Supporting Information:

Selective amphiphilic polyelectrolyte complex bilayers with sub-nanometer effective pore sizes and high permeance

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1. Copolymer synthesis and characterization

Synthesis of A+. This copolymer was described in a previous publication [1], where it was labeled C+. Briefly, the two monomers, TAEMA (4.00 g) and TFEMA (4.00 g), were dissolved in 32 mL of DMSO. 0.008 g AIBN was added. The flask was then sealed. After 30 minutes of nitrogen purging, the flask was placed in an oil bath set to 60 °C with stirring at 300 rpm for 17 hours. At the end of the reaction, 0.8 g of MEHQ was added. The polymer was then precipitated in acetone (0.8 L) and purified by stirring two fresh portions of 1:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72 hours at 60 °C. ^{1}H-NMR spectrum of A+ was reported in our previous publication[1] and is reproduced with permission below:

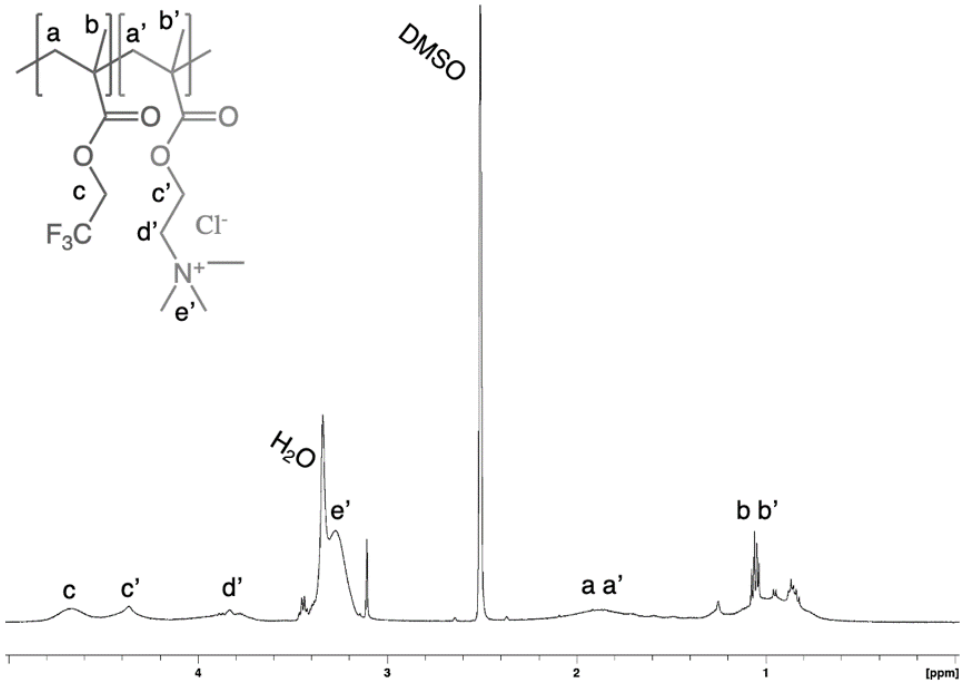

Figure S1. ^{1}H-NMR spectrum of A+ and peak assignments. Reproduced with permission from the Supporting Information file for [1]. Copyright 2024 American Chemical Society.

Synthesis of S-. As reported earlier,[1] 4.00 g each of SEMA and TFEMA were dissolved in 32 mL of DMSO. AIBN (0.008 g) was added, and the flask was sealed and purged with nitrogen for 30 minutes. The flask was stirred at 300 rpm in an oil bath set to 60 °C for 17 hours. At the end of the reaction, the flask was removed, and 0.8 g of MEHQ was added to terminate the reaction. The polymer was precipitated in 1:3 ethanol to hexane volume ratio (0.8 L) and purified by stirring two fresh portions of 2:3 ethanol to hexane volume ratio for at least 3 hours. Finally, the copolymer was dried in the vacuum oven for 72 hours at 60 °C. ^{1}H-NMR spectrum, reproduced below, was used to determine its composition.

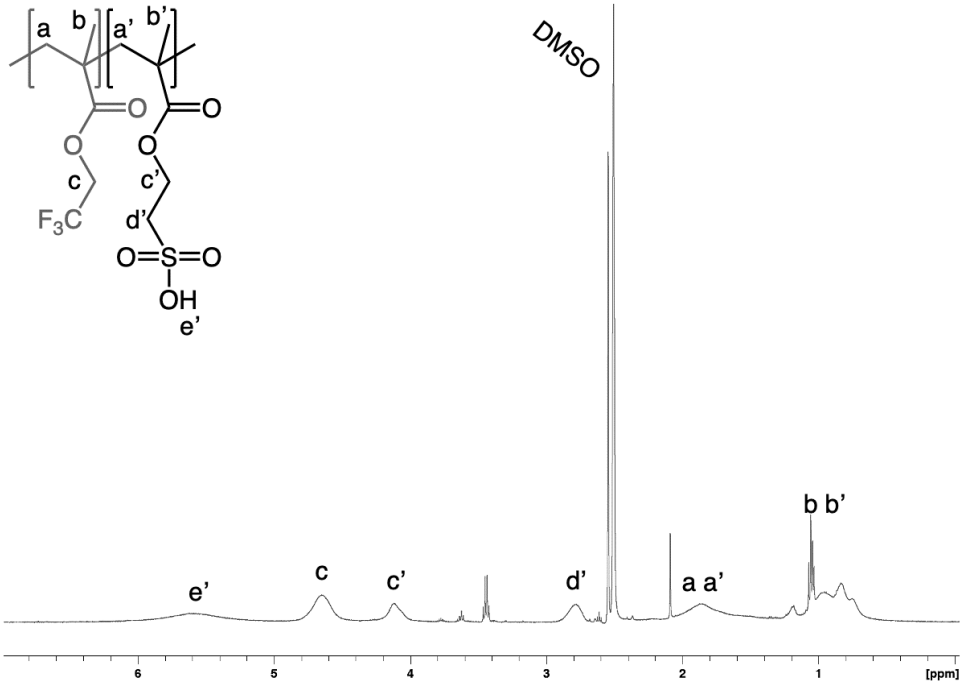

Figure S2. ^{1}H-NMR spectrum of S- and peak assignments. Reproduced with permission from the Supporting Information file for [1]. Copyright 2024 American Chemical Society.

Synthesis of A*+. A*+, a copolymer similar to A+ but with a higher fraction of the hydrophobic monomer TFEMA, was synthesized as described in the main document. Its ^{1}H-NMR spectrum, shown below, was used to calculate its composition.

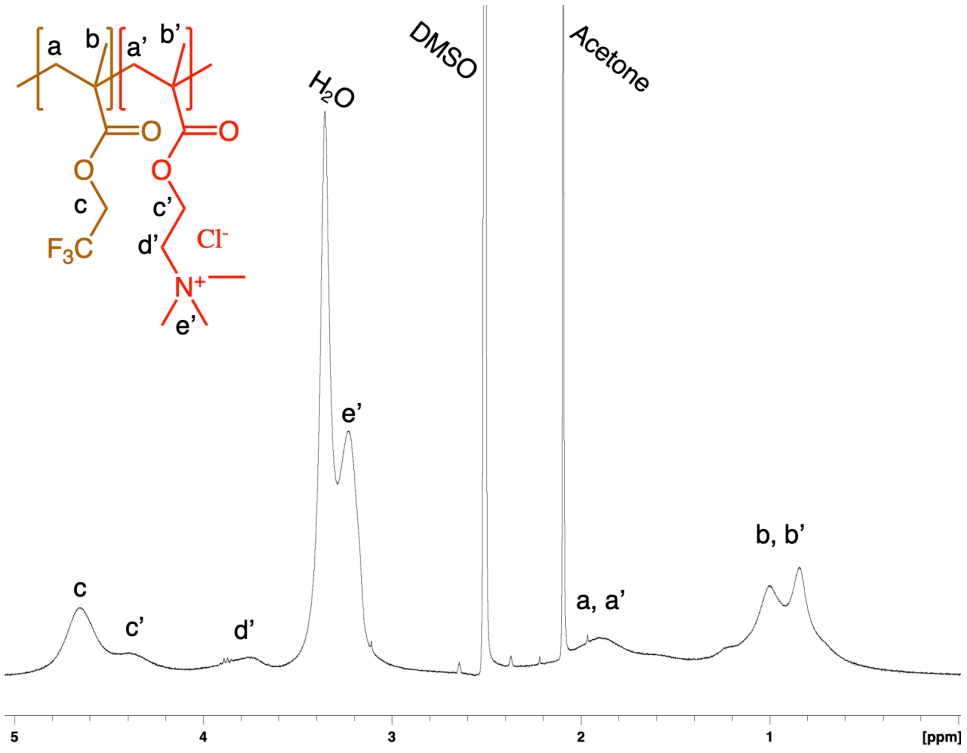

Figure S3. ^{1}H-NMR spectrum of A*+ and peak assignments.

Table S1. Water uptake by copolymers and APEC bilayer free standing films.

	S-	AS	A*S	A+	A*+
Water uptake (%)	289 ± 14	69 ± 8	41 ± 6	1020 ± 130	384 ± 56

2. Membrane characterization

TFC membranes were characterized by a Phenom G2 Pure Tabletop scanning electron microscope (SEM) using 5 kV. Dried membranes were immersed in liquid nitrogen and severed with a razor blade for cross-sectional imaging. Samples were sputter coated (Cressington 108 Manual, Ted Pella Inc., CA) with Au/Pd (60/40) in argon atmosphere.

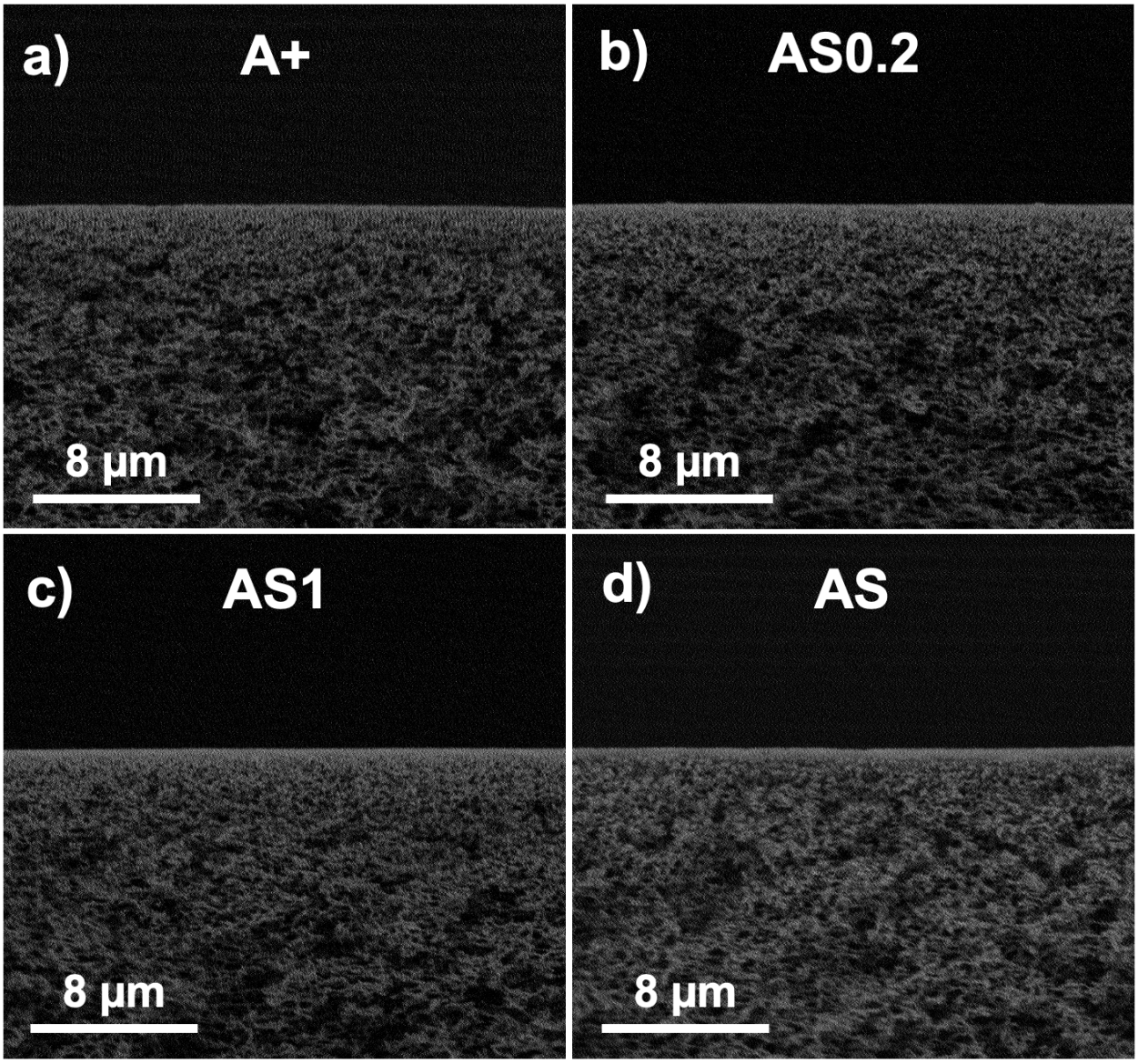

Figure S4. Cross-sectional SEM images of (a) single layer A+, (b) AS0.2 bilayer, (c) AS1 bilayer, (d) AS bilayer. It is possible to see bilayers with an approximate thickness of ~200-500 nm (10 000× magnification).

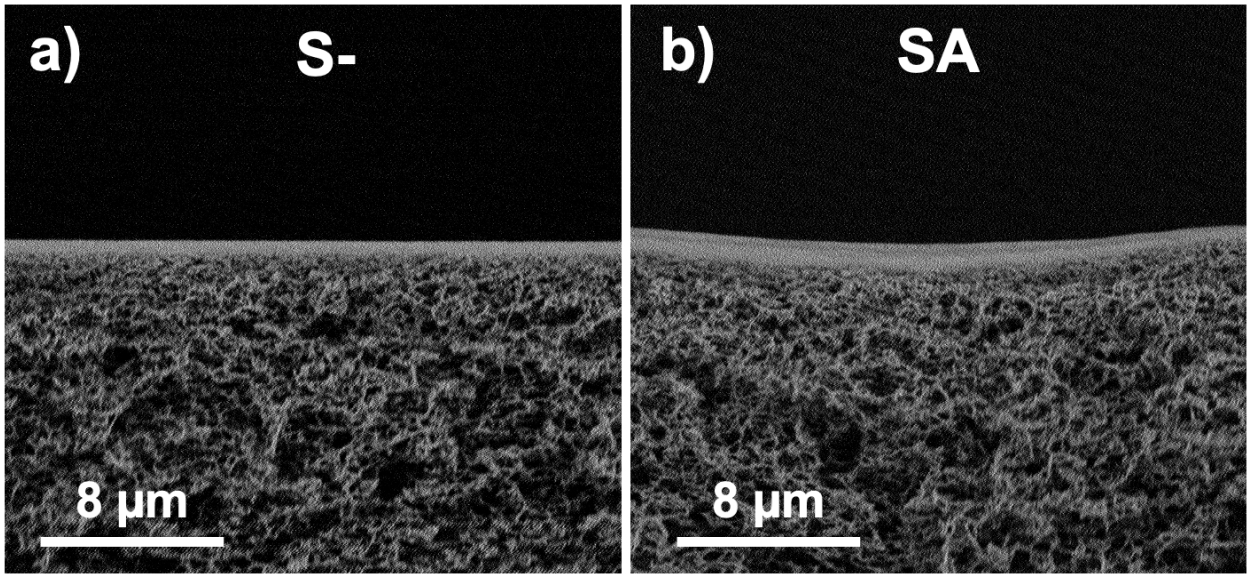

Figure S5. Cross-sectional SEM images of (a) single layer S-, (b) SA bilayer. It is possible to see the S- single layer with an approximate thickness of ~400 nm, and an SA bilayer with an approximate thickness of ~800 nm (10 000× magnification).

3. Filtration experiments

Table S2. Stokes diameter and net charge of solutes used to evaluate the effective pore size of the selective layers.

	Stokes diameter (nm)	**Net charge**
Vitamin B12	1.48 [a)]	0 [c)]
Sucrose	0.958 [b)]	0
Glucose	0.73 [b)]	0
Glycerol	0.47 [b)]	0

[a)]Reported by Bowen [2]; [b)]Calculated by Gin [3]; [c)]Net charge is zero at the tested pH.

Table S3. Permeance, dye rejections, and salt rejections of APEC bilayer membranes with different top layer amounts of A+.

	S-	SA0.2	SA1	SA
Permeance ($L/m^2.h.bar$)	4.0 ± 1.1	3.8 ± 1.0	3.2 ± 1.1	3.1 ± 1.0
Vitamin B12 rejection (%)	58.0 ± 3.4	60.9 ± 5.9	99.1 ± 0.1	99.7 ± 0.3
Riboflavin rejection (%)	12.8 ± 2.9	13.7 ± 4.1	84.0 ± 3.4	86.9 ± 3.2
NaCl rejection (%) 1 mM; 10 mM	72.1 ± 3.7; 34.2 ± 2.7	75.6 ± 2.6; 31.4 ± 3.3	75.8 ± 2.3; 32.2 ± 1.6	67.6 ± 3.5; 31.4 ± 2.2
Na_2SO_4 rejection (%) 1 mM; 10 mM	93.2 ± 0.9; 86.0 ± 1.2	90.5 ± 1.1; 80.2 ± 1.5	95.3 ± 0.9; 95.3 ± 0.9	92.5 ± 1.0; 93.0 ± 0.8
$MgCl_2$ rejection (%) 1 mM; 10 mM	12.5 ± 1.1; 1.2 ± 0.5	14.3 ± 1.3; 5.3 ± 0.9	44.2 ± 2.9; 23.2 ± 2.1	68.9 ± 1.9; 36.8 ± 3.2

Table S4. Permeance, dye rejections, and salt rejections of APEC bilayer membranes with different top layer amounts of S-.

	A+	AS0.2	AS1	AS
Permeance ($L/m^2.h.bar$)	82 ± 16	28 ± 7	21 ± 6	20 ± 5
Vitamin B12 rejection (%)	8.3 ± 1.5	65.0 ± 6.2	99.8 ± 0.2	99.8 ± 0.2
Riboflavin rejection (%)	1.2 ± 0.6	15.1 ± 5.1	92.1 ± 3.2	91.0 ± 2.5
NaCl rejection (%) 1 mM; 10 mM	26.4 ± 2.1; 3.7 ± 0.8	72.3 ± 3.9; 27.7 ± 2.5	73.5 ± 3.1; 37.1 ± 2.5	67.3 ± 2.6; 29.9 ± 1.6
Na_2SO_4 rejection (%) 1 mM; 10 mM	18.3 ± 2.6; 5.0 ± 1.8	30.8 ± 3.9; 12.4 ± 1.9	91.4 ± 0.7; 91.5 ± 1.1	91.9 ± 0.8; 91.5 ± 1.1
$MgCl_2$ rejection (%) 1 mM; 10 mM	58.7 ± 3.9; 4.2 ± 0.9	89.0 ± 1.7; 58.2 ± 1.6	84.3 ± 1.9; 72.2 ± 1.4	83.4 ± 2.3; 71.8 ± 1.6

Table S5. Permeance, vitamin B12 rejection, and salt rejections of APEC bilayer membranes with different evaporation times prior to immersion in deionized water.

	AS – 30 min (Standard)	AS – 1 min	AS – 5 s
Permeance ($L/m^2.h.bar$)	20.0 ± 2.5	20.2 ± 3.5	20.6 ± 2.7
Vitamin B12 rejection (%)	99.8 ± 0.2	99.8 ± 0.1	99.7 ± 0.1
NaCl rejection (%) 1 mM; 10 mM	67.3 ± 2.6; 29.9 ± 1.6	66.9 ± 4.7; 29.7 ± 2.2	66.2 ± 2.4; 30.1 ± 3.7
Na_2SO_4 rejection (%) 1 mM; 10 mM	91.9 ± 0.8; 91.5 ± 1.1	91.7 ± 1.7; 91.5 ± 1.3	91.6 ± 2.0; 91.4 ± 2.7

Table S6. Permeance, dye rejections, and salt rejections of APEC bilayer membrane with more hydrophobic cationic copolymer A*+ compared with cationic single layer A*+ and support membrane (PSf).

	PSf	A*+	A*S
Permeance ($L/m^2.h.bar$)	1100 ± 150	59 ± 11	8.5 ± 1.0
Vitamin B12 rejection (%)	6.9 ± 1.1	10.5 ± 1.8	100 ± 0.0
Riboflavin rejection (%)	1.0 ± 0.5	1.6 ± 0.4	99.6 ± 0.1
NaCl rejection (%) 1 mM; 10 mM	1.3 ± 0.4; 1.0 ± 0.3	28.3 ± 1.3; 4.2 ± 0.5	69.7 ± 1.6; 48.6 ± 1.6
Na_2SO_4 rejection (%) 1 mM; 10 mM	2.2 ± 0.2; 1.6 ± 0.3	21.9 ± 1.5; 6.0 ± 0.6	98.3 ± 0.5; 98.2 ± 0.8
$MgCl_2$ rejection (%) 1 mM; 10 mM	2.3 ± 0.5; 1.8 ± 0.5	64.9 ± 1.7; 6.6 ± 0.5	88.6 ± 1.2; 88.9 ± 1.9

Table S7. Small neutral solute rejections of APEC bilayer membrane with more hydrophobic cationic copolymer A*+ compared with AS, SA, and single layers S-, and A+.

	A+	S-	SA	AS	A*S
Sucrose rejection (%)	1.5	14.3	91.3	94.9	99.9
Glucose rejection (%)	0.9	4.4	62.2	65.9	88.1
Glycerol rejection (%)	0.1	0.2	13.4	15.2	37.2

Table S8. Charged dye rejections of APEC bilayer membranes and single layers.

	S-	A+	SA	AS
Ethyl orange (%)	97.3 ± 2.4	32.6 ± 8.2	99.5 ± 0.4	99.7 ± 0.1
Chicago sky blue (%)	99.2 ± 0.7	58.3 ± 9.1	99.8 ± 0.2	100.0 ± 0.0

4. Benchmarking Membrane Performance

Commercial membranes whose MWCO and permeances are reported in Figure 9 and the references that include this information are shown below.

Table S9. Permeances and MWCO values of commercial NF and RO membranes in Figure 9.

Membrane		Reported MWCO (Da)	Water permeance ($L/m^2.h.bar$)	Reference
APEC bilayer	AS	340	20	This study
	A*S	190	8	This study
Commercial NF	NF270	400	14.6	[4]
	NP030	500	1	[4]
	NF200	740	8	[4]
	NF90	800	7.6	[4]
	UA60	1000	12.5	[4]
	NP010	1000	8.1	[4]
	GE	1100	1.6	[4]
	GH	1200	3.6	[4]
Commercial RO	BW30-400FR	100	2.5	[5]
	AK	162	0.09	[6]
	ESPA	162	0.07	[6]
	XLE	220	3.9	[7, 8]
	SC 3100	250	1.3	[8]

5. Chemical stability of APEC bilayer membranes

The chemical stability of the APEC bilayer AS membrane when exposed to acidic and alkaline environments was characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy of the selective layer chemistry before and after two days of storage in pH 4, 7, and 10 buffers (Hydrion). We first dried an AS bilayer membrane in a vacuum oven at room temperature for 24 hours. Then, the ATR-FTIR spectrum was acquired using an FT/IR-6200 spectrophotometer (JASCO Corp.) equipped with a ZnSe crystal. ATR-FTIR spectra were averaged across 32 scans with a resolution of 4 cm^{-1} in the 4000-600 cm^{-1} region. Then, each membrane swatch was stored in the selected buffer for two days and dried. ATR-FTIR spectroscopy was performed once more.

The AS membrane spectrum (**Figure S6)** shows the characteristic peaks for APEs. The asymmetric stretching of sulfonate groups ($-SO_3^-$) from the SEMA units is represented by the peak at ~1225-1185 cm^{-1}, whereas the symmetric S=O stretching of sulfonate is attributed to the peak at ~1060-1030 cm^{-1}.[1] The ester C=O stretching from the methacrylate backbone seen in all repeat units is attributed to the absorption at around 1725-1740 cm^{-1}. The characteristic in the ~1180-1120 cm^{-1} area is related to C-F stretching of the CF_3 groups from TFEMA, which overlaps with ester C-O-C vibrations of the methacrylate backbone, while the absorption at ~970-950 cm^{-1} is attributed to C-N^+ stretching of the quaternary ammonium groups from TAEMA.[1, 9]

The ATR-FTIR spectra of AS membranes exposed to pH 4, 7, and 10 buffers do not exhibit new absorption bands. Characteristic methacrylate, sulfonate, or quaternary ammonium peaks are preserved, implying that there was no detectable chemical degradation or irreversible chemical change of the polymer functional groups. Small variations in relative peak intensities between samples likely arise from variations in relative thicknesses of A and S layers between swatches, consistent with variation among unexposed samples.

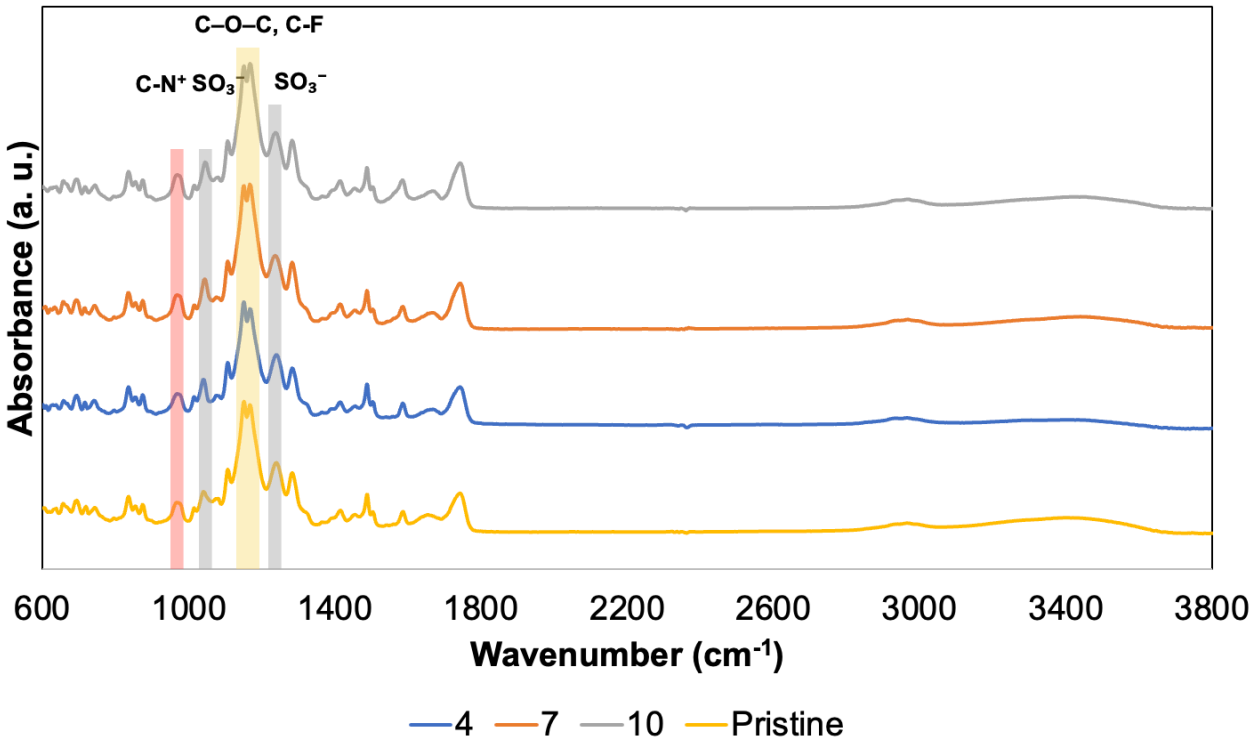

Figure S6. ATR-FTIR spectra for chemical stability analysis of the AS bilayer membrane before and after soaking in solutions at pH 4, pH 7, and pH 10 for 2 days.

References

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