

## Electronic Supplementary Information

### **Microporous poly(triaminoguanidinium-amide) nanofilms with sub-nm precision for ultra-low molecular weight cut-off in nanofiltration**

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## **Materials and chemicals.**

Polyacrylonitrile was received from Indian Petrochemicals Corporation Limited (IPCL), India. Trimesoyl chloride (TMC, 98%), LR white resin, and the benzoyl peroxide catalyst were purchased from Sigma Aldrich, India. Hydrazine hydrate (~80%) was purchased from Spectrochem Pvt. Ltd., India. Bovine serum albumin (BSA, 98%), n-hexane 99% HPLC, sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>, 99.5%), magnesium chloride (MgCl<sub>2</sub>, 99%), sodium chloride (NaCl, 99.9%), magnesium sulphate (MgSO<sub>4</sub>, 99%), sodium hydroxide (NaOH, extrapure, 98%), glycerol (99%), D-glucose (extrapure, >99%), and sucrose (extrapure AR, ACS) were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), India. Guanidine hydrochloride (> 98.0%), 6-hydroxy-2-naphthalene sulfonic acid sodium salt (> 97%), methyl orange, orange G, acid fuchsin, and brilliant blue R were purchased from TCI Chemicals (India) Pvt. Ltd. Isopropanol, methanol, and dimethylformamide (DMF) were of AR grade and were purchased from SD. Fine-Chem Limited, India. N-type <100> silicon wafers were used as a substrate for atomic force microscopy (AFM) and scanning electron microscopy (SEM) study and were purchased from University wafer, Boston, USA. Silicon wafers with 100 nm thick gold coating (PLATYPUS™) were used for the X-ray photoemission spectroscopy (XPS) study and were purchased from Agar Scientific, UK. Polyester nonwoven fabric (Nordlys-TS100-100-500-T76/96, Polymer Group Inc., France) was used to make ultrafiltration support membranes via phase inversion. Pure water (conductivity < 2 μS) was prepared from a double pass reverse osmosis system and used to synthesize composite membrane and study the nanofiltration performance.

## Synthesis of triaminoguanidinium chloride (TG) monomer:

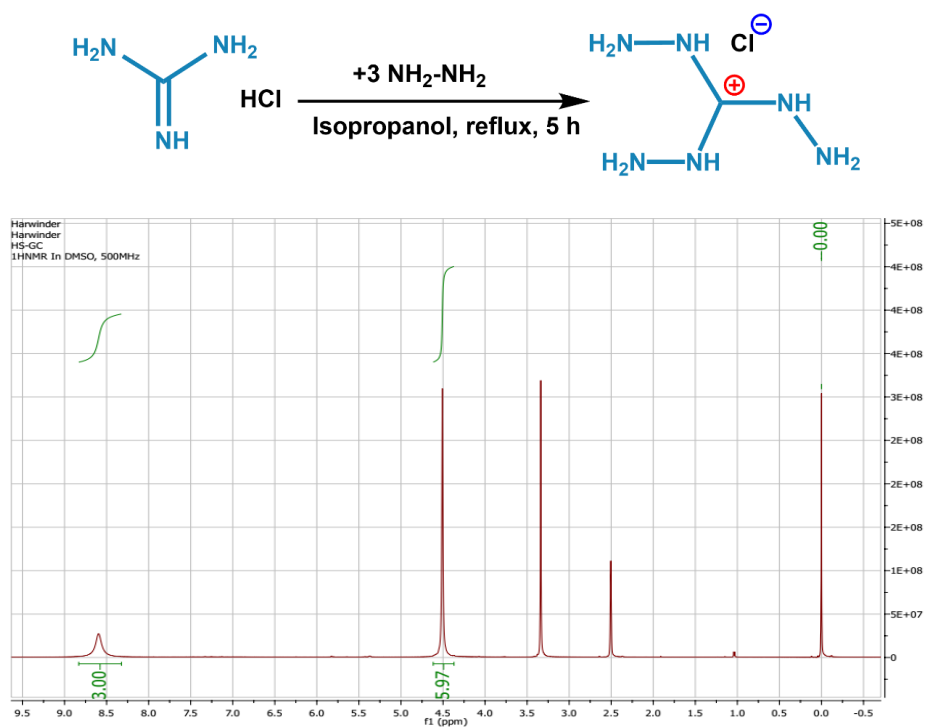


Fig. S1.  $^1\text{H NMR}$  of triaminoguanidinium (TG) in DMSO.

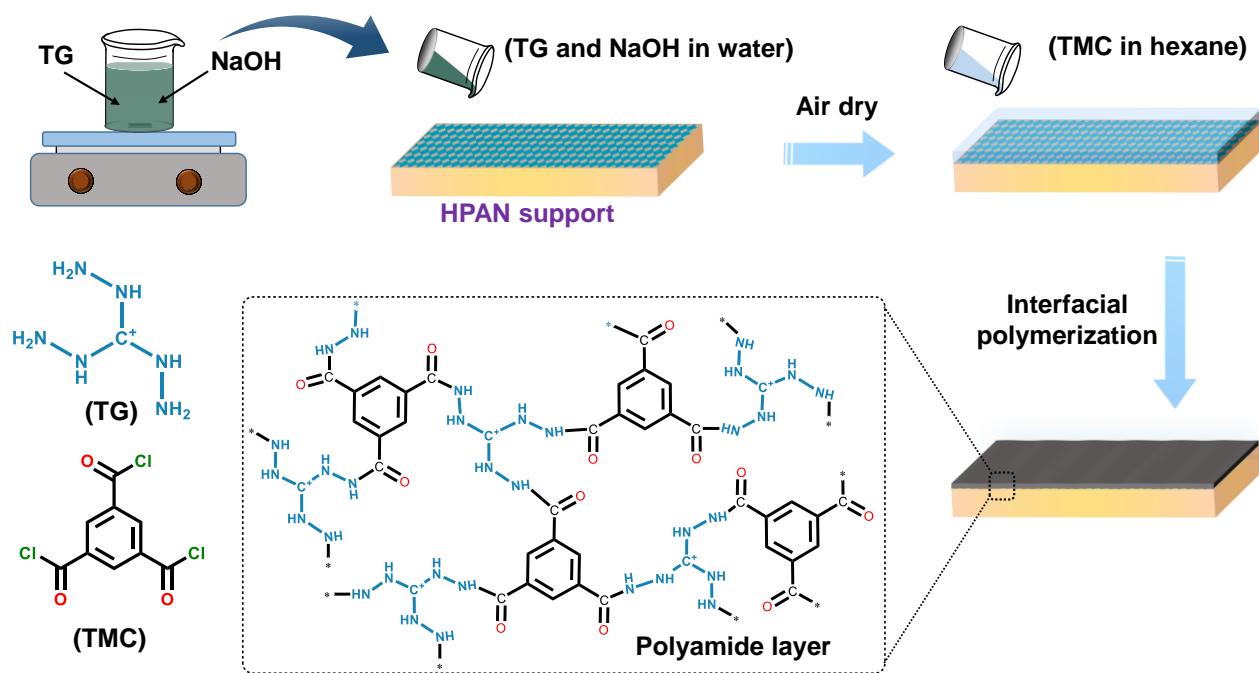
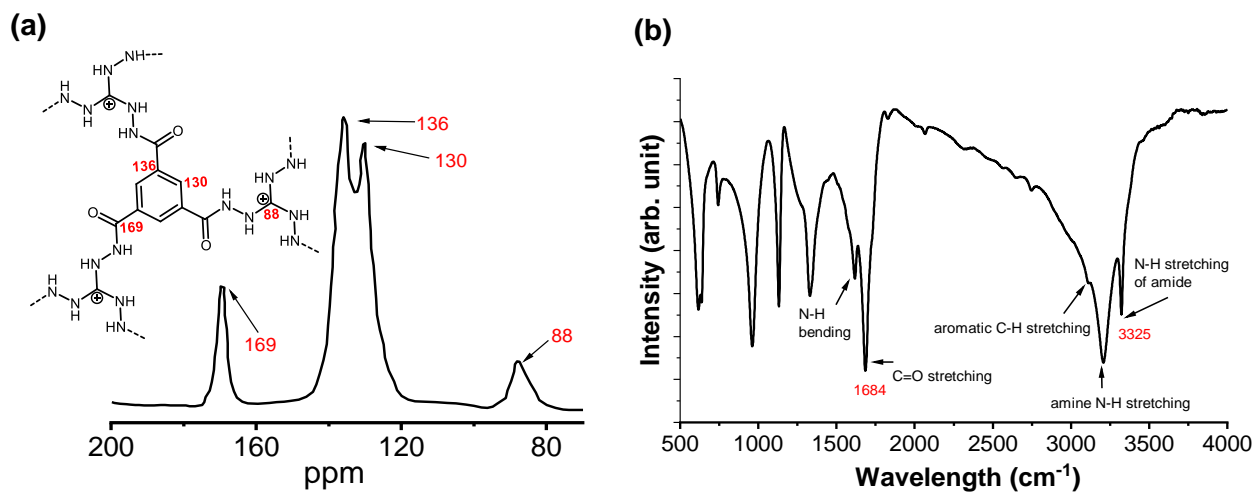


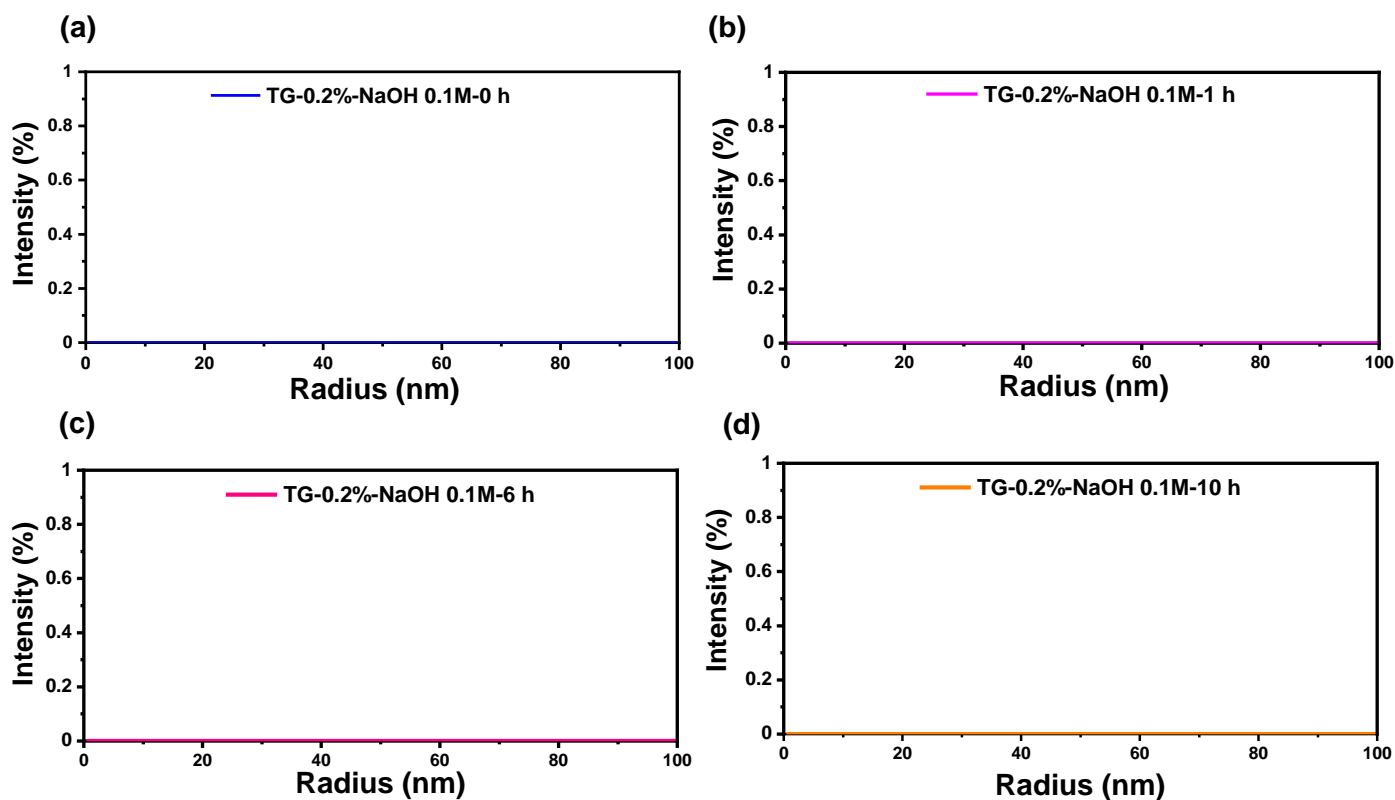
Fig. S2. The fabrication process of poly(triaminoguanidinium-amide) nanofilm composite membrane via interfacial polymerization.



**Fig. S3.** (a)  $^{13}\text{C}$  solid-state NMR, and b) FTIR spectra of poly(triaminoguanidinium-amide) nanofilm. Several milligrams of nanofilm powder samples were collected by vigorous mixing at the bulk liquid-liquid interface. The sample was washed repeatedly in water and acetone and dried in a hot air oven at  $45 (\pm 1) ^\circ\text{C}$  for 2 h.

### Dynamic light scattering (DLS) study:

We used a dynamic light scattering (DLS) instrument to study the behaviour of triaminoguanidinium chloride (TG) monomer in the presence of NaOH in the aqueous solution. 0.2 wt% TG monomer and 0.1 M sodium hydroxide were mixed in water and stirred for different aging times. Four TG and NaOH mixed solutions were prepared with different aging times (0, 1, 6, and 10 hours) and studied using DLS (Fig. S4).



**Fig. S4.** The particle size distribution study of triaminoguanidinium chloride (TG) monomer in the presence of NaOH in the aqueous solution by using the dynamic light scattering (DLS) method. The solution was prepared by mixing 0.2 wt% TG monomer and 0.1 M sodium hydroxide in water under the stirring condition at different aging times (0 hour, 1 hour, 6 hour, and 10 hour).

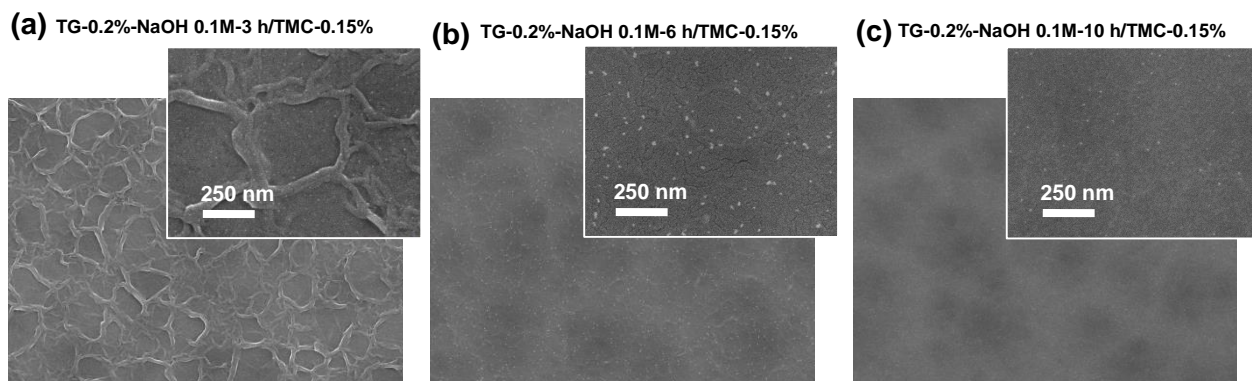
## Preparation condition of poly(triaminoguanidinium-amide) composite membranes:

**Table S1.** Preparation conditions of poly(triaminoguanidinium-amide) nanofilm composite membranes via interfacial polymerization by using triaminoguanidinium chloride (TG) and NaOH in the aqueous phase and TMC in the organic (hexane) phase. Post-treatment was done by annealing at 70 ( $\pm$ 1) °C for 1 minute in a hot air oven.

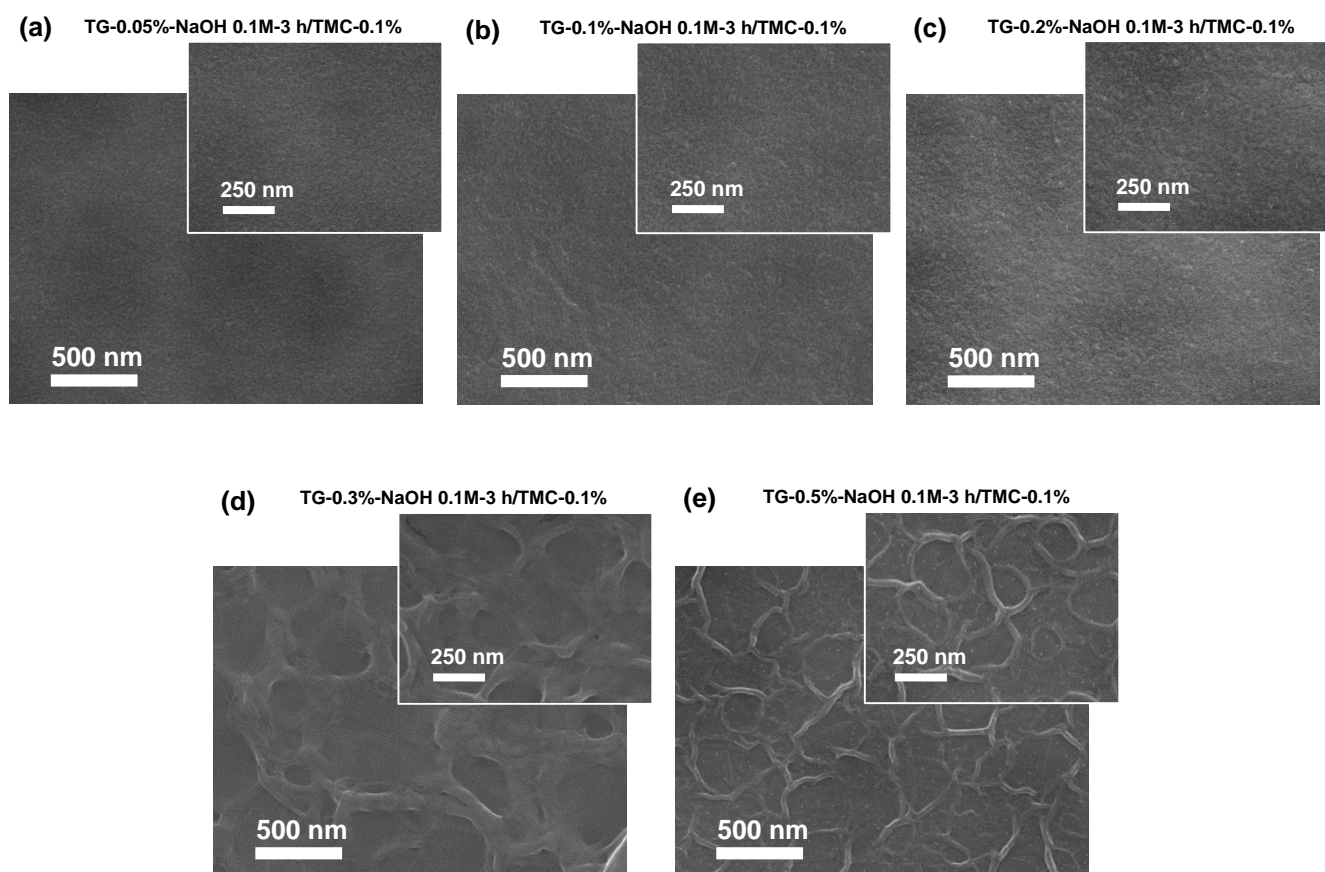
Preparation conditions: TG amine- w/w%-NaOH [M]-aging (stirring) time/TMC-w/w%	Aqueous solution containing amine [w/w%] and NaOH [M]			TMC in organic phase [w/w%]	IP time [sec]	Post- annealing condition
	TG [w/w%]	NaOH [M]	Stirring time [h]			
TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	TG [0.2]	0.1	0	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%	TG [0.2]	0.1	1	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%	TG [0.2]	0.1	3	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%	TG [0.2]	0.1	4	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%	TG [0.2]	0.1	6	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%	TG [0.2]	0.1	10	TMC [0.15]	10	70 °C /1 min
TG-0.05%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.05]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.1%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.1]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.2]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.3%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.3]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.5%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.5]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.2%-NaOH 0.0M-0 h/TMC-0.15%	TG [0.2]	0.0	0	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.01M-0 h/TMC-0.15%	TG [0.2]	0.01	0	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.05M-0 h/TMC-0.15%	TG [0.2]	0.05	0	TMC [0.15]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-3 h/TMC-0.05%	TG [0.2]	0.1	3	TMC [0.05]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-3 h/TMC-0.1%	TG [0.2]	0.1	3	TMC [0.1]	10	70 °C /1 min
TG-0.2%-NaOH 0.1M-3 h/TMC-0.2%	TG [0.2]	0.1	3	TMC [0.2]	10	70 °C /1 min
#TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%- FSU	TG [0.2]	0.1	0	TMC [0.15]	10	NA
#TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%- RSU	TG [0.2]	0.1	0	TMC [0.15]	10	NA

TG: triaminoguanidinium chloride; TMC: trimesoyl chloride. #Nanofilms were made at the bulk water-hexane interface, followed by the transfer of the nanofilm onto the water surface and then onto the gold-coated silicon wafer support. FSU: Front side up, RSU: Rear side up.

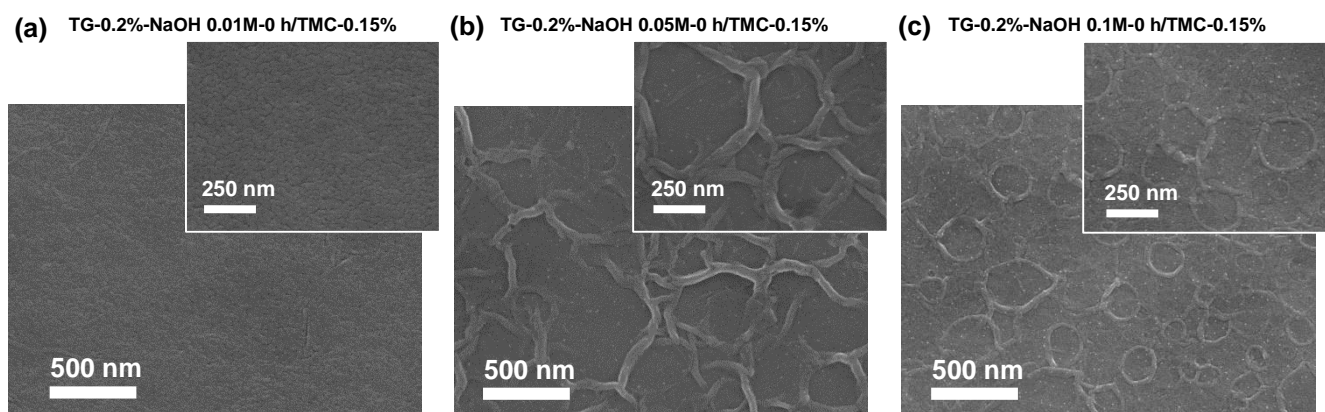
## Nanofilms made on cross-linked HPAN support – characterization by SEM:



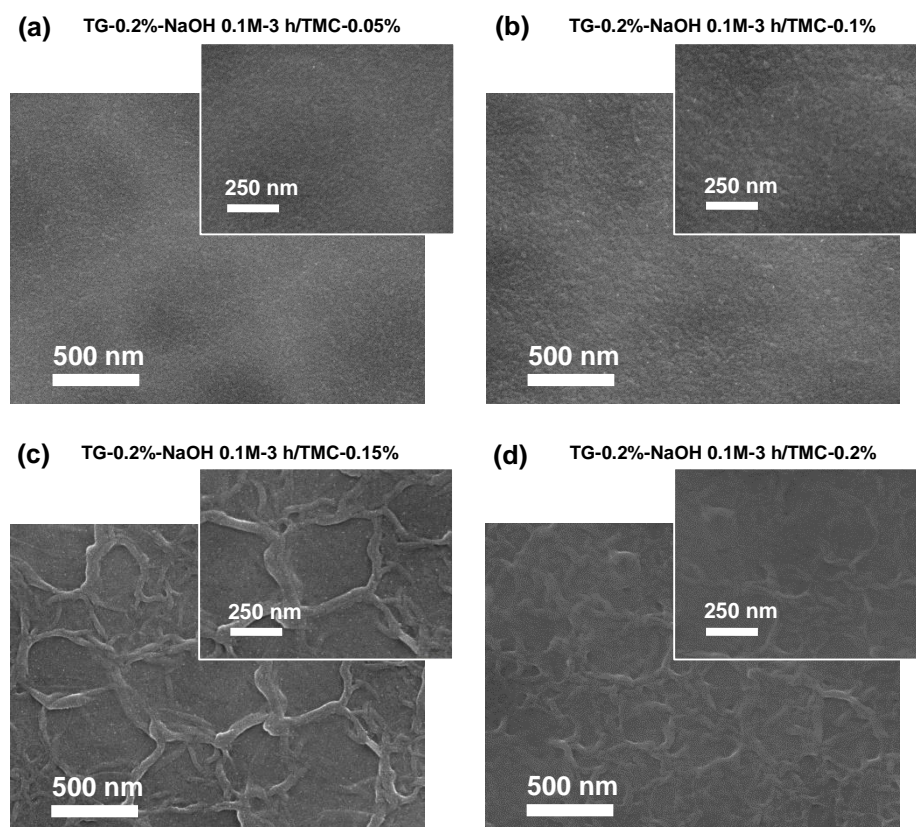
**Fig. S5.** The surface morphology of the poly(triaminoguanidinium-amide) nanofilm composite membranes prepared on HPAN support was observed under SEM at different times after adding NaOH. (a) TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, (b) TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%, and (c) TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%.



**Fig. S6.** Surface morphology of the poly(triaminoguanidinium-amide) nanofilm composite membranes prepared on HPAN support observed under SEM at different amine concentrations. (a) TG-0.05%-NaOH 0.1M-3 h/TMC-0.1%, (b) TG-0.1%-NaOH 0.1M-3 h/TMC-0.1%, (c) TG-0.2%-NaOH 0.1M-3 h/TMC-0.1%, (d) TG-0.3%-NaOH 0.1M-3 h/TMC-0.1%, and (e) TG-0.5%-NaOH 0.1M-3 h/TMC-0.1%.



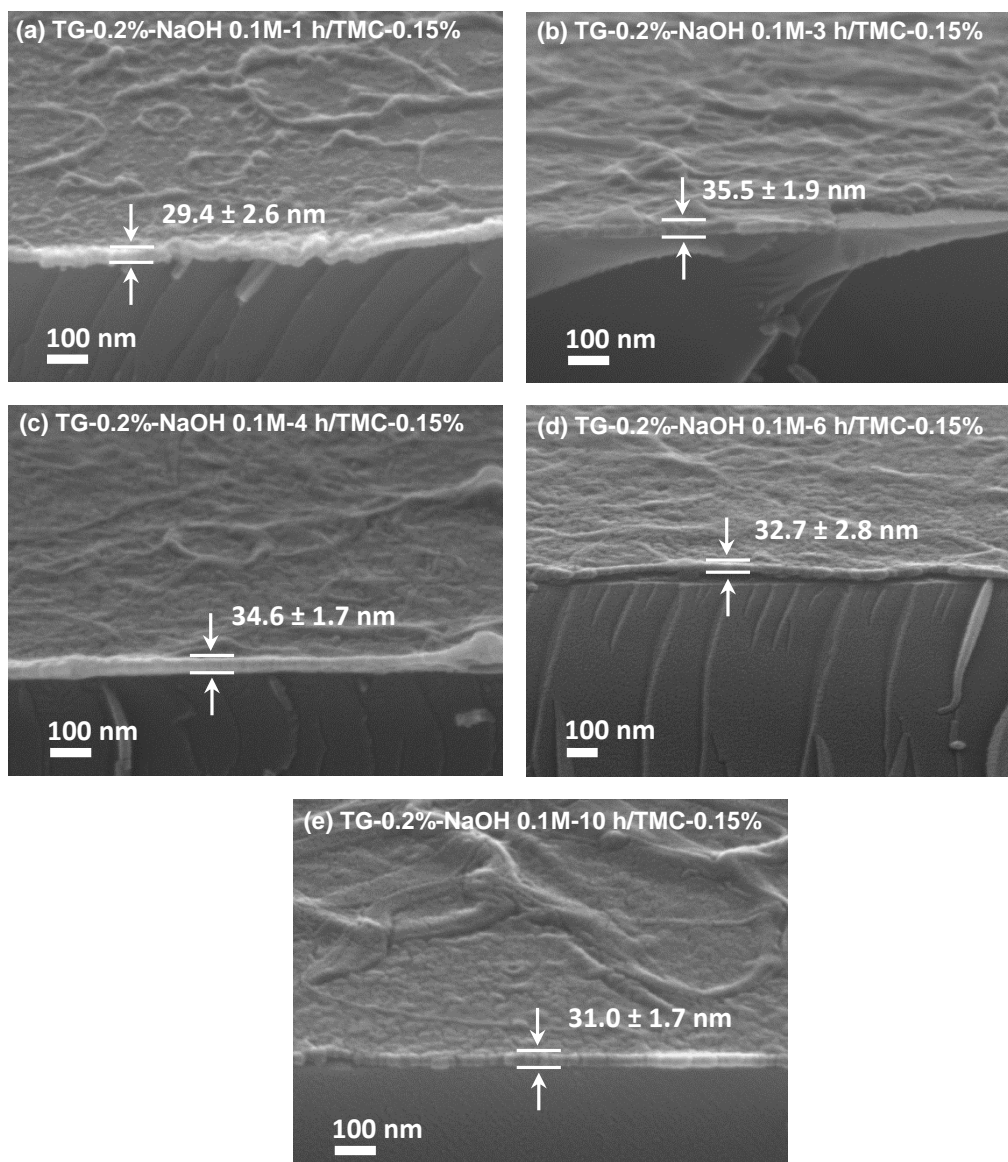
**Fig. S7.** Surface morphology of the poly(triaminoguanidinium-amide) nanofilm composite membranes prepared on HPAN support observed under SEM at different NaOH concentrations. (a) TG-0.2%-NaOH 0.01M-0 h/TMC-0.15%, (b) TG-0.2%-NaOH 0.05M-0 h/TMC-0.15%, and (c) TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%.



**Fig. S8.** Surface morphology of the poly(triaminoguanidinium-amide) nanofilm composite membranes prepared on HPAN support observed under SEM at different TMC concentrations. (a) TG-0.2%-NaOH 0.1M-3 h/TMC-0.05%, (b) TG-0.2%-NaOH 0.1M-3 h/TMC-0.1%, (c) TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, and (d) TG-0.2%-NaOH 0.1M-3 h/TMC-0.2%.



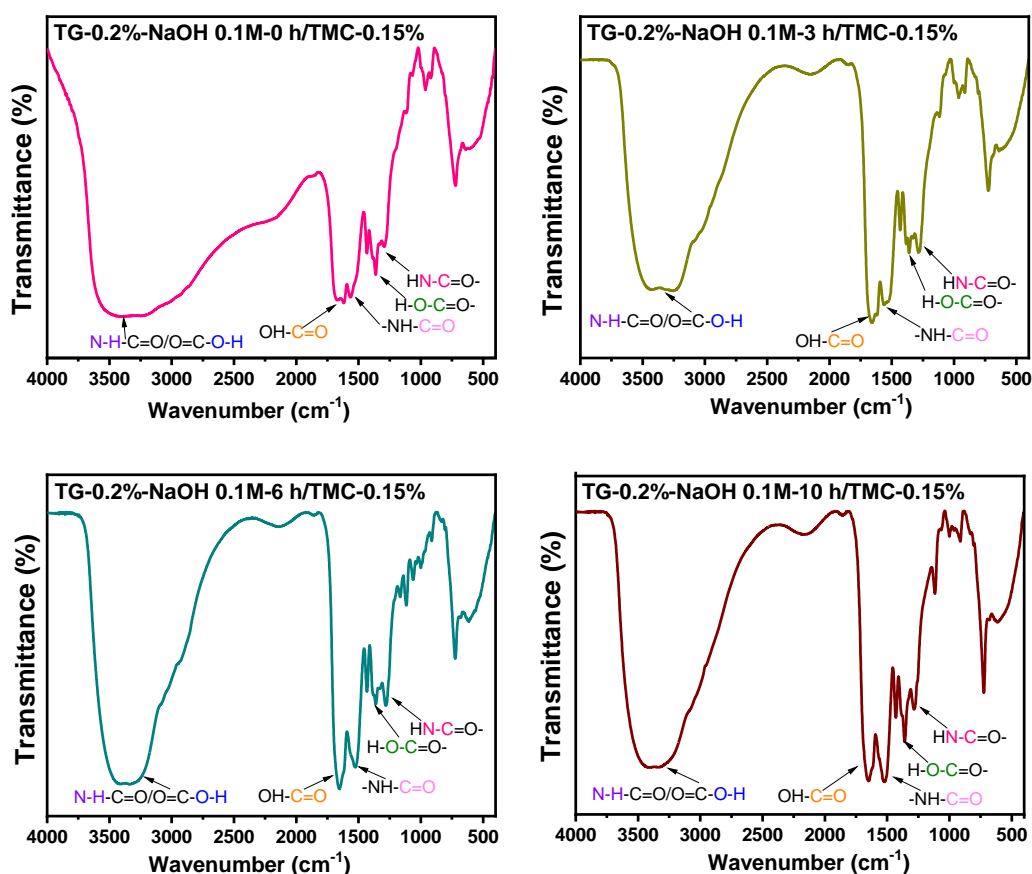
**Surface morphology and analysis of the thickness of the freestanding poly(triaminoguanidinium-amide) nanofilms from SEM:**



**Fig. S9.** Surface morphology and the estimation of the thickness of the freestanding poly(triaminoguanidinium-amide) nanofilms from SEM. (a, e) SEM images of the freestanding nanofilm transferred onto the silicon wafer. Interfacial polymerization conditions are: (a) TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%, (b) TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, (c) TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%, (d) TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%, and (e) TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%.

## Characterization of the poly(triaminoguanidinium-amide) nanofilms using the Fourier-transform infrared spectroscopy (FT-IR) method:

The poly(triaminoguanidinium-amide) nanofilms with different aging times were further characterized by using FT-IR. The IR frequency measurements exhibit features corresponding to different functional groups of the nanofilms. Nanofilms were prepared at the bulk water-hexane interface using 0.2 w/w% TG and 0.1 M NaOH in the aqueous and reacted with TMC (0.15 w/w%) via interfacial polymerization. The aging time between TG and NaOH was varied from 0 to 10 h. After interfacial polymerization for 10s, the bulk polymers were filtered and washed with pure water to remove the excess monomers and NaOH. Then the polymers were dried at room temperature for 1 day, then in a hot air oven at 40 °C for 6 – 7 hours. All the polymers prepared with different aging times, and their corresponding FT-IR spectra, shows the presence of stretching frequencies for  $\text{O}=\text{C}-\text{OH}$ ,  $\text{HN}-\text{C}=\text{O}$ ,  $\text{O}=\text{C}-\text{O}-\text{H}$ , and  $\text{H}-\text{N}-\text{C}=\text{O}$  groups at  $\sim 1667\text{ cm}^{-1}$ ,  $\sim 1548\text{ cm}^{-1}$ ,  $\sim 1357\text{ cm}^{-1}$ , and  $\sim 1275\text{ cm}^{-1}$  respectively (Fig. S10).



**Fig. S10.** FT-IR spectra of the poly(triaminoguanidinium-amide) nanofilm composite membranes with varying time. Membranes were prepared with different aging times after adding NaOH to the aqueous TG solution. (a) TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%, (b) TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, (c) TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%, and (d) TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%.

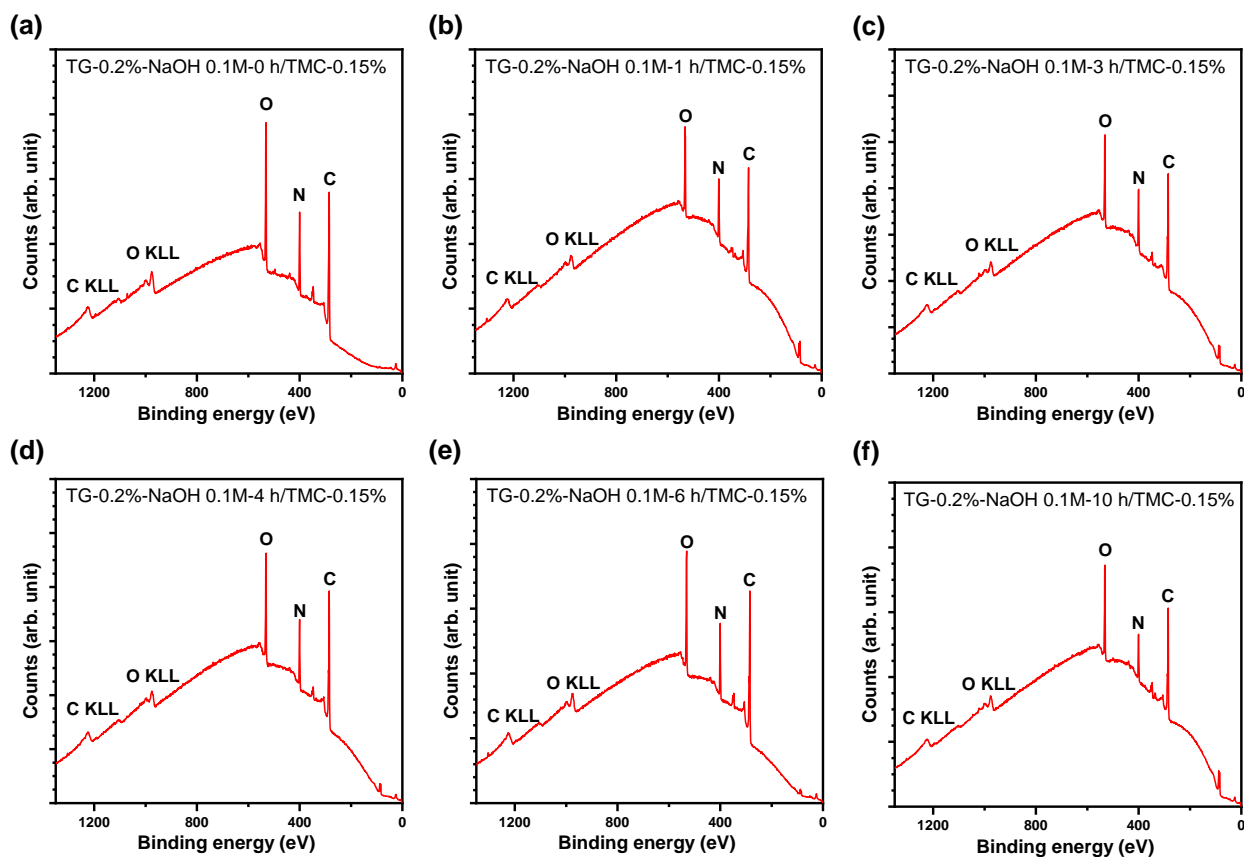
## Chemical characterization of the poly(triaminoguanidinium-amide) nanofilms by XPS:

The elemental composition of the poly(triaminoguanidinium-amide) nanofilms were determined by using XPS analysis after transferring the nanofilms onto a gold-coated silicon wafer surface. C1s, O1s, and N1s core level XPS spectra were studied to determine the elemental composition (C, N, and O). The XPS results from the survey spectra, C1s, O1s, and N1s core level XPS spectra were presented in Tables S2 – S4 and Figures S11 – S15.

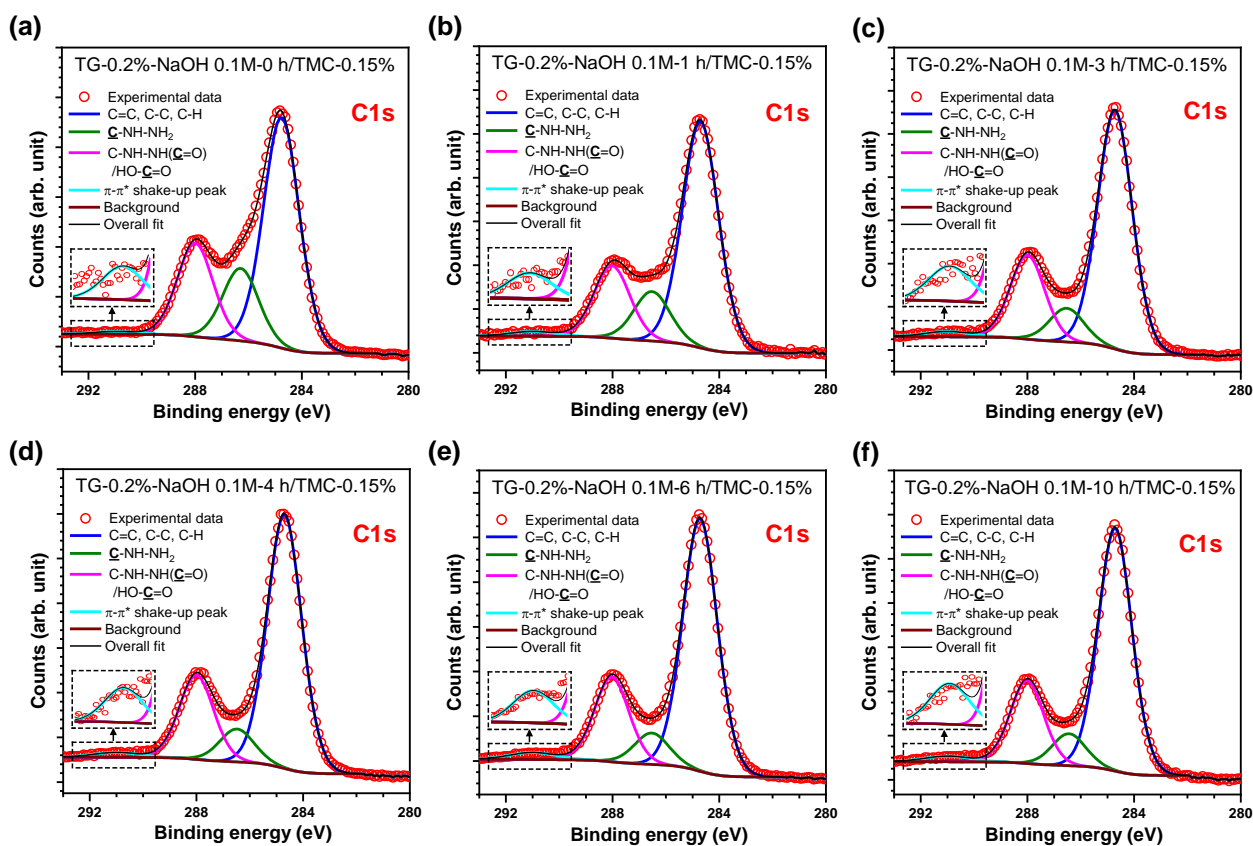
**Table S2.** C, N, and O results from the survey spectra of the freestanding polyamide nanofilms.

Preparation conditions	C (at %)	N (at %)	O (at %)	O/N	COOH from O1s [overall COOH in the nanofilm] (at%)
<b>Nanofilms were made on top of PAN support*</b>					
TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	63.7 ± 0.3	16.5 ± 0.8	19.8 ± 1.0	1.2 ± 0.1	4.6 ± 0.1 [0.9]
TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%	63.7 ± 0.5	19.3 ± 0.4	17.0 ± 0.4	0.9 ± 0.03	4.0 ± 0.4 [0.7]
TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%	63.4 ± 0.8	18.2 ± 1.1	18.4 ± 0.3	1.0 ± 0.1	5.0 ± 0.2 [0.9]
TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%	65.2 ± 0.7	16.7 ± 0.7	18.1 ± 0.1	1.1 ± 0.04	3.9 ± 0.1 [0.7]
TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%	64.3 ± 0.6	17.0 ± 0.5	18.7 ± 0.5	1.1 ± 0.05	3.0 ± 0.3 [0.6]
TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%	63.9 ± 0.3	15.8 ± 0.7	20.3 ± 0.5	1.3 ± 0.1	2.6 ± 0.2 [0.5]
<b>Nanofilms were made at the water-hexane interface#</b>					
#TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%-FSU	63.5 ± 0.2	13.8 ± 0.3	22.7 ± 0.3	1.6 ± 0.1	7.5 ± 0.3 [1.7]
#TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%-RSU	63.5 ± 0.2	21.0 ± 0.0	15.6 ± 0.2	0.7 ± 0.01	6.7 ± 0.4 [1.0]

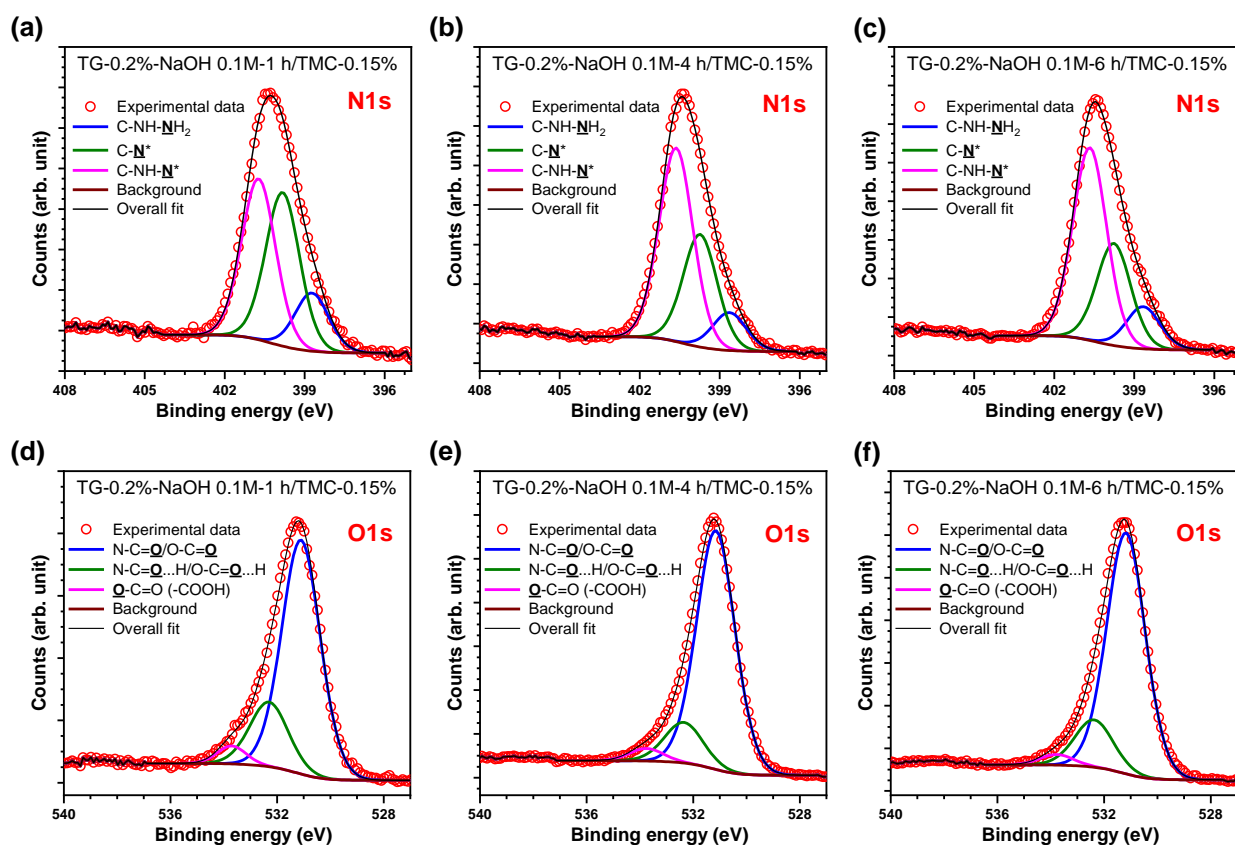
\*Nanofilms were made on top of PAN support, followed by the transfer of the nanofilm onto the DMF surface and then onto the gold-coated silicon wafer support. #Nanofilms were made at the bulk water-hexane interface, followed by the transfer of the nanofilm onto the water surface and then onto the gold-coated silicon wafer support. FSU: Front side up, RSU: Rear side up. The species N-C=O...H and O-C=O...H in O1s are the amide and carboxylic acid groups of poly(triaminoguanidinium-amide), which are hydrogen-bonded to water or intramolecular hydrogen-bonded between amide and carboxylic acid group, or intramolecular hydrogen-bonded between carboxylic acid groups. Overall COOH (at%) in the nanofilm = [COOH (at%) from O1s] x [O (at%) from the survey spectrum].



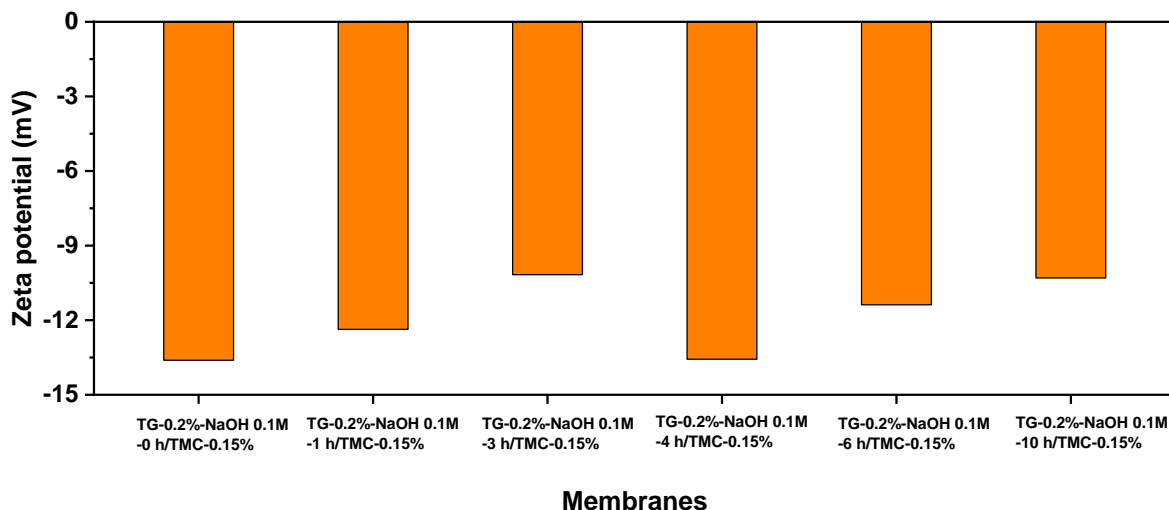
**Fig. S11.** XPS survey spectra of the freestanding poly(triaminoguanidinium-amide) nanofilms transferred onto the gold-coated silicon wafer. (a) for TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%, (b) for TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%, (c) for TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, (d) for TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%, (e) for TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%, and (f) for TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%.



**Fig. S12.** XPS C1s spectra of the freestanding poly(triaminoguanidinium-amide) nanofilms transferred onto the gold-coated silicon wafer. (a) for TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%, (b) for TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%, (c) for TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%, (d) for TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%, (e) for TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%, and (f) for TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%.

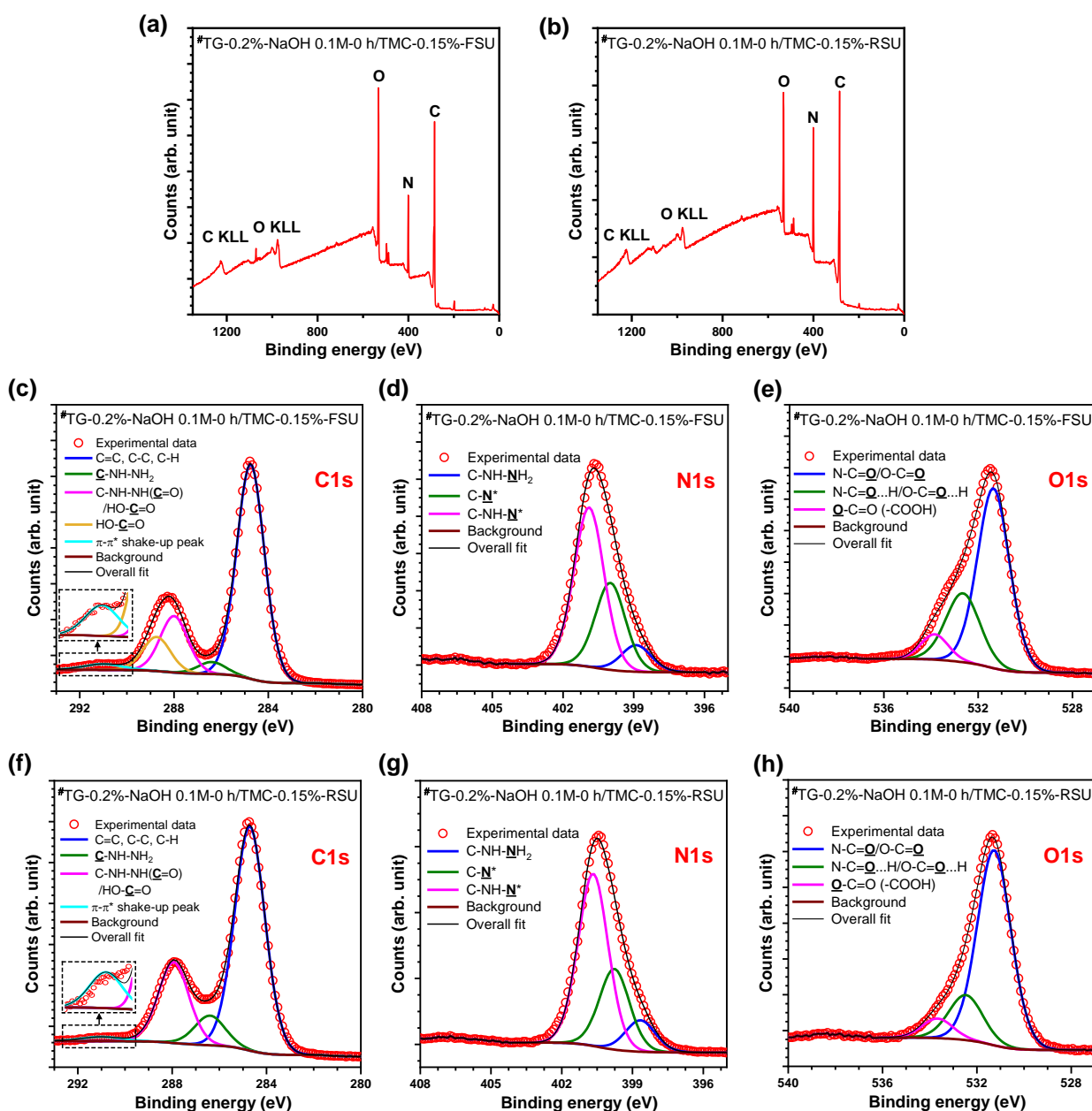


**Fig. S13.** XPS N1s and O1s spectra of the freestanding poly(triaminoguanidinium-amide) nanofilms transferred onto the gold-coated silicon wafer. (a, d) for TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%, (b, e) for TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%, and (c, f) for TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%.



**Fig. S14.** Surface zeta potential of the poly(triaminoguanidinium-amide) nanofilm composite membranes. Membranes were prepared with different mixing (stirring) times (0 to 10 hours) after adding NaOH to the aqueous TG solution.

The elemental compositions of the poly(triaminoguanidinium-amide) nanofilms facing both the hexane phase (front side up) and the aqueous phase (rear side up) were studied by using XPS. Nanofilms were prepared at the bulk water-hexane interface using 0.2 w/w% TG and 0.1 M NaOH in the aqueous and reacted with TMC (0.15 w/w%) via interfacial polymerization. After interfacial polymerization for 10s, nanofilms were transferred onto the water surface to remove the excess monomers and NaOH. Then, the nanofilms were transferred on the gold-coated silicon wafer surface, facing (a) front side up (FSU) or surface facing organic solution during interfacial polymerization and (b) rear side up (RSU) or surface facing the aqueous solution during interfacial polymerization. Figure S15 shows the survey, C1s, N1s, and O1s spectra of the nanofilms.



**Fig. S15.** XPS survey, C1s, N1s, and O1s spectra of the freestanding poly(triaminoguanidinium-amide) nanofilms transferred onto the gold-coated silicon wafer. (a, c, d, e) for #TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%-FSU, and (b, f, g, h) for #TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%-RSU.

**Table S3.** XPS results of the freestanding poly(triaminoguanidinium-amide) nanofilms prepared on the top of PAN support.

Membrane	C1s			N1s			O1s		
	Energy (eV)	Species	(at %)	Energy (eV)	Species	(at %)	Energy (eV)	Species	(at %)
TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	284.8	C=C, C-C, C-H	57.7 ± 0.3	398.9	C-NH-NH <sub>2</sub>	19.4 ± 1.6	531.2	N-C=O/O-C=O	72.3 ± 1.6
	286.3	C-NH-NH <sub>2</sub>	18.2 ± 0.3	400.0	C-N*	52.4 ± 1.1	532.4	N-C=O...H/O-C=O...H	23.1 ± 1.5
	288.0	C-NH-NH(C=O)/HO-C=O	23.2 ± 0.3	400.9	C-NH-N*	28.2 ± 2.4	533.8	O-C=O	4.6 ± 0.1
	291.0	π-π* shake-up peak	1.0 ± 0.2						
TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%	284.7	C=C, C-C, C-H	64.0 ± 0.3	398.8	C-NH-NH <sub>2</sub>	14.9 ± 0.7	531.2	N-C=O/O-C=O	76.0 ± 1.2
	286.6	C-NH-NH <sub>2</sub>	13.6 ± 0.6	399.9	C-N*	41.8 ± 0.6	532.4	N-C=O...H/O-C=O...H	20.0 ± 0.8
	288.1	C-NH-NH(C=O)/HO-C=O	20.8 ± 0.4	400.8	C-NH-N*	43.3 ± 0.1	533.8	O-C=O	4.0 ± 0.4
	291.0	π-π* shake-up peak	1.7 ± 0.1						
TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%	284.7	C=C, C-C, C-H	66.1 ± 0.8	398.6	C-NH-NH <sub>2</sub>	13.0 ± 0.7	531.2	N-C=O/O-C=O	79.2 ± 0.7
	286.5	C-NH-NH <sub>2</sub>	9.5 ± 0.3	399.7	C-N*	34.1 ± 0.9	532.4	N-C=O...H/O-C=O...H	15.7 ± 0.6
	288.0	C-NH-NH(C=O)/HO-C=O	22.5 ± 0.7	400.6	C-NH-N*	52.9 ± 0.5	533.8	O-C=O	5.0 ± 0.2
	291.0	π-π* shake-up peak	1.9 ± 0.7						
TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%	284.7	C=C, C-C, C-H	67.3 ± 0.3	398.6	C-NH-NH <sub>2</sub>	11.6 ± 0.6	531.1	N-C=O/O-C=O	81.6 ± 0.6
	286.5	C-NH-NH <sub>2</sub>	9.0 ± 0.3	399.7	C-N*	34.1 ± 1.4	532.3	N-C=O...H/O-C=O...H	14.6 ± 0.5
	288.0	C-NH-NH(C=O)/HO-C=O	22.0 ± 0.3	400.6	C-NH-N*	54.3 ± 1.8	533.7	O-C=O	3.9 ± 0.1
	291.0	π-π* shake-up peak	1.7 ± 0.0						
TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%	284.7	C=C, C-C, C-H	66.6 ± 0.6	398.6	C-NH-NH <sub>2</sub>	13.1 ± 1.2	531.2	N-C=O/O-C=O	81.6 ± 0.8
	286.5	C-NH-NH <sub>2</sub>	9.3 ± 0.9	399.7	C-N*	30.6 ± 0.6	532.4	N-C=O...H/O-C=O...H	15.5 ± 0.9
	288.0	C-NH-NH(C=O)/HO-C=O	21.8 ± 0.7	400.6	C-NH-N*	56.3 ± 1.0	533.8	O-C=O	3.0 ± 0.3
	291.0	π-π* shake-up peak	2.2 ± 0.3						
TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%	284.7	C=C, C-C, C-H	66.6 ± 0.5	398.6	C-NH-NH <sub>2</sub>	12.1 ± 0.2	531.2	N-C=O/O-C=O	81.2 ± 1.5
	286.4	C-NH-NH <sub>2</sub>	8.8 ± 0.4	399.7	C-N*	27.5 ± 1.8	532.4	N-C=O...H/O-C=O...H	16.3 ± 1.7
	288.0	C-NH-NH(C=O)/HO-C=O	22.6 ± 0.4	400.6	C-NH-N*	60.4 ± 1.6	533.8	O-C=O	2.6 ± 0.2



291.0  $\pi$ - $\pi^*$  shake-up peak  $2.0 \pm 0.2$

C-N\*: C-NH-NH<sub>2</sub> (H-bonded), C-NH-NH<sub>2</sub>, C-N\*H-NH<sub>2</sub>, C-NH-NH (-C=O)

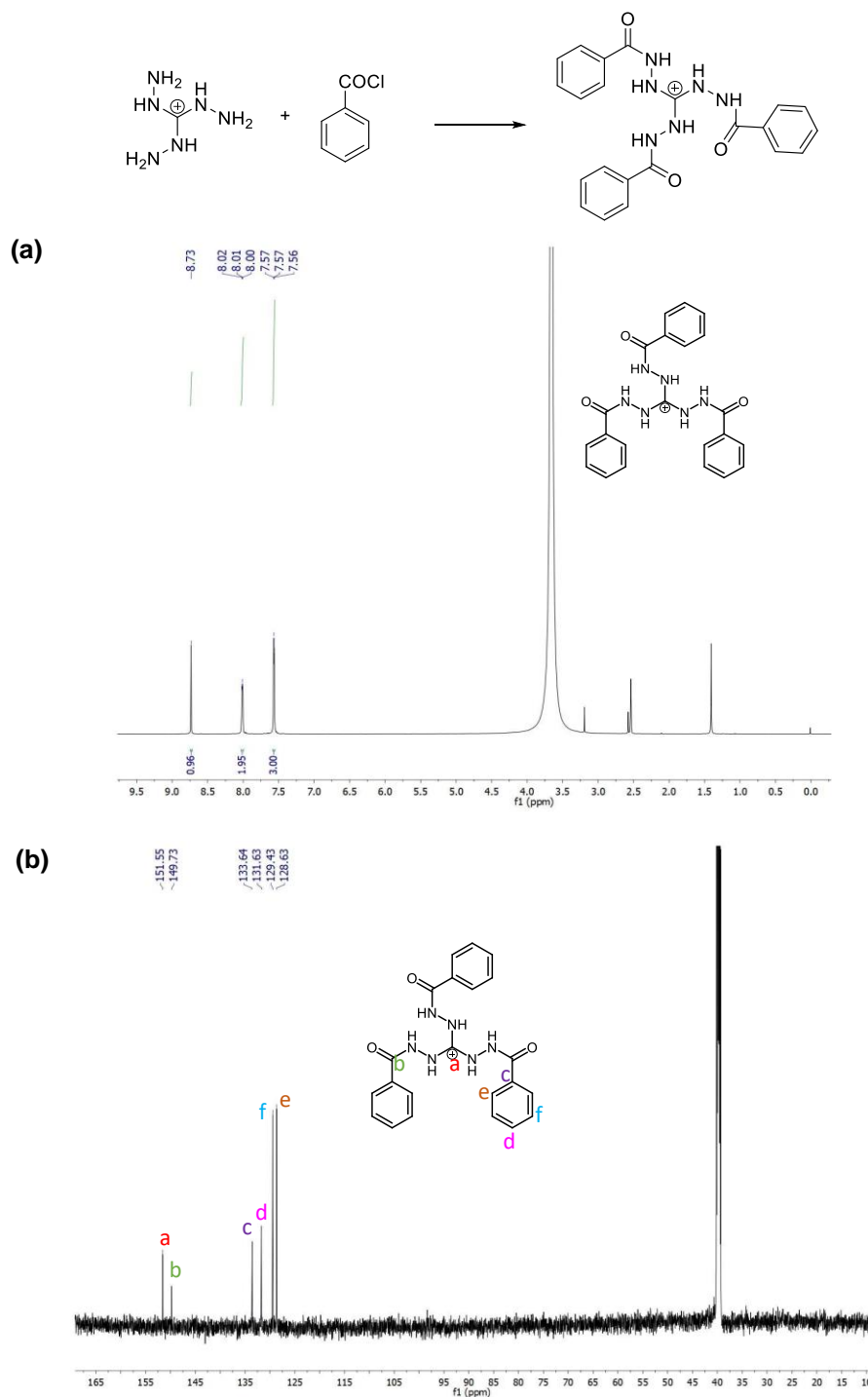
C-NH-N\*: C-NH-NH (-C=O) (H-bonded), C-NH-NH (-C=O), C-NH-NH<sub>3</sub><sup>+</sup> (protonated form)

**Table S4.** XPS results of the freestanding poly(triaminoguanidinium-amide) nanofilms prepared at the aqueous-hexane interface.

Membrane	C1s			N1s			O1s		
	Energy (eV)	Species	(at %)	Energy (eV)	Species	(at %)	Energy (eV)	Species	(at %)
#TG-0.2%-NaOH 0.1M-0 h/TMC- 0.15%-FSU (front side up)	284.8	C=C, C-C, C-H	66.2 ± 0.5	398.9	C-NH- <u>N</u> H <sub>2</sub>	9.5 ± 0.7	531.3	N-C= <u>O</u> /O-C= <u>O</u>	66.1 ± 0.6
	286.4	<u>C</u> -NH-NH <sub>2</sub>	3.7 ± 0.1	400.0	C- <u>N</u> *	31.5 ± 1.4	532.6	N-C= <u>O</u> ...H/O-C= <u>O</u> ...H	26.4 ± 0.3
	288.0	C-NH-NH( <u>C</u> =O)	17.2 ± 0.6	400.9	C-NH- <u>N</u> *	59.0 ± 2.1	533.8	<u>O</u> -C=O	7.5 ± 0.3
	288.7	HO- <u>C</u> =O	10.5 ± 0.9						
	291.0	$\pi$ - $\pi^*$ shake-up peak	2.4 ± 0.1						
#TG-0.2%-NaOH 0.1M-0 h/TMC- 0.15%-RSU (rear side up)	284.7	C=C, C-C, C-H	65.9 ± 0.4	398.7	C-NH- <u>N</u> H <sub>2</sub>	10.8 ± 0.2	531.3	N-C= <u>O</u> /O-C= <u>O</u>	76.1 ± 0.6
	286.4	<u>C</u> -NH-NH <sub>2</sub>	8.7 ± 0.0	399.8	C- <u>N</u> *	28.9 ± 0.4	532.5	N-C= <u>O</u> ...H/O-C= <u>O</u> ...H	17.2 ± 0.3
	288.0	C-NH- NH( <u>C</u> =O)/HO- <u>C</u> =O	23.9 ± 0.4	400.7	C-NH- <u>N</u> *	60.3 ± 0.2	533.7	<u>O</u> -C=O	6.7 ± 0.4
	291.0	$\pi$ - $\pi^*$ shake-up peak	1.6 ± 0.1						

### Synthesis of amide oligomer:

Triaminoguanidinium chloride (10 mmol) and benzoyl chloride (50 mmol) was refluxed in 50 ml of dry THF for 6 h under an N<sub>2</sub> environment. After cooling the reaction mixture to room temperature, the white precipitate was filtered and washed with an aqueous bicarbonate solution to remove excess benzoic acid and finally dried in the vacuum at 80 °C. The oligomer was characterized by <sup>1</sup>H NMR.



**Fig. S16.** (a) <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>): δ (in ppm) 8.73 (1 H, s), 8.01 (2 H, t, J = 1.2), 7.57 (3 H, d, J = 2.4). (b) <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ (in ppm) 128.63, 129.43, 131.63, 133.64, 149.73, 151.55.

**Table S5.** Nanofiltration performance of the poly(triaminoguanidinium-amide) nanofilm composite membranes fabricated on HPAN support.

Membrane	Nanofiltration performance of the membrane						Selectivity (NaCl to Na <sub>2</sub> SO <sub>4</sub> )
	Feed →	Pure water	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	MgCl <sub>2</sub>	NaCl	
TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	9.2 ± 1.2	7.0 ± 0.5	6.9 ± 0.4	5.8 ± 0.3	6.4 ± 0.3	37.5
	Salt rejection (%)	-	99.6 ± 0.2	99.1 ± 0.6	85.0 ± 2.3	85.0 ± 2.0	
TG-0.2%-NaOH 0.1M-1 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	11.4 ± 0.8	8.9 ± 0.6	8.7 ± 0.7	8.2 ± 0.8	8.4 ± 0.5	74.8
	Salt rejection (%)	-	99.7 ± 0.1	98.5 ± 0.6	63.7 ± 2.4	73.8 ± 1.4	
TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	16.1 ± 1.9	11.9 ± 0.7	12.2 ± 0.4	12.2 ± 0.5	12.8 ± 0.3	76.2
	Salt rejection (%)	-	99.5 ± 0.2	97.3 ± 1.0	48.1 ± 2.4	59.6 ± 1.5	
TG-0.2%-NaOH 0.1M-4 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	19.2 ± 1.9	12.3 ± 1.0	13.4 ± 1.2	15.2 ± 1.7	14.4 ± 1.7	52.6
	Salt rejection (%)	-	99.0 ± 0.6	91.2 ± 3.3	27.3 ± 3.9	46.3 ± 4.0	
TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	22.6 ± 2.0	13.9 ± 0.8	15.8 ± 0.6	18.6 ± 0.8	16.8 ± 0.8	45.3
	Salt rejection (%)	-	98.7 ± 0.3	86.5 ± 3.3	21.5 ± 1.8	41.6 ± 2.2	
TG-0.2%-NaOH 0.1M-10 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	26.8 ± 2.8	15.0 ± 1.6	17.7 ± 1.8	22.7 ± 2.4	17.6 ± 1.8	13.5
	Salt rejection (%)	-	95.8 ± 1.1	83.4 ± 1.6	22.2 ± 2.1	43.5 ± 1.2	
TG-0.05%-NaOH 0.1M-3 h/TMC-0.1%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	20.5 ± 0.1	13.4 ± 0.4	17.5 ± 0.8	16.6 ± 0.2	16.3 ± 0.2	51.5
	Salt rejection (%)	-	99.1 ± 0.2	86.6 ± 1.8	31.2 ± 2.3	54.2 ± 3.0	
TG-0.1%-NaOH 0.1M-3 h/TMC-0.1%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	19.0 ± 0.5	11.8 ± 0.6	12.8 ± 0.6	14.6 ± 0.5	15.5 ± 0.4	138.6
	Salt rejection (%)	-	99.7 ± 0.1	98.2 ± 0.2	39.6 ± 2.8	51.5 ± 2.9	
TG-0.2%-NaOH 0.1M-3 h/TMC-0.1%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	18.8 ± 1.3	11.3 ± 0.7	10.3 ± 0.6	10.9 ± 0.8	11.3 ± 0.8	63.1
	Salt rejection (%)	-	99.4 ± 0.1	98.5 ± 0.2	54.1 ± 3.8	61.5 ± 2.7	
TG-0.3%-NaOH 0.1M-3 h/TMC-0.1%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	13.4 ± 0.7	8.7 ± 0.2	10.6 ± 0.3	9.7 ± 0.4	9.3 ± 0.4	47.4
	Salt rejection (%)	---	99.3 ± 0.3	98.3 ± 0.5	66.7 ± 3.2	65.9 ± 3.1	
TG-0.5%-NaOH 0.1M-3 h/TMC-0.1%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	13.4 ± 0.5	8.7 ± 0.3	10.6 ± 0.3	9.5 ± 0.3	9.3 ± 0.3	53.3
	Salt rejection (%)	-	99.3 ± 0.6	98.0 ± 1.7	75.9 ± 2.0	64.3 ± 1.9	
TG-0.2%-NaOH 0.0M-0 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	No membrane was formed					
	Salt rejection (%)	No membrane was formed					
TG-0.2%-NaOH 0.01M-0 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	39.5 ± 1.7	20.3 ± 1.4	30.5 ± 6.3	35.1 ± 9.7	35.9 ± 1.4	6.7
	Salt rejection (%)	-	87.2 ± 5.0	33.9 ± 8.8	6.0 ± 2.5	14.8 ± 2.9	
TG-0.2%-NaOH 0.05M-0 h/TMC-0.15%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	8.3 ± 1.2	6.4 ± 0.8	7.3 ± 0.9	5.9 ± 0.7	6.2 ± 0.9	21.1
	Salt rejection (%)	-	99.2 ± 0.6	98.9 ± 0.4	89.5 ± 1.2	82.7 ± 2.0	
TG-0.2%-NaOH 0.1M-3 h/TMC-0.05%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	20.7 ± 0.5	12.6 ± 0.3	12.2 ± 0.1	12.4 ± 0.3	12.8 ± 0.4	89.8
	Salt rejection (%)	-	99.5 ± 0.1	98.6 ± 0.3	63.4 ± 2.9	58.7 ± 1.4	
TG-0.2%-NaOH 0.1M-3 h/TMC-0.2%	Water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	10.2 ± 0.7	7.3 ± 0.3	7.0 ± 0.3	6.9 ± 0.4	8.1 ± 0.5	51.3
	Salt rejection (%)	-	99.5 ± 0.3	99.3 ± 0.2	69.1 ± 3.3	73.3 ± 3.3	

### Acid and base stability test of the poly(triaminoguanidinium-amide) nanofilm composite membranes:

To investigate the acid and base stability of the poly(triaminoguanidinium-amide) nanofilm composite membranes, the membranes were prepared with 0 h aging time after adding NaOH to the aqueous TG solution (TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%). Membranes were annealed at 70 ( $\pm 1$ ) °C for 1 min in a hot air oven after interfacial polymerization for 10 s. After a 24-hour treatment period in the designated pH solutions (pH 1, 3, 11 and 12), the membranes were rinsed in pure water to achieve a pH of 7.0.

### Liquid transport mechanism through poly(triaminoguanidinium-amide) nanofilm composite membranes:

The permeance of the poly(triaminoguanidinium-amide) nanofilm composite membranes was measured with varying viscosity of the feed solution (Table S6). Pure water and water-methanol mixture at different temperatures were used as a feed with known viscosity.

**Table S6.** The permeance of the poly(triaminoguanidinium-amide) nanofilm composite membranes fabricated on HPAN support with varying viscosity of the feed solution.

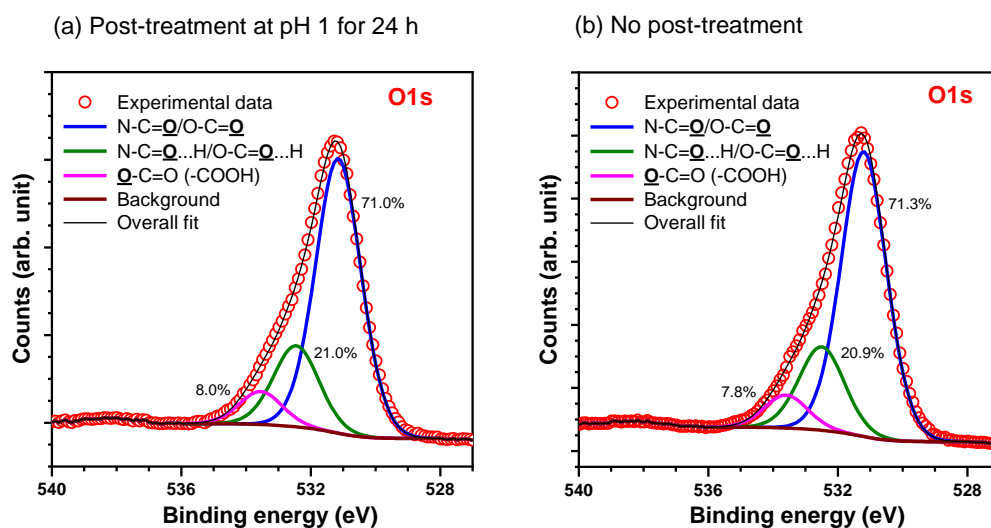
Feed solution	Viscosity (cP)	Permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	
		TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%
Pure water @ 25 °C	0.89	9.2 $\pm$ 1.2	22.6 $\pm$ 2.0
Pure water @ 20 °C	1.00	8.9 $\pm$ 0.7	18.7 $\pm$ 1.8
Pure water @ 15 °C	1.14	7.6 $\pm$ 0.5	14.0 $\pm$ 1.8
MeOH:Water (1:9 by v/v %) @ 25 °C	1.21	5.8 $\pm$ 0.4	12.9 $\pm$ 1.9
MeOH:Water (1:9 by v/v %) @ 20 °C	1.32	4.8 $\pm$ 0.3	10.8 $\pm$ 1.7
MeOH:Water (1:4 by v/v %) @ 25 °C	1.43	3.6 $\pm$ 0.3	8.5 $\pm$ 1.3
MeOH:Water (1:4 by v/v %) @ 20 °C	1.60	2.8 $\pm$ 0.2	7.1 $\pm$ 1.2
MeOH:Water (1:4 by v/v %) @ 15 °C	1.82	2.3 $\pm$ 0.1	5.7 $\pm$ 1.0

### Determination of the molecular weight cut-off (MWCO) of the poly(triaminoguanidinium-amide) nanofilm composite membranes:

The molecular weight cut-off (MWCO) is an indirect way to measure the retention efficiency or pore size of porous membranes. Typically, the solute size that is retained by at least 90% is used to indicate the MWCO of the membrane. To evaluate the MWCO of various poly(triaminoguanidinium-amide) nanofilm composite membranes, uncharged or neutral solutes (glycerol, glucose, and sucrose) with different molecular weights and a concentration of 0.2 g L<sup>-1</sup> were used in the aqueous feed. Using a Total Organic Carbon analyzer (TOC), the concentration of neutral solutes in the permeate and feed was determined. The rejection was then plotted against the molecular weight of the solutes (inset of Fig. 5a). The MWCO of the membrane (inset of Fig. 5a) was determined by identifying the molecular weight corresponding to the 90% rejection value.

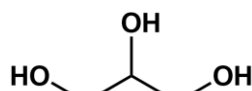
**Table S7.** Mean pore size and standard deviation of the membranes.

Membrane	Mean pore diameter (Å)	Standard deviation (Å)
TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%	11.3	1.3
TG-0.2%-NaOH 0.1M-3 h/TMC-0.15%	12.3	1.3
TG-0.2%-NaOH 0.1M-6 h/TMC-0.15%	13.5	1.3

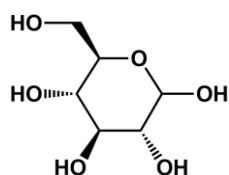


**Fig. S17.** O1s XPS spectra of the poly(triaminoguanidinium-amide) nanofilms made on HPAN support. (a) After post-treatment with pH 1 acidic solution for 24 h, and (b) no post-treatment (kept in pure water of pH 7).

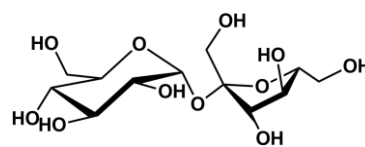
List of the organic dyes used for molecular separation:



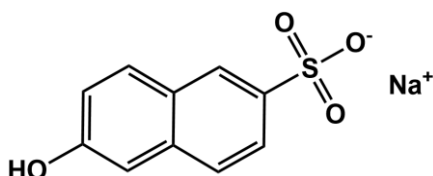
Glycerol ( $C_3H_8O_3$ )  
Molecular weight  
( $g\ mol^{-1}$ ): 92.09  
Charge: Neutral



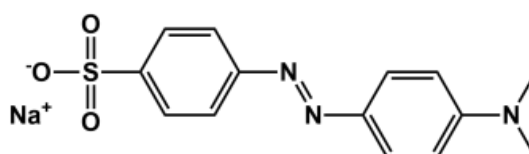
Glucose ( $C_6H_{12}O_6$ )  
Molecular weight  
( $g\ mol^{-1}$ ): 180.15  
Charge: Neutral



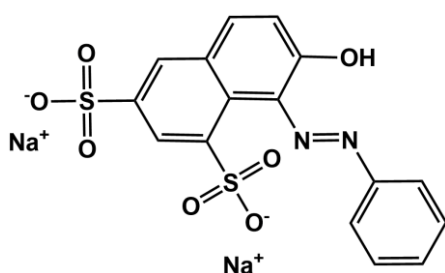
Sucrose ( $C_{12}H_{22}O_{11}$ )  
Molecular weight  
( $g\ mol^{-1}$ ): 342.3  
Charge: Neutral



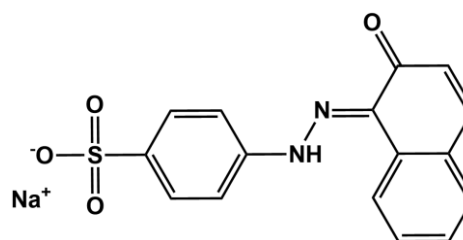
HNSA: 6-hydroxy-2-naphthalenesulfonic acid  
sodium salt; ( $C_{10}H_7NaO_4S$ )  
Molecular weight ( $g\ mol^{-1}$ ): 246.2  
Charge: Negative



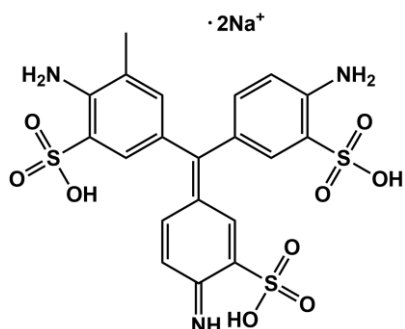
Methyl orange ( $C_{14}H_{14}N_3NaO_3S$ )  
Molecular weight ( $g\ mol^{-1}$ ): 327.3  
Charge: Negative



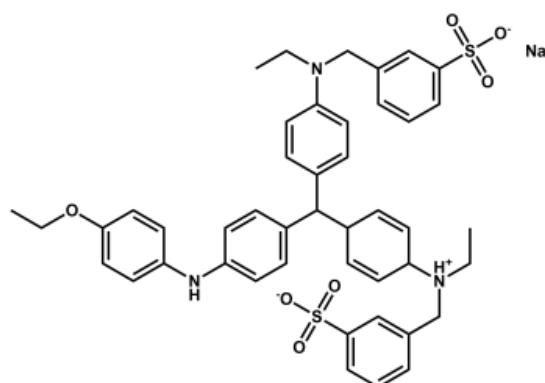
Orange G ( $C_{16}H_{10}N_2Na_2O_7S_2$ )  
Molecular weight ( $g\ mol^{-1}$ ): 452.4  
Charge: Negative



Acid orange 7 ( $C_{16}H_{11}N_2NaO_4S$ )  
Molecular weight ( $g\ mol^{-1}$ ): 350.3  
Charge: Negative



Acid fuchsin ( $C_{20}H_{17}N_3Na_2O_9S_3$ )  
Molecular weight ( $g\ mol^{-1}$ ): 585.5  
Charge: Negative

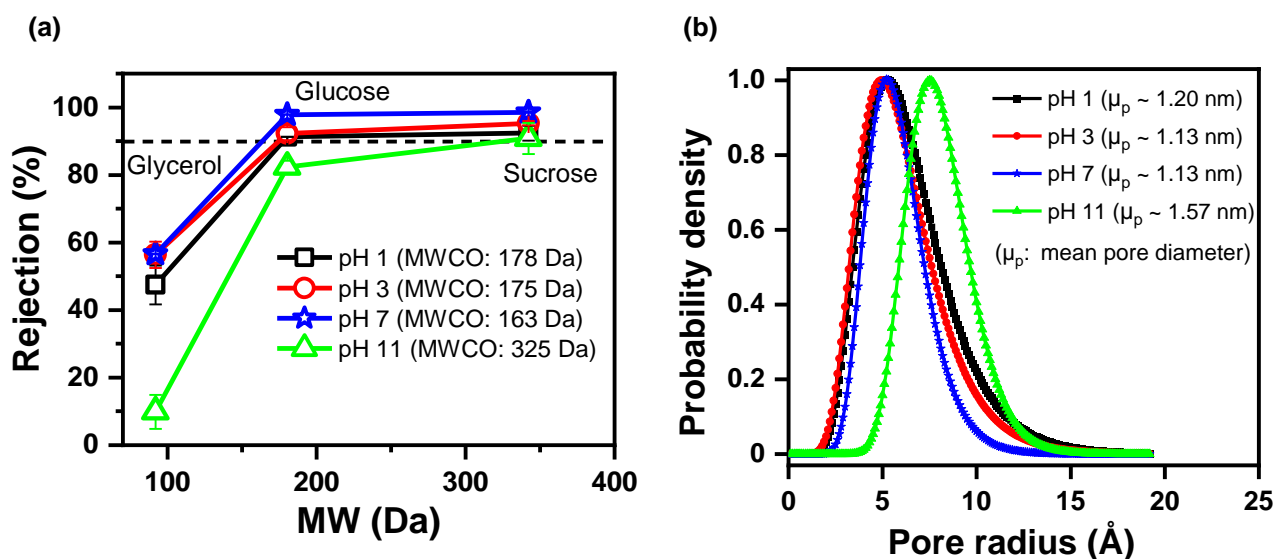


Brilliant blue R ( $C_{45}H_{44}N_3NaO_7S_2$ )  
Molecular weight ( $g\ mol^{-1}$ ): 825.9  
Charge: Negative

**Fig. S18.** Molecular structure and the properties of neutral and negative charged solutes used in this work.

### pH stability of the membranes:

To study the effect of acid and base treatment on MWCO of the poly(triaminoguanidinium-amide) nanofilm, we adopted a 24-hour treatment in the designated pH solutions (pH 1, 3, and 11). The membranes were rinsed in pure water to achieve a pH of 7.0. The separation behavior of uncharged or neutral solutes was studied with different molecular weights with a feed concentration of 0.2 g L<sup>-1</sup>. The MWCO and pore size distribution plots of the membranes after acid and base treatment are shown in Fig. S19.

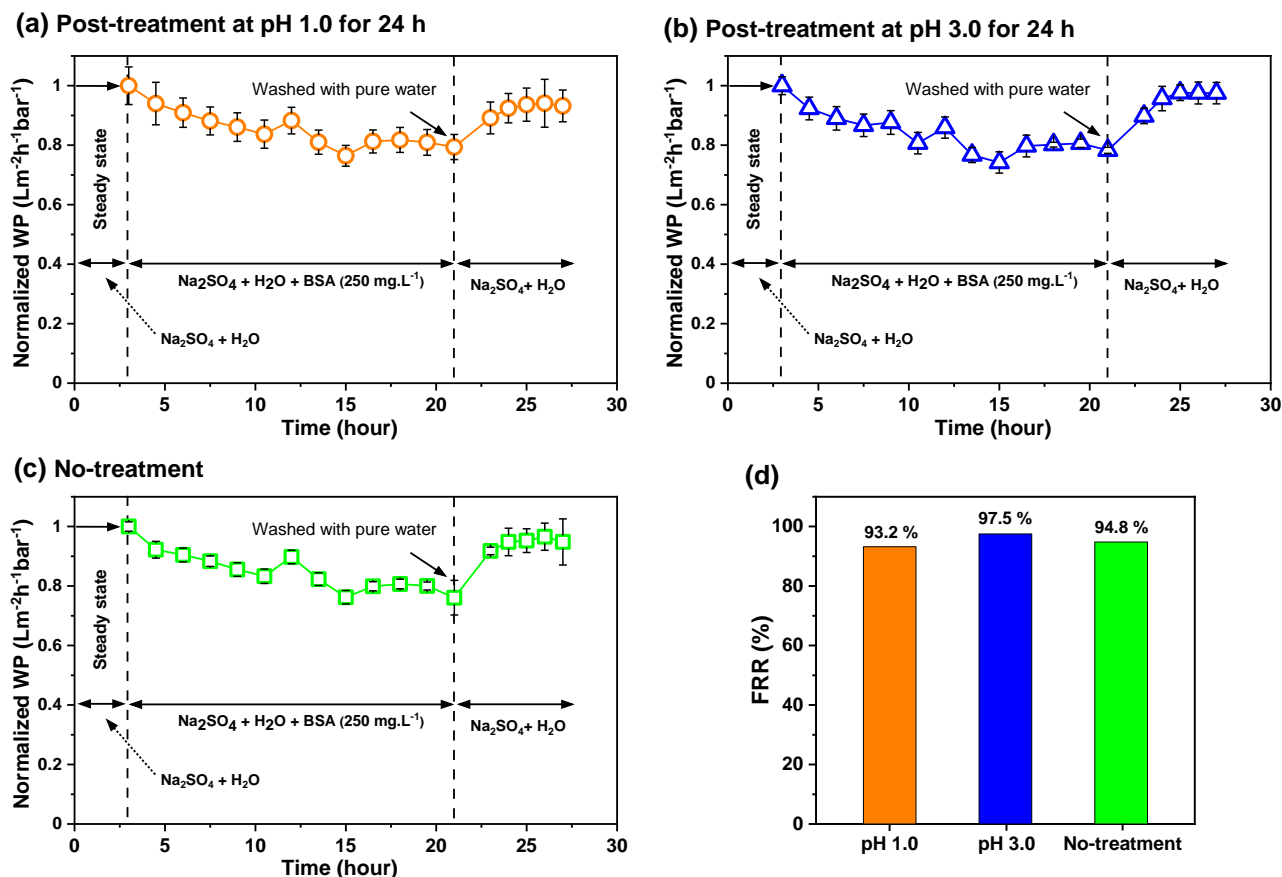


**Fig. S19.** The molecular weight cut-off (MWCO) curve and corresponding pore size distribution plot of the poly(triaminoguanidinium-amide) nanofilm composite membranes after acid and base treatments. (a) The plot of MWCO after post-treatment at various pH solutions (pH 1 to pH 11), (b) The plot of pore size distribution function (normalized) of the membranes after post-treatment at various pH solutions. The membrane was prepared with 0 hour aging time after adding NaOH to the aqueous TG solution (TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%). Black line – pH 1, red line – pH 3, blue line – no treatment, and green line – pH 11. (Glycerol, MW: 92.09 Da; Glucose, MW: 180.15 Da; Sucrose, MW: 342.3 Da).

### Fouling study of the poly(triaminoguanidinium-amide) nanofilm composite membranes:

To investigate the fouling behavior of the membranes, we included bovine serum albumin (BSA) in the aqueous feed solution along with Na<sub>2</sub>SO<sub>4</sub>. The membranes were pre-compacted for 3 hours under 4 bar pressure and at a cross-flow velocity of 40 L h<sup>-1</sup>, with a Na<sub>2</sub>SO<sub>4</sub> feed solution concentration of 2 g L<sup>-1</sup>. Afterward, 0.25 g L<sup>-1</sup> of BSA was added to the feed solution, and the water permeance of each membrane was recorded at 1.5-hour intervals. The experiments were conducted continuously for 20 hours, after which the system was cleaned with pure water for 2 hours. Water permeance was measured again using a Na<sub>2</sub>SO<sub>4</sub> feed solution with a concentration of 2 g L<sup>-1</sup> under 4 bar pressure. The results are presented in Fig. S20. We calculated the flux recovery ratio (FRR %) of the membranes

by comparing the water permeance before and after filtration of the BSA solution followed by washing with pure water.



**Fig. S20.** Fouling study of the poly(triaminoguanidinium-amide) nanofilm composite membranes with BSA. (a – c) Normalized water permeance (WP) with time after adding BSA in the feed solution and the recovery in permeance after washing with pure water. (d) Flux recovery ratio (FRR (%)) of the membranes post-treated at different acidic pH (pH 1 and 3; adjusted with HCl) for 24 h. The membrane was prepared with 0 hour aging time after adding NaOH to the aqueous TG solution (TG-0.2%-NaOH 0.1M-0 h/TMC-0.15%).

### Long-term performance stability study of the poly(triaminoguanidinium-amide) nanofilm composite membranes:

The separation performance of the poly(triaminoguanidinium-amide) nanofilm composite membranes was studied in a cross-flow filtration system at  $25 (\pm 1.0) ^\circ\text{C}$  under 4 bar applied pressure. Water permeance and salt rejection were recorded with time using  $2 \text{ g L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  in the feed solution to investigate their long-term stability. The water permeance and  $\text{Na}_2\text{SO}_4$  rejection of the membranes were measured for three successive days. Results are shown in Fig. 5d.



**Table S8.** Nanofiltration performance of the reported nanofilm composite membranes fabricated using different monomers.

Membrane	Pure water permeance (Lm <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	MWCO (Da)	Reference	
PIP-TMC	12.6 ± 0.7	274	<i>Nat. Commun.</i> , 2020, 11, 2015.	<b>S1</b>
PEI-TMC	28.3 ± 0.9	449		
β-CD-TMC	5.6	400	<i>Adv. Mater.</i> , 2018, 30, 1705933.	<b>S2</b>
Glucose/TMC-5.0	33.7 ± 1.4	327.3	<i>J. Membr. Sci.</i> , 2021, 619, 118786.	<b>S3</b>
PIP-TMC	19.3	300	<i>Adv. Funct. Mater.</i> , 2021, 31, 2007054.	<b>S4</b>
PMPD-TMC	20.2	613	<i>Sep. and Puri. Tech.</i> , 2020, 251, 117380.	<b>S5</b>
NF 270	17	250	<i>J. Membr. Sci.</i> , 2011, 381, 132–141.	<b>S6</b>
	11.5	200	<i>J. Membr. Sci.</i> 2008, 320, 325–334.	
	8.5	170	<i>Sep. and Puri. Tech.</i> , 2007, 54, 139–146.	
	10.3	270	<i>Sep. and Puri. Tech.</i> , 2011, 76, 303–307.	
	7.6	200	<i>Environmental Technology</i> 2013, 34 (24):3183–89.	
	Average: 11.0 ± 3.7	Average: 218 ± 41		
Sucrose/TMC	52.4	783	<i>J. Hazard. Mater.</i> , 2022, 421, 126716.	<b>S7</b>
PE-TMC	10.7	820	<i>Appl. Surf. Sci.</i> , 2017, 416, 152-159.	<b>S8</b>
DETA/TMC	3.35	420	<i>Desalination</i> 2014, 333, 59–65.	<b>S9</b>
TETA/TMC	4.35	400		
TEPA/TMC	5.1	370		
PIP/TMAAM	12.1	364	<i>RSC Adv.</i> 2018, 8, 15102–15110.	<b>S10</b>
PIP-MPD/TMC	4.8	170	<i>Sep. and Puri. Tech.</i> , 2021, 279, 119692.	<b>S11</b>
RE8040–BE	3.0	102	<i>J. Environ. Eng.</i> <b>2009</b> , 135 (9), 788–795.	<b>S12</b>
RE8040–FE	3.0	102		
RE8040–nFE	3.0	102		
RE8040–BLN	4.9	102		