Supporting Information

Simultaneous use of MOFs MIL-101(Cr) and ZIF-11 in thin film nanocomposite membranes for organic solvent nanofiltration

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MOF SYNTHESIS

MIL-101(Cr) was crystalized following a hydrothermal synthesis,[1] based on the first reported synthesis by Khan et al:[2] 2.001 g of $Cr(NO_3)_3 \cdot 9H_2O$ (≤ 98%, Sigma Aldrich) and 0.830 g of terephthalic acid (98%, Sigma Aldrich) were dissolved in 25 mL of deionized water. The obtained solution was autoclaved at 220 ºC during 8 h. The synthesized nanocrystals were activated as follows: firstly, by two stages of washing with deionized water and centrifugation at 10,000 rpm during 15 min, and secondly by treatment at 200 ºC in an autoclave with DMF (99.5%, Scharlau) during 24 h. Finally, the nanocrystals were washed overnight with methanol (99.9%, Scharlau) under reflux followed by two stages of washing with methanol at room temperature and centrifuged at 10,000 rpm during 15 min.

Nano ZIF-11 crystals were synthesized following the method reported by Sanchez-Laínez et al.,[3] which involves 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 (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 nanoparticles were activated by three stages of washing with methanol at room temperature and centrifugation at 10,000 rpm during 7 min.

MOF CHARACTERIZATION

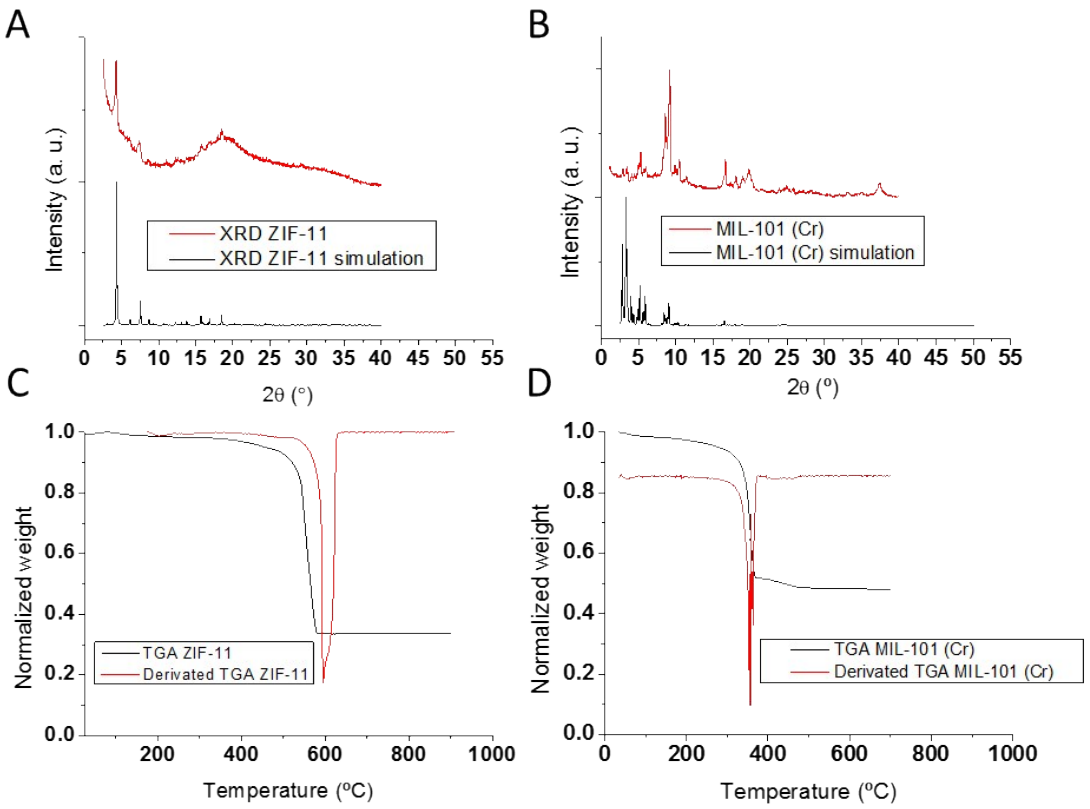

Fig. S1. XRD patterns of nano ZIF-11 (A) and MIL-101(Cr) (B). TGA diagrams of nano ZIF-11 (C) and MIL-101(Cr) (D)

MEMBRANE CHARACTERIZATION

Table S1. EDX quantification of the whole area contained in Fig. S2.

Element	Atomic (%)
C	51.5
O	37.4
Cr	10.9
Zn	0.1

Table S2. MOF content in non-supported MOF-PA nanocomposites

	MOF content in PA	
	Theoretical (%)	Experimental (%)
MIL-101(Cr)	61.2	73.7
ZIF-11		29.0
MIL-101(Cr)+ZIF-11		46.1

Table S3. Permeance and rejection values with errors for the four membrane types tested in this work. In general, two membranes were tested for every case. Conditions: 19 °C and 20 bar of feed pressure.

	Methanol + SY			
	Permeance ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	**Error ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)**	**Rejection (%)**	**Error (%)**
TFC	3.3	0.9	91.0	4.7
TFNMIL101	3.9	1.0	91.1	4.1
TFNZIF11	4.9	1.0	84.1	0.8
TFNMIL101-ZIF11	4.8	1.2	87.9	2.4
	Methanol + AO			
	Permeance ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	**Error ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)**	**Rejection (%)**	**Error (%)**
TFC	2.6	0.1	92.8	8.7
TFNMIL101	3.1	0.1	99.0	1.4
TFNZIF11	3.1	0.3	98.1	5.7
TFNMIL101-ZIF11	2.9	0.6	98.5	2.6

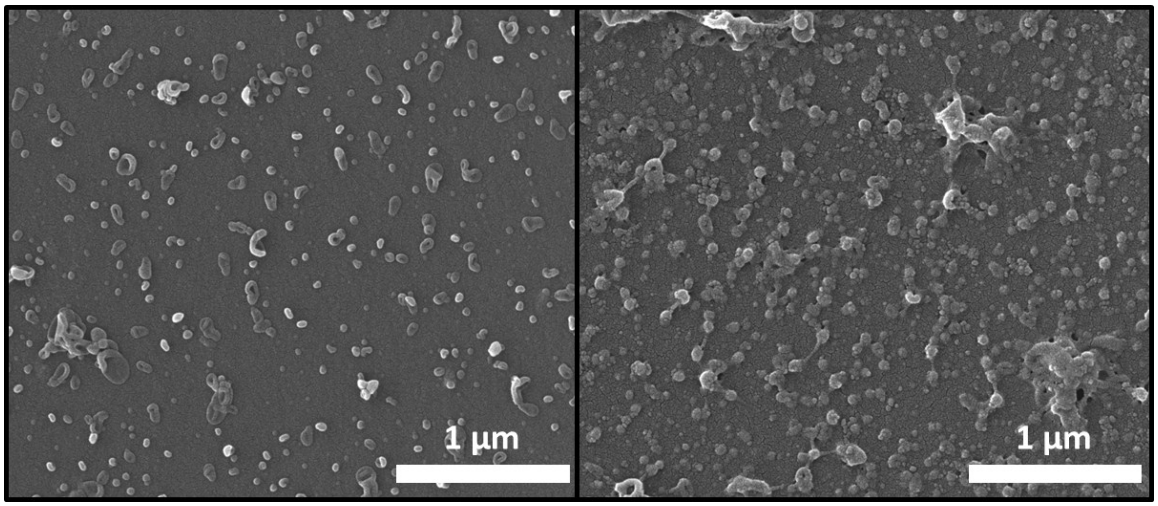

Fig. S2. SEM of a TFC membrane with no post-treatment (left) and a TFN membrane with a DMF filtration post-treatment (right)

Table S4. Contact angles of the synthesized membranes.

Membranes	Contact angle (º)
TFC	71 ± 2
TFNZIF-11	72 ± 3
TFNMIL-101	57 ± 4
TFNMIL-101+ZIF-11	71 ± 5

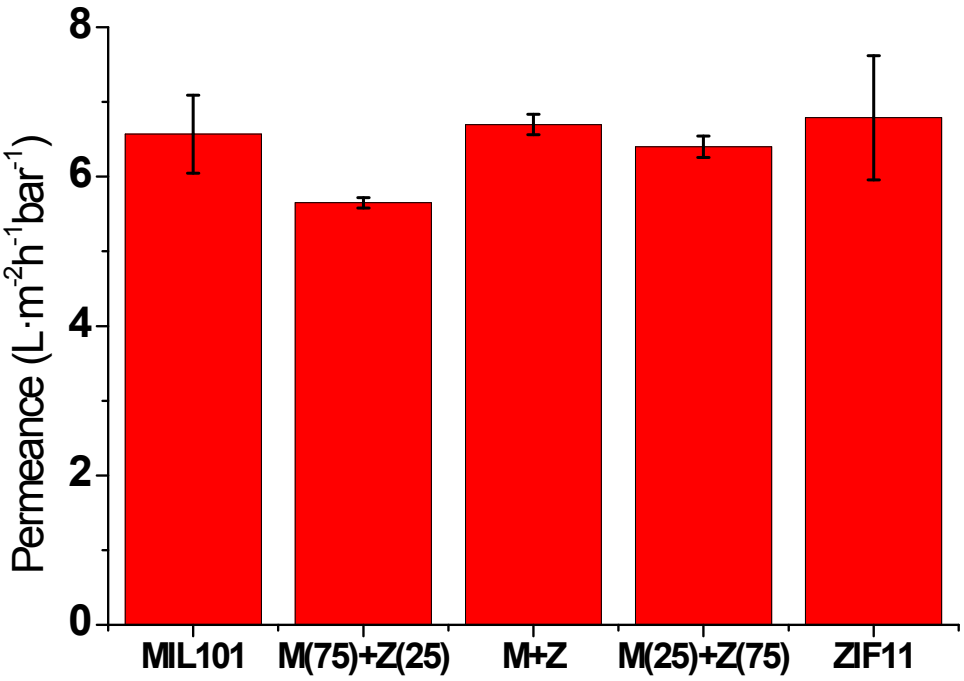

Fig. S3. Effect in the OSN of different proportions (written in brackets) of MOFs mixtures embedded in the thin film. "M" and "Z" represents MIL-101(Cr) and ZIF-11 respectively

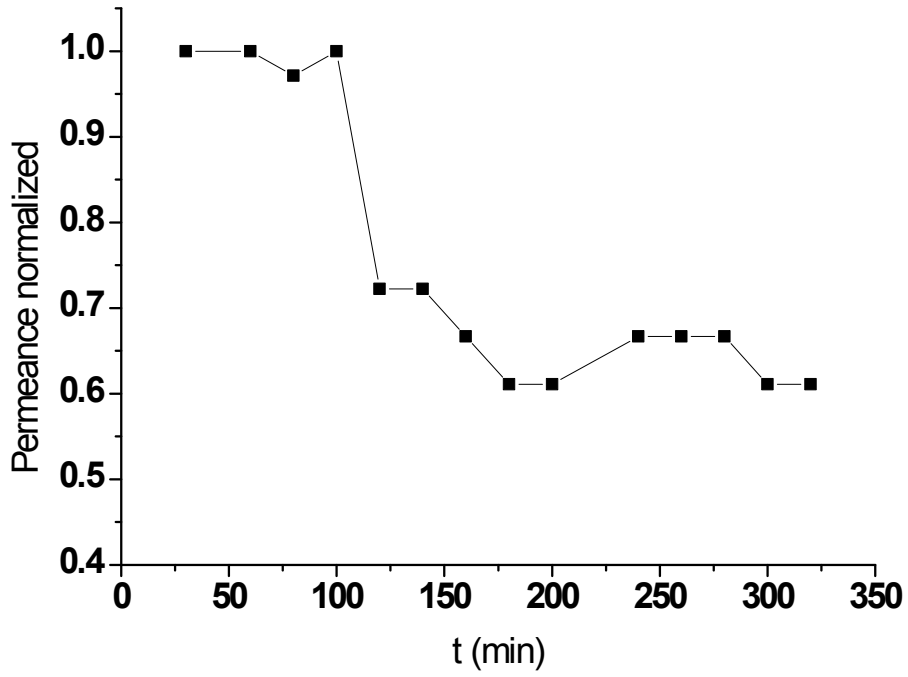

Fig. S4. Evolution of permeance of solvent through a TFC membrane pos-treated with DMF filtration in time. The feed solution consisted of methanol and AO and the test was carried out in the same dead-end module used for the other experiments in this work.

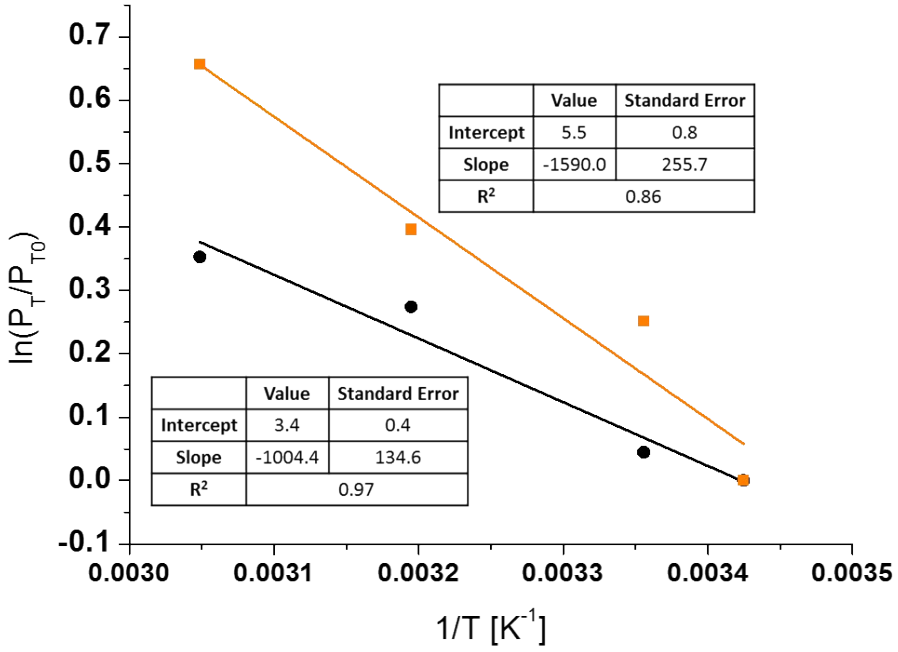

Fig. S5. Linear fit (Arrhenius plot) corresponding to permeate data in Fig. 3 when filtering methanol with SY (black) and when filtering pure methanol (orange).

NOTES AND REFERENCES

1. T. Zhao, F. Jeremias, I. Boldog, B. Nguyen, S. K. Henninger and C. Janiak, *Dalton Trans.*, 2015, **44**, 16791-16801.

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

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.