Supporting Information

Flexible Aliphatic-Aromatic Polyamide Thin Film Composite Membrane for Highly Efficient Organic Solvent Nanofiltration

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Table of Contents

1. Figures

1.1 SEM images of the PEI/TMC TFC membrane surface

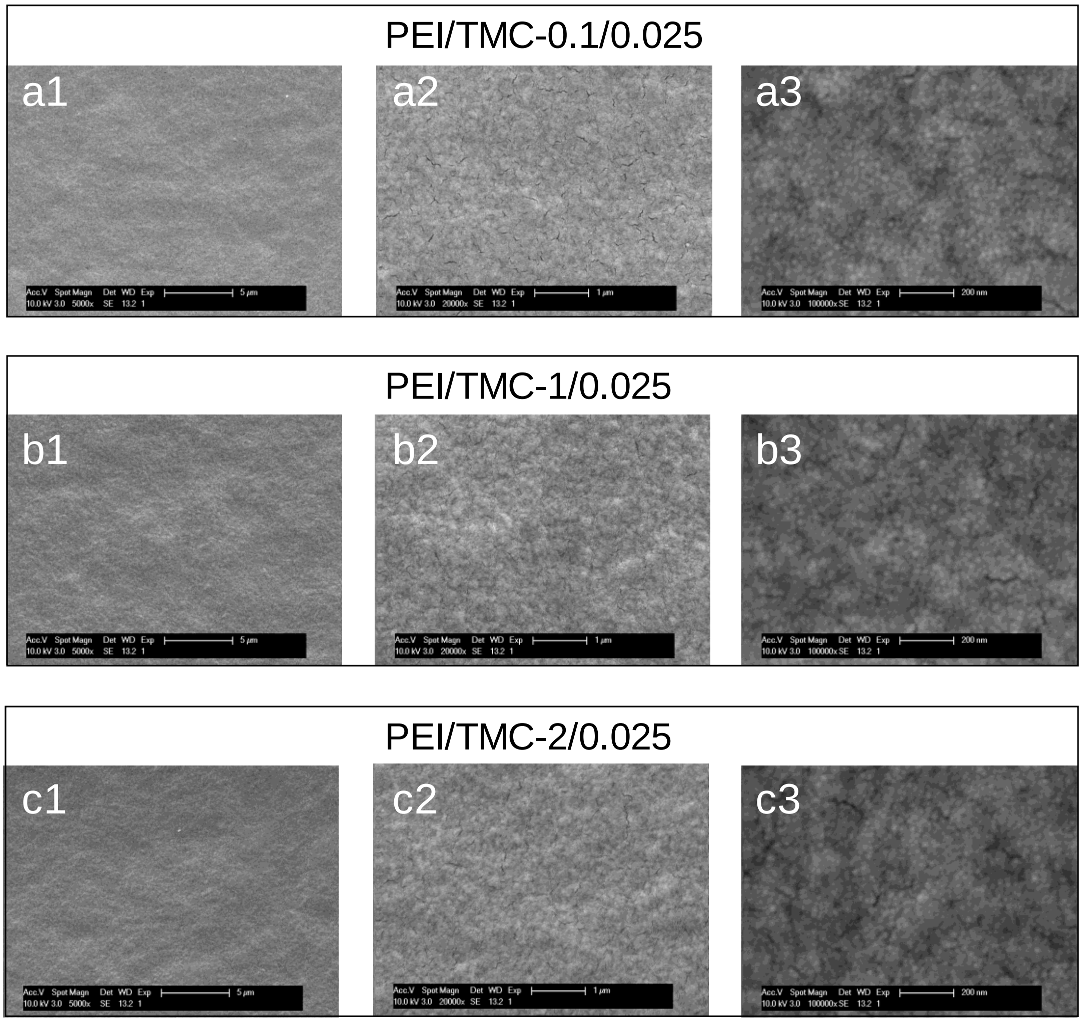

Figure S1. The membrane surface of the PEI/TMC composite membrane. a1- a3: PEI/TMC-0.1/0.025 membrane; b1- b3: PEI/TMC-1/0.025 membrane; c1- c3: PEI/TMC- 2/0.025 membrane.

1.2 Cross-sectional SEM images of the activated PEI/TMC TFC membrane

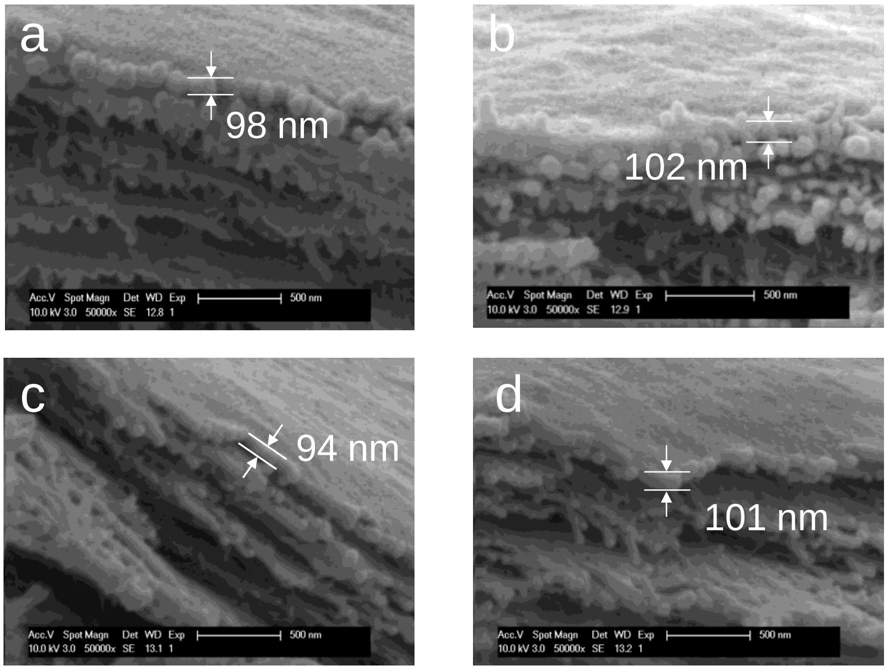

Figure S2. The cross-sectional SEM images of the PEI/TMC TFC membrane after different activation durations in DMF. (a) 30 min; (b) 60 min; (c) 180 min; (d) 1440 min.

1.3 Synthesis of the PEI/TMC polymer

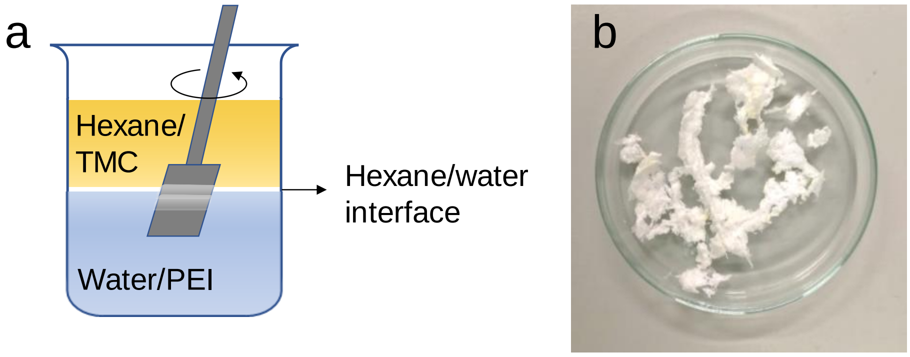

Figure S3. (a) Synthesis of the cross-linked PEI/TMC polymer. (b) The powder of the PEI/TMC polymer.

The cross-linked PEI/TMC polymer is synthesized through a support free oil/water interface, as shown in Figure S3a. The solution of PEI (0.25 wt%) and TMC (0.025 w/v%) was poured in a glass beaker. The synthesized PEI/TMC polymer was collected by continuously wrapping the nanofilm on a stainless steel sheet. The collected cross-linked polymer was further washed with plenty of methanol and DI water for three times to remove the residue monomers and tiny polymers. After washing, the PEI/TMC polymer was moved to a vacuum oven and dried at 60°C for 24 hours. The obtained polymer is shown in Figure S3b.

1.4 OSN performances of the pristine membrane without DMF activation

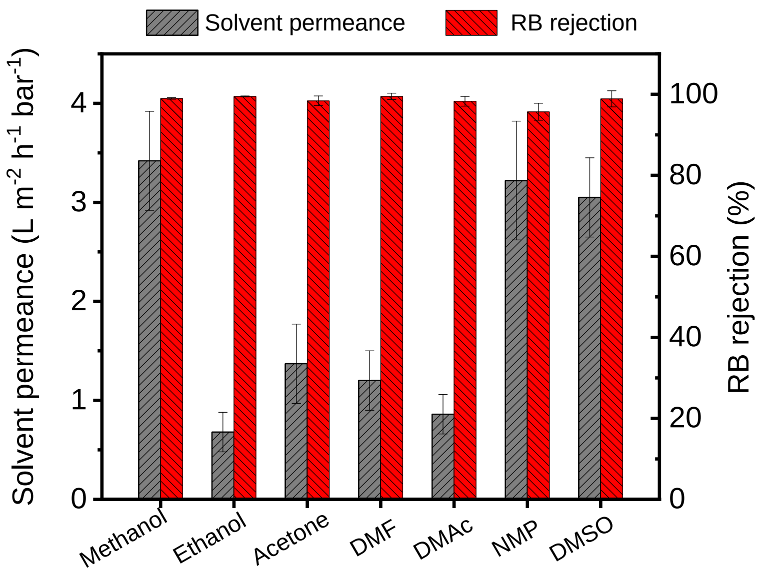

Figure S4. (a) OSN performances of TFC-8 membrane in various organic solvents using RB as the solute with concentration of 30 mg L^{-1}. Tested at 6 bar, 600 rpm and room temperature.

1.5 Long-term filtration performances in methanol and acetone

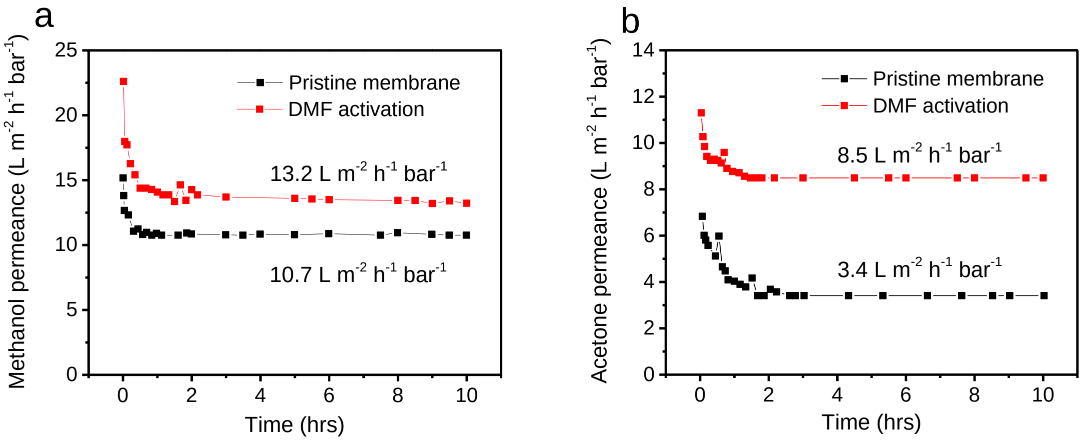

Figure S5. A 10-hour filtration of the pristine membrane and the DMF activated membrane in pure methanol and acetone, respectively. (a) methanol; (b) acetone.

1.6 MWCO of the pristine membrane without DMF activation

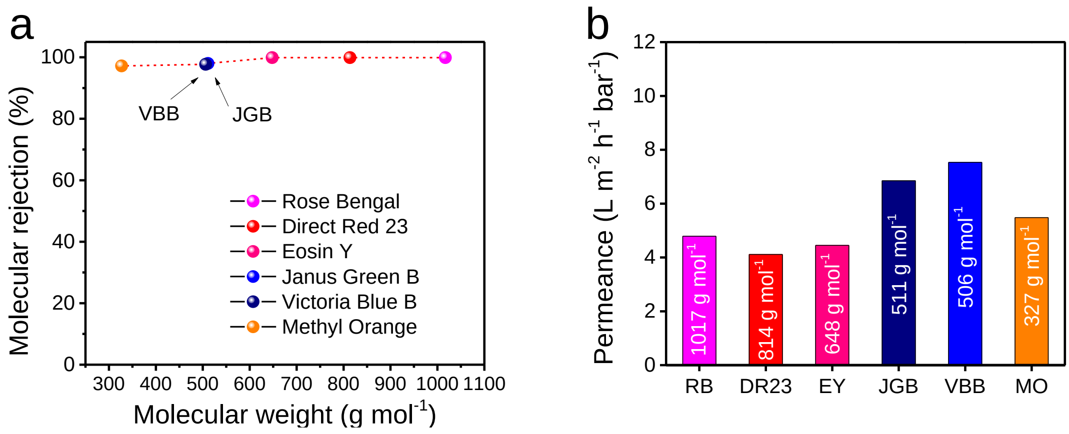

Figure S6. Molecular rejection (a) and solvent permeance (b) of the TFC-8 membrane in methanol/dye separations. (rose Bengal (RB, 1017 g mol^{-1}), direct red 23 (DR23, 814 g mol^{-1}), eosin Y (EY, 648 g mol^{-1}), Janus green B (JGB, 511 g mol^{-1}), victory Blue B (VBB, 506 g mol^{-1}), methyl orange (MO, 327 g mol^{-1}))

1.7 UV-Vis absorption spectrums

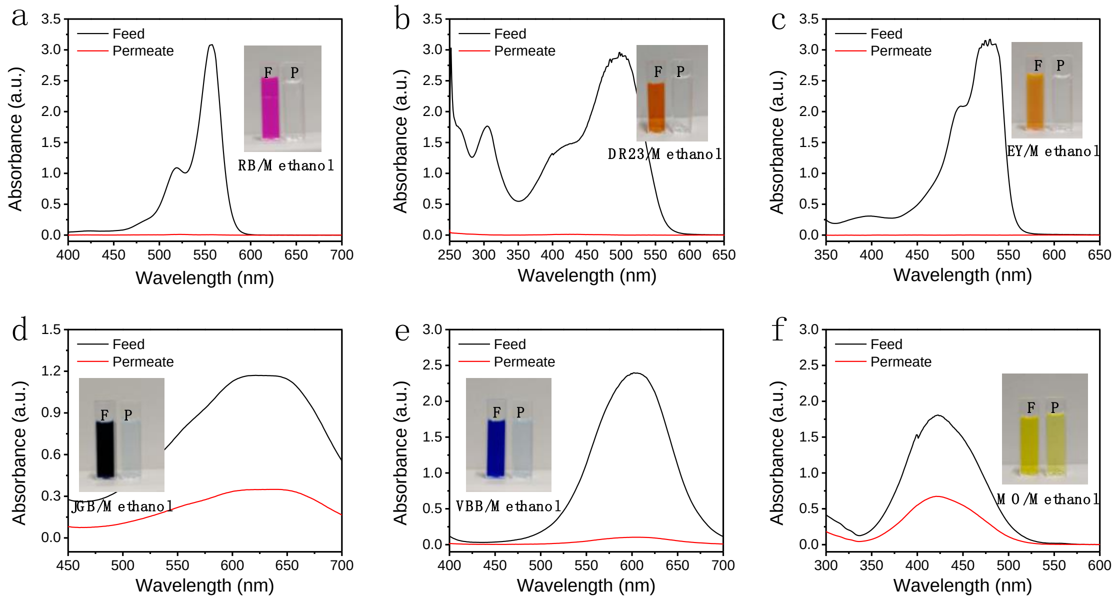

Figure S7. The UV-Vis absorption of the methanol/dye solution in the permeate and the feed.

1.8 The set-up of the METcell Cross-Flow System

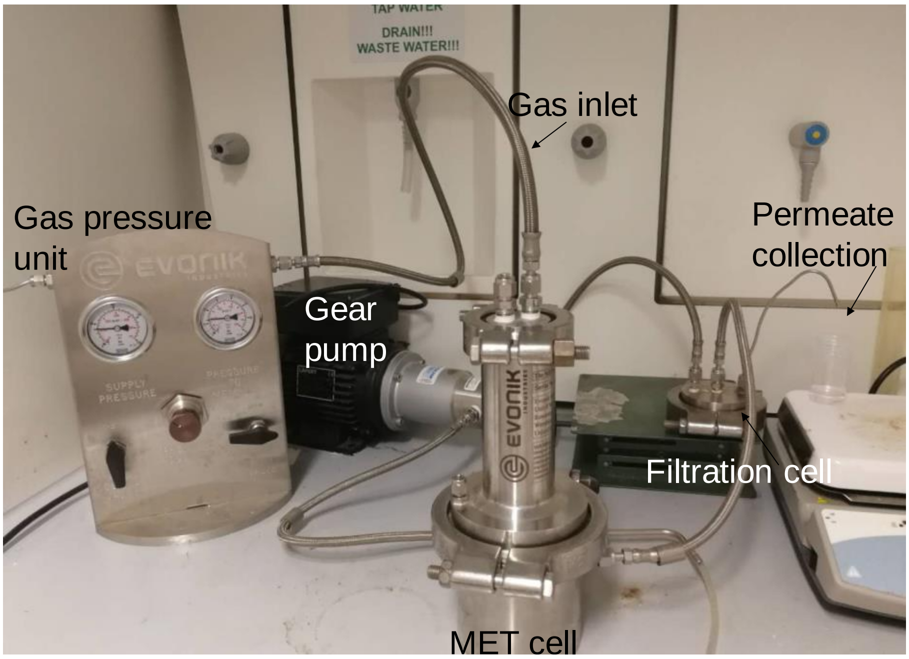

Figure S8. Assembled METcell Cross-Flow System.

2. Tables

2.1 OSN performances comparison with literatures

Table S1. OSN performances comparison with the reported crosslinked PEI/TMC TFC OSN membranes.

Membrane	PEI Mw/Da	Substrate	Thickness/nm	Solvent	Marker / Da	Permeability / L m^{-2} h^{-1} bar^{-1}	Rejection/ %	MWCO/Da	Ref.
PEI-CDs/TMC	20,000	PAN	200	Acetone	PEG (800)	1.5	> 90	800	[1]
PEI-	20,000	PAN	482	Acetone	PEG	1.3	99	200	[2]

GO/TMC					(1000)				
				Ethanol		0.8			
PEI-MOF/TMC	10,000	PAN	230	Methanol	RB (1018)	10~20	95~97	1018	3
				Ethanol		6~13	96~98		
PEI-ZIF-8-GO/GA[a]	60,000	Ceramic substrate	850	Methanol	MB (800)	5.0	99	800	4
PEI-silica/TMC	20,000	PAN	/	Isopropanol	PEG (1000)	0.6	99.9	394	5
PEI-SiO2-Py/TMC	20,000	PAN	368	Ethanol	PEG (1000)	2.1	97.3	564	6
PEI/TMC	800	ANF hydrogel	98	Methanol	MO (327)	5.5	97.2	327	This work
				Methanol (DMF activation)	VBB (506)	10.3	98.6	506	
				DMF	RB (1018)	6.4	99.2	648	
					DR23 (814)	6.5	99.5		
					EY (648)	6.9	95.6		
				DMSO	RB (1018)	4.3	98.9	814	
					DR23 (814)	3.4	98.4		

[a] The membrane was prepared from vacuum-assisted assembly method.

2.2 Raw data of solvent swelling degree and solvent uptake

Table S2. Raw data of solvent swelling of the PEI/TMC TFC membrane.

Solvent	W_{wet} (g)	W_{dry} (g)	Solvent swelling degree (%)	Solvent uptake (cm^3 g^{-1})
MeOH	0.0819	0.0391	109.5	1.4
EtOH	0.0793	0.0416	90.6	1.2
Acetone	0.0860	0.0394	118.3	1.5
DMF	0.0946	0.0394	140.1	1.5
DMAc	0.0973	0.0392	148.2	1.6
NMP	0.1008	0.0381	164.6	1.6
DMSO	0.1180	0.0404	192.1	1.8

Table S3. Raw data of solvent swelling of the ANF sublayer membrane.

Solvent	W_{wet} (g)	W_{dry} (g)	Solvent swelling degree (%)	Solvent uptake (cm^3 g^{-1})
MeOH	0.0960	0.0468	105.1	1.3
EtOH	0.0932	0.0434	114.8	1.5
Acetone	0.1078	0.050	115.6	1.5
DMF	0.1083	0.0428	153.0	1.6
DMAc	0.1335	0.050	167.0	1.8
NMP	0.1121	0.0404	177.5	1.7
DMSO	0.1365	0.0470	190.4	1.7

Table S4. Raw data of solvent swelling of the cross-linked PEI/TMC polymer.

Solvent	W_{dry} (g)	W_{wet} (g)	Solvent swelling degree (%)	Solvent uptake (cm^3 g^{-1})
MeOH	0.0323	0.1230	280.8	3.6
EtOH	0.0404	0.1371	239.4	3.0
Acetone	0.0294	0.0799	171.8	2.2
DMF	0.0091	0.0515	465.9	5.0
DMAc	0.0085	0.0636	648.2	7.0
NMP	0.0065	0.0802	1133.9	11.0
DMSO	0.0081	0.1116	1277.9	11.6

2.3 Effect of monomer concentrations on OSN performances

Table S5. The separation performances of PEI/TMC ANF TFC membranes in DMF/RB solution. (rose Bengal concentration: 30 mg/L; Tested at pressure of 6 bar with stirring of 600 rpm in a dead-end filtration)

Membrane	PEI conc. (wt%)	TMC conc. (w/v%)	DMF permeance (L m^{-2} h^{-1} bar^{-1})	Rose Bengal rejection (%)
TFC-1	2	0.05	0.5 ± 0.2	97.1 ± 1.2

TFC-2	2	0.025	3.3 ± 0.8	93.4 ± 1.5
TFC-3	2	0.01	18.6 ± 2.0	70.9 ± 3.5
TFC-4	1	0.025	2.1 ± 0.1	97.7 ± 1.0
TFC-5	1	0.01	6.5 ± 2.1	92.6 ± 3.9
TFC-6	0.5	0.025	1.1 ± 0.1	98.5 ± 0.8
TFC-7	0.5	0.01	3.5 ± 1.7	95.1 ± 2.3
TFC-8	0.25	0.025	1.1 ± 0.1	99.4 ± 0.1
TFC-9	0.25	0.01	2.8 ± 0.7	96.8 ± 0.4
TFC-10	0.1	0.025	1.9 ± 0.9	99.4 ± 0.4
TFC-11	0.1	0.01	2.8 ± 1.5	95.6 ± 0.6
TFC-12	0.1	0.05	0.1 ± 0.1	99.5 ± 0.2

The effect of monomer concentrations on the OSN performances of the aliphatic polyamide TFC membrane was systemically investigated. The separation performances of the prepared membranes were evaluated in DMF/RB organic solution as shown in Table S5. When fixing the PEI concentration, a higher TMC concentration shows a better RB rejection but a lower DMF permeance. For example, when the PEI concentration was 2 wt%, the membranes prepared with TMC concentration of 0.05, 0.025 and 0.01 w/v% has a RB rejection in a decreasing sequence of: 97.1 ± 1.2% (TFC-1) > 93.4 ± 1.5% (TFC-2) > 70.9 ± 3.5% (TFC-3). While, the DMF permeances display an increasing trend of 0.5 ± 0.2 L m^{-2} h^{-1} bar^{-1} (TFC-1) < 3.3 ± 0.8 L m^{-2} h^{-1} bar^{-1} (TFC-2) < 18.6 ± 2.0 L m^{-2} h^{-1} bar^{-1} (TFC-3). Interestingly, it can also be found that a higher PEI/TMC monomer concentration does not give a higher solute rejection. In other words, a lower monomer concentration produces a more selective aliphatic polyamide thin film but a denser membrane with a lower solvent permeability. As examples of TFC-3, TFC-5, TFC-7, TFC-9 and TFC-11 membranes. The TMC concentration was fixed at 0.01 w/v% and the PEI concentration was varied from 2 wt% to 0.1 wt%. The resultant DMF permeance decreased significantly but the RB rejection increased. This could be explained by the higher monomer concentration leading to a fast reaction rate The excessive heat released during the IP reaction introduces the defects and the imperfect cross-linking reaction.[7] However, a permselective membrane with perfect solute rejection is highly desirable in OSN process. Therefore, TFC-8, TFC-10 and TFC-12 are the promising candidates for OSN application by considering their exceptional RB rejections (> 99%), though the DMF permeances were less than 2.0 L m^{-2} h^{-1} bar^{-1}. Among the three membranes, TFC-8 membrane is considered to be the most stable and reproducible membrane in terms of the standard deviation (± 0.1) for both DMF permeance and RB rejection. Thus, this membrane was selected as the typical nanofibrous TFC membrane for the following experiments.

2.4 Physical properties of organic solvent

Table S6. Solvent physical properties.

Solvent	Viscosity (η, mPa · s)	Molar volume (V_m, cm^3 mol^{-1})	Density (g cm^{-3})	Hansen Solubility Parameter ($MPa^{1/2}$)			Pure solvent permeance (L m^{-2} h^{-1} bar^{-1})
				δ_d	δ_p	δ_h	

Methanol	0.54	40.46	0.79	15.1	12.3	22.3	13.2±0.2
Ethanol	1.07	58.32	0.79	15.8	8.8	19.4	5.1±1.0
Acetone	0.32	73.52	0.79	15.5	10.4	7.0	8.5±0.4
DMF	0.8	76.94	0.95	17.4	13.7	11.3	6.9±0.1
DMAc	0.92	92.68	0.94	16.8	11.5	10.2	3.3±0.5
NMP	1.65	96.24	1.03	18.0	12.3	7.2	2.3±0.3
DMSO	1.987	71.03	1.1	18.4	16.4	10.2	7.9±0.7

2.5 OSN permeance of PEI/TMC membranes

Table S7. Molecular separation performances comparison for the PEI/TMC-0.25/0.025 composite membrane with and without DMF activation. The membranes were tested in methanol at 6 bar, 600 rpm.

Dye	PEI/TMC-0.25/0.025		PEI/TMC-0.25/0.025 (DMF activation: 30 min)	
	Rejection (%)	Permeance (L m^{-2} h^{-1} bar^{-1})	Rejection (%)	Permeance (L m^{-2} h^{-1} bar^{-1})
RB	99.9	4.8	99.9	5.5
DR23	99.9	4.1	99.9	5.3
EY	99.9	4.5	99.9	4.6
JGB	90.0	6.9	98.4	9.9
VBB	94.7	7.5	98.6	10.3
MO	97.2	5.5	63.0	10.7

2.6 UV-Vis data for molecular separation in DMSO

Table S8. The separation of MO from DR23 in DMSO.

Molecule	Wavelength (nm)	UV-Vis absorption (a. u.)			Rejection (%)
		Feed	Permeate	Retentate	
MO	430	0.48	0.57	1.04	-
DR23	507	1.22	0.00	3.48	99.9

Table S9. The separation of EY from DR23 in DMSO.

Molecule	Wavelength (nm)	UV-Vis absorption (a. u.)			Rejection (%)
		Feed	Permeate	Retentate	
EY	530	2.34	0.31	3.18	86.8
DR23+EY	507	1.75	0.15	2.65	-
DR23	430	0.71	0.0	1.11	99.9

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