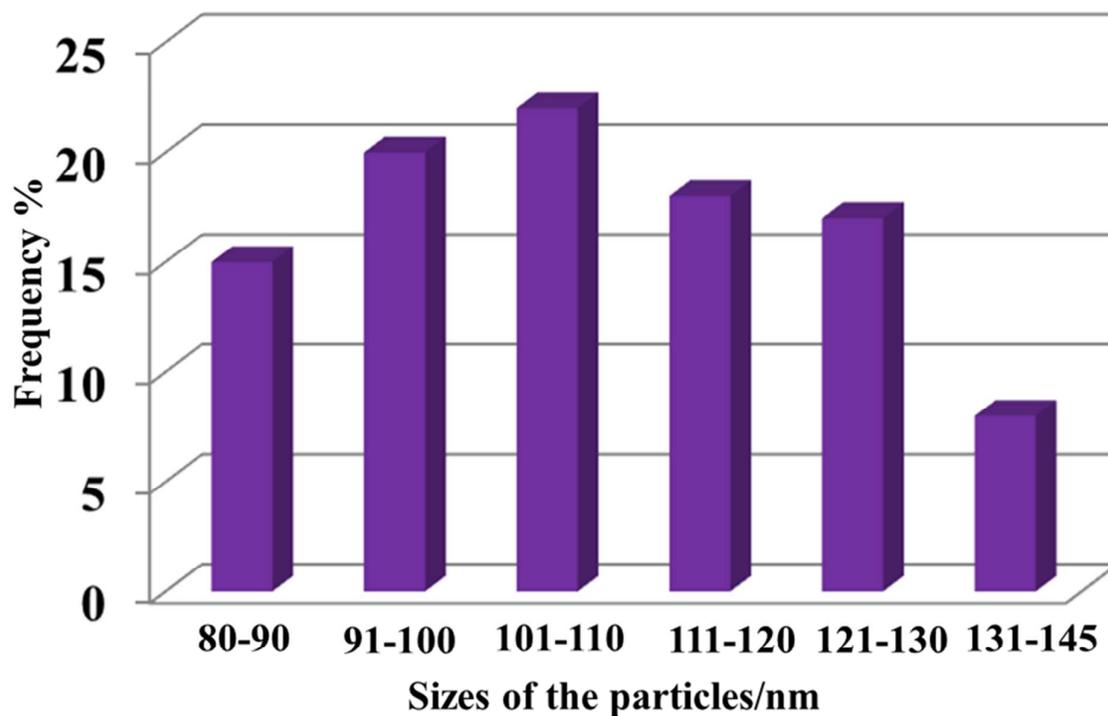


Figure S10. The size distribution histogram plots of ZIF-8@AC-4.

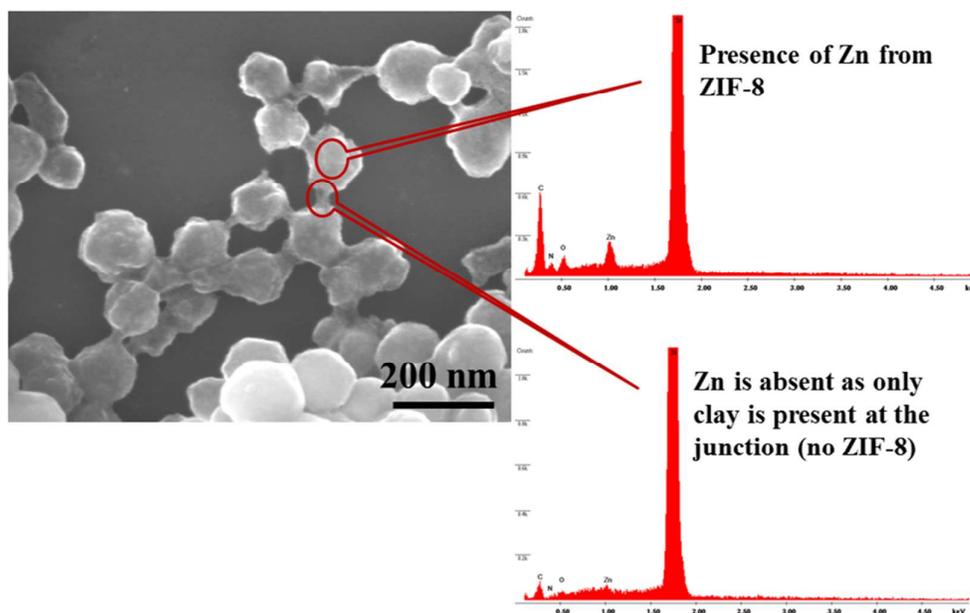


Figure S11. FESEM image and EDX study on ZIF-8@AC-3. Point EDX study on a specific particle shows presence of both Zn (from ZIF-8) and Si (from aminoclay); while a junction contains only Si and no Zn was found.

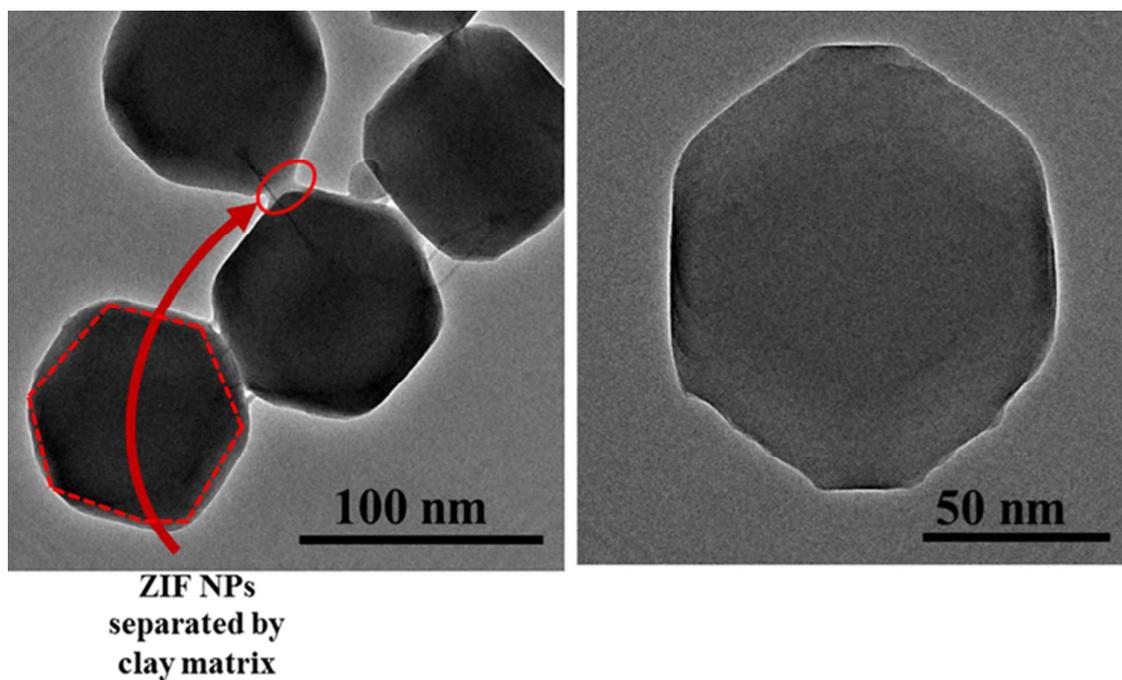


Figure S12. TEM images of **ZIF-8@AC-1**. A ZIF-8 NP with darker contrast has been highlighted. The NPs are separated by aminoclay matrix. Right: A single nanoparticle has been shown. The clay layers are visible at the edges of the particle.

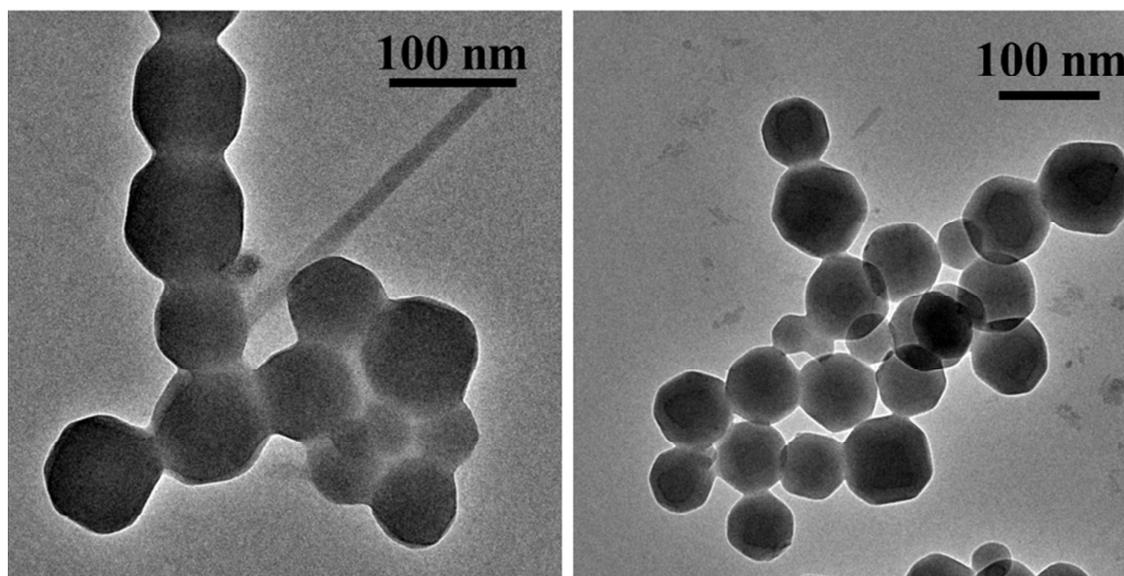


Figure S13. TEM images of **ZIF-8@AC-2**.

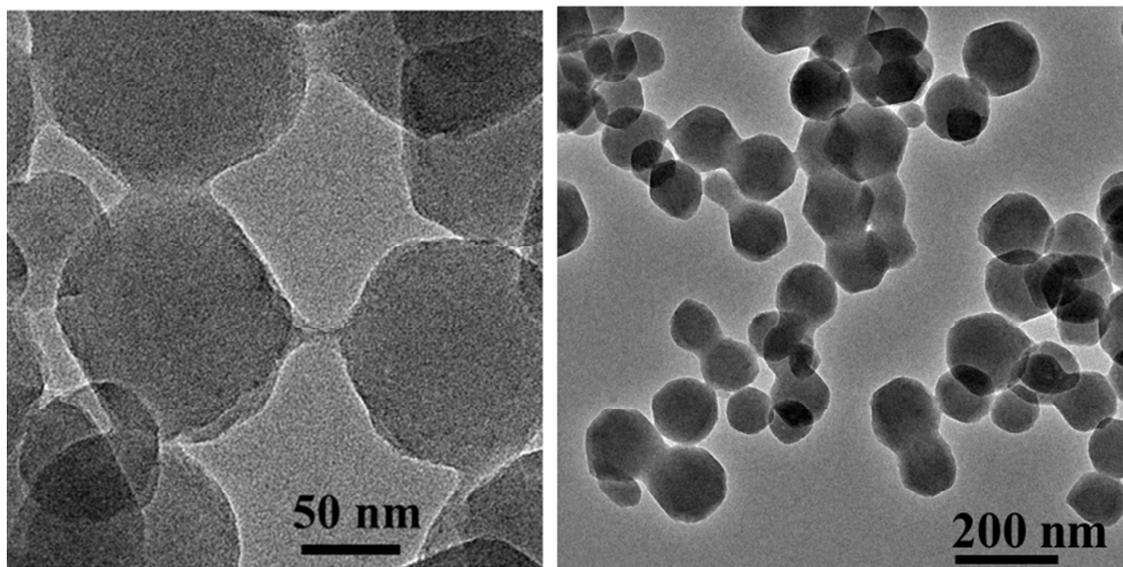


Figure S14. TEM images of ZIF-8@AC-3.

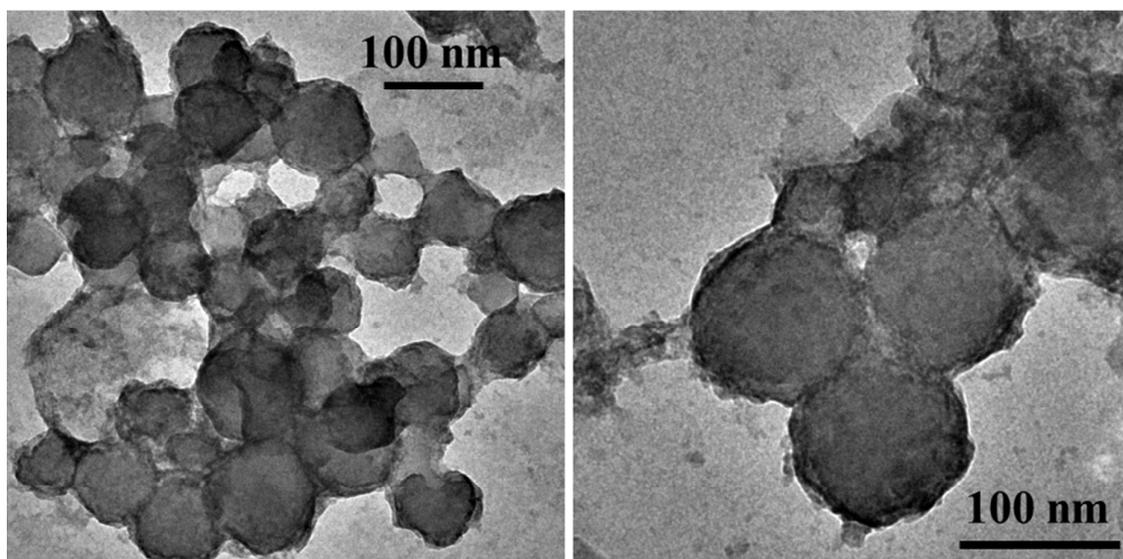


Figure S15. TEM images of ZIF-8@AC-4.

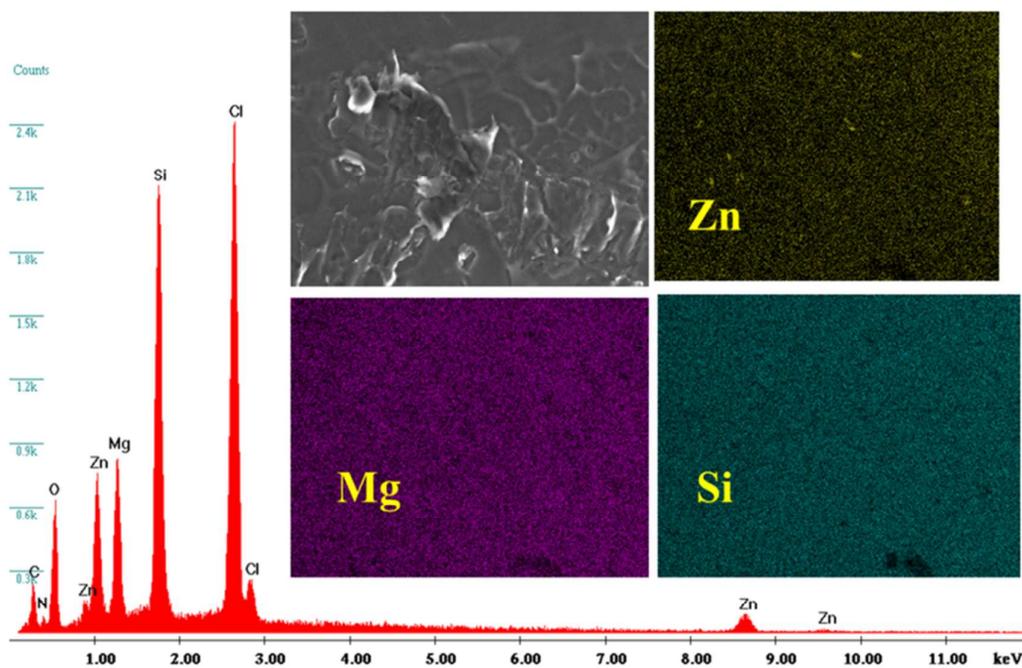


Figure S16. EDX spectrum of the Zn@AC solid showing the presence of Zn. Inset shows elemental mapping showing the homogeneous distribution of the elements (Zn, Mg and Si) throughout the sample.

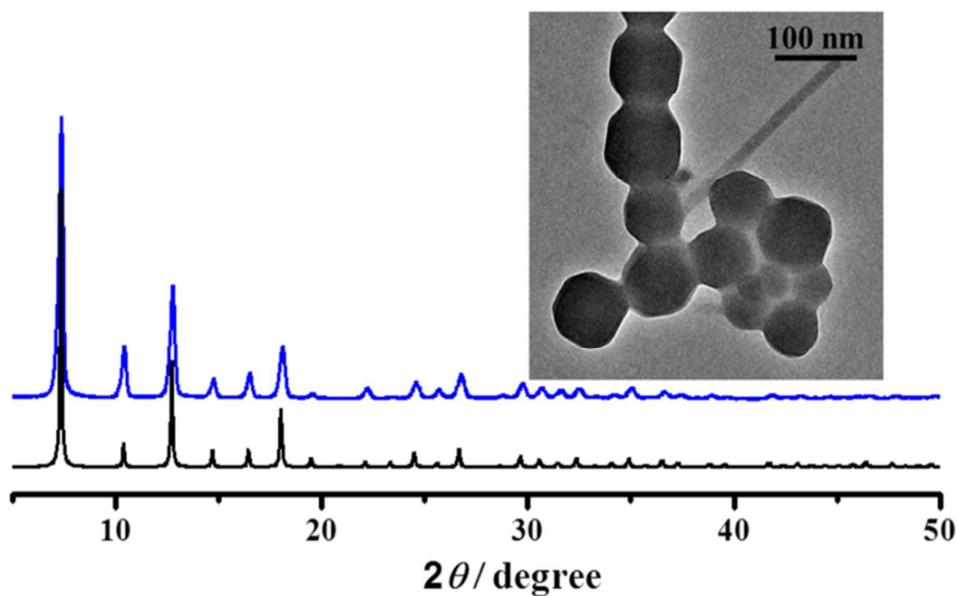


Figure S17. PXRD patterns of simulated ZIF-8 (black) and the solid (blue) obtained from the reaction of Zn@AC and 2-methylimidazole. Inset shows the TEM image.

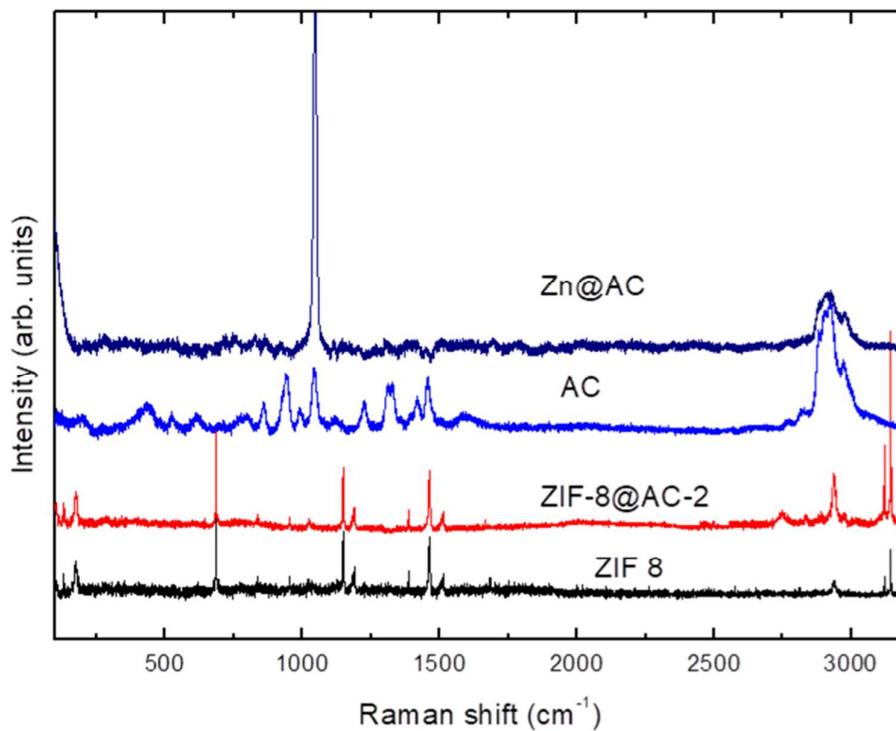


Figure S18. Raman spectra of ZIF-8, **ZIF-8@AC-2**, pristine AC and Zn@AC from 100-3200 cm⁻¹.

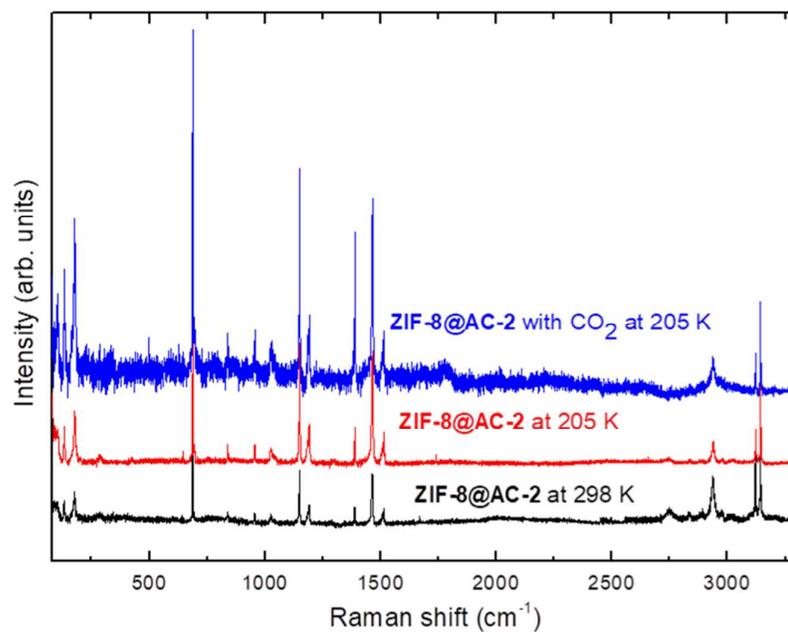


Figure S19. Raman spectra of **ZIF-8@AC-2** at 298 K, **ZIF-8@AC-2** at 205 K and **ZIF-8@AC-2** with CO₂ at 205 K.

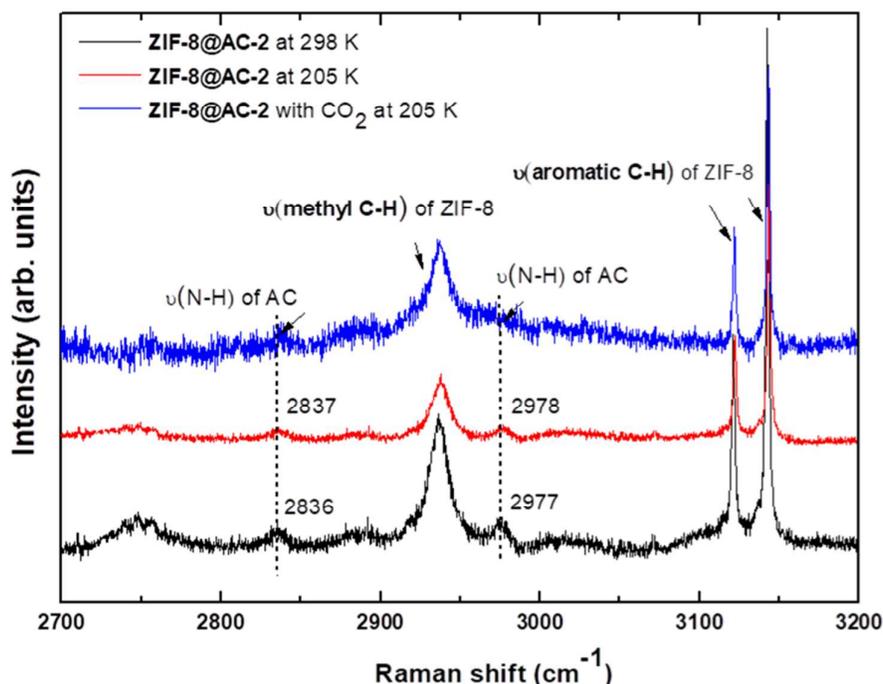


Figure S20. Raman spectra of **ZIF-8@AC-2** at 298 K, **ZIF-8@AC-2** at 205 K and **ZIF-8@AC-2** with CO₂ at 205 K from 2700-3200 cm⁻¹.

Details of methods to calculate surface area, pore volume and pore size

The surface area, pore volume and pore size distribution were calculated from the N₂ adsorption data of the corresponding samples using the ASiQwin software. The surface area was calculated using the Brunauer–Emmett–Teller (BET) theory, which is an extension of the Langmuir theory (monolayer adsorption), to multilayer adsorption.¹⁸ Following are some important hypotheses of BET theory:

1. Physical adsorption of gas molecules occurs on a solid in layers infinitely.
2. No interaction between each adsorption layer is considered.
3. The Langmuir theory can be applied to each layer.

The BET equation is:

$$\frac{1}{v \left[\left(\frac{P_0}{P} \right) - 1 \right]} = \frac{c - 1}{v_m c} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c}$$

P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity, and v_m is the monolayer adsorbed gas quantity, c is the BET constant and can be expressed as:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction.

The BET equation is an adsorption isotherm and can be plotted as a straight line with $1/[v(P_0/P)-1]$ on the y-axis and P/P_0 on the x-axis according to the experimental N_2 isotherms. The value of the slope and the y-intercept of the straight line can be used to calculate the monolayer adsorbed gas quantity (v_m) and the BET constant. The total surface area S_{total} and the specific surface area S_{BET} are given by:

$$S_{total} = (v_m N s)/V$$

$$S_{BET} = S_{total}/a$$

where N is Avogadro's number, s is the adsorption cross section of the adsorbing species, V is the molar volume of the adsorbate gas (N_2), and a is the mass of the solid adsorbent. We calculated the multi-point BET surface area of different samples using ASiQwin software in the P/P_0 range of 0.05 to 0.35.

The total pore volume is calculated from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate. The pore volume and pore size distributions were calculated using the Density Functional Theory (DFT), which can provide sorption and phase behavior of fluids in narrow pores on a molecular level. Indeed, the Non-Local Density Functional Theory (NLDFE) and Grand Canonical Monte Carlo simulation (GCMC) methods can describe the local fluid structure near curved solid walls accurately; the adsorption isotherms in model pores are determined based on the intermolecular potentials of the fluid-fluid and solid-fluid interactions. The relation between isotherms derived from the above approaches and the experimental isotherm on a porous solid can be interpreted in terms of a Generalized Adsorption Isotherm (GAI) equation:

$$N\left(\frac{P}{P_0}\right) = \int_{W_{MIN}}^{W_{MAX}} N\left(\frac{P}{P_0}, W\right) f(W) dw$$

where

$N(P/P_0)$ = experimental adsorption isotherm data

W = pore width

$N(P/P_0, W)$ = isotherm on a single pore of width W

$f(W)$ = pore size distribution function

The assumption which is reflected from the GAI equation is that the total isotherm consists of a number of individual “single pore” isotherms multiplied by their relative distribution, $f(W)$, over a range of pore sizes. The set of $N(P/P_0, W)$ isotherms (kernel) for a given system can be obtained by the DFT as indicated above. The pore size distribution can then be derived by solving the GAI equation numerically via a fast non-negative least square algorithm. We have used the ASiQwin software to calculate the pore size distribution using the NLDFT- N_2 -carbon equilibrium transition kernel at 77 K based on a slit-pore model.

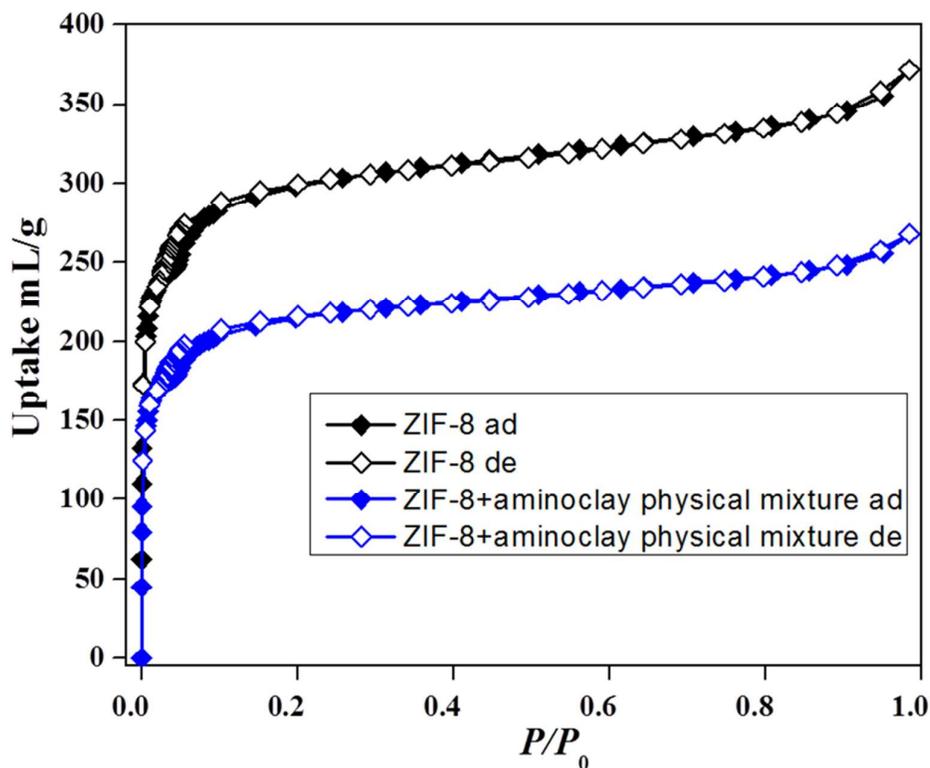


Figure S21. N_2 adsorption isotherms at 77 K of ZIF-8 and physical mixture of ZIF-8 and aminoclay (clay content 27.2 wt%)

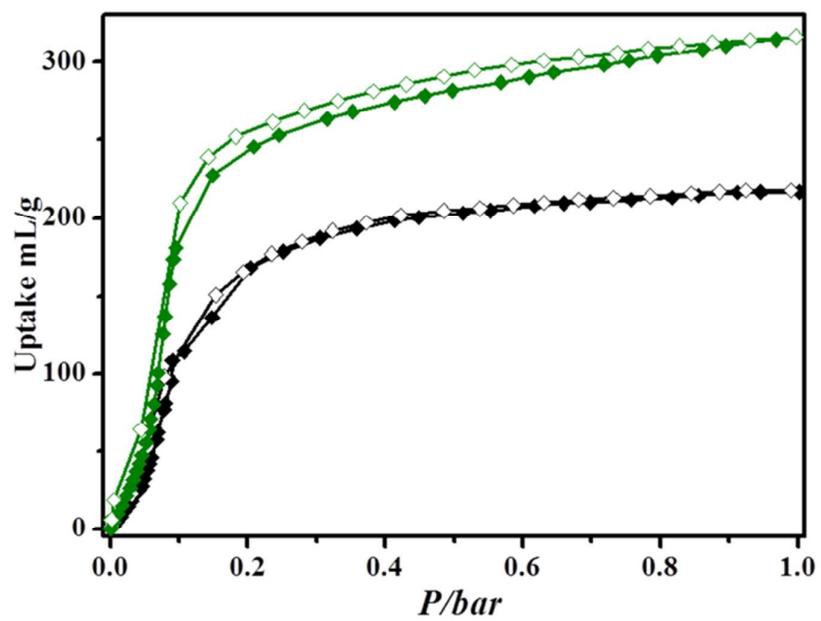


Figure S22. CO₂ adsorption isotherms at 195 K of ZIF-8 NPs (black) and ZIF-8@AC-2 (green).