Supporting Information

Switch of Surface Adhesion to Cohesion by Dopa-Fe^{3+} Complexation in Response to Microenvironment at the Mussel Plaque-Substrate Interface

Byeongseon Yang[†], Chanoong Lim[‡], Dong Soo Hwang[‡], and Hyung Joon Cha[*,†]

[†]Department of Chemical Engineering, [‡]School of interdisciplinary Bioscience and Bioengineering, Pohang University of Science and Technology, Pohang 37673, Republic of Korea

*e-mail: hjcha@postech.ac.kr

Table S1. Thickness of *dr*fp-3F film on mica surface measured by SFA under the following four different conditions: in 0.1 M acetic acid (pH ~3) without Fe^{3+}, in 0.1 M acetic acid (pH ~3) with Fe^{3+}, in 0.1 M Tris buffer (pH 8.0) without Fe^{3+}, and in 0.1 M Tris buffer (pH 8.0) with Fe^{3+}.

Condition	Asymmetric thickness	Symmetric thickness
pH 3	2.0 ± 0.6 nm	11.0 ± 10.1 nm
pH 3 + Fe^{3+}	3.3 ± 2.7 nm	12.3 ± 2.7 nm
pH 8	4.2 ± 0.2 nm	~50–300 nm
pH 8 + Fe^{3+}	6.7 ± 2.4 nm	~30–150 nm

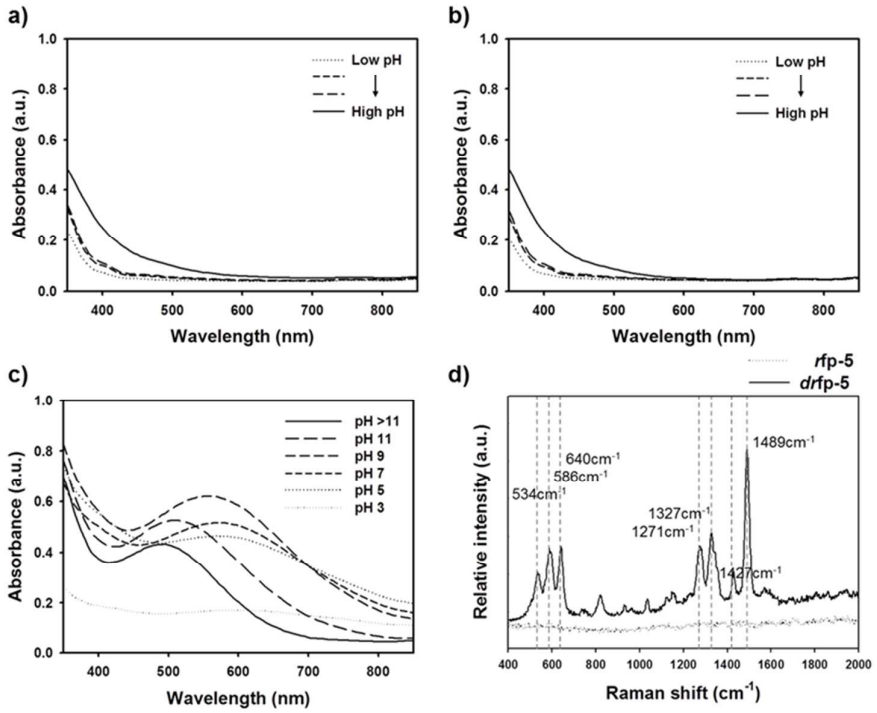

Figure S1. Dopa-Fe^{3+} complexation of *r*fp-3F, *r*fp-5 and *dr*fp-5. (a) The UV-Vis absorbance of *r*fp-3F at different pH. The UV-Vis absorbance of (b) *r*fp-5 and (c) *dr*fp-5 at different pH. (d) Resonance Raman spectroscopy of *r*fp-5 and *dr*fp-5 with Dopa-Fe^{3+} complexation.

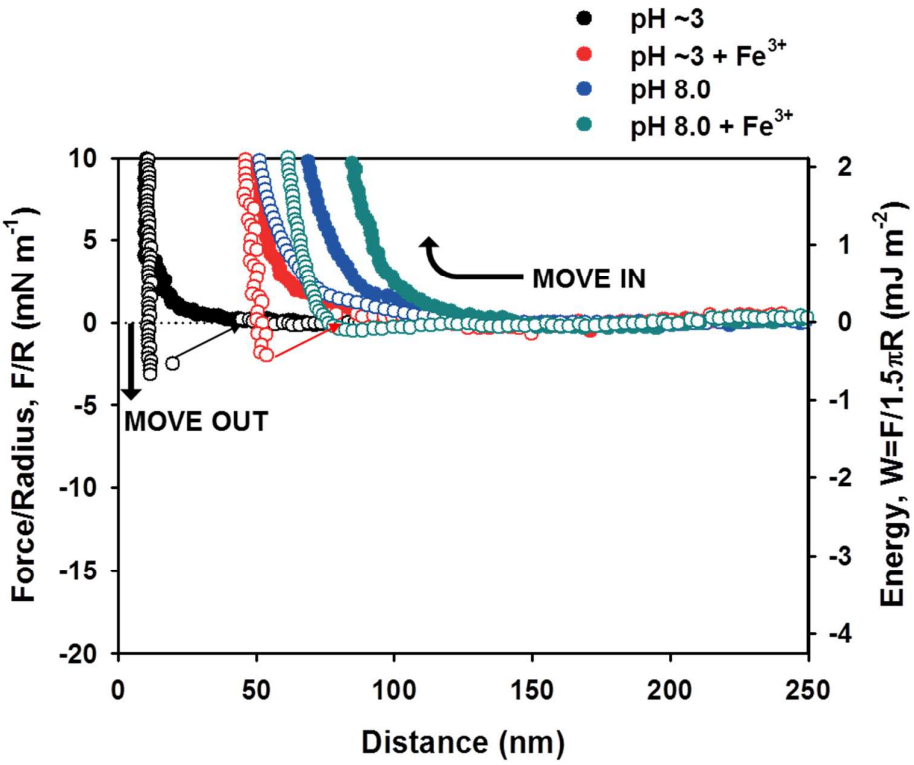

Figure S2. SFA analyses of the cohesive interactions of *r*fp-3F. To measure the cohesive interactions of *r*fp-3F, both mica surfaces were coated with *r*fp-3F and Fe^{3+}-spiked *r*fp-3F solution was deposited between two symmetric *r*fp-3F films. SFA measurements were conducted under the following four different conditions: 1) in 0.1 M acetic acid (pH ~3) without Fe^{3+}, 2) in 0.1 M acetic acid (pH ~3) with Fe^{3+} (tyrosine:Fe^{3+} molar ratio of 3:1), 3) in 0.1 M Tris buffer (pH 8.0) without Fe^{3+}, and 4) in 0.1 M Tris buffer (pH 8.0) with Fe^{3+} (tyrosine:Fe^{3+} molar ratio of 3:1). The normalized forces, F/R, are shown on the left ordinate, whereas the corresponding interaction energies per unit area (defined as F/1.5πR) are on the right ordinate.

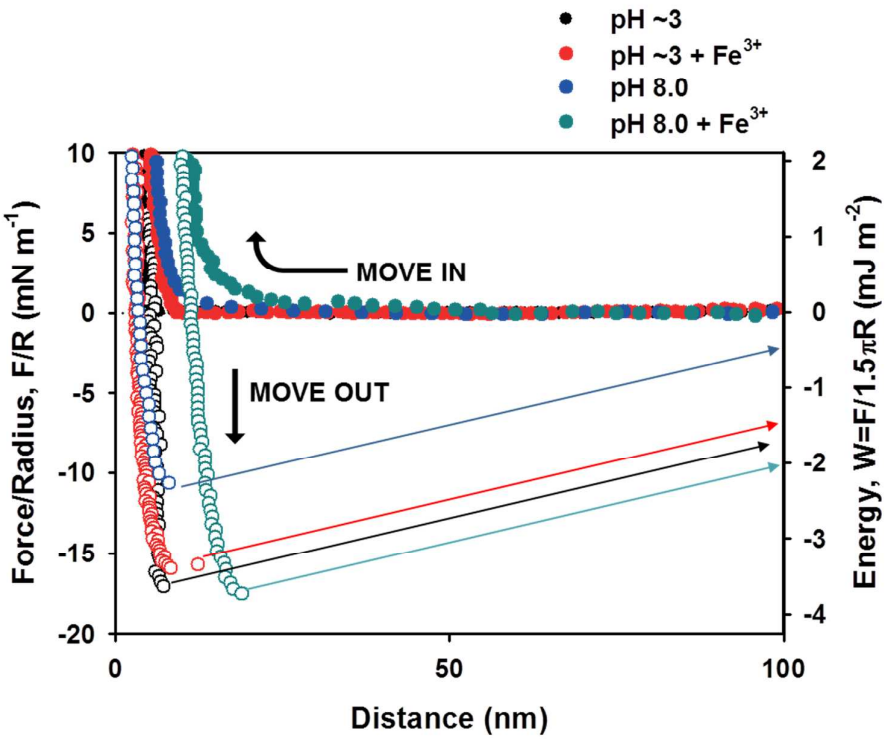

Figure S3. SFA analyses of the surface adhesive interactions of *r*fp-3F. To measure the surface adhesive interactions of *r*fp-3F, only one mica surface was coated with *r*fp-3F. SFA measurements were conducted under the following four different conditions: 1) in 0.1 M acetic acid (pH ~3) without Fe^{3+}, 2) in 0.1 M acetic acid (pH ~3) with 0.5 μM of Fe^{3+}, 3) in 0.1 M Tris buffer (pH 8.0) without Fe^{3+}, and 4) in 0.1 M Tris buffer (pH 8.0) with 0.5 μM of Fe^{3+}. The normalized forces, F/R, are shown on the left ordinate, whereas the corresponding interaction energies per unit area (defined as F/1.5πR) are on the right ordinate.

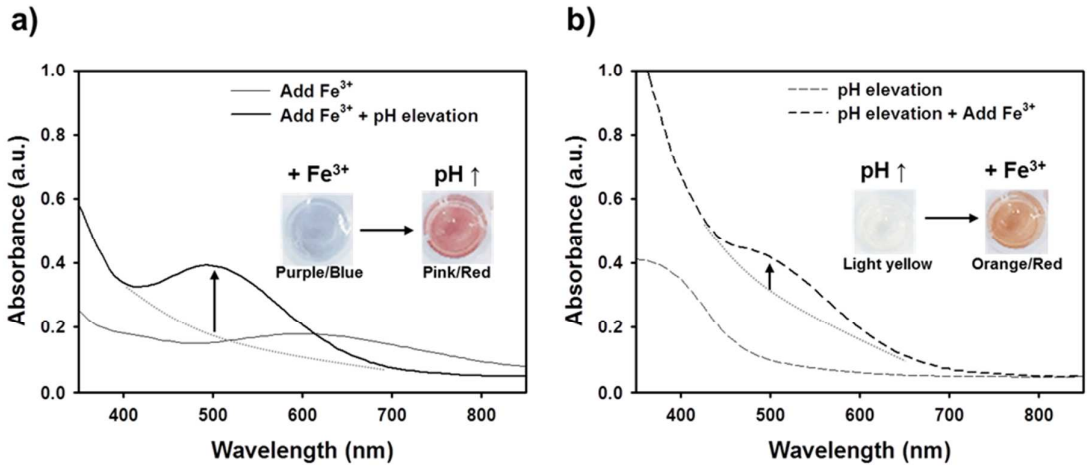

Figure S4. UV-Vis absorbance analysis of different Dopa-Fe^{3+} complexation pathways. Dopa-Fe^{3+} complexation (a) with pH elevation after adding Fe^{3+} and (b) with Fe^{3+} addition to *dr*fp-3F after pH elevation. The color changes are shown in the insets. The black arrow in the graph indicates the absorbance intensity at base-line (gray-dotted line).

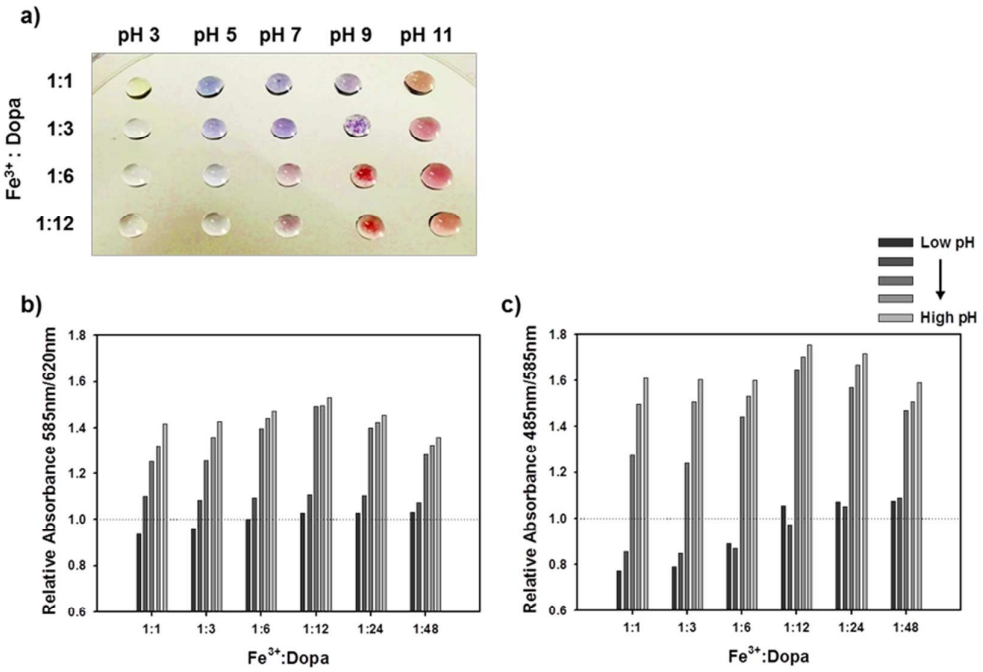

Figure S5. Dopa-Fe^{3+} complexation depending on Dopa:Fe^{3+} ratio and pH. (a) The color changes resulting from Dopa-Fe^{3+} complexation. (b) The 585 nm/620 nm absorbance ratio shows the ratio of bis-complex compared to mono-complex. (c) The 485 nm/585 nm absorbance ratio shows the ratio of tris-complex compared to bis-complex. The pH was gradually increased from pH ~3 (light gray bar) to pH >11 (black bar) with NaOH.