Supporting Information

Low-fouling, mixed-charge poly-L-lysine polymers with anionic oligopeptide side-chains

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Table S6. The graft densities of OEG-maleimide calculated by ^{1}H-NMR data.

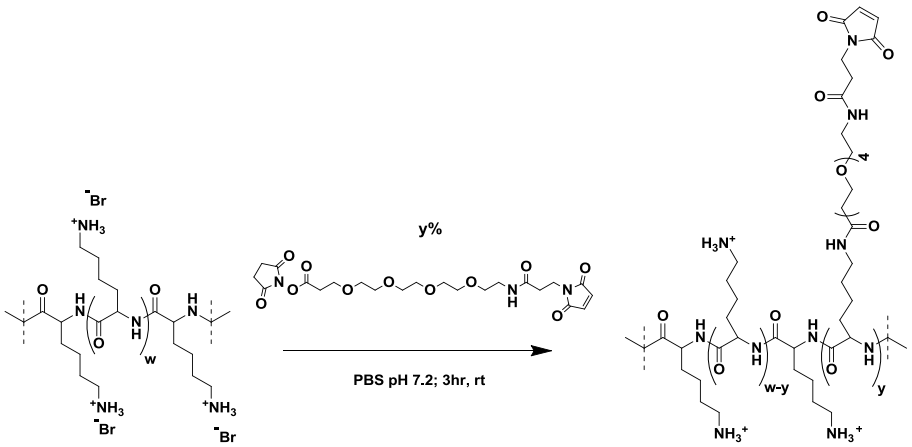


Figure S1. Scheme of PLL-mal(y%) synthesis.

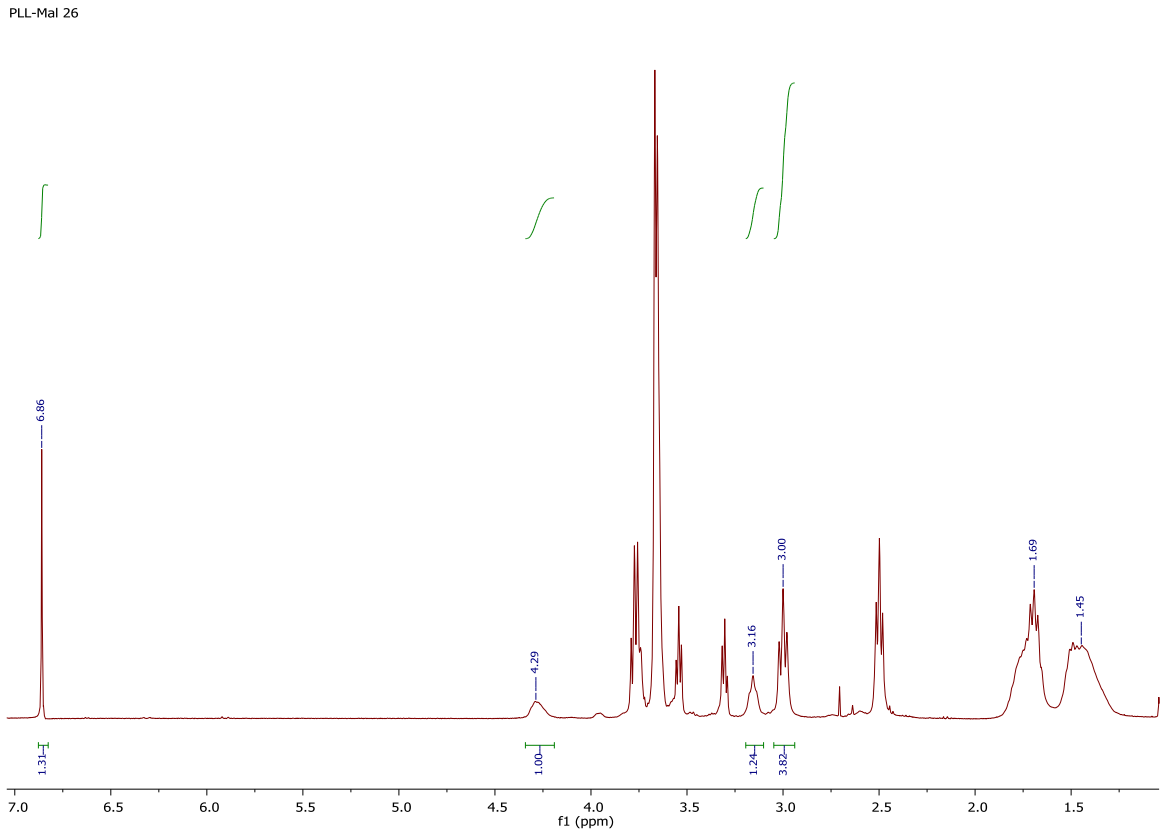


Figure S2. ^{1}H-NMR spectrum of PLL-mal(26%) after purification recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm with tetramethylsilane as an internal standard.

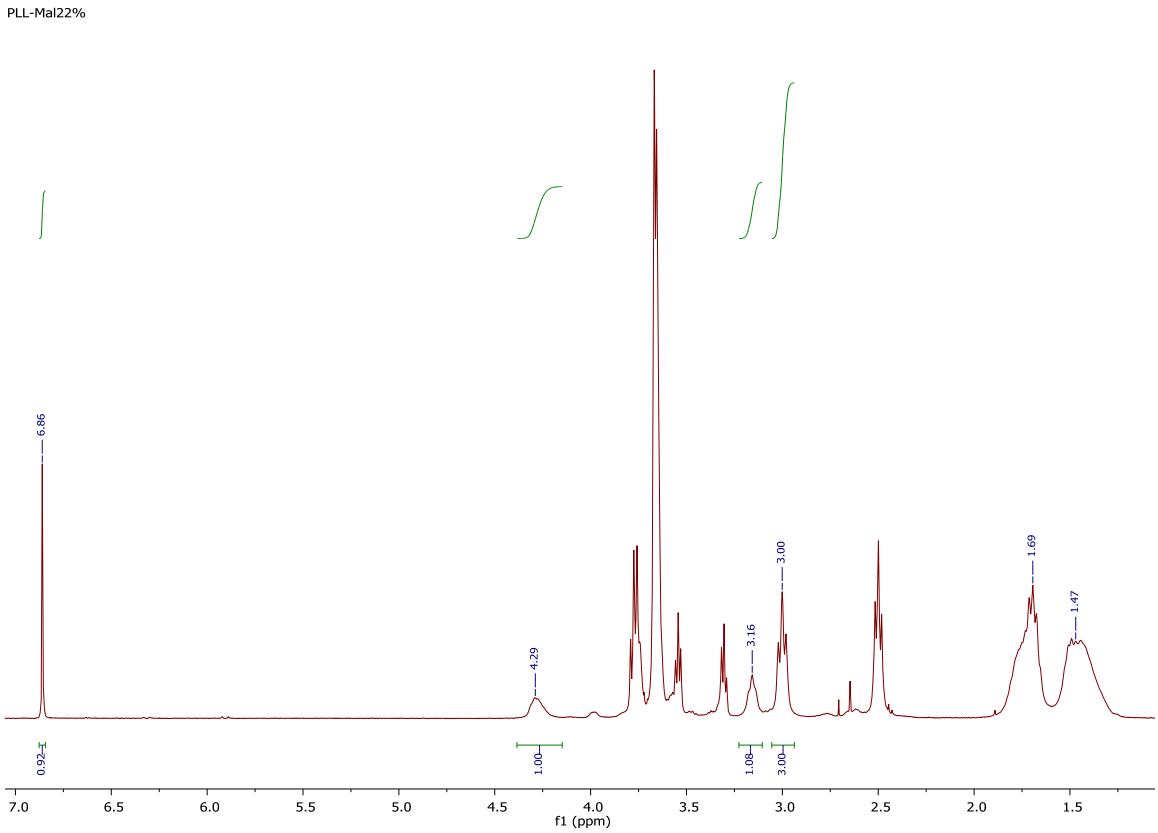
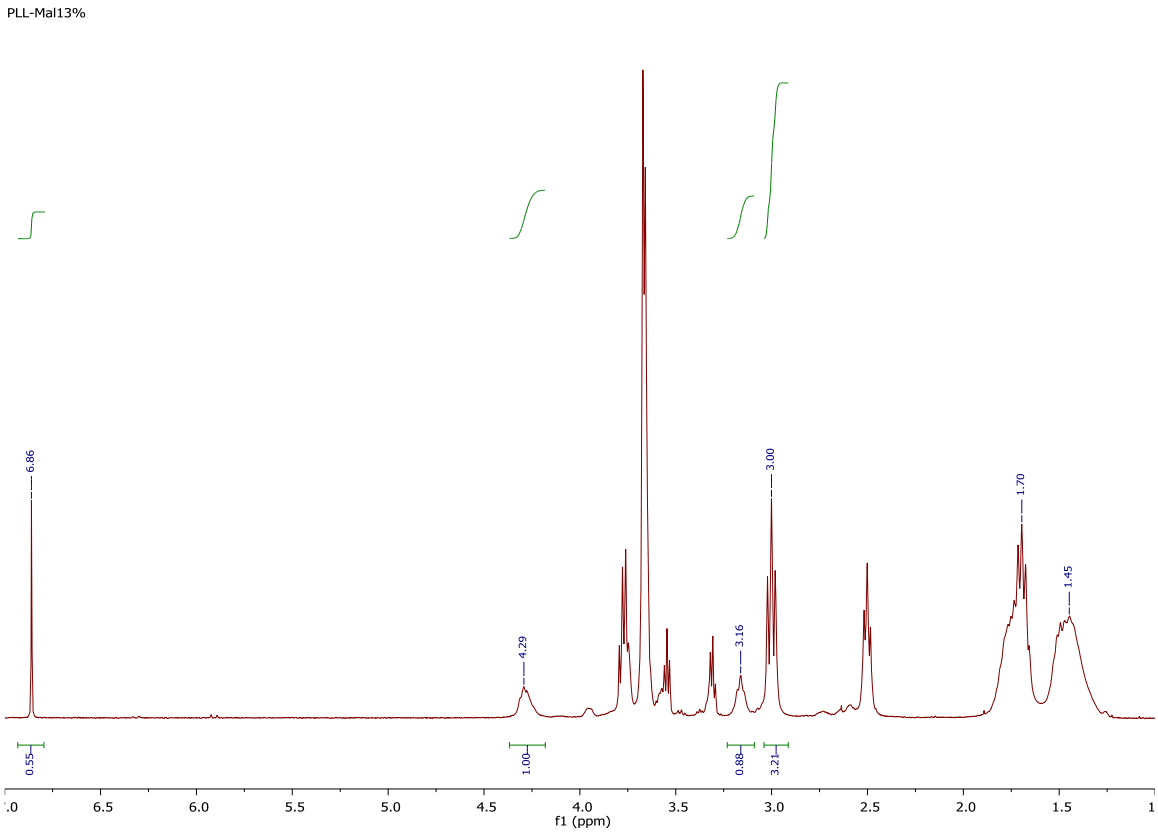


Figure S3. ^{1}H-NMR spectrum of PLL-mal(22%) after purification recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm with tetramethylsilane as an internal standard.

The ^{1}H NMR spectra of PLL-mal(y%), used to characterize the formation of such copolymers, were substituted in the Supporting Information.

The final grafting ratio (the percentage of the OEG-Mal chains) was determined by using the subsequent formula where the relative areas of the lysine side-chain peak (–N–CH_2) at 3.00 ppm and the OEG peak (CH_2–O–) at 3.16 ppm and the maleimide peak (HC=CH) at 6.86 ppm in ^{1}H NMR. The percentages of maleimide chains (y%) were calculated by the subsequent formula:

$$\%\ of\ functionalization = \frac{integral\ of\ the\ maleimide\ peak}{integral\ of\ the\ free\ lysine + integral\ of\ the\ coupled\ lysine}$$



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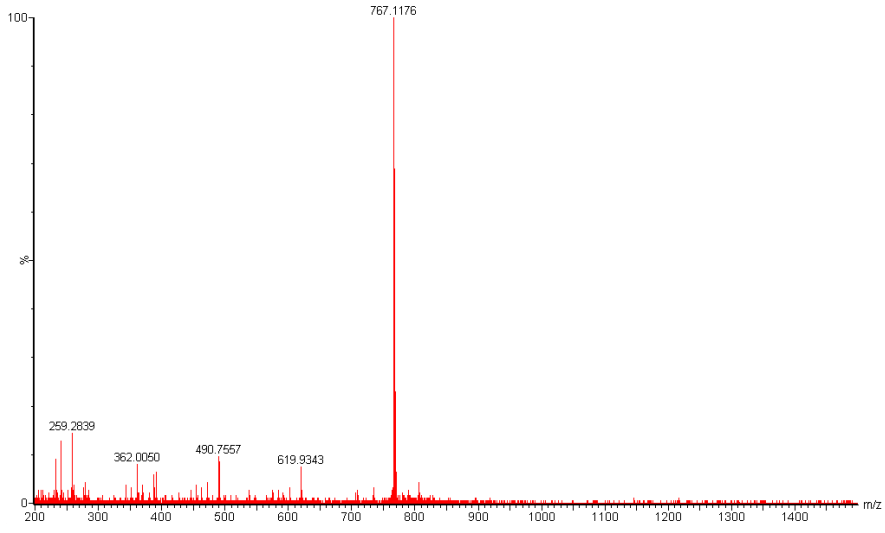


Figure S5. Mass spectrum of oligopeptide CEEEEE after purification, using 90 % Milli-Q water and 10 % acetonitrile.

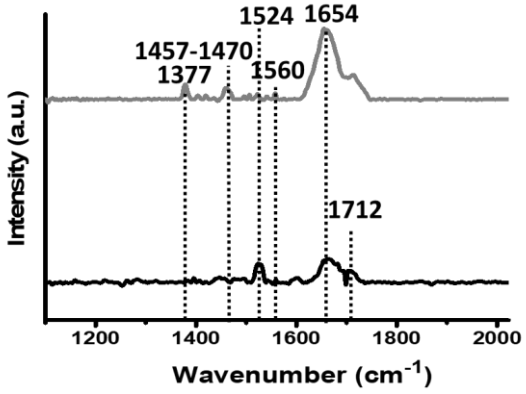
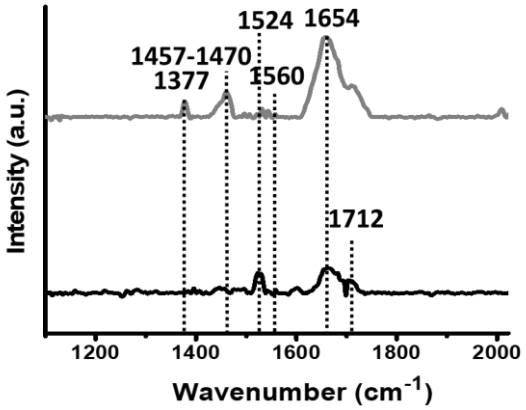


Figure S6. PM-IRRAS spectra of PLL–mal(22%) deposited on a gold chip (black line, bottom), and PLL-mal(22%)-CEEEEE (grey line, top) after the coupling reaction with CEEEEE.



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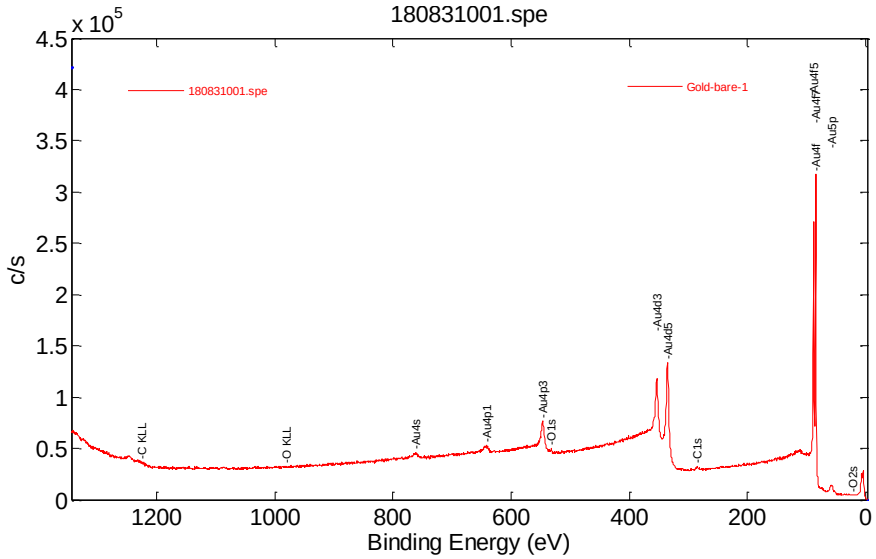
Explanation of the increase in the values of the contact angle after coupling reaction of CEEEEE to the PLL-mal(y%)

To explain the increase of contact angle values after the functionalization of PLL-mal(y%) with CEEEEE, we should introduce the hydropathy index (HI) of an amino acid, which is a number representing the hydrophobic or hydrophilic properties of its sidechain. It was proposed in 1982 by Jack Kyte and Russell F. Doolittle J. Mol. Biol. 157:105-132(1982).

The larger the HI number is, the more hydrophobic the amino acid. From ProtScale (https://web.expasy.org/protscale/pscale/Hphob.Doolittle.html) we found that the HI value for cysteine residue is 2.500, for glutamic acid -3.500 and for lysine -3.900. By comparing the HI values of single amino acids, we could explain that PLL-mal(y%) polymer, which is formed by only lysine residues, is more hydrophilic that the cysteine and glutamic acid.

Moreover, by calculating the grand average of hydropathy (GRAVY) value for CEEEEE sequence, that is defined by the sum of hydropathy values of all amino acids divided by the peptide length, we found that GRAVY index for CEEEEE is -2.5 (http://www.gravy-calculator.de/index.php).



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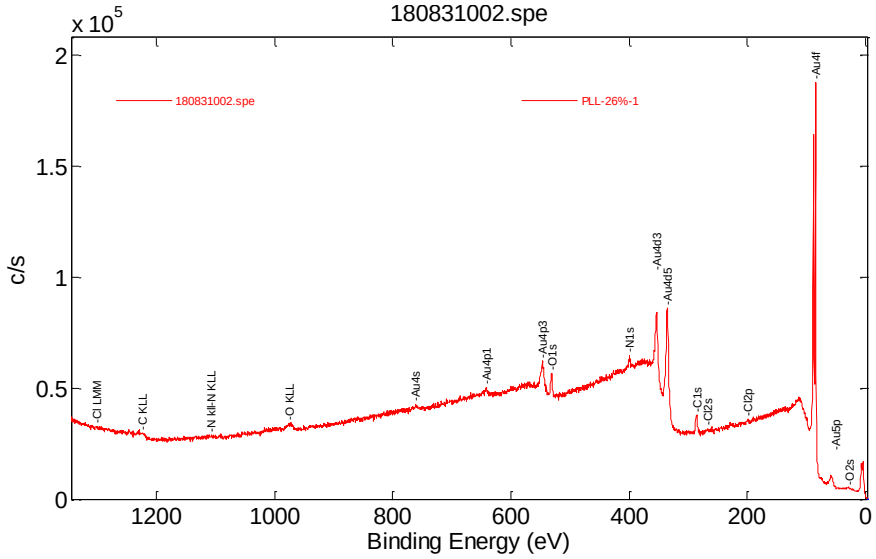


Figure S9. XPS Survey spectrum of PLL-mal(26%), from -5 eV - 1345 eV, Pass Energy = 224 eV and δE = 0.4eV for 3 cycles.

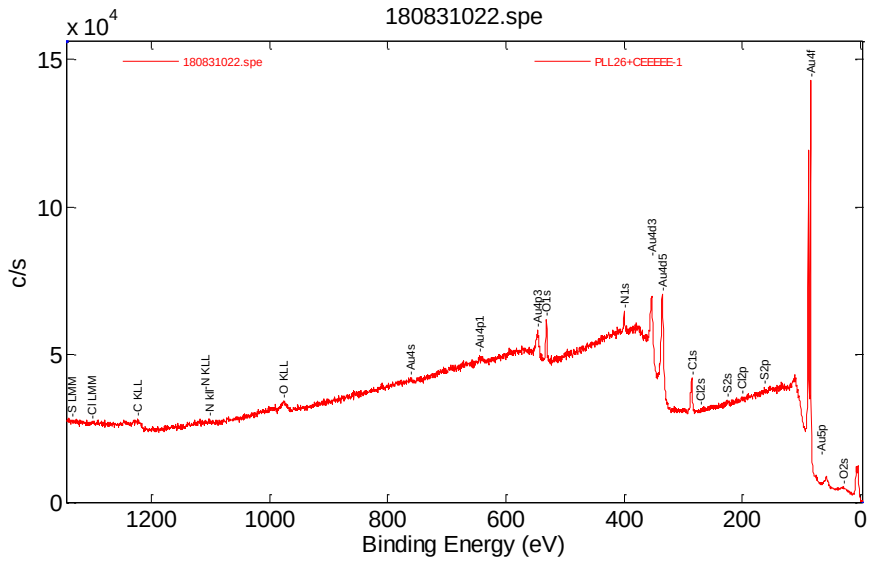
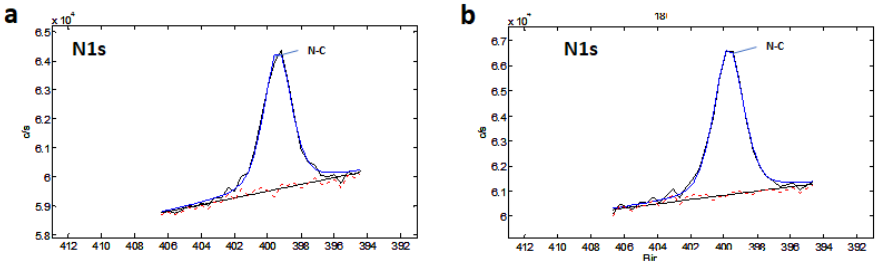


Figure S10. XPS Survey spectrum of PLL-mal(26%)-CEEEEE, from -5 eV - 1345 eV, Pass Energy = 224 eV and δE = 0.4eV for 3 cycles.



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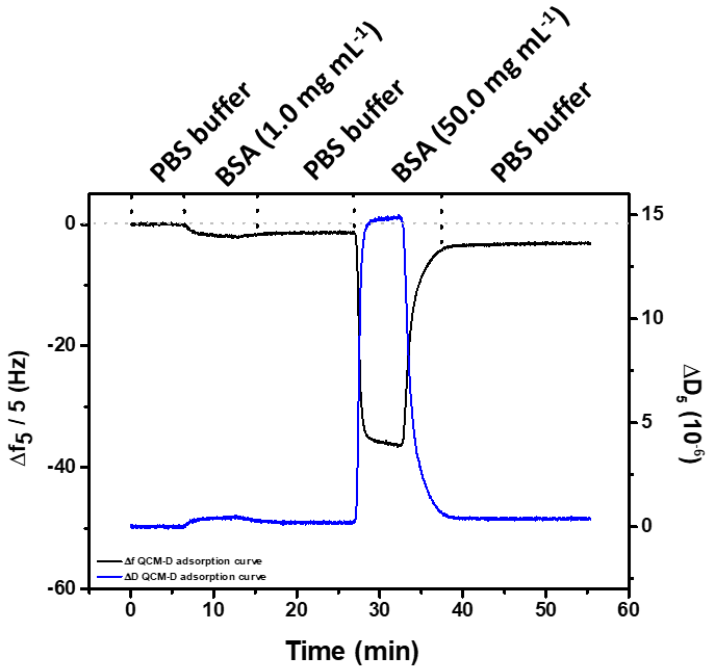

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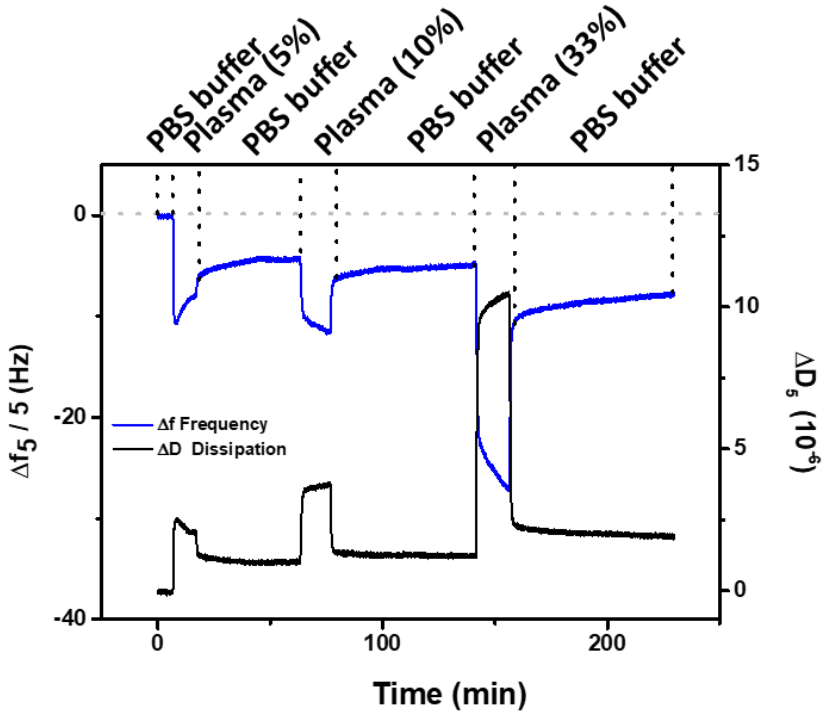

Figure S13. QCM-D antifouling tests using diluted human plasma samples and PLL-mal(26%)-CEEEEE on silicon oxide surface. Frequency (blue line) and energy dissipation (black line) shifts corresponding to the adsorption of protein from diluted human plasma samples are observed in QCM-D measurement.

Table S1. XPS signals from core spectra of PLL and PLL-CEEEEE layers.

Surface	C [at%]	N [at%]	O [at%]	Na [at%]	S [at%]	Cl [at%]	Br [at%]	Au [at%]
PLL	41.50	7.78	9.34	0.94	0.02	1.25	1.05	38.12
PLL-CEEEEE	47.07	12.49	15.28	0.95	1.55	0.46	1.20	21.00

Table S2. XPS signals from core spectra of Au bare, PLL-mal(13%), PLL-mal(22%) and PLL-mal(26%) layers.

Surface	C [at%]	N [at%]	O [at%]	S [at%]	Cl [at%]	Au [at%]
Au bare	20.67	-	-	-	-	79.33
PLL-mal(13%)	36.24	8.16	12.68	0.00	1.13	41.78
PLL-mal(22%)	41.59	9.36	14.82	0.30	1.94	31.98
PLL-mal(26%)	41.62	10.42	16.20	0.08	-	31.67

Table S3. Surface coverage (ng cm^{-2}) of PLL-mal(26%), CEEEEE and molar ratio of CEEEEE to the PLL-mal(26%) for the evaluation of the coupling efficiency estimated by SPRI.

SPRI areal mass (ng cm^{-2})				
PLL-mal(26%)	**CEEEEE**	**mol CEEEEE/ mal(26%)**	**[BSA] 1.0 mg mL^{-1}**	**[BSA] 50.0 mg mL^{-1}**
138	282	2.4	9(2)	13(2)

Table S4. Surface coverage (ng cm^{-2}) of BSA adsorption on PLL-mal(26%)-CEEEEE silicon oxide surface measured by QCM-D on silicon oxide surface.

QCM-D areal mass (ng cm^{-2})	
[BSA] 1.0 mg mL^{-1}	**[BSA] 50.0 mg mL^{-1}**
24	55

Table S5. Surface coverages of protein (ng cm^{-2}) from diluted human plasma samples on PLL-mal(26%)-CEEEEE silicon oxide surface estimated byQCM-D.

Human plasma in PBS	QCM-D (ng cm^{-2})
5%	78
10%	88
33%	139

Table S6. The graft densities of OEG-maleimide calculated by ^{1}H-NMR data.

NMR % of the polymer	Free lysine (signal at 3.00 ppm)	Coupled lysine (signal at 3.16 ppm)	Maleimide (signal at 6.86 ppm)
PLL-mal(26%)	75.49	24.51	25.89
PLL-mal(22%)	73.53	26.47	22.55
PLL-mal(13%)	78.48	21.52	13.45