Supplemental Information

1. The fraction of APFO molecules on the PEM surface

It is known that the contact angle of water on a smooth surface with aligned $-CF_3$ groups, an extremely low surface energy material, can reach 119° .¹ Here, trichloro (1H, 1H, 2H, 2H-perfluorocotyl) silane (FDTS) has been chosen to react with the Si substrate using a phase separation method in order to create a well-packed self-assembled monolayer.² The cleaned Si substrate is immersed into a plastic vial containing toluene (8 mL) and FDTS (10 uL). The reaction takes 1 hour and the substrate is then rinsed with toluene, ethanol, and water successively. The substrate is dried in an oven at 120° C for 10 min. The contact angle measured was 119.21° .

The wetting of a flat and chemically heterogeneous surface with two-component is typically modelled using the Cassie equation (Eq 1),³

$$\cos\theta_A^C = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{Eq 1}$$

where θ_A^c is the apparent contact angle, f_1 and f_2 are the area fractions of materials 1 and 2 ($f_1 + f_2 = 1$), and θ_1 and θ_2 are the contact angles on pure materials 1 and 2, respectively. Fig. S1 shows that the proportion of counterions on the surface of the PDAC-SPS PEMs reaches approximately 90% when the multilayers are assembled with 200 mmol L⁻¹ or higher NaCl concentrations in the polyelectrolyte assembly baths.



Fig. S1 f_{APFO} value calculated from contact angles according to Cassie's model for PEMs with surfaces that had been counterion exchanged with APFO. When NaCl concentration in the assembly exceeds 200 mmol L⁻¹, the fraction of fluorinated groups on the PEM surface reaches approximately 90%.⁴⁻⁵

2. Increase in thickness ratio after APFO dipping

Due to the displacement of SPS and diffusion of APFO surfactant into the film, the thickness of the PEM significantly increases after 5 min of exposure to APFO. The thickness ratio was obtained through normalization with the PDAC-SPS PEM before exposure to APFO. When the APFO ion exchange solution is a higher concentration, such as 100 mmol L^{-1} , the thickness ratio is almost 140%. Decreasing the APFO solution concentrations to 5 and 25 mmol L^{-1} will decrease the thickness ratio somewhat but they are still over 100%, meaning that the film increases in thickness in all cases.



Fig. S2 Thickness (closed symbols) and thickness ratio (open symbols) of 10.5 bilayers PDAC-SPS PEMs before and after APFO (5, 25, and 100 mmol L^{-1}) dipping for 5 min. The thicknesses increase up to 140% by displacement and diffusion of APFO surfactant.

3. SPS removal kinetics during the APFO dipping process

The APFO diffusion process is investigated by dipping 250 mmol L⁻¹ NaCl assembled PDAC-SPS PEMs into 5, 25, and 100 mmol L⁻¹ APFO solution for different time. Fig. S3 shows absorbance of peaks around 199 nm with dipping into APFO solutions for different time. Peaks around 199 nm and 225 nm correspond to π - π * transition of phenol group of SPS.⁶ The amount of SPS decrease a lot initially based on Lambert-Beer Law and come to saturated values exponentially with time going on. The amount in SPS removal also increases with increasing the concentration of APFO dipping solutions.



(a) 100 mmol L⁻¹ APFO

(b) 25 mmmol L⁻¹ APFO



(d) SPS removal kinetics during APFO dipping

Fig. S3 UV-vis spectra of 10.5 bilayers PDAC-SPS PEMs dipped in (a) 100 mmol L⁻¹, (b) 25 mmol L⁻¹, and (c) 5 mmol L⁻¹ APFO solution for different times; and (d) SPS removal kinetics during APFO dipping when locating the maximum absorbance of SPS at 199 nm.

Fig. S4 shows FTIR spectra of APFO counterion exchange/diffusion kinetics into PDAC-SPS PEMs and the removal of SPS. The bands at approximately 1208 and 1035 cm⁻¹ are assigned to asymmetric and symmetric vibrations of SO_3^- groups, respectively.⁷ The bands at 1206 and 1149 cm⁻¹ represent the C-F stretching vibration.⁸ For high APFO dipping concentration PEMs, intensities of SO₃ groups decrease as increasing these of C-F with time going on. However, intensities of SO₃ groups do not change a lot and the C-F peak at 1149 cm⁻¹ shows at shoulder for low APFO dipping concentration PEMs.



Fig. S4 FTIR spectra of 250 mmol L^{-1} NaCl assembled 10.5 bilayers PDAC-SPS PEMs dipped in (A) 100 mmol L^{-1} , (B) 25 mmol L^{-1} , and (C) 5 mmol L^{-1} APFO solution for different times. A1-C1 are from ATR mode with PEM on glass substrate and A2-C2 are from transmission mode with PEM on a ZnSe crystal substrate.

4. Wenzel model-the relationship between the wettability and surface roughness

In order to explain the relationship between the contact angle of a droplet on a smooth surface or a rough surface made of the same materials, Wenzel⁹ derived the following equation in 1936.

$$\cos\theta_r = r\cos\theta \tag{Eq 2}$$

where θ_r and θ are the contact angles of same materials on the rough surface and smooth surface respectively. And r is the surface roughness factor. Here, we can see that rough surface will let the hydrophilic surface becomes more hydrophilic, while hydrophobic surface becomes more hydrophobic.

5. The APFO existence in APFO co-assembled PDAC-SPS PEM through FTIR

The bands around 1208 and 1035 cm⁻¹ are assigned to asymmetric and symmetric vibrations of SO_3^- groups, respectively.⁷ The bands at 1206 and 1149 cm⁻¹ represent the C-F stretching vibration.⁸ The shoulder peak at 1149 cm⁻¹ (blue circle) increase with increasing APFO co-assembly concentration. The peak of S=O symmetric vibration around 1035 cm⁻¹ (red circle) decreases when the APFO concentration is as high as 25 mmol L⁻¹. In this case more APFO molecules were existed in the PEM to interact with positive charged PDAC layer and result to less SPS absorption.



Fig. S5 FTIR spectra of APFO co-assembled PDAC-SPS PEM by varying APFO assembly concentrations. Shoulder peak of APFO can be detected at low concentration as 0.5 mmol L^{-1} (blue circle). The decrease in S=O symmetric vibration (red circle) can be observed at higher concentration as 25 mmol L^{-1} .

6. Ionic strength influence on the growth of APFO co-assembled PDAC-SPS PEM



(A)

(B)

Fig. S6 (A) UV-vis spectra of APFO co-assembled PDAC-SPS PEMs varying NaCl concentration in polyelectrolyte solutions and (B) their relative SPS absorption at 199 nm. (C) thickness of APFO co-assembled 10.5 trilayer PDAC-SPS PEMs with different NaCl Concentration in polyelectrolyte solutions. The concentration of APFO during assembly is fixed as 5 mmol L⁻¹. The amount of SPS absorption will increase with increasing the multilayer thickness.



Fig. S7 FTIR spectra of APFO co-assembled PDAC-SPS PEMs with different NaCl concentration in polyelectrolyte solutions. The concentration of APFO during assembly is fixed as 5 mmol L⁻¹.

Ionic strength of polyelectrolyte solutions during assembly is another way to modulate the wettability properties in controlling with the morphology of each polyelectrolyte chain. In the same time of contact angle increase, amount of SPS and APFO as well as thickness of PEMs will increase with increasing the NaCl concentration in the polyelectrolyte solutions.

Fig. S6 shows the SPS absorption peak around 199 nm, corresponds to a π - π * transition of benzene group of SPS,⁶ increase with continuous increasing the ionic strength to be a thicker film. In this case, amount of SPS will increase due to the thickness increase as raising the NaCl assembly concentrations. However, the SPS absorbance can not be detected for the PEM with salt concentration as 1000 mmol L^{-1} because the PEM is too thick and amount of SPS inside is too much to be over UV detection limit. Moreover, the amounts of APFO also increase when raising the NaCl assembly concentrations with increasing the intensity of shoulder peak of C-F stretching vibration at 1149 cm^{-1,8} as shown in Fig. S7. The amount of APFO and SPS are increase in the same time to increase the PEMs thickness to high values.

Lastly we measured the surface roughness of the APFO co-assembled films using a stylus profilometer, the results of which can be seen in Fig. S8.



APFO Assembly Concentration (mmol L⁻¹)

Fig. S8 RMS surface roughness of the 10.5 trilayer APFO co-assembled PDAC-SPS PEMs terminated in PDAC-APFO layers over varying surfactant assembly concentrations always with 250 mmol L^{-1} NaCl in the polyelectrolyte assembly solutions.

References

- 1 R.J. El-Khouri and M.S. Johal, *Langmuir*, 2003, 19, 4880.
- 2 D. Yoo, S.S. Shiratori, M.F. Rubner, *Macromolecules*, 1998, 31, 4309.
- 3 L. Gao and T.J. McCarthy, JACS, 2006, 128, 9052.
- 4 A.B.D. Cassie, Discuss Faraday Soc., 1948, 3, 11.
- 5 M. Jarn, Q. Xu and M. Linden, *Langmuir*, 2010, **26**, 111330.
- 6 M.A. Rahim, W.S. Choi, H.J. Lee and I.C. Jeon, *Langmuir*, 2010, 26, 4680.
- 7 K. Katagiri, A. Matsuda and F. Caruso, *Macromolecules*, 2006, 39, 8067.
- 8 W.W Simons, The Sadtler Handbooks of Infrared Spectra, Sadtler Research Laboratories, Philadelphia 2004.
- 9 R.N. Wenzel, Ind. Eng. Chem., 1936, 28, 988.