Electronic Supporting Information

High flux thin film nanocomposite membranes based on MOFs for organic solvent nanofiltration

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MOFs synthesis

ZIF-8: For the synthesis of ZIF-8 crystals, 0.3 g of zinc nitrate hexahydrate, ($Zn(NO_3)2{\cdot}6H_2O$, >98%, Sigma-Aldrich) was dissolved in 11.3 g of methanol (MeOH, HPLC grade, 99.99%, Scharlau). A solution consisting of 0.66 g of 2-methylimidazole ($C_4H_6N_2$, 99%, Aldrich) and 11.0 g of methanol was added to the nitrate solution and vigorously stirred for 5 min. The resultant solution was transferred to a Teflon-lined stainless steel autoclave and heated under autogenous pressure in a conventional oven at 150 °C for 5 h. After cooling, the solids were separated by centrifugation and washed with methanol. The resultant ZIF-8 powder was dried overnight.

NH_2-MIL-53(Al): 1.6 g of aluminum nitrate nonahydrate ($AlN_3O_9{\cdot}9H_2O$, >98%, Aldrich) and 1.1 g of 2-aminoterephthalic acid (99%, Aldrich) were dissolved in 30 mL of N,N-dimethylformamide (DMF, >95%, Scharlau), after which the solution was transferred to an autoclave and solvothermally treated at 130 °C for 3 days. The yellow product obtained after cooling to room temperature was washed three times with acetone and activated at 75 °C with methanol overnight. The solid was collected by centrifugation and dried overnight.

MIL-53(Al): 0.8 g of aluminum nitrate nonahydrate and 0.5 g of terephthalic acid (98%, Sigma-Aldrich) were dissolved in 15 mL of DMF, after which the solution was transferred to an autoclave and solvothermally treated at 120 °C for 1 day. The product obtained after cooling to room temperature was washed three times with acetone and activated at 75 °C with methanol overnight. The solid was collected by centrifugation and dried overnight.

MIL-101(Cr): 0.7 g of chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, >98, Aldrich) and 26 mL of water were mixed; 0.45 g of terepthalic acid was added and the synthesis was carried out in a microwave at 180 °C for 30 min. The product was recovered by centrifugation, washed with water and dried overnight. To remove the free terephthalic acid remaining after the synthesis, the material was purified with DMF at 120 °C overnight and then by refluxing with methanol for 12 h, and dried.

MOFs characterization

XRD analysis

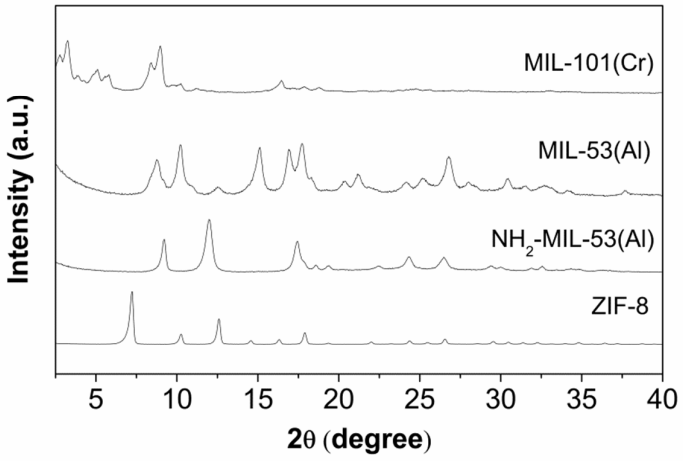

Figure S1. X-ray diffraction of the MOF powders ZIF-8, NH_2-MIL-53 (Al), MIL-53(Al) and MIL-101(Cr).

Thermogravimetric analysis of MOFs

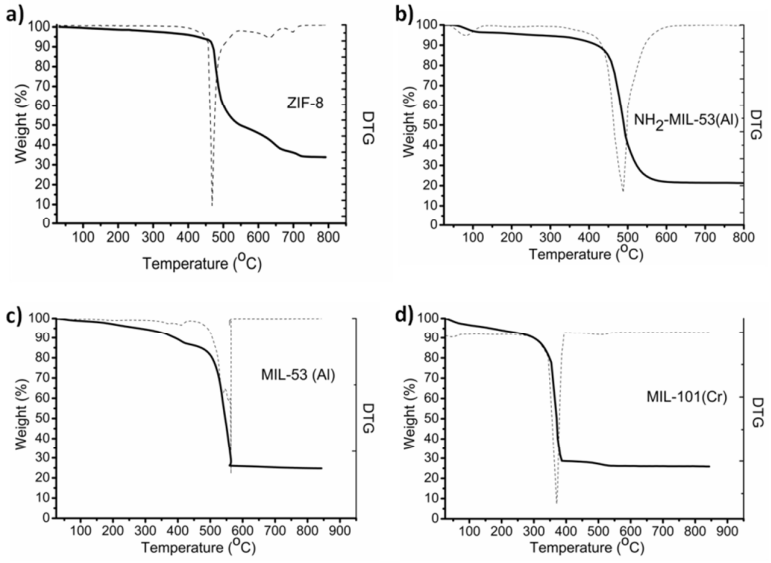

Figure S2. TGA and DTG curves of the MOFs: a) ZIF-8, b) NH_2-MIL-53 (Al), c) MIL-53(Al) and d) MIL-101(Cr).

Thermogravimetric analyses of MOFs after water adsorption

To evaluate the hydrophobicity/hydrophilicity of the different MOFs water adsorption experiments were carried out. The experiments were conducted by conditioning different samples for 1 week at room temperature in closed plastic flasks containing liquid water, ensuring that all samples were in an atmosphere saturated with water but not in direct contact with water. TG measurements were performed to quantify the amount of water adsorbed (Figure S3).

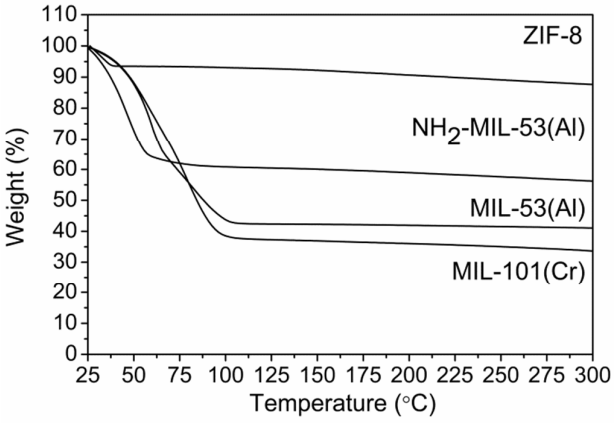

Figure S3. TGA curves of ZIF-8, NH2-MIL-53(Al) and MIL-101(Cr) after water adsorption experiments.

OSN results for TFC and TFN-ZIF-8 membranes with different post-treatments

Table S1. MeOH and THF fluxes and MWCO at 30 bar applied pressure for TFC and TFN-ZIF-8 membranes, after different post-treatments.

Membrane	THF/PS flow ($L \cdot m^{-2} \cdot h^{-1}$)	THF MWCO	MeOH/PS flow ($L \cdot m^{-2} \cdot h^{-1}$)	MeOH MWCO
TFC	7.3	295	15.4	232
TFC –PT1 (hot water)	6.8	232	6.2	232
TFC- PT2 (dipping DMF)	15.8	295	19.3	232
TFC- PT3 (hot water+dipping DMF)	6.0	232	27.0	232
TFC- PT4 (filtration DMF)	50.0	295	44.0	232
TFC-PT5 (hot water+ filtration DMF)	25.7	295	35.2	232
TFN-**ZIF-8**	3.8	232	13.7	232
TFN-**ZIF-8** -PT1 (hot water)	3.0	295	11.2	232
TFN-**ZIF-8**- PT2 (dipping DMF)	8.6	232	22.7	232
TFN-**ZIF-8**- PT3 (hot water+dipping DMF)	14.6	232	31.3	232
TFN-**ZIF-8**- PT4 (filtration DMF)	128	295	63.2	232
TFN-**ZIF-8**-PT5 (hot water+ filtration DMF)	112	295	53.6	232

Characterization of TFC/TFN membranes

SEM observation

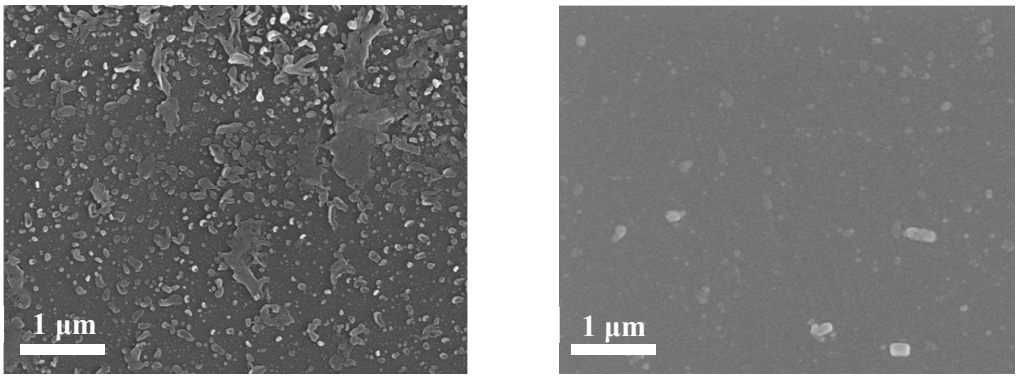

Figure S4. SEM image of TFC surface membrane before (left) and after (right) DMF dipping.

EDX analysis

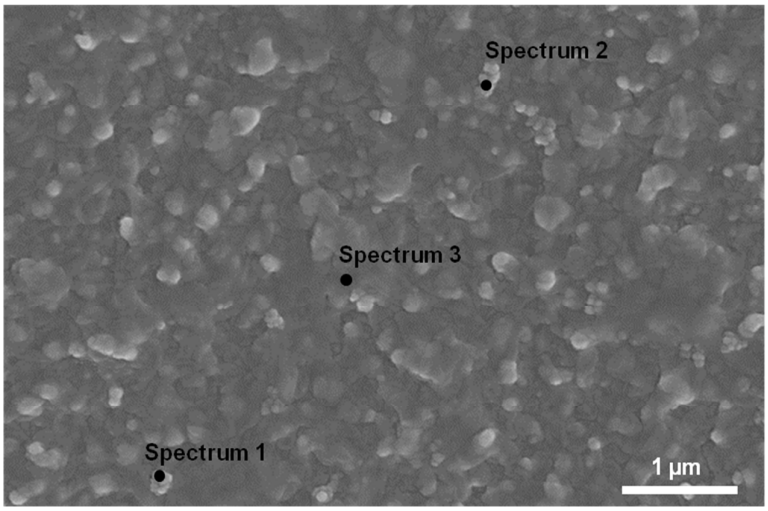

Figure S5. SEM image of 0.2% (w/v) TFN-MIL-101(Cr) surface membrane after DMF dipping.

Table S2. Cr EDX analysis for 0.2% (w/v) TFN-MIL-101(Cr) surface membrane.

Spectrum	Cr (wt%)
1	7.3
2	2.0
3	6.6

In this case, EDX is a qualitative technique, and the element % (w/w) showed in table S2 are just approximate values.

OSN performance of TFN-MIL-101(Cr) membranes with different post-treatments

Table S3. MeOH/PS and THF/PS permeances for TFC and TFN-MIL-101(Cr), 0.2% (w/v) membranes, before and after DMF post- treatments.

Membrane	Permeance MeOH/PS ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	Permeance THF/PS ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)
TFC	0.5	0.2
TFC-PT2 (dipping DMF)	0.6	0.5
TFC-PT4 (filtration DMF)	1.5	1.7
TFN-MIL-101(Cr)	0.6	0.6
TFN-MIL-101(Cr)-PT2 (dipping DMF)	1.7	1.9
TFN-MIL-101(Cr)-PT4 (filtration DMF)	3.9	10.0