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ARTICLE

Supporting Information

Beyond the H_2/CO_2 upper bound: one-step crystallization and separation of nano-sized ZIF-11 by centrifugation and its application in mixed matrix membranes

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MOF characterization

TEM

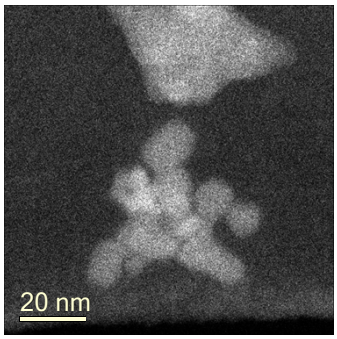

Figure S1. nZIF-11 TEM image at 1min

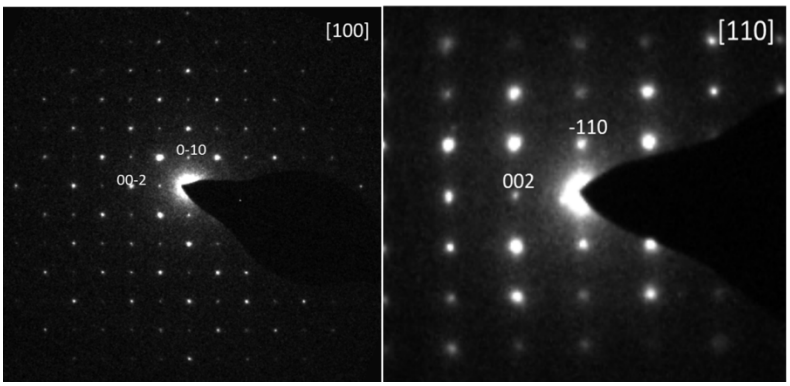

Figure S2. SAED patterns along [110] and [100] directions of ZIF-11 micro-sized particles

Crystal size distribution

Table S1. Average and predominant size of the different samples synthesized by centrifugal acceleration.

Sample	2 min	5 min	10 min	15 min	30 min
Average size (µm)	0.039±0.006	0.035±0.006	0.036±0.006	1.90±1.55	16.61±2.33
Predominant size (µm)	0.042	0.024	0.031	0.300	14.051

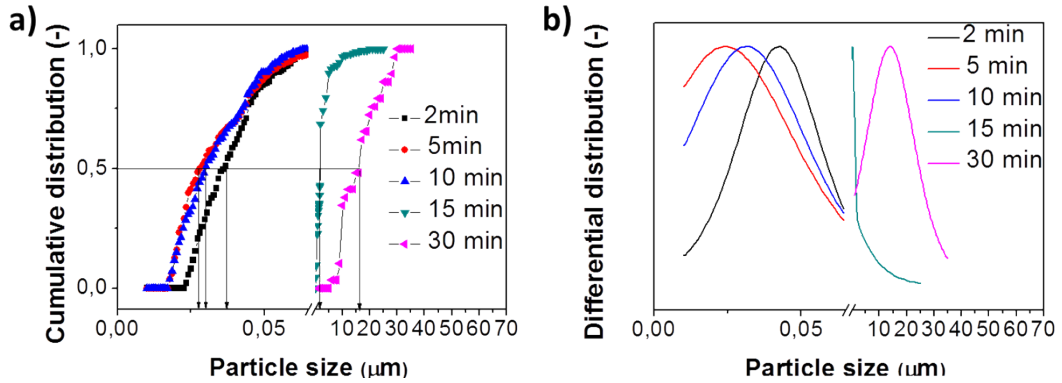

Figure S3. (a) Cumulative distribution and (b) differential distribution of the different samples synthesized by centrifugation.

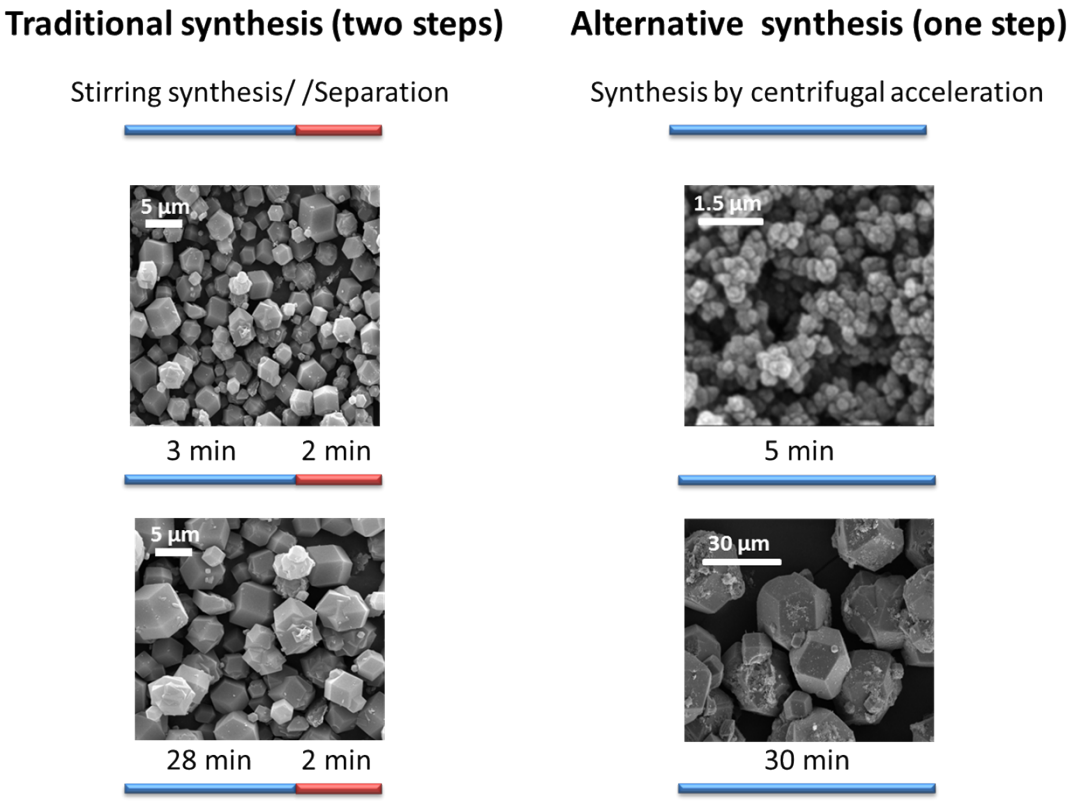

Figure S4. Crystal growth comparison between traditional and centrifugal syntheses.

Thermogravimetric analysis

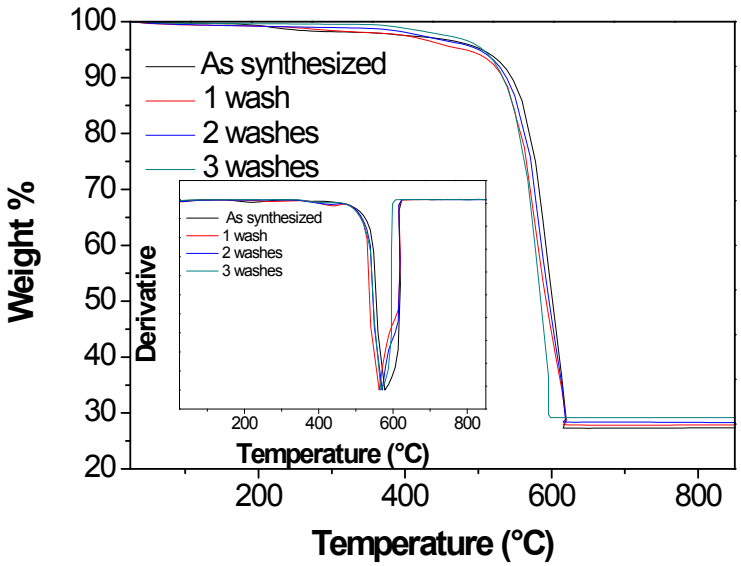

Figure S5. TGA and derivative (insert) of nZIF-11 as synthesized and for different washes.

Small weight loss at around 400 ^{0}C in Fig. S3 corresponds to residual toluene remaining in the particle pores. As the number of washes increases, this weight loss becomes smaller until it finally disappears for 3 washes.

FTIR analysis

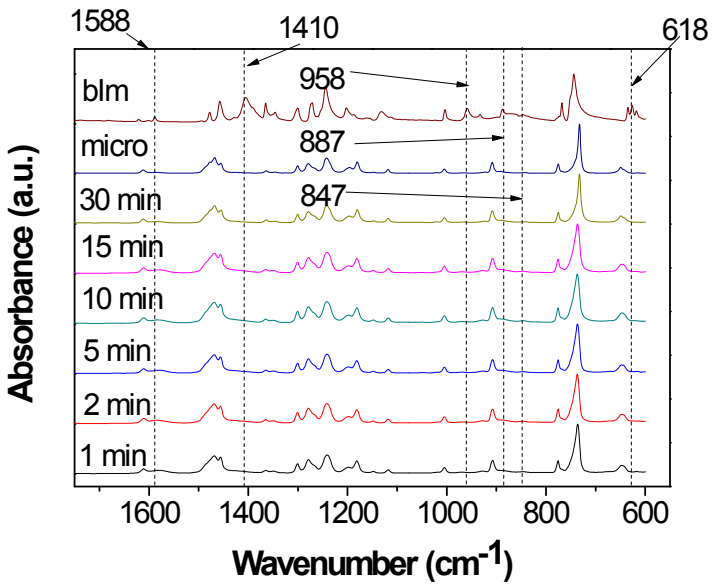

Figure S6. FTIR spectra of the samples synthesized at different times, micro-sized ZIF-11 and organic linker.

Fig. S4 shows the FTIR spectra of all the samples synthesized by centrifugal acceleration within times from 1 to 30 min, together with those of the micro-sized crystals and the organic linker. They are represented only from 2000 to 500 cm^{-1} so that the more representative peaks become better defined. The band found in the region 1620-1450 cm^{-1} is derived essentially from aromatic C-C and C-N stretching modes.[1] It

can also be appreciated the C-N stretch mode at 1584 cm^{-1}.[2] The band in the region of 600-1500 cm^{-1} is attributed to the entire ring stretching or bending, while the C-C stretches in the aromatic ring is associated with the peak at 1611 cm^{-1}.[3] Differences between the organic liker and the MOF can be observed. Peaks at 1410, 958, 887 and 847 cm^{-1}, present in bIm spectrum and related to benzene CH-wag, ring stretch, imidazole ring bend and imidazole CH-wag respectively, disappear in ZIF-11 spectra, even when synthesizing the MOF for only 1 min in the centrifuge. The peaks at 1588 and 618 cm^{-1}, caused by N-H in plane bend and In-plane ring bend, respectively, move to higher wavelengths.[4]

Colloidal suspension stability

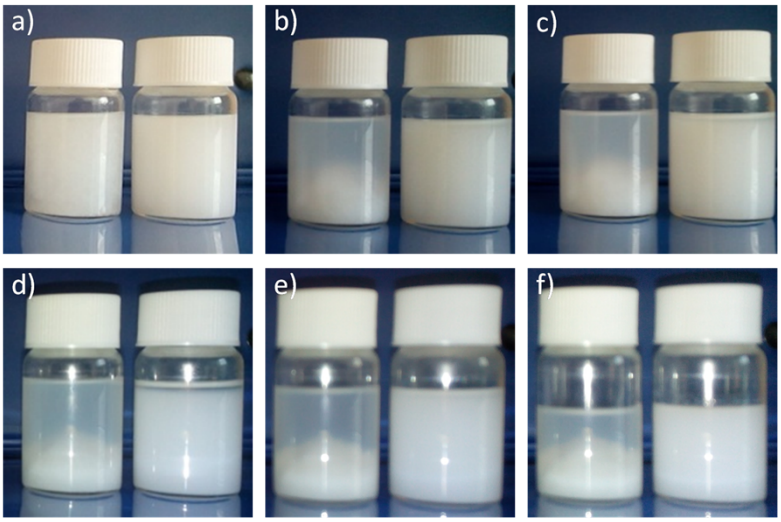

Figure S7. Pictures of nZIF-11 suspensions in chloroform taken at different times: a) 0 hours , b) 1 hour, c) 2 hours, d) 1 day, e) 8 days and f) 20 days. In each one picture the left one correspond to the previously dried MOF sample where the right one is the colloidal MOF suspension.

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The colloidal suspension stability study shows how the material dispersed after drying starts to precipitate in only one hour, while the wet one keeps stable for 20 days. Agglomeration explains this behaviour. When dried, the material tends to aggregate and cannot be fully dispersed though sonication, which make it precipitate fast. On the other hand, when the material is kept in wet state it continues fully dispersed and can remain stable for days.

Membrane performance

Table S2. H_2/CO_2 gas separation performance for different MMMs collected from literature.

ZIF	Polymer	Loading [% wt]	Temperature [ºC]	H_2Permeability [Barrer]	H_2/CO_2 selectivity	Reference
ZIF-8	Matrimid®	40	35	71.22	2.90	5
ZIF-7	PBI	-	220	293	13.6	6
ZIF-7	PBI	50	120	202	9.2	7
ZIF-8	PBI	60	35	669.9	2.8	8
ZIF-8	PBI	60	35	1749.9	4.1	9
ZIF-11	PBI	39.5	35	464.7	3.6	10
ZIF-90	PBI	45	180	228	13.21	11
ZIF-8	PIM-1	43	35	14430	0.74	12
MSS-Z8[a]	PSF	32	35 120	56.1 224.1	2.2 3.7	13
nZIF-11	Matrimid®	25 15	35 200	95.9 535	4.4 9.1	This work

[a]Silica-(ZIF-8) core shell spheres.

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