Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

A water-based at room temperature synthesized ZIF-93, for CO_2 adsorption

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Supporting Information

1.- Powder XRD

The XRD measurements on the materials were recorded in the 10–90º 2ϑ range (scan speed = 20 s, step = 0.04°) by powder X-Ray diffraction (PXRD) using a Shimadzu 600 Series Diffractometer employing CuKα radiation (λ=1.5418 Å).

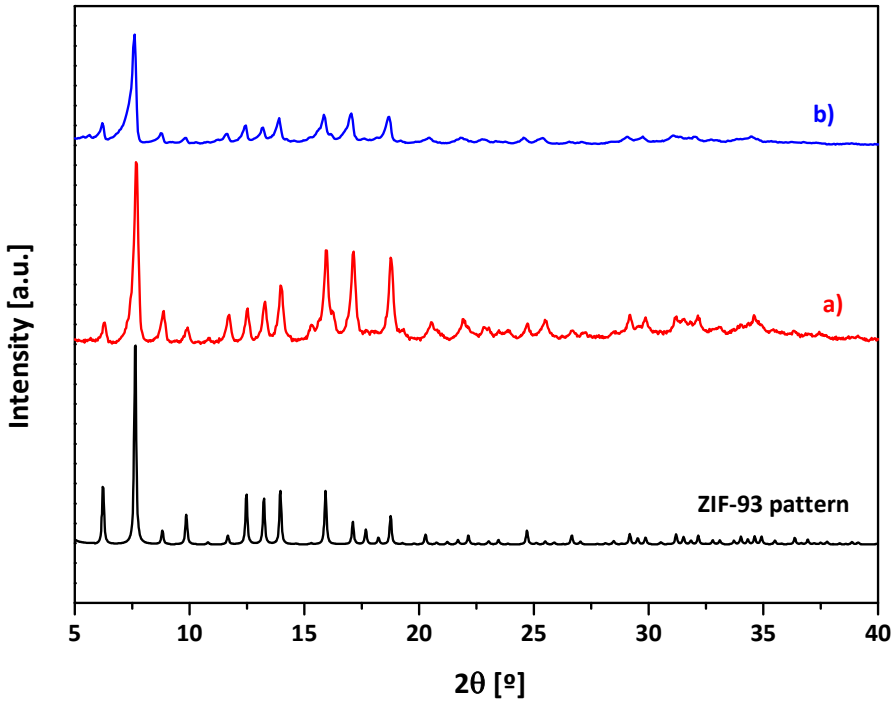

Figure S1.- Figure 1. PXRD pattern of as-synthesized ZIF-93 at different H_2O molar ratio and synthesis time, a) 1:2:1:135, 18 h and b) 1:2:1:33, 2 h.

2.- SEM

The morphology of the resulting materials was studied using a FESEM instrument, model Merlin VP Compact (ZEISS).

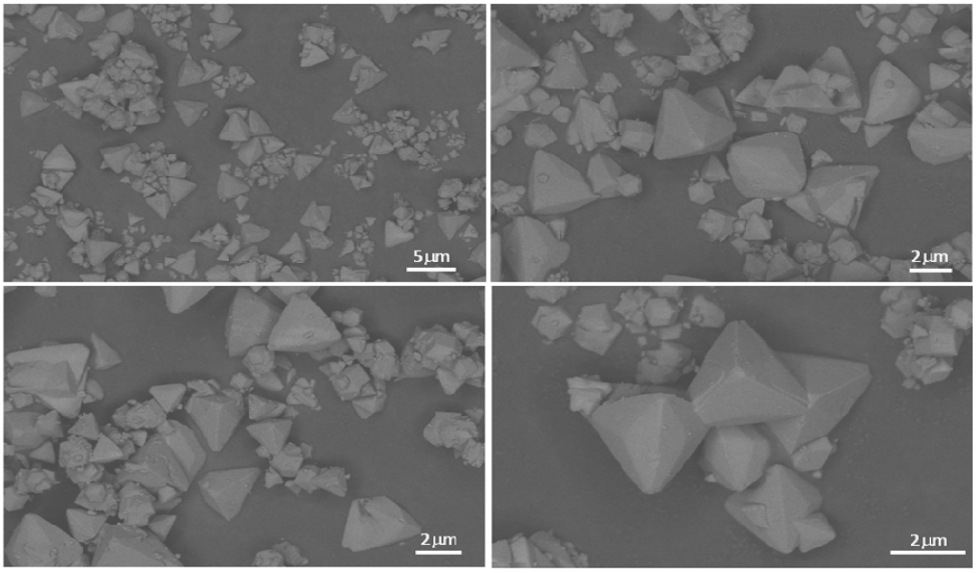

Figure S2.- SEM pictures of ZIF-93 powder

3.- TGA

The thermogravimetric analysis (TGA) was measured on Mettler Toledo TG/ SDTA analyzer. For this purpose, ca.10 mg of sample were filled into alumina crucibles and heated in a flow of air with a ramp of 10 K·min^{-1} from room temperature up to 973 K.

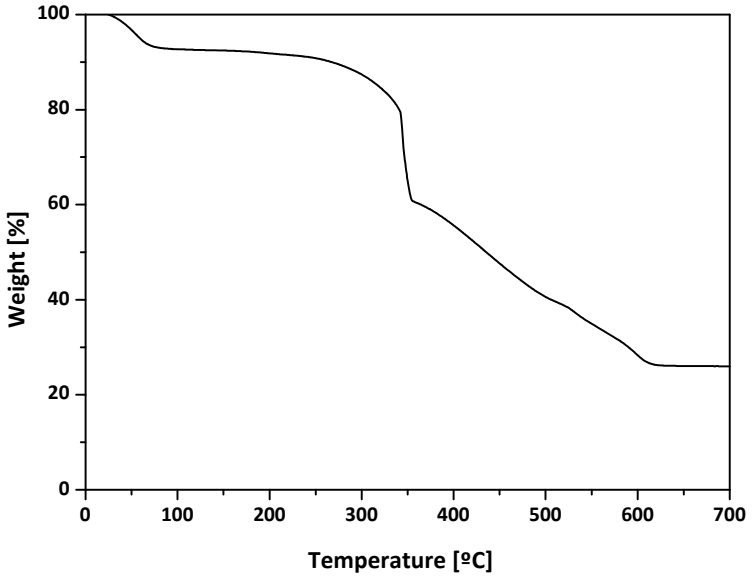

Figure S3.- TG curve of ZIF-93 powder

4.- Gas sorption analysis

Nitrogen adsorption isotherm measurements at 77 K were performed in a home-made fully automated manometric equipment designed and constructed by the Advanced Materials Group (LMA), and now commercialized as N2GSorb-6 (Gas to Materials Technologies; www.g2mtech.com). Before the adsorption experiments, the samples were outgassed at 473 K for 8h under vacuum (10^{-3} Pa). Nitrogen adsorption data were used to determine: (i) the total pore volume V_t at a relative pressure of 0.95, ii) the BET specific surface area (SBET), and iii) the micropore volume VDR, after application of the Dubinin-Radushkevich equation.

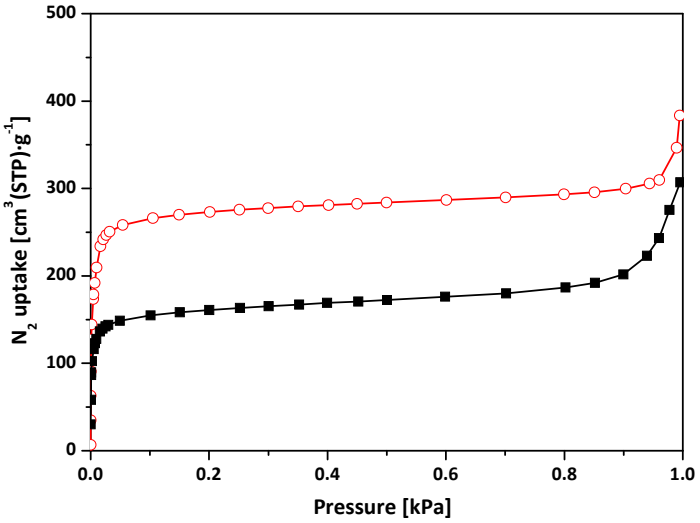

Figure S4.- N_2 isotherms measured at 77 K of ZIF-93 prepared in water in this work (close symbols) and prepared in DMF (open symbols).

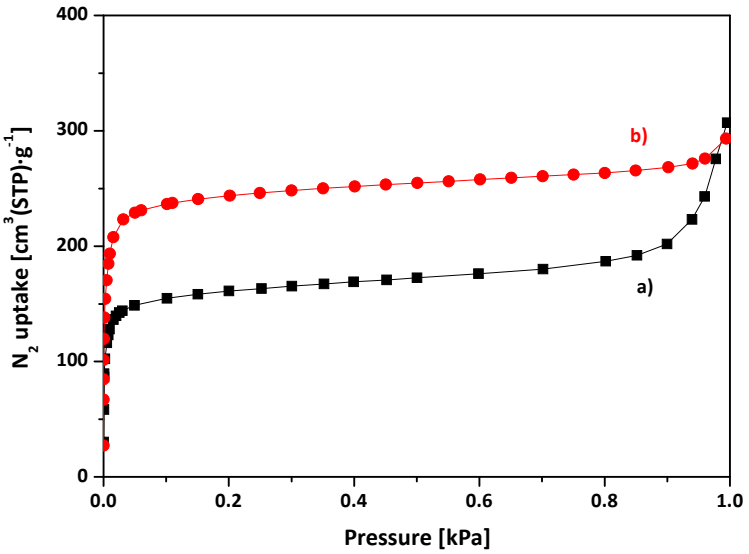

Figure S5.- N_2 isotherms measured at 77 K of as-synthesized ZIF-93 at different H_2O molar ratio and synthesis time, a) 1:2:1:135, 18 h and b) 1:2:1:33, 2 h.

The CO_2 and N_2 adsorption/desorption isotherms at 303 K were performed in a AUTOSORB-6 apparatus. Before the adsorption experiments, the samples were outgassed at 473 K for 4 h under vacuum.

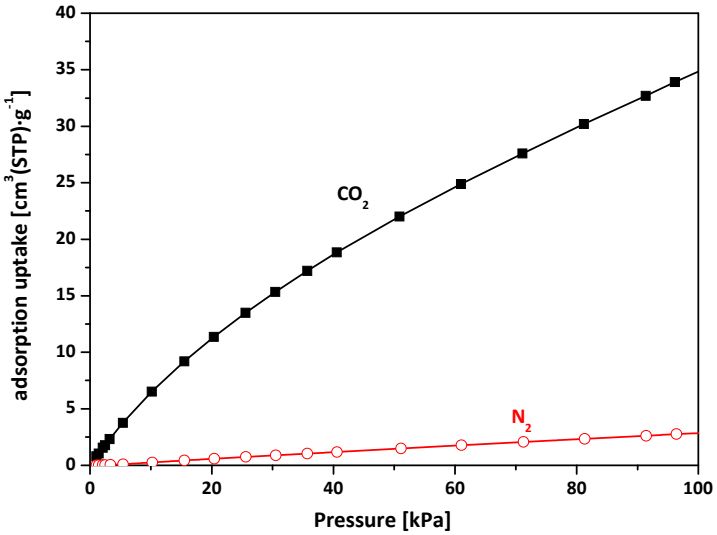

Figure S6.- CO_2 and N_2 isotherms up to 1 bar at 303 K of the material synthesized in aqueous solution.

5.- Breakthrough experiments

Experiments are carried out in a u-shaped glass column. 0.4 g of sample is loaded into the column with an inner diameter of 5 mm and a pack bed height of around 4 cm. The adsorbent is sieved between 500 µm and 1 mm to keep the ratio of column-to particle radius above 5.[1-2] In order to check how our bed deviates from ideal plug flow, we use H_2 as inert gas. H_2 profile not only shows us the deviation from ideal plug flow but also the time zero.

Prior to measurements, the activation of the adsorbent is carried out at 423 K in an electric furnace under a flow of 50 mL·min^{-1} of inert gas. Then the sample is cooled down to measurement temperature.

For the breakthrough experiments a total flow rate of 12 mL(STP)·min^{-1} of a N_2/CO_2 mixture (75:25, v/v) and inert gas (H_2) was fed to the column at 298 K and a total pressure of 110 kPa.

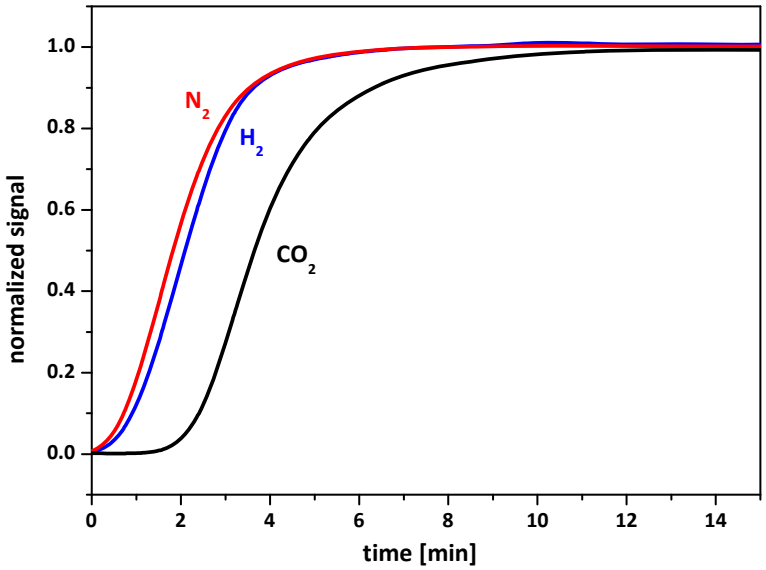

Figure S7.- Breakthrough curves of a CO_2/N_2 mixture with H_2 as reference.

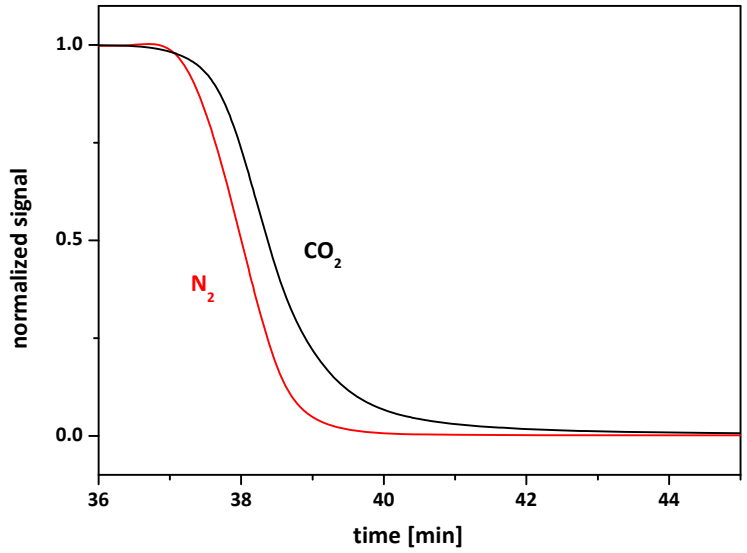

Figure S8.- Desorption curves at 298 K and 100 kPa of the adsorbed CO_2 and N_2 after the breakthrough experiment presented in Figure 3 (He flow of 5 cm^3 (STP)/min).

In order to understand the lack of roll-up in the N_2 profile, we performed more breakthrough experiments, changing the quantity of dead volume.

a) breakthrough experiment at 298 K with the initial configuration (Figure S9a)

b) breakthrough experiment at 298 K, filling the dead volume downstream with small glass balls, to minimize the dead volume (Figure S9b)

c) breakthrough experiment at 298 K with an adsorption configuration in which a large dead volume was set after the bed (Figure S9c)

d) breakthrough experiment at 273 K with the initial configuration (Figure S9d)

In configuration (*a*) the standard and N_2 breaks at the same time, meaning N_2 is not adsorbed, and roll-up is not showing. To minimize this effect, we performed the same experiment, but filling the dead volume downstream with small glass balls, to lessen the dead volume (*b*), showing similar curves. In configuration (*c*), we added a large dead volume was set after the bed, and again, breakthrough curves are comparable, therefore, again there is not N_2 adsorption and roll-up. Lastly, we have carried out the experiment using the second configuration (*b*) at lower temperature (273K) to induce the adsorption of N_2 and consequently the roll-up. Now we can see that N_2 is adsorbed and later displaced by CO_2, and at that moment, we see the roll-up.

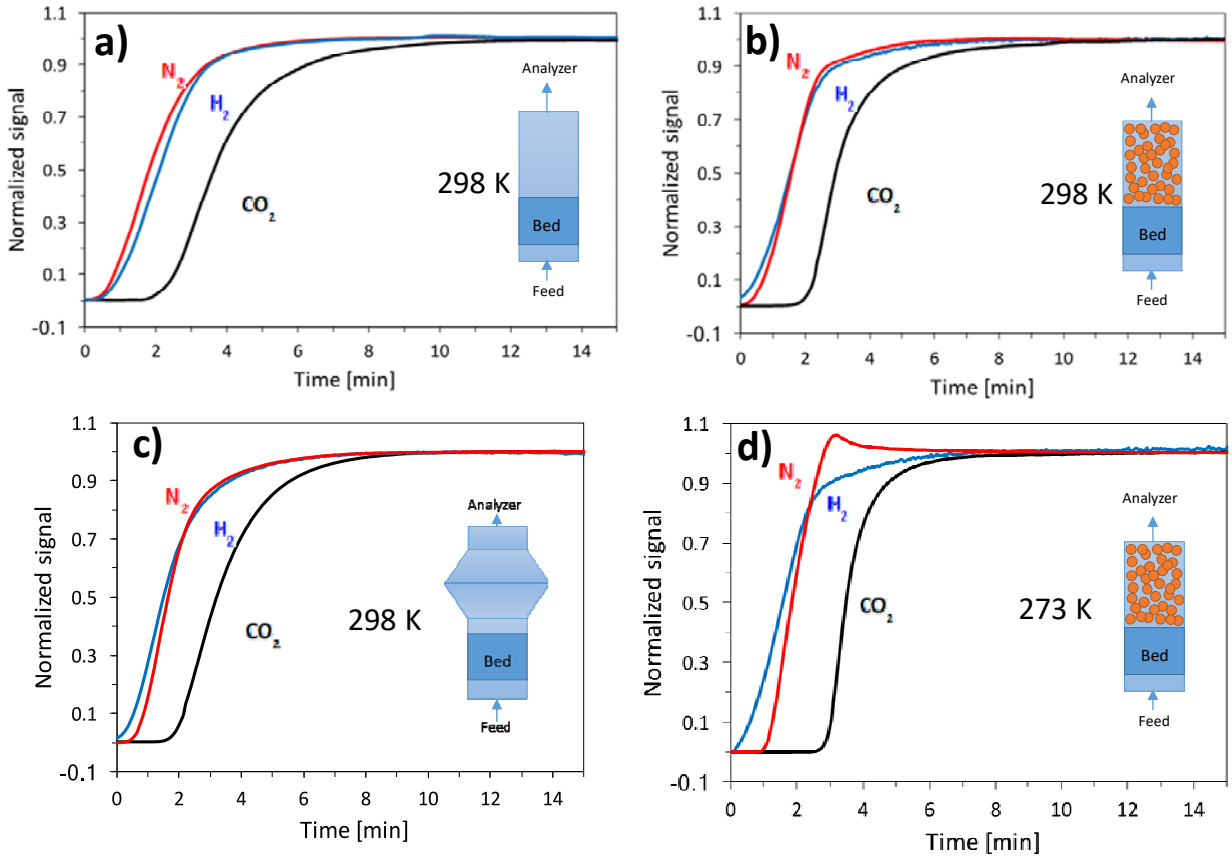

Figure S9.- Breakthrough curves of a CO_2/N_2 mixture with H_2 as reference. a) at 298 K (same as Figure S7); b) at 298K, filling the dead volume downstream with small glass balls; c) at 298K, with a large dead volume and d) at 273 K, filling the dead volume downstream with small glass balls.

1. P. Fosbøl, N. von Solms, A. Gladis, K. Thomsen and G. M. Kontogeorgis, in *Process Systems and Materials for CO2 Capture*, John Wiley & Sons, Ltd, 2017, pp. 43-78.
2. R. F. P. M. Moreira, T. L. P. Dantas, F. M. T. Luna, I. J. Silva, Jr., D. C. S. de Azevedo, C. A. Grande and A. E. Rodrigues, *Proc. Annu. Int. Pittsburgh Coal Conf.*, 2010, **27**, 2332–2343