

Supplementary information to:

Zwitterion-functionalized MIL-125-NH₂ based thin-film nanocomposite forward osmosis membrane: Towards improved performance for salt rejection and heavy metal removal

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Materials and chemicals

Polyethersulfone (PES) (Ultrason® E 6020, Mw: 58,000) was purchased from BASF Co. Polyethylene glycol 300 (PEG-300), *m*-phenylenediamine (MPD), trimesoyl chloride (TMC), potassium carbonate (K_2CO_3), sodium bicarbonate ($NaHCO_3$), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), magnesium sulfate ($MgSO_4$), monopotassium phosphate (KH_2PO_4), ammonium chloride (NH_4Cl), *N,N*-dimethylformamide (DMF), *n*-hexane, methanol, and acetone were purchased from Merck Co. Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), bovine serum albumin (BSA), titanium isopropoxide (TTIP), 2-aminoterephthalic acid (BDC-NH₂), cyanuric chloride (CC), l-cysteine hydrochloride (l-Cys.HCl) and sodium alginate (SA) were purchased from Sigma Aldrich Co. Sodium chloride (NaCl) was purchased from Iranian Mineral Salts Companies. Except for acetone which must be dried before use, all other applied chemicals in the present work have been used without further purification.

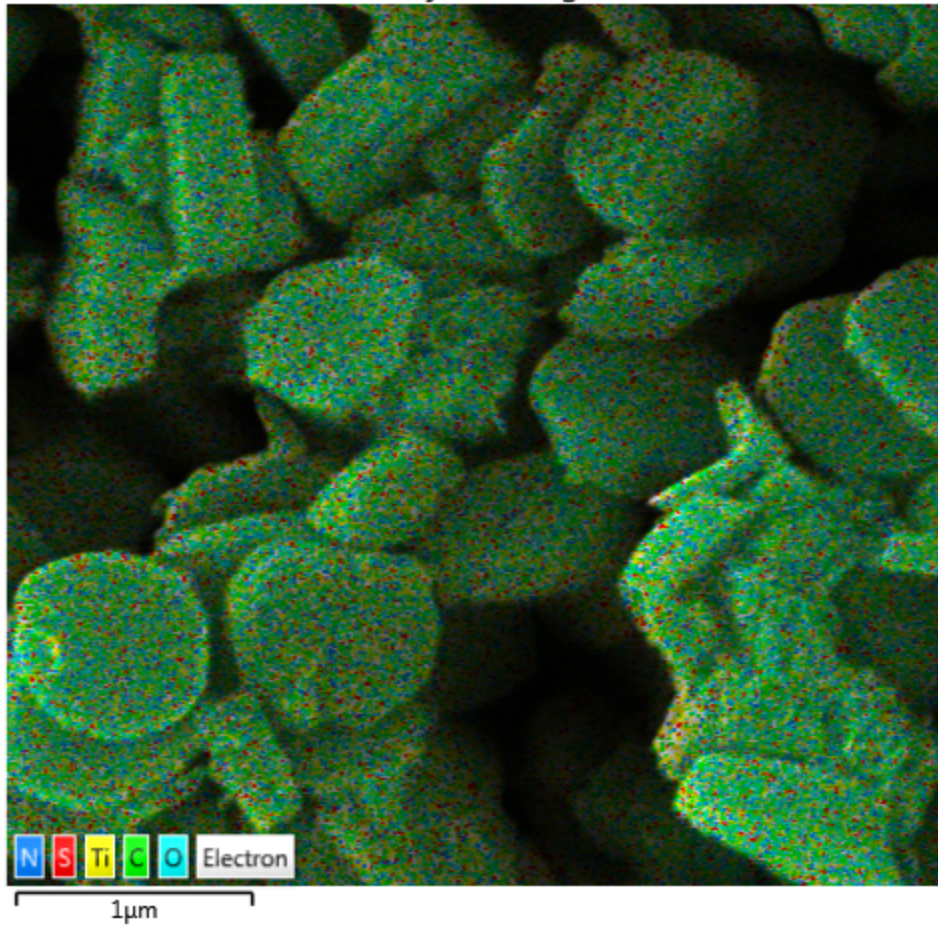
Instruments

Fourier transform infrared spectroscopy (FTIR) of nanofillers and membranes was recorded with a Unicam Matson1000 instrument with the wavenumber ranging from 400 cm^{-1} to 4000 cm^{-1} . Powder X-ray diffraction (XRD) patterns were collected by an XPERT-PRO diffractometer system (MPD PANalytical Company) within the 2θ range from 5° to 80° using a Cu K α radiation source. N₂ adsorption-desorption isotherms were recorded by using Belsorp-mini II instrument at -196°C . The morphology and chemical compositions of the membranes were investigated by field emission scanning electron microscopy (FE-SEM) MIRA3 TESCAN-XMU model equipped with energy-dispersive X-ray spectroscopy (EDS). Before taking FE-SEM images, all samples were coated with a uniform thin layer of conductive gold or platinum metal. Furthermore, the structure and surface roughness of TFC and TFN-M_x membranes were analyzed by atomic force microscope (AFM), ENTEGRA AFMNT-MDT model. Scanning area for each sample was $5\ \mu\text{m} \times 5\ \mu\text{m}$ that scanned at a rate of 0.5 Hz. Water contact angle (WCA) analysis was employed to determine the hydrophilicity behavior of the fabricated membranes surface using a contact angle goniometer (Dataphysics, OCA 15 plus). The surface wettability of membranes was measured at least in five different points of each membrane surface and the data were averaged.

Membrane substrate preparation

Primarily, the polymer powder was dried for daytime to eliminate remnant moisture before executing the next steps. For the preparation of PES membrane substrates, the casting solution was prepared by dissolving 2 g PES in a mixture of 5.6 g PEG and 8.4 g DMF for 6 h in ambient temperature ^{1,2}. The obtained solution was kept untouched for 24 hours to let enclosed air bubbles to leave. The membrane substrate was cast over a tidy polished glass plate exploiting a hand-casting knife with 150 μ in length and immediately dipped in a water bath to allow phase inversion reaction to begin. The final-resulting substrate was hoarded in fresh deionized water for 24 hours before any further modification or alteration.

EDS Layered Image 1



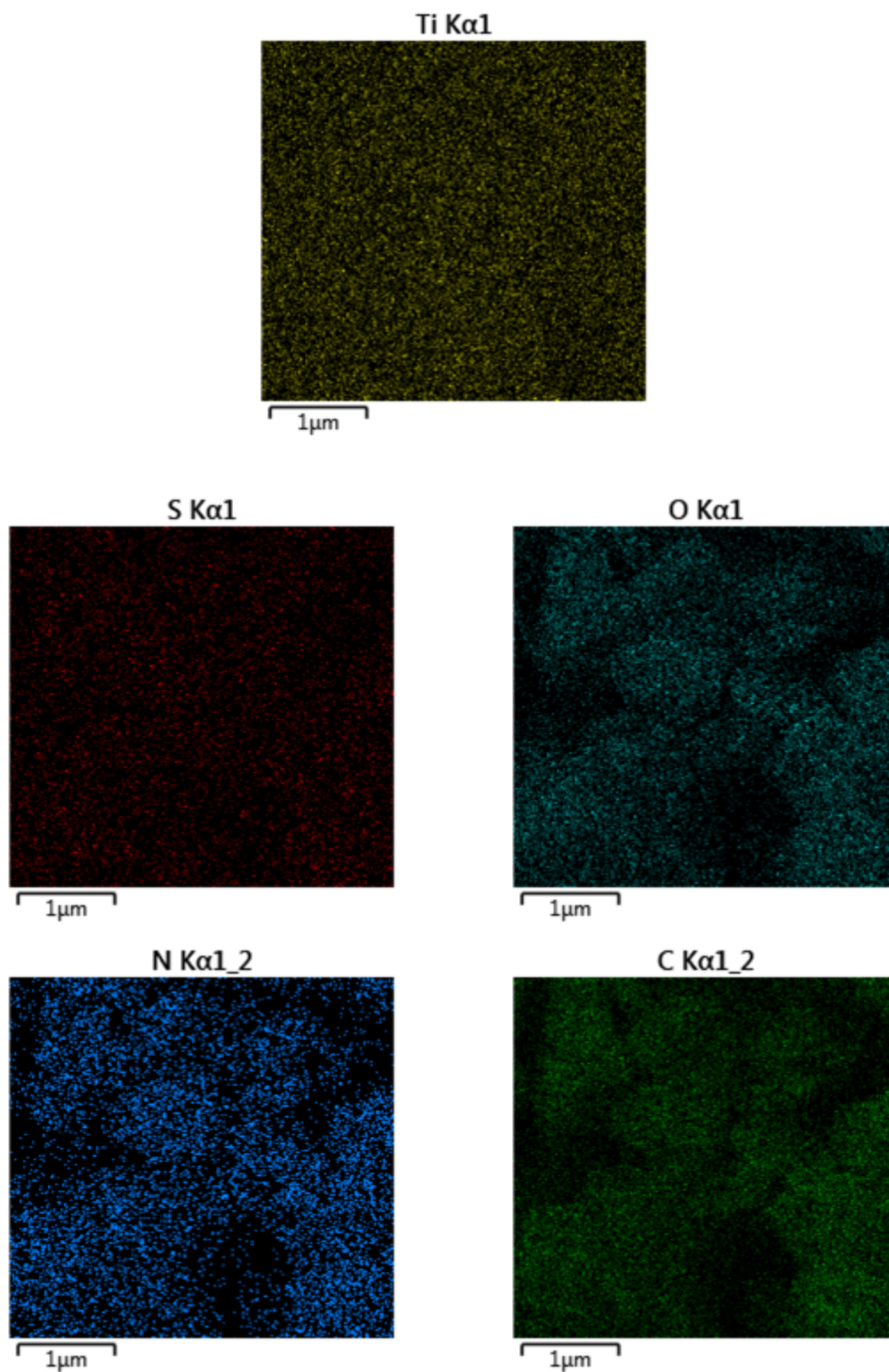


Fig. S1 EDS elemental mapping of C, N, O, S, and Ti elements for MIL-125-NH-CC-Cys nanoparticles.

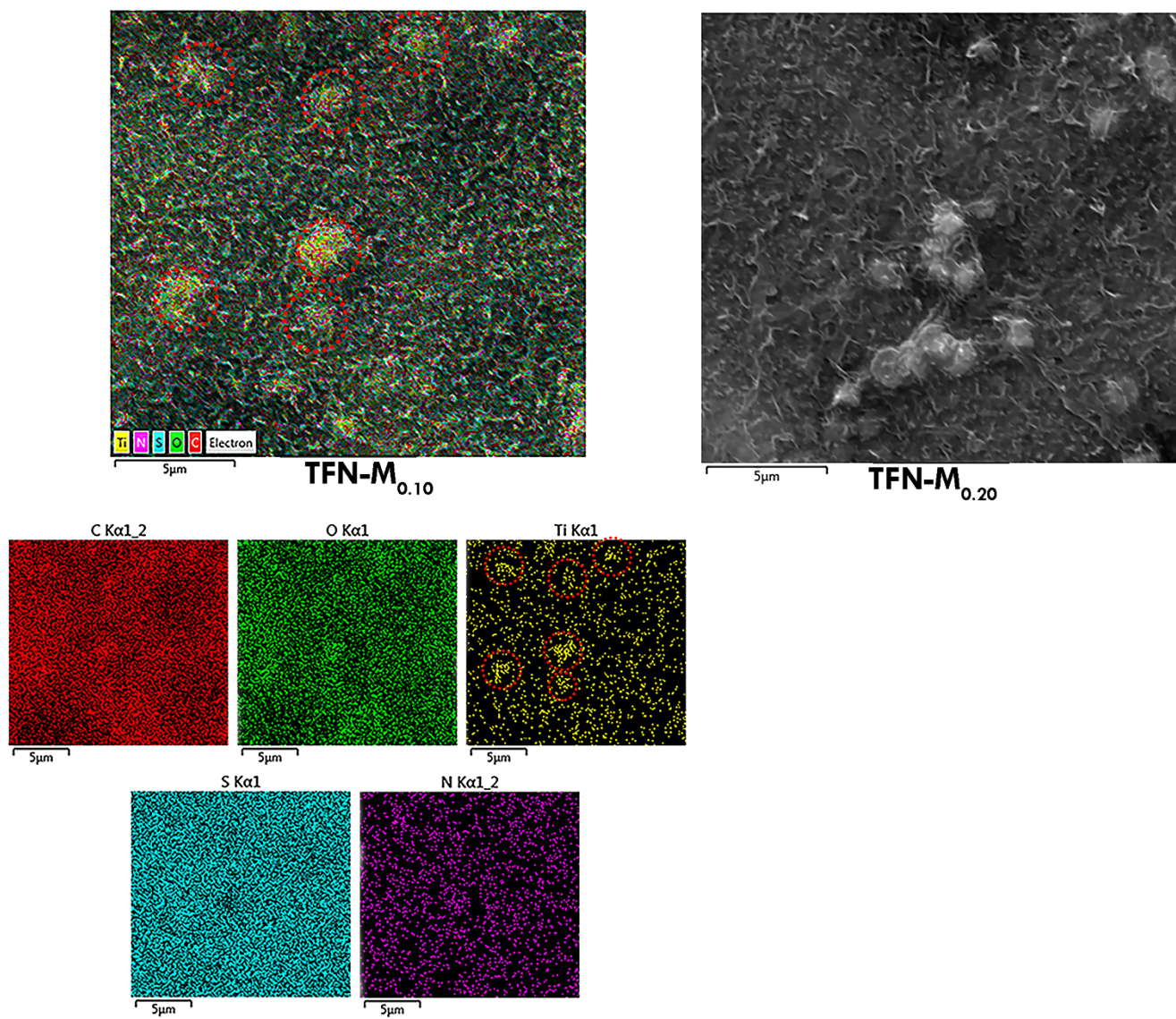


Fig. S2 Top surface EDS elemental mapping of the TFN-M_{0.10} (left) and top surface FESEM images of TFN-M_{0.20} at NPs aggregation region (right).

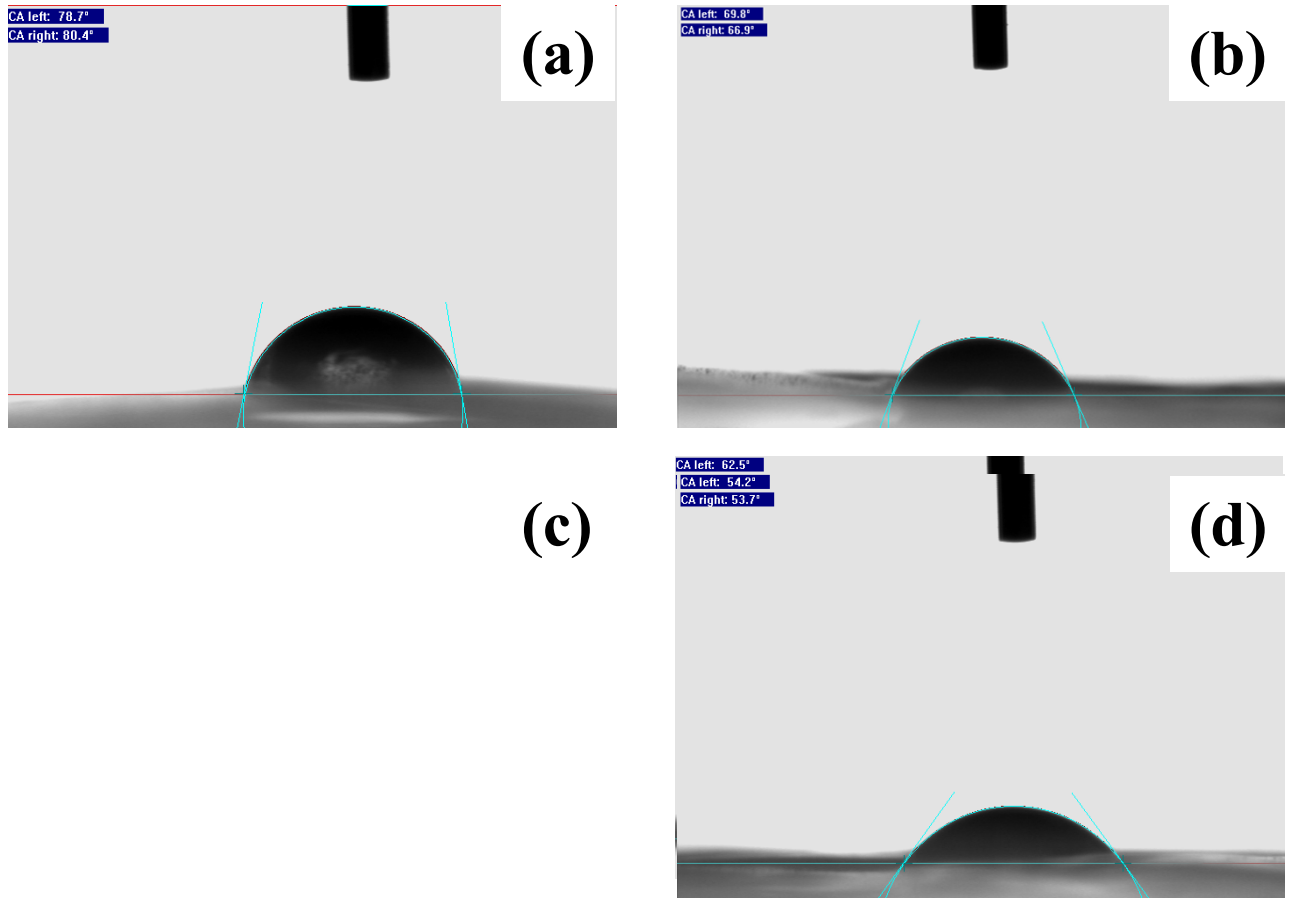


Fig. S3 Selected water contact angle (WCA) images of the (a) TFC, (b) TFN-M₁₀₀, (c) TFN-M₂₀₀ and (d) TFN-M₄₀₀ membranes.

Table S1 A journey to the literature toward the comparison between different inorganic compounds as draw solute

The draw solute	pH (2 M condition)- Approximately	The osmotic pressure (2 M condition)- Approximately	Maximum M of the solubility	The flux of water (experimental data; $\mu\text{m s}^{-1}$)	The diffusion of reverse salt ($\text{g m}^{-2} \text{h}^{-1}$)	References
KNO ₃	6	65	3.3	4.4	176	3
NH ₄ H ₂ PO ₄	3.9	86	3.7	4.3	28.5	3
NaNO ₃	6	81	10.5	5.7	85	3
NH ₄ Cl	4.7	88	7.5	5.3	64	3
NH ₄ NO ₃	4.9	65	84	4.1	228	3
Na ₂ SO ₄	7.5	95	1.8	2.1	2.7	4,5
NaCl	7	100	5.5	2.7	7.2	4,5
MgCl ₂	5.6	256	5	2.3	4.8	4,5
KHCO ₃	8	80	2	2.2	1.4	5
CaCl ₂	6.3	218	7.5	2.6	8	5
KCl	6.8	90	4.6	6.3	60	3
KBr	7	90	4.5	2.8	22	5
MgSO ₄	6.7	55	2.8	1.5	1.2	4,5
NH ₄ HCO ₃	7.7	66	3	2	18.5	5
K ₂ SO ₄	7.3	32	3.6	2.5	3.7	5

Table S2 Intrinsic permeability and structural parameters for TFC and TFN-M_x membranes, which calculated by the Matlab-based algorithm.

Membrane	A (LMH bar⁻¹)	B (LMH)	S (μm)	B/A (bar)	R² (J_w)	R² (J_s)
TFC	1.55 ± 0.21	0.393 ± 0.037	417 ± 11	0.25	0.97	0.97
TFN-M _{0.05}	2.37 ± 0.14	0.526 ± 0.024	419 ± 10	0.22	0.95	0.95
TFN-M _{0.10}	2.79 ± 0.12	0.571 ± 0.025	405 ± 12	0.20	0.99	0.99
TFN-M _{0.20}	2.53 ± 0.10	0.518 ± 0.022	401 ± 9	0.20	0.96	0.96

Table S3 Comparison between the FO performances of TFN-M_{0.10} membrane with relevant previously reported membranes

Entry	Membranes with filler wt.% (Nanoparticles)	Feed and draw solution, respectively	J_w (LMH)	J_s (gMH)	J_s/J_w (g/L)	Membrane orientation	Flux recovery ratios (FRR) in fouling experiment (%)		References
							SA	BSA	
1	TFN-M _{0.10} MIL-125-NH-CC-His	NaCl 1 M and DI water	39.56	10.56	0.27	PRO	-	-	Present work
			25.48	5.62	0.22	FO	87	90	
	23.85		8.18	0.34	PRO	-	-		
	15.85		4.94	0.32	FO	68	74		
2	TFN-U2 (UiO-66)	NaCl 1 M and DI water	36.7	7.1	0.20	PRO	-	-	6
			20.7	4.3	0.21	FO	NR*	NR	
3	M1 M2 (Ag-MOF)	NaCl 1 M and DI water	~31	~5.61	~0.18	FO	~77	NR	7
			~23	~5.73	~0.25		~60	NR	
4	TFN _{w0.2} QNP@WPO M	NaCl 1 M and DI water	45.9	15.9	0.35	PRO	-	-	8
			30.2	8.5	0.35	FO	~>90	~85-90	
5	TFN0.1 NaY	NaCl 1 M and DI water	38.7	15	0.39	PRO	-	-	9
			17.5	7.5	0.43	FO	NR	NR	
6	TFN-2 LDH/GO	NaCl 1 M and DI water	23.6	6.9	0.29	PRO	-	-	10
			13.4	6.2	0.46	FO	NR	NR	
7	HTI TFC (commercially available)	NaCl 1 M and DI water	46.4	24.9	0.46	PRO	-	-	11
			22.9	6.4	0.34	FO	NR	NR	

*Not reported

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