Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Improved mechanical stability of HKUST-1 in confined nanospace

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Experimental Section

Synthesis of hybrids HKUST-1@AC: 0.420 g of trimesic acid (0.7 mmol) was dissolved in 12ml of ethanol (solution 1). Activated carbon (AC) in proportions of 10, 25 and 50 wt% was added to this solution. Percentages are calculated assuming 100% of yield in the HKUST-1 synthesis. In a separate flask, 1 g of $Cu(NO_3)_2.3H_2O$ (4 mmol) was dissolved in 12 ml of distilled water (solution 2) plus 1 ml of dimethylformamide (DMF). The solution 2 was slowly added to the solution 1 under stirring at room temperature for 30 minutes. This mixture was transferred to a 50 ml Teflon autoclave and cooked at 80ºC for 20 h. It is essential to maintain the agitation during the whole synthesis to favor the contact between reactants. After cooling, the solid was filtered and washed with water for several times. The final material was called MOF@AC10, MOF@AC25, MOF@AC50, respectively. Pure MOF was prepared in the same condition for the sake of comparison. The activated carbon selected as a host material for this study was prepared from petroleum pitch (VR93) using anhydrous KOH (6:1 wt.%/wt.% ratio) as activating agent (sample LMA726). Further details about the sample preparation are described in ref. [1].

Results and discussion

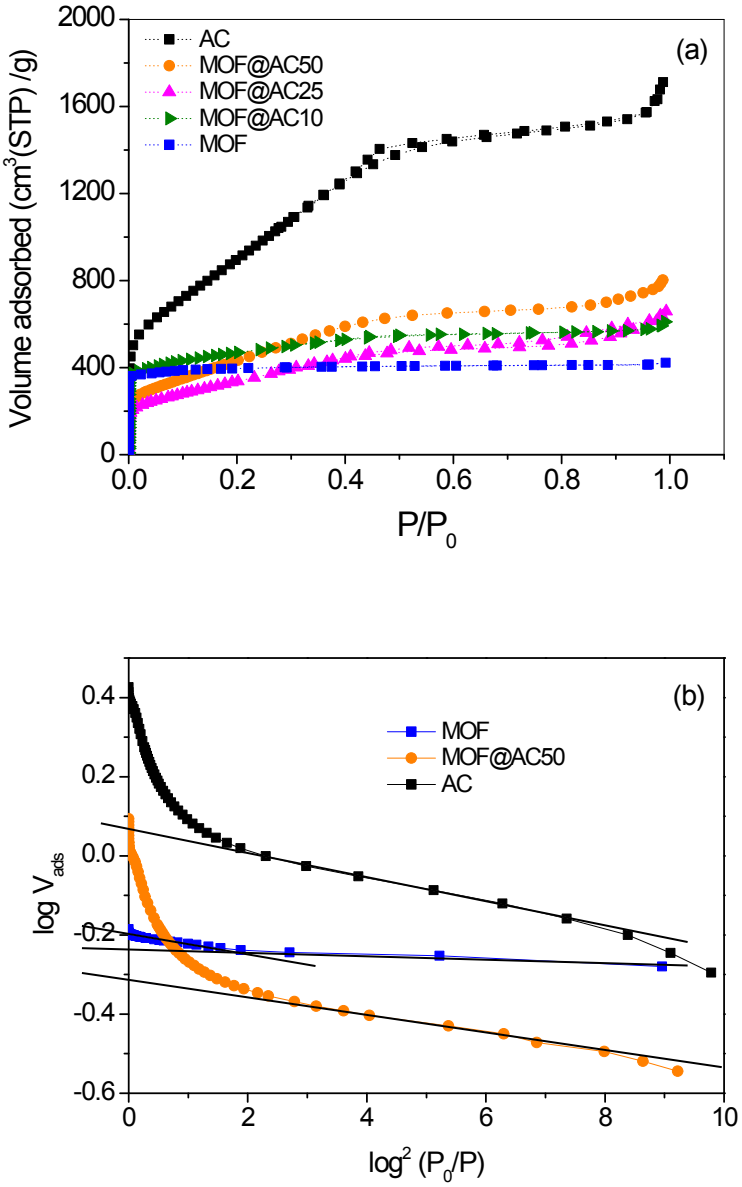

Figure S1. (a) Nitrogen adsorption/desorption isotherms at -196ºC for the individual host (AC) and guest (MOF) components, and the corresponding hybrid materials MOF@ACx (where x = wt.% AC); **(b)** Dubinin-Radushkevich (DR) plot for samples AC, MOF and MOF@AC (the range considered for the calculation of the micropore volume is also included).

Figure S1b shows that the DR equation applied to MOF (sample HKUST-1) gives rise to two well-defined slopes, a first one in the $\log^2(P_0/P)$ range 2-12, with a V_{DR} = 0.59 cm^3/g, and a second slope in the range 0.5-2, with a V_{DR} = 0.63 cm^3/g. This behavior is characteristic of samples with a bimodal pore size distribution. In the case of AC and MOF@AC samples, the presence of a widely developed micro/mesoporous structure (upward deviation in the low $\log^2(P_0/P)$ region) gives rise to a single straight line in the range $\log^2(P_0/P)$ ~ 2-8. In the case of HKUST-1, only the first V_{DR} value has been considered.

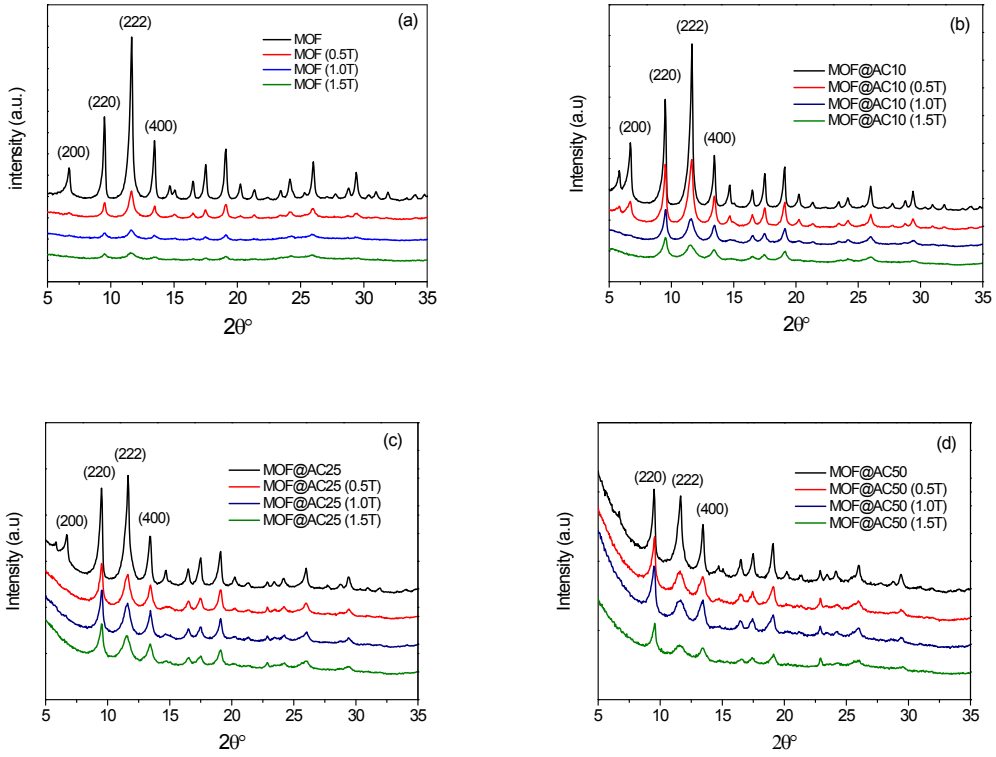

Figure S2. XRD profile for the different samples (a) MOF (HKUST-1), (b) hybrid MOF@AC10, (c) hybrid MOF@AC25 and (d) hybrid MOF@AC50, as synthesized and after a mechanical treatment at 0.5, 1.0 and 1.5 Tons.

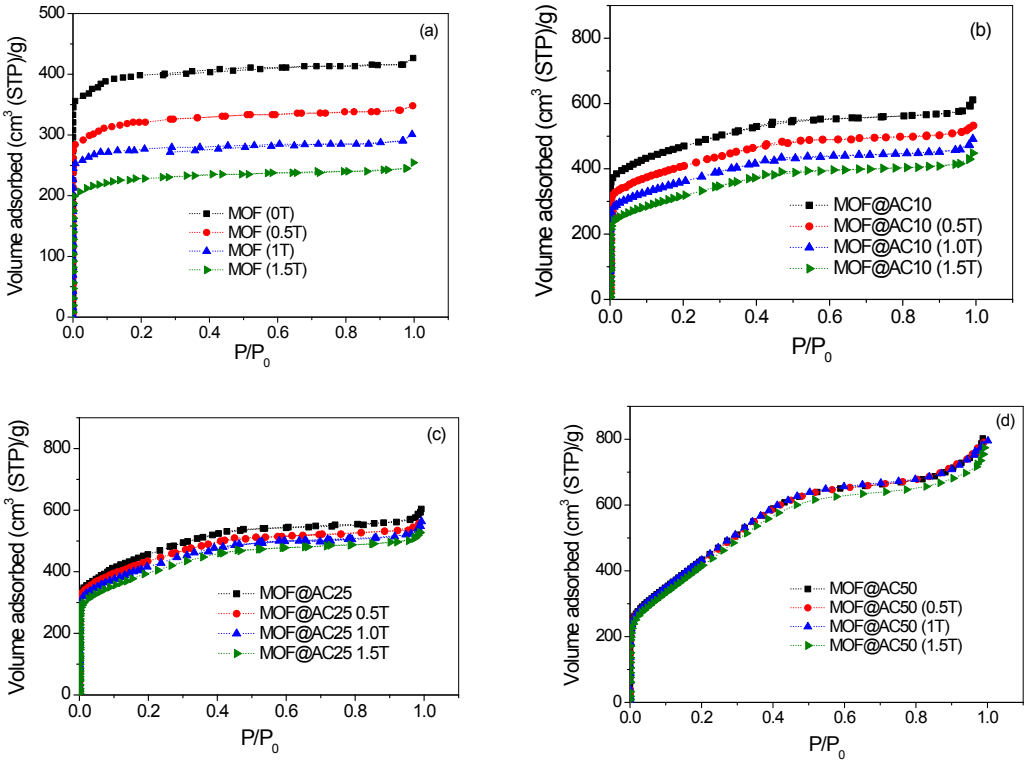

Figure S3. Nitrogen adsorption/desorption isotherms at -196ºC for (a) MOF (HKUST-1), (b) hybrid MOF@AC10, (c) hybrid MOF@AC25 and (d) hybrid MOF@AC50, as synthesized and after a mechanical treatment at 0.5, 1.0 and 1.5 Tons.

Table S1. Textural properties calculated from the N_2 adsorption data at -196ºC, bulk density and excess methane adsorption capacity for the different hybrid HKUST-1@AC materials, and the original HKUST-1 and AC.

Sample	Textural Properties			Gravimetric Capacity (CH_4)			Volumetric Capacity (CH_4)	
	S_{BET} (m^2/g)	V_{DR} (cm^3/g)	V_t (cm^3/g)	Excess Methane (10 MPa, 25 ºC)	Excess Methane (10 MPa, 25 ºC)*	ρ (g/cm^3)¥	Excess Methane (10MPa, 25ºC)	Excess Methane (10 MPa, 25ºC)*
MOF	1590	0.58	0.64	0.16 g/g	0.06 g/g	0.88	198 V/V	68V/V
MOF@AC10	1700	0.64	0.88	0.15 g/g	0.08 g/g	0.83	179 V/V	95 V/V
MOF@AC25	1635	0.59	0.87	0.16 g/g	0.11 g/g	0.75	163 V/V	119 V/V
MOF@AC50	1600	0.51	1.10	0.15 g/g	0.14 g/g	0.63	134 V/V	126 V/V
AC	3790	1.19	2.40	0.23 g/g	0.23 g/g	0.54	171 V/V	171 V/V

* Excess methane after a conforming step at 1.0 Ton

References

[1]. M.E. Casco, M. Martinez-Escandell, E. Gadea-Ramos, K. Kaneko, J. Silvestre-Albero, F. Rodriguez-Reinoso, *Chem. Mater.* 2015, **27**, 959.