Supporting Information

MOF Nanoparticles of MIL-68(Al), MIL-101(Cr) and ZIF-11 for Thin Film Nanocomposite Organic Solvent Nanofiltration

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MOF SYNTHESIS

MIL-101(Cr) was crystalized following a hydrothermal synthesis:[1] 0.70 g of $CrCl_3 \cdot 6H_2O$ (≤ 98%, Sigma Aldrich) and 0.45 g of therephthalic acid (98%, Sigma Aldrich) in 26 mL of deionized water. The obtained solution was heated at 180 ºC during 30 min in a microwave (Anton Paar, Multiwave 3000). The synthesized nanocrystals were activated as follows: firstly, two stages of washing and centrifugation at 10,000 rpm during 15 min with deionized water. Secondly, a washing stage at 200 ºC with DMF (99.5%, Scharlau) during 24 h. Finally, a washing overnight with methanol (99.9%, Scharlau) at 70 ºC with two stages of washing and centrifugation at 10,000 rpm during 15 min with methanol.

MIL-68(Al) nanocrystals were synthesized through a solvothermal synthesis with THF:[2] 1.40 g of $Al(NO_3)_3 \cdot 9H_2O$ (≥98%, Sigma Aldrich) were mixed with 0.60 g of therephthalic acid in 32.0 mL of anhydrous THF (≥99.9, Sigma Aldrich). The synthesis took place during three days at 70 ºC. Afterwards, the resulted solution was centrifuged at 10,000 rpm during 15 min. The obtained nanocrystals were washed

and centrifuged in two stages at 10,000 rpm and 15 min with THF. Finally, the MIL-68(Al) nanocrystals were activated at 300 ºC during 8 h.

Nano ZIF-11 crystals were synthesized following the method reported by Sanchez-Lainez et al.[3] which implies the preparation of two solutions. Solution 1: 0.24 g of benzimidazole (98%, Sigma Aldrich) was mixed with 6.40 g of methanol, 9.20 g of toluene (≥ 99.5%, Sigma Aldrich) and 2.40 g of NH_4OH (Ammonia 25%, Panreac). Solution 2: 0.22 g of zinc acetate (Sigma Aldrich) was dissolved in 3.20 g of methanol. Both solutions were mixed and immediately centrifuged at 10,000 rpm during 7 min. The obtained nanocrystals were activated by three stages of washing and centrifugation at 10,000 rpm during 7 min with methanol.

In all three cases, the resulted nanocrystals were stored in fresh solvent to be used afterwards in TFN formation.

MOF CHARACTERIZATION

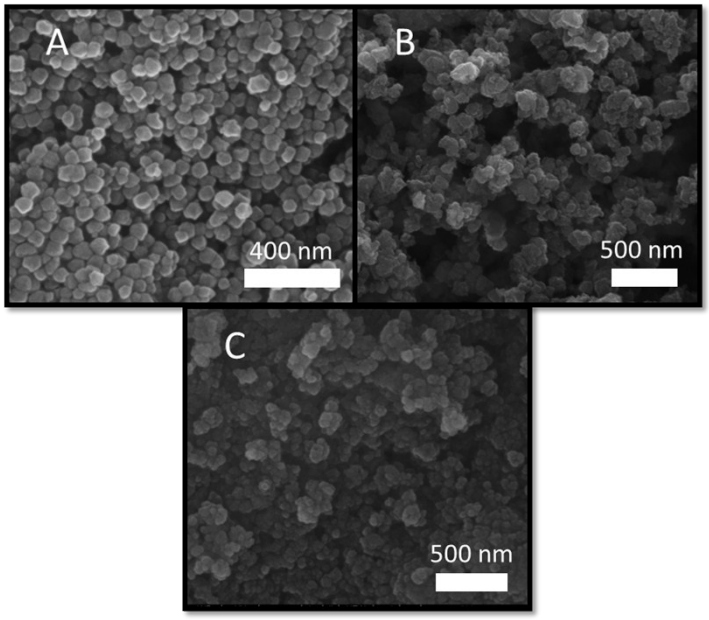

Fig. S1. SEM images of MOF particles. MIL-101(Cr) (A), MIL-68(Al) (B) and ZIF-11 (C).

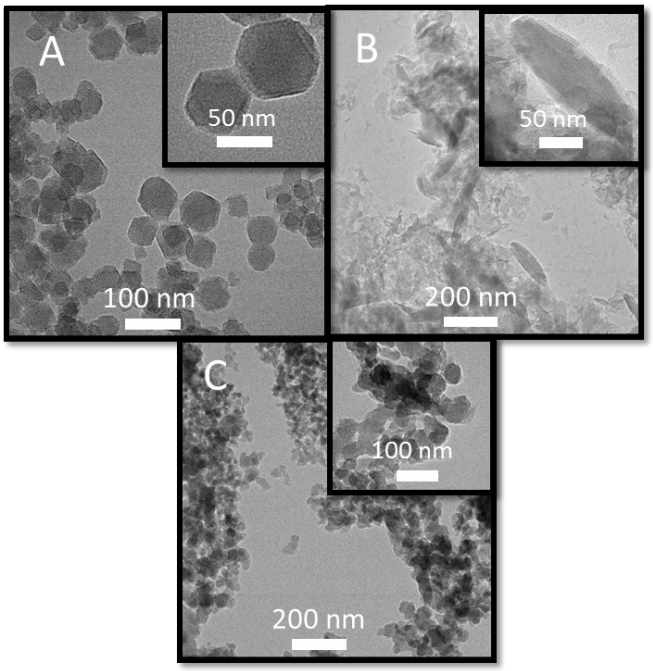

Fig. S2. TEM images of MOF particles. MIL-101(Cr) (A), MIL-68(Al) (B) and ZIF-11 (C).

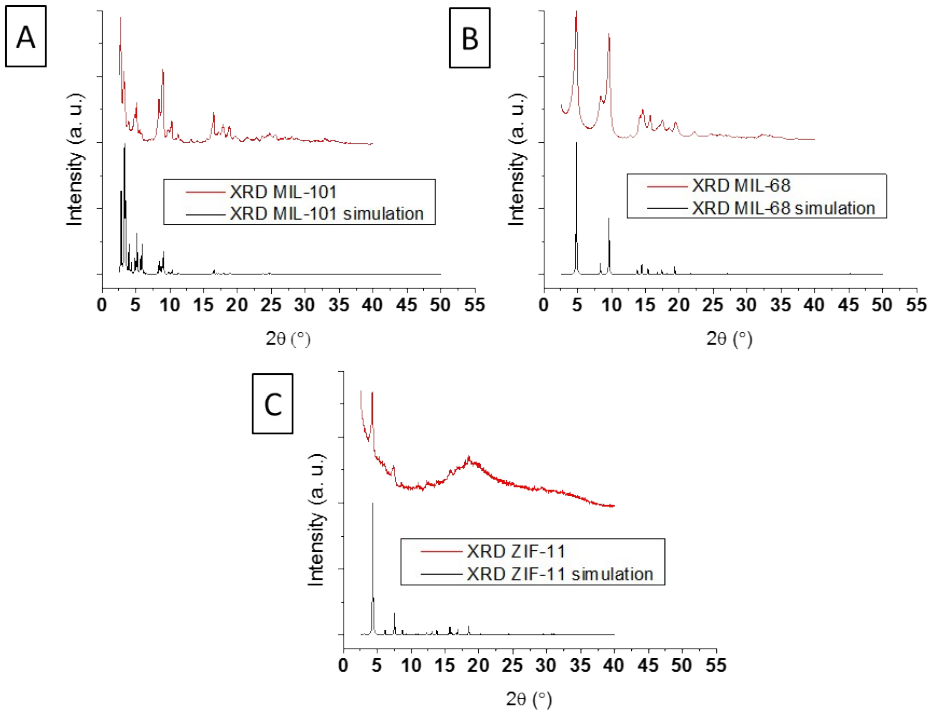

Fig. S3. XRD patterns of MIL101 (Cr) (A), MIL-68(Al) (B) and ZIF-11 (C). In this case the observed peaks correspond to the presence of a small amount of crystalline ZIF-11.[3]

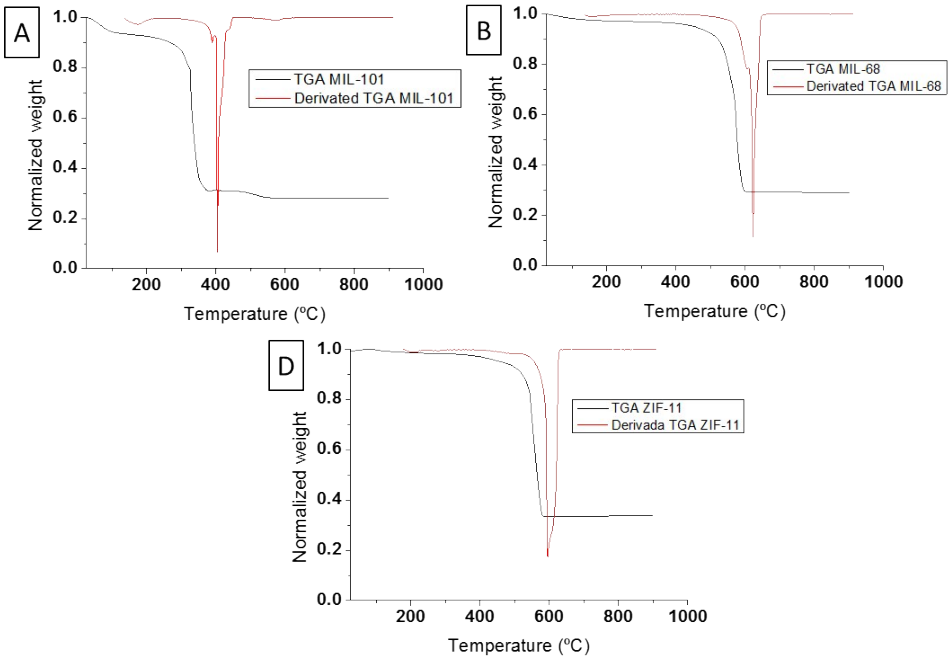

Fig. S4. TGA curves of MIL101 (Cr) (A), MIL-68(Al) (B) and ZIF-11 (C).

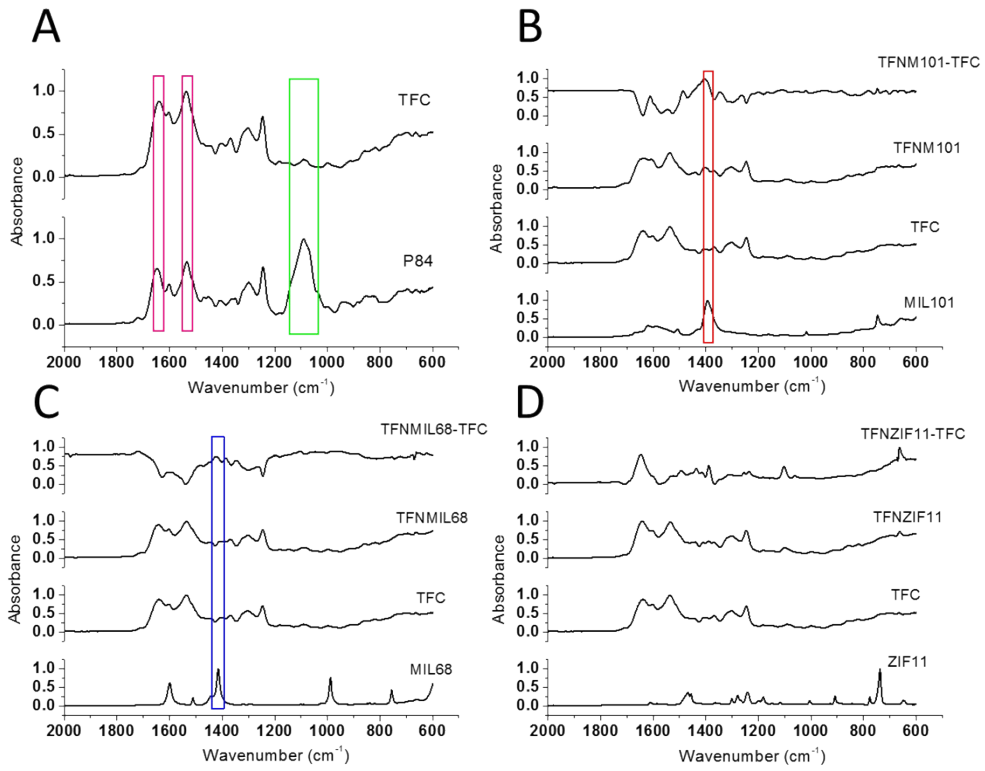

Fig. S5. FTIR-ATR analysis of MOFs, P84® support, TFC membranes, TFN membranes and the TFN membranes spectra after subtraction of the TFC membrane spectrum. A corresponds to MIL-101(Cr), B to MIL-68(Al), C to ZIF-11 and D to P84® and TFC membrane comparison.

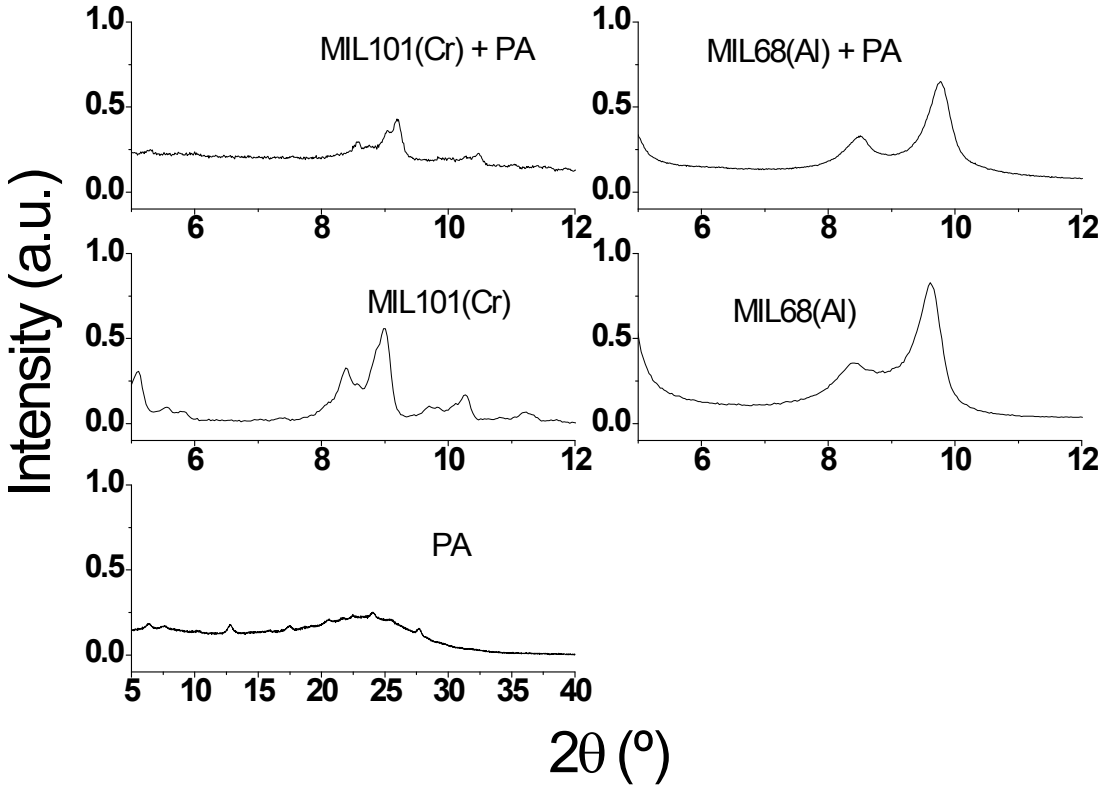

Fig. S6. XRD patterns of PA and MIL-101(Cr) and PA and MIL-68(Al) composites, MIL-101(Cr) and MIL-68(Al) crystals and bare PA.

REFERENCES

1. N. A. Khan, I. J. Kang, H. Y. Seok and S. H. Jhung, *Chem. Eng. J.*, 2011, **166**, 1152-1157.

2. B. Seoane, V. Sebastian, C. Tellez and J. Coronas, *CrystEngComm*, 2013, **15**, 9483-9490.

3. J. Sanchez-Lainez, B. Zornoza, A. Mayoral, A. Berenguer-Murcia, D. Cazorla-Amoros, C. Tellez and J. Coronas, *J. Mater. Chem. A*, 2015, **3**, 6549-6556.