The structural characterization of monomers is as follows:



Figure S1. 1H NMR spectra of ASC₈ and AGC₈ monomers.

¹H-NMR of ASC₈ (400 MHz, D₂O, ppm): δ 0.88 (3H, t, -CH₂CH₃), 1.30-1.35 (10H, m, -CH₂CH₂(CH₂)₅CH₃), 1.81 (2H, m, -CH₂CH₂(CH₂)₅CH₃), 1.97 (3H, s, -C=CCH₃), 3.30 (6H, -N-CH₃), 3.41-3.58 (2H, m, -CH₂CH₂(CH₂)₅CH₃), 3.80 (2H, t, OCH₂CH₂), 4.54 (2H, t, -OCH₂CH₂), 5.93 (1H, s, -CH₂=C-), 6.48 (1H, s, CH₂=C-). ¹H-NMR of AGC₈ (400 MHz, D₂O, ppm): δ 0.88 (6H, t, -CH₂CH₃), 1.29-1.3 5 (20H, m, -(CH₂)₅-), 1.78-1.82 (4H, m, -N-CH₂CH₂), 3.22 (12H, d, -N-(CH₃)₂), 3.41 (4H, m, -N-CH₂-), 3.69-3.75 (2H, d, -N-CH₂-CH), 3.98-4.08 (2H, m, -N-CH₂-CH), 5.93 (1H, d, -CH₂=CH-), 6.23-6.34 (1H, q, -CH₂=CH-), 6.63-6.73 (1H, d, CH₂=CH-). Figure S2 shows variations of intensity ratio I_1/I_3 versus the concentration of homopolymers in aqueous solution and the critical aggregate concentration values of PASC₈ and PAGC₈ were obtained through steady-state fluorescence. The plots have a usual sigmoid shape with a rapid decrease of I_1/I_3 at measured concentration, which are sensitive to the environment polarity. With the increase of concentration, the I_1/I_3 ratios of PAGC₈ decreased sharply while those of PASC₈ decreased tardily after a certain concentration region, showing significant variation in the polarity of the hydrophobic microdomain and little difference in the critical aggregation concentration value. Differently, I_1/I_3 values almost reach a constant value at measured concentration of PASC₁, indicating that PASC₁ molecules cannot form aggregates due to the lack of polarity segments.



Figure S2. Fluorescence intensity ratio I_1/I_3 curves of PEs: PASC₁, PASC₈ and

PAGC₈ in aqueous solution.

"Wet" and "dry" mass obtained from QCM-D and LSPR measurements can be compared in order to determine the hydration fraction of the adsorbate, as presented in Figure S3.



Figure S3. Wet and dry mass for (a) $PASC_1$, (b) $PASC_8$, (c) $PAGC_8$ PE layers onto

silica surface at different concentration.

A smooth and homogeneous surface with an average root mean-square roughness (RMS) of \sim 0.5 nm can be firstly observed for the bare substrate.



Figure S4. Contact angle of water on fresh silica surfaces.

The shifts in frequency (Δf) and dissipation (ΔD) of DOPA adsorption on the bare substrste as a function of time are presented in Figure S5. The frequency approaches to about -23.0 Hz, while the dissipation to about 4.4 × 10⁻⁶.



Figure S5. Shifts in frequency and dissipation for DOPA adsorption on the bare

substrste surfaces.



Figure S6. (a) and (b): The plot of Ψ and Δ against λ for DOPA adsorption on different SAMs. The data are fitted by the dash lines. (c) The plot of mean-squareerror (MSE) against h for DOPA adsorption on the corresponding SAMs

Further anticorrosion evidence can be found in typical potentiodynamic polarization curves for different surfaces in 0.1 mol/L HCl solution (Figure S6). Compared with bare gold substratese, it can be seen that the current decreases to a range of 2.80~2.99 μ A·cm⁻² after PEs adsorption, and the current decreases greatly after the DOPA-PEs multilayers formed, with the corrosion current decreasing to a range of 0.13~0.34 μ A·cm⁻². It is indicated that the corrosion current of PE adlayers decreases to an extent, indicating an partially protection to the acid corrosion. For the DOPA-PEs multilayers, the corrosion current decreases greatly, particularly for the DOPA-PEs multilayers at the concentration of 2.0 × CAC. We concluded that DOPA-PEs multilayers have a good corrosion resistance capability, owing to their compact network microstructure and the growing of thickness which could prevent the penetration of acid molecules and water to the substrates.



Figure S7. Potentiodynamic polarization curves of different surfaces in acid solution.

Homopolymer	$M_{\rm n}$ (g/mol)	$M_{\rm w}({\rm g/mol})$	M_z (g/mol)	$M_{\rm w}/M_{\rm n}$
PAGC ₈	9.89×10^{3}	1.13×10^4	1.35×10^4	1.14
PASC ₈	9.83×10^{3}	$1.10 imes 10^4$	$1.28 imes 10^4$	1.12
PASC ₁	9.70×10^{3}	$1.03 imes 10^4$	$1.09 imes 10^4$	1.06

Table S1. Molecular weights and polydispersity of different surfaces

	Thickness	Wet mass	$\Delta \lambda_{\max}$	Dry mass	Water content
	(nm)	(ng/cm ²)	(nm)	(ng/cm ²)	(%)
70mg/L PASC ₁	0.48	28.5	0.09	15	47.4
140mg/L PASC ₁	0.69	73.6	0.17	29	60.6
0.5CAC PASC ₈	2.05	206.0	0.72	128	37.0
2.0CAC PASC ₈	3.47	409.6	1.29	241	41.2
0.5CAC PAGC ₈	3.11	336.0	0.89	164	51.2
2.0CAC PAGC ₈	5.03	519.0	1.37	270	47.7

Table S2. Fitted thickness, wet mass, $\Delta \lambda_{max}$, dry mass and water content of different polymer adlayers caculated from QCM-D and LSPR

		Slope of $\Delta D/\Delta f$ (×10 ⁻⁶ /Hz)
70mg/L PASC ₁	$k_{I} = k_{II}$	0.023
140mg/L PASC ₁	$k_{I} = k_{II}$	0.025
0.5CAC PASC ₈	k I	0.023
	k∎	0.075
2.0CAC PASC ₈	k I	0.014
	kш	<u>0.120</u>
0.5CAC PAGC ₈	k I	0.010
	k∎	0.086
2.0CAC PAGC ₈	k I	0.011
	k <u>∎</u>	<u>0.14</u>

Table S3. Slopes of $\Delta D/\Delta f$ of adsorption processes for different polymer adlayers

	Frequency	Wet mass	Thickness	Dry mass	Water content
	(Hz)	(ng/cm ²)	(nm)	(ng/cm ²)	(%)
DOPA on 70mg/L PASC ₁	12.1	440.3	8.3	373.5	15.1
DOPA on 140mg/L	20.3	638.3	10.9	490.5	23.1
PASC ₁					
DOPA on 0.5CAC PASC ₈	28.2	1225.5	17.4	783.0	36.1
DOPA on 2.0CAC PASC ₈	62.8	1792.6	30.4	1368.2	23.7
DOPA on 0.5CAC PAGC ₈	43.6	1334.1	20.5	922.5	30.9
DOPA on 2.0CAC PAGC ₈	74.5	2095.9	36.7	1651.5	21.2

Table S4. Wet mass, dry mass and water content of DOPA adsorbed on the different

surfaces estimated from QCM-D and ellipsometry.

Sample	$I_{\rm corr}/\mu {\rm A}\cdot {\rm cm}^{-2}$
Bare substrate	60.39
140 mg/L PASC ₁	2.93
2.0 CAC PASC ₈	2.80
2.0 CAC PAGC ₈	2.99
DOPA on bare substrate	8.23
DOPA on 140mg/L PASC ₁	0.34
DOPA on 2.0 CAC PASC ₈	0.17
DOPA on 2.0 CAC PAGC ₈	0.13

Table S5. I_{corr} of different surfaces derived from Tafel plots.