

Supporting Information

Superior Antifouling Performance of a Zwitterionic Peptide Compared to an Amphiphilic, Non-Ionic Peptide

Huijun Ye,[†] Libing Wang,[†] Renliang Huang,^{*,‡} Rongxin Su,^{*,†,§,#} Boshi Liu,[†] Wei Qi,^{†,§,#} and Zhimin He[†]

[†] State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China

[‡] Tianjin Key Laboratory of Indoor Air Environmental Quality Control, School of Environmental Science and Engineering, Tianjin University, Tianjin 300072, P. R. China

[§] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

[#] Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin University, Tianjin 300072, P. R. China

* Author to whom any correspondence should be addressed

E-mail: tjuhl@tju.edu.cn (R. H.), surx@tju.edu.cn (R. S.)

Tel: +86 22 27407799. Fax: +86 22 27407599.

Supplementary Figures

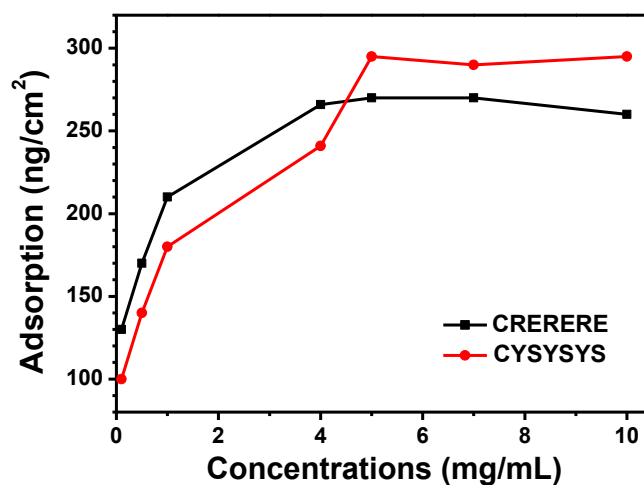


Figure S1. The adsorption amounts of peptides on bare Au surfaces with different concentrations of peptide solutions.

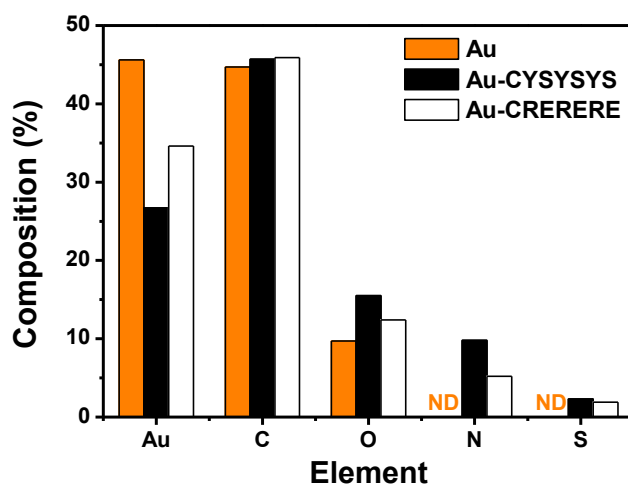


Figure S2. XPS surface compositions. Percent elemental surface compositions of Au, C, O, N, and S for bare Au (orange), Au-CYSYSYS (black) and Au-CRERERE (white) peptide SAMs. Note: “ND” represents that no N1S and S2P peak was determined.

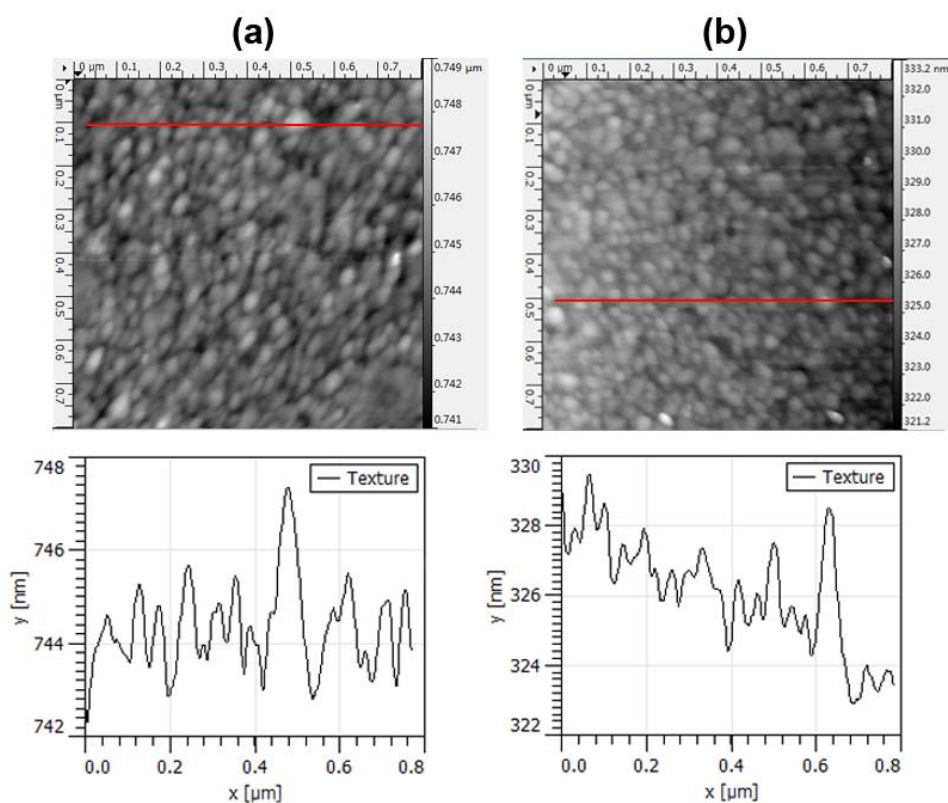


Figure S3. AFM images of the (a) CRERERE peptide SAM and (b) CYSYSYS peptide SAM.

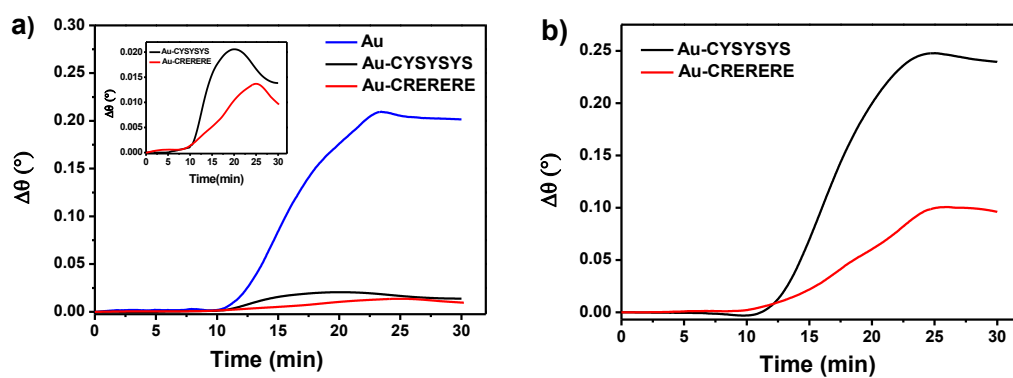


Figure S4. SPR sensorgrams showing the non-specific protein adsorption from BSA solution (a) and soybean milk (b) onto Au-CYSYSYS and Au-CRERERE surfaces.

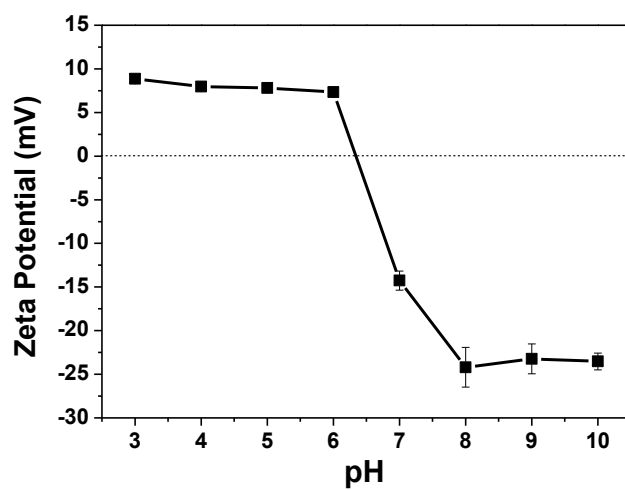


Figure S5. Zeta potentials of the CRERERE peptide at different pH values.

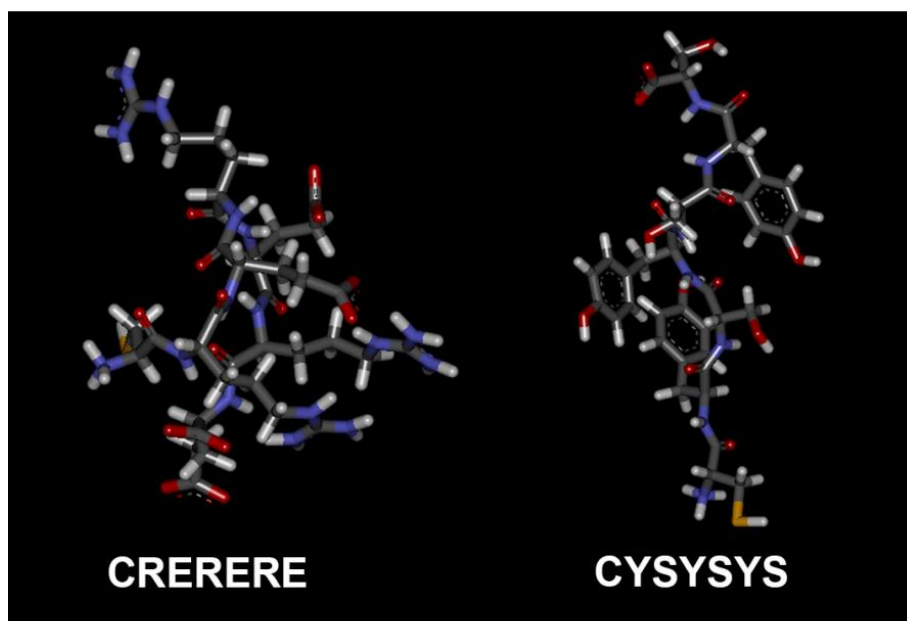


Figure S6. The molecular conformations of CRERERE (left) and CYSYSYS (right) peptide in water.

Supplementary Tables

Table S1 The nonspecific adsorption from single protein solutions and protein complexes-containing media on bare Au surface

Sample	Adsorption (ng/cm ²) ^a
BSA	162.67±10.21
Lysozyme	63.93±5.97
β-lactoglobulin	152.90±11.19
Serum	581.67±17.16
Soybean milk	378±19.08
Cow milk	468±25.53

^a All the measurements were repeated for three times.

Table S2 Summary of the antifouling surfaces and the corresponding non-specific protein adsorption

Antifouling surfaces		protein adsorption (ng/cm ²) ^a		Ref.
		BSA	Lys	
Hydrophilic/ Zwitterionic polymer/peptide	Poly(ethyleneoxide) end-tethered to polydopamine	/	<20	[1]
	Hyaluronic acid	7.7	4.6	[2]
	Poly(carboxybetaine)(pCB ₂ -catechol ₂)	/	<0.3	[3]
	Poly(N-acryloylamino-ethoxyethanol)	<0.3	<0.3	[4]
	EKEKEK-PPPPC	/	3.5	[5]
	CRERERE peptide	4.8	1.967	This study
Amphiphilic polymer/peptide	CYSYSYS peptide	7.75	11.78	This study
	PHEMA-PFA copolymer	25 ^b	/	[6]
Hydrophobic polymer	Poly(perfluorodecyl-acrylate)	500 ^b	/	[6]

^a 1 mg/mL BSA or lysozyme was used unless otherwise noted.

^b The concentration of BSA was 10 mg/mL.

Table S3 The protein concentrations of milk, soybean milk and human serum blood

Sample	Concentration (mg/mL)
Milk	25.86
Soybean milk	7.603
Human blood serum	52.40

Table S4 Summary of hydrogen bonds in the CYSYSYS peptide

DONOR	ACCEPTORH	ACCEPTOR			
atom# :res@atom	atom# :res@atom	atom# :res@atom	%occupied	distance	angle
74 :5@OG	43 :3@HG	42 :3@OG	0.79	2.959 (0.23)	40.39 (14.04)
91 :6@OH	43 :3@HG	42 :3@OG	0.66	2.975 (0.18)	27.86 (14.98)
106 :7@OG	28 :2@HH	27 :2@OH	0.53	2.877 (0.20)	20.42 (14.45)
106 :7@OG	43 :3@HG	42 :3@OG	0.31	2.907 (0.20)	23.32 (14.30)
42 :3@OG	75 :5@HG	74 :5@OG	0.21	3.017 (0.24)	31.13 (16.01)
74 :5@OG	107 :7@HG	106 :7@OG	0.17	3.153 (0.19)	44.64 (8.20)
27 :2@OH	107 :7@HG	106 :7@OG	0.16	2.915 (0.16)	21.76 (12.49)
91 :6@OH	60 :4@HH	59 :4@OH	0.13	3.114 (0.19)	26.09 (14.16)
27 :2@OH	92 :6@HH	91 :6@OH	0.09	3.043 (0.18)	31.77 (12.89)
59 :4@OH	28 :2@HH	27 :2@OH	0.06	3.115 (0.23)	34.41 (14.20)
42 :3@OG	107 :7@HG	106 :7@OG	0.06	3.133 (0.24)	38.47 (18.83)
42 :3@OG	92 :6@HH	91 :6@OH	0.04	3.232 (0.24)	25.78 (13.19)
106 :7@OG	75 :5@HG	74 :5@OG	0.03	3.018 (0.32)	13.39 (4.63)
106 :7@OG	60 :4@HH	59 :4@OH	0.02	2.862 (0.01)	38.70 (18.12)
27 :2@OH	43 :3@HG	42 :3@OG	0.02	3.272 (0.09)	38.32 (18.10)
91 :6@OH	107 :7@HG	106 :7@OG	0.01	3.494 (0.00)	56.79 (0.00)
91 :6@OH	75 :5@HG	74 :5@OG	0.01	3.305 (0.00)	58.77 (0.00)
59 :4@OH	92 :6@HH	91 :6@OH	0.01	2.967 (0.00)	17.26 (0.00)
59 :4@OH	75 :5@HG	74 :5@OG	0.01	3.338 (0.00)	50.11 (0.00)

59 :4@OH	solvent acceptor		0.31	3.064 (0.25)	27.26 (18.31)
106 :7@OG	solvent acceptor		0.28	2.968 (0.17)	25.65 (12.46)
solvent donor	60 :4@HH	59 :4@OH	0.24	2.877 (0.20)	19.74(13.69)
solvent donor	28 :2@HH	27 :2@OH	0.22	2.932 (0.23)	26.14(15.45)
solvent donor	92 :6@HH	91 :6@OH	0.19	2.846 (0.23)	26.32(14.92)
27 :2@OH	solvent acceptor		0.19	2.991 (0.22)	31.78 (14.39)
solvent donor	75 :5@HG	74 :5@OG	0.17	2.786 (0.15)	20.42(7.48)
solvent donor	107 :7@HG	106 :7@OG	0.15	2.899 (0.24)	23.1 (14.08)
91 :6@OH	solvent acceptor		0.13	2.994 (0.21)	25.46(13.12)
42 :3@OG	solvent acceptor		0.12	3.038 (0.17)	36.22(13.37)
solvent donor	43 :3@HG	42 :3@OG	0.11	2.888 (0.24)	20.10(11.19)
74 :5@OG	solvent acceptor		0.09	2.947 (0.20)	30.41(16.52)

Table S5 Summary of hydrogen bonds in the CRERERE peptide

DONOR		ACCEPTORH		ACCEPTOR		%occupied	distance	angle
atom#	:res@atom	atom#	:res@atom	atom#	:res@atom			
49	:3@OE1	112	:6@HH21	111	:6@NH2	74.90	2.946 (0.23)	31.62 (13.52)
50	:3@OE2	112	:6@HH21	111	:6@NH2	74.60	2.964 (0.23)	33.01 (13.74)
50	:3@OE2	106	:6@HE	105	:6@NE	66.30	2.980 (0.22)	30.91 (12.91)
49	:3@OE1	106	:6@HE	105	:6@NE	63.20	3.004 (0.22)	31.61 (13.41)
49	:3@OE1	32	:2@HH12	30	:2@NH1	28.30	2.911 (0.19)	37.09 (12.02)
49	:3@OE1	35	:2@HH22	33	:2@NH2	25.50	2.892 (0.19)	35.00 (12.51)
50	:3@OE2	32	:2@HH12	30	:2@NH1	18.70	2.942 (0.21)	35.92 (13.41)
50	:3@OE2	35	:2@HH22	33	:2@NH2	15.90	2.903 (0.20)	36.13 (12.47)
88	:5@OE1	73	:4@HH21	72	:4@NH2	5.00	2.827 (0.11)	24.76 (10.46)
88	:5@OE1	67	:4@HE	66	:4@NE	3.90	3.044 (0.23)	36.12 (8.30)
89	:5@OE2	73	:4@HH21	72	:4@NH2	2.10	2.922 (0.20)	32.73 (11.55)
89	:5@OE2	67	:4@HE	66	:4@NE	1.90	2.946 (0.18)	31.54 (10.44)
89	:5@OE2	70	:4@HH11	69	:4@NH1	1.30	2.843 (0.13)	33.71 (11.62)
88	:5@OE1	71	:4@HH12	69	:4@NH1	1.20	2.942 (0.18)	27.03 (9.05)
89	:5@OE2	113	:6@HH22	111	:6@NH2	0.70	3.110 (0.26)	47.19 (11.97)
88	:5@OE1	70	:4@HH11	69	:4@NH1	0.70	2.981 (0.24)	38.88 (14.74)
89	:5@OE2	71	:4@HH12	69	:4@NH1	0.60	3.129 (0.24)	44.55 (9.61)
88	:5@OE1	110	:6@HH12	108	:6@NH1	0.60	3.104 (0.30)	37.34 (15.19)
89	:5@OE2	110	:6@HH12	108	:6@NH1	0.50	2.859 (0.17)	24.95 (9.83)
88	:5@OE1	74	:4@HH22	72	:4@NH2	0.40	2.869 (0.10)	43.68 (5.21)
89	:5@OE2	74	:4@HH22	72	:4@NH2	0.30	2.863 (0.19)	46.04 (2.79)
88	:5@OE1	113	:6@HH22	111	:6@NH2	0.20	2.970 (0.30)	49.17 (7.56)
50	:3@OE2	34	:2@HH21	33	:2@NH2	0.20	2.953 (0.01)	40.60 (1.41)
50	:3@OE2	113	:6@HH22	111	:6@NH2	0.10	3.453 (0.00)	57.85 (0.00)
50	:3@OE2	28	:2@HE	27	:2@NE	0.10	2.716 (0.00)	38.06 (0.00)

89	:5@OE2	solvent acceptor				8.40	2.827 (0.24)	22.94 (14.58)
88	:5@OE1	solvent acceptor				7.90	2.794 (0.24)	21.14 (13.23)
49	:3@OE1	solvent acceptor				5.90	2.791 (0.20)	21.32 (12.55)
127	:7@OE1	solvent acceptor				5.40	2.855 (0.26)	22.54 (14.09)
128	:7@OE2	solvent acceptor				4.90	2.815 (0.23)	22.53 (12.09)
50	:3@OE2	solvent acceptor				4.40	2.786 (0.25)	22.58 (14.08)
solvent donor		73	:4@HH21	72	:4@NH2	2.60	2.994 (0.21)	31.17 (11.75)
solvent donor		113	:6@HH22	111	:6@NH2	2.30	3.041 (0.18)	32.20 (11.91)
solvent donor		110	:6@HH12	108	:6@NH1	2.30	2.978 (0.20)	24.85 (13.43)
solvent donor		70	:4@HH11	69	:4@NH1	2.10	2.937 (0.18)	24.31 (12.11)
solvent donor		67	:4@HE	66	:4@NE	2.00	3.101 (0.27)	37.20 (13.47)
solvent donor		109	:6@HH11	108	:6@NH1	1.70	3.030 (0.21)	29.27 (12.50)
solvent donor		74	:4@HH22	72	:4@NH2	1.70	3.012 (0.19)	38.58 (15.75)
solvent donor		71	:4@HH12	69	:4@NH1	1.70	3.055 (0.23)	35.30 (14.78)

solvent donor	32	:2@HH12	30	:2@NH1	1.40	3.001 (0.15)	31.80 (13.87)
solvent donor	31	:2@HH11	30	:2@NH1	1.10	3.003 (0.12)	21.97 (9.56)
solvent donor	35	:2@HH22	33	:2@NH2	0.80	3.082 (0.24)	42.15 (14.84)
solvent donor	106	:6@HE	105	:6@NE	0.50	3.236 (0.23)	39.56 (17.16)
solvent donor	112	:6@HH21	111	:6@NH2	0.30	3.149 (0.10)	49.11 (6.89)
solvent donor	34	:2@HH21	33	:2@NH2	0.10	3.331 (0.00)	49.93 (0.00)
solvent donor	28	:2@HE	27	:2@NE	0.10	3.499 (0.00)	58.20 (0.00)

References

- [1] Pop-Georgievski, O.; Verreault, D.; Diesner, M.-O.; Proks, V.; Heissler, S.; Rypacek, F.; Koelsch, P. Nonfouling poly(Ethylene Oxide) layers end-tethered to polydopamine. *Langmuir* **2012**, *28*, 14273–14283.
- [2] Liu, X.; Huang, R.; Su, R.; Qi, W.; Wang, L.; He, Z. Grafting hyaluronic acid onto gold surface to achieve low protein fouling in surface plasmon resonance biosensors. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13034–13042.
- [3] Gao, C.; Li, G.; Xue, H.; Yang, W.; Zhang, F.; Jiang, S. Functionalizable and ultra-low fouling zwitterionic surfaces via adhesive mussel mimetic linkages. *Biomaterials* **2010**, *31*, 1486–1492.
- [4] Chen, H.; Zhang, M.; Yang, J.; Zhao, C.; Hu, R.; Chen, Q.; Chang, Y.; Zheng, J. Synthesis and characterization of antifouling poly(N-Acryloylaminoethoxyethanol) with ultralow protein adsorption and cell attachment. *Langmuir* **2014**, *30*, 10398–10409.
- [5] Nowinski, A. K.; Sun, F.; White, A. D.; Keefe, A. J.; Jiang, S. Sequence, structure, and function of peptide self-assembled monolayers. *J. Am. Chem. Soc.* **2012**, *134*, 6000–6005.
- [6] Baxamusa, S. H.; Gleason, K. K. Random copolymer films with molecular-scale compositional heterogeneities that interfere with protein adsorption. *Adv. Funct. Mater.* **2009**, *19*, 3489–3496.