

Supporting Information

to

**Direct Label-free Electrochemical Detection of
Proteins Using the Polarized Oil/Water Interface**

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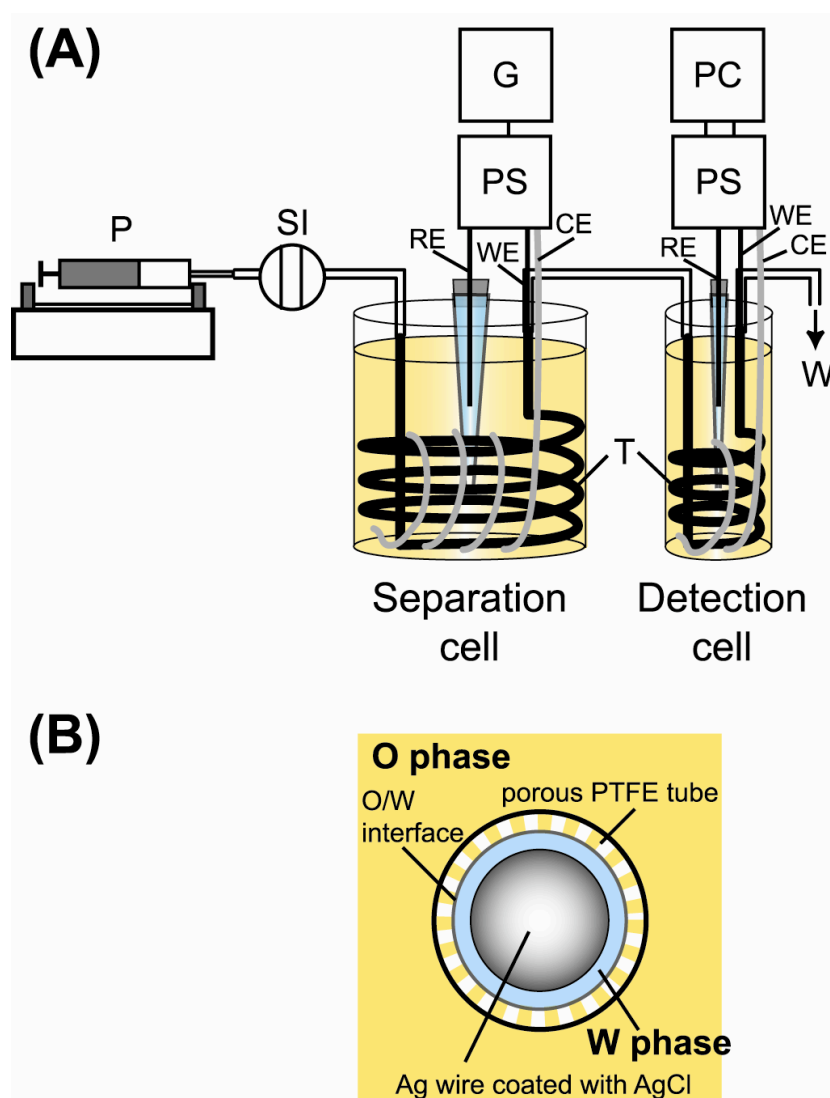


Figure S1. (A) Scheme of the O/W-type flow-cell system and (B) the cross section of the porous PTFE tube with a Ag/AgCl wire electrode inside. P, syringe pump; SI, sample injector; T, porous PTFE tube with a Ag/AgCl wire electrode inside; WE, working electrode; CE, platinum counter electrode; RE, reference electrode; W, waste; PS, potentiostat; G, programmable function generator; PC, personal computer. Colorized and reprinted with permission from ref 20. Copyright 2010 The Japan Society for Analytical Chemistry.

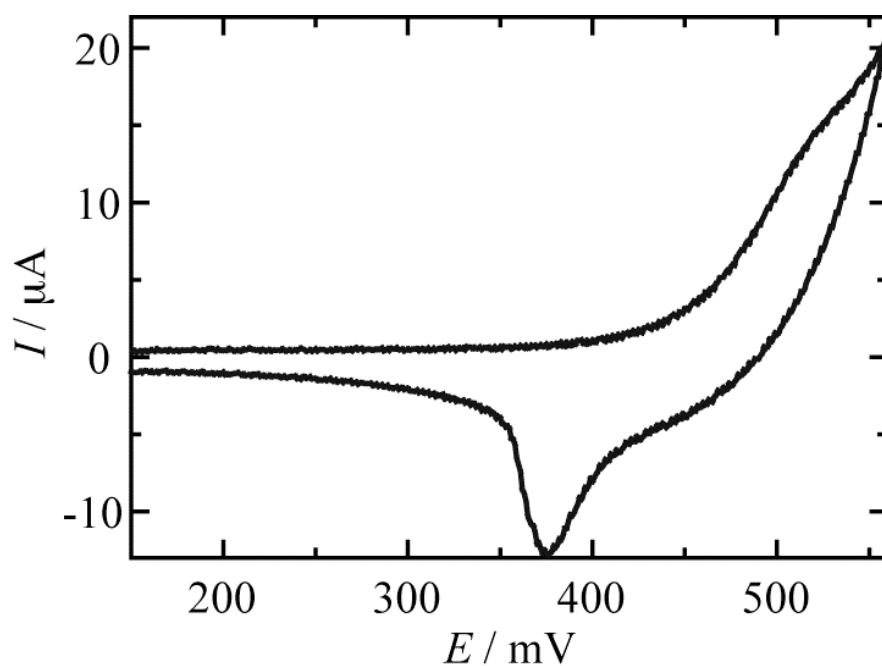


Figure S2. Cyclic voltammogram for 0.1 mM Cyt c at the DCE/W interface in the absence of DNNS. pH = 3.1. Scan rate: 100 mV s⁻¹.

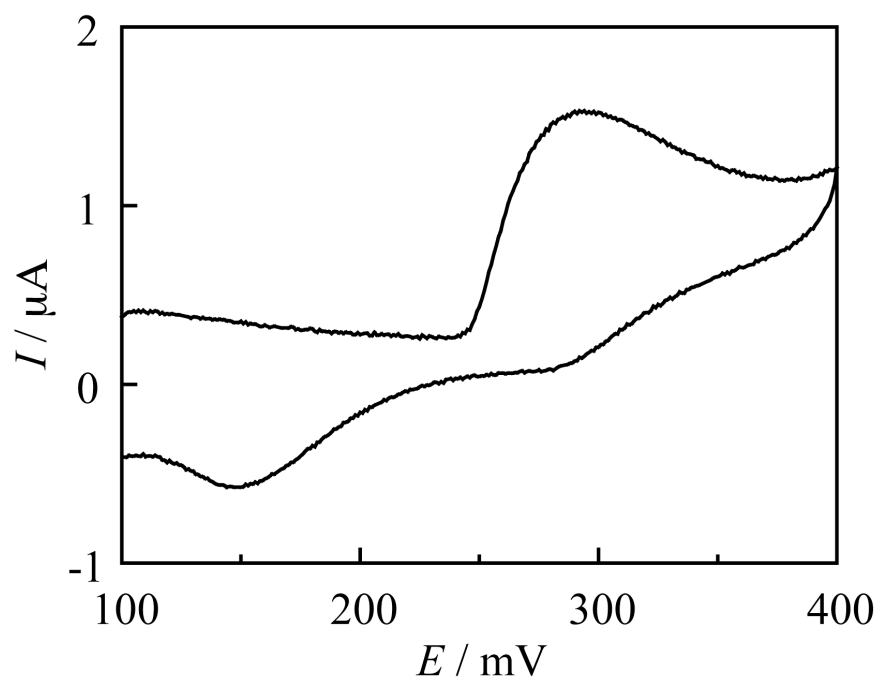


Figure S3. Cyclic voltammogram for 0.1 mM protamine at the DCE/W interface in the presence of 1.0 mM DNNS in DCE. pH = 3.2. Scan rate: 20 mV s⁻¹.

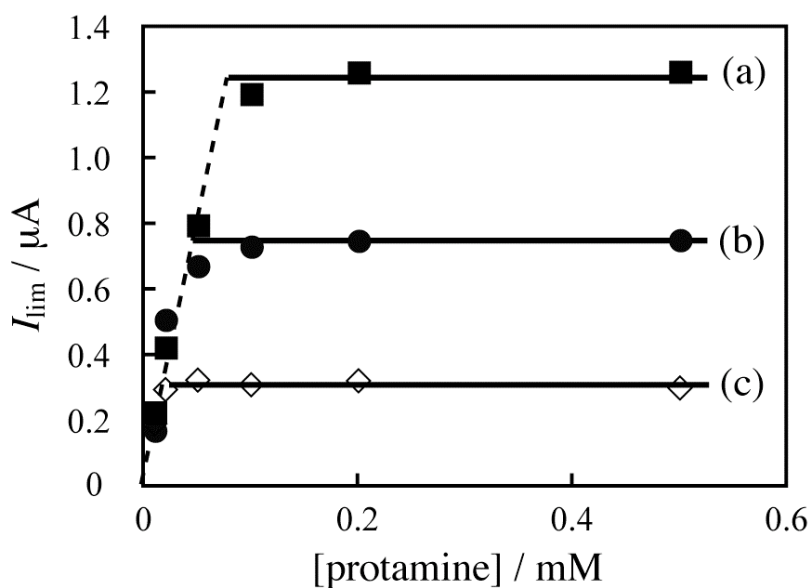


Figure S4. Dependence of I_{lim} (at $t = 5.0$ s) on the concentration of protamine in W (pH 3.2) for various [DNNS] values: (a) 2.0, (b) 1.0, (c) 0.5 mM. The dashed line and the horizontal solid lines represent the “protamine diffusion-controlled” and “DNNS diffusion-controlled” currents, respectively.

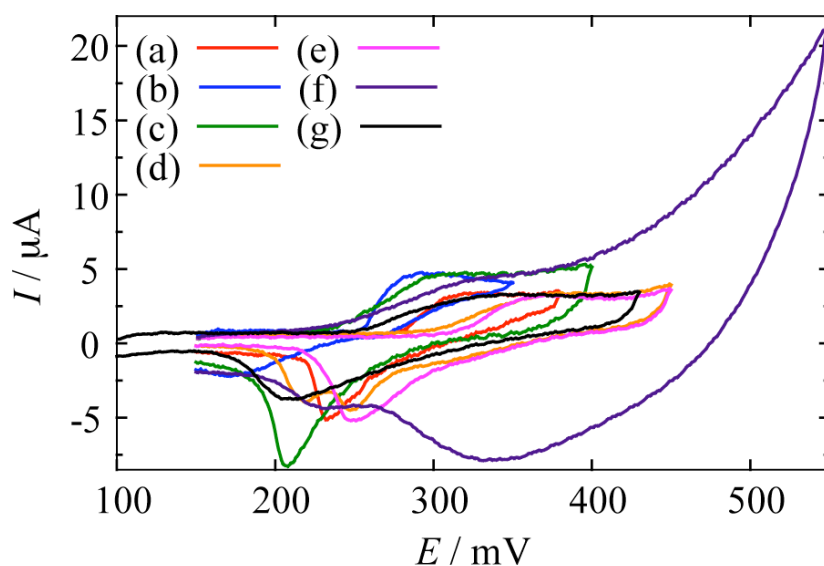


Figure S5. Cyclic voltammograms for (a) 0.1 mM Cyt c, (b) 0.1 mM protamine, (c) 0.1 mM myoglobin, (d) 0.1 mM lysozyme, (e) 0.1 mM ribonuclease, (f) 0.05 mM albumin, and (g) 0.1 mM α -lactalbumin at the DCE/W interface in the presence of 1.0 mM AOT in DCE. pH = 3.2. Scan rate: 100 mV s^{-1} .

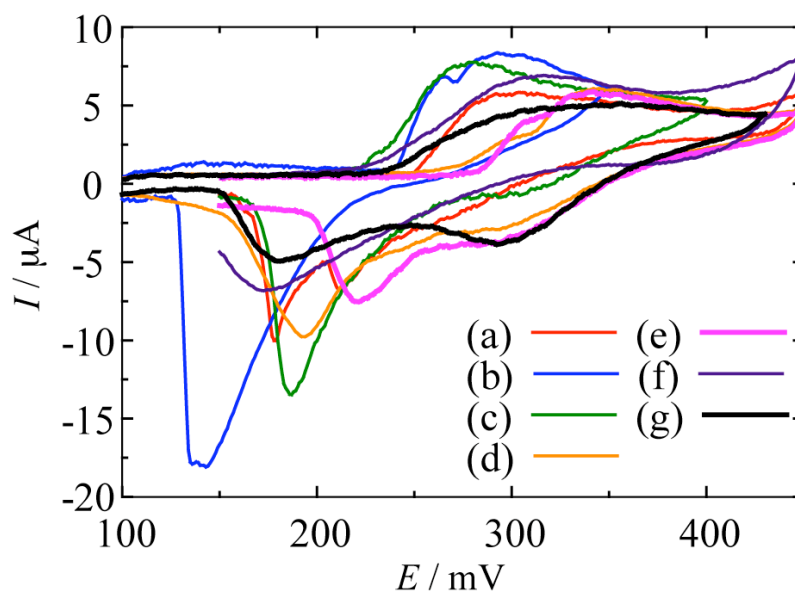


Figure S6. Cyclic voltammograms for (a) 0.1 mM Cyt c, (b) 0.1 mM protamine, (c) 0.1 mM myoglobin, (d) 0.1 mM lysozyme, (e) 0.1 mM ribonuclease, (f) 0.05 mM albumin, and (g) 0.1 mM α -lactalbumin at the DCE/W interface in the presence of 1.0 mM BDFHS in DCE. pH = 3.2. Scan rate: 100 mV s^{-1} .

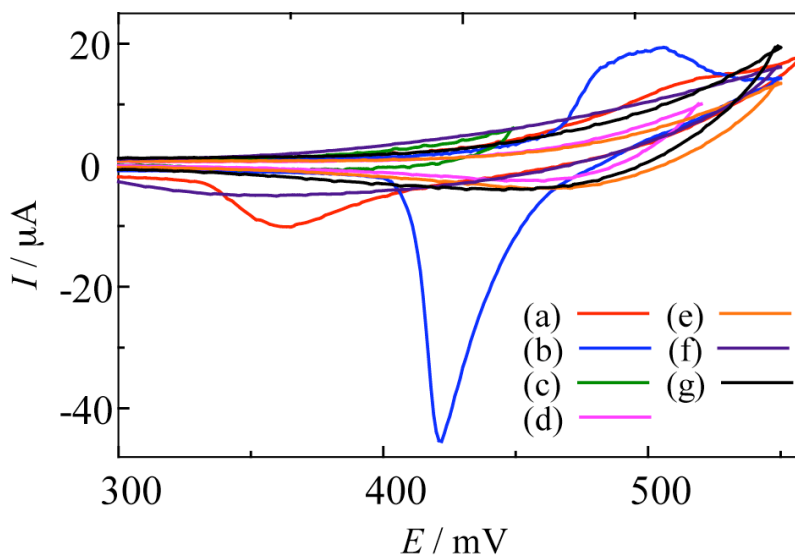


Figure S7. Cyclic voltammograms for (a) 0.1 mM Cyt c, (b) 0.1 mM protamine, (c) 0.1 mM myoglobin, (d) 0.1 mM lysozyme, (e) 0.1 mM ribonuclease, (f) 0.05 mM albumin, and (g) 0.1 mM α -lactalbumin at the DCE/W interface in the presence of 1.0 mM BEHP in DCE. pH = 3.2. Scan rate: 100 mV s^{-1} .

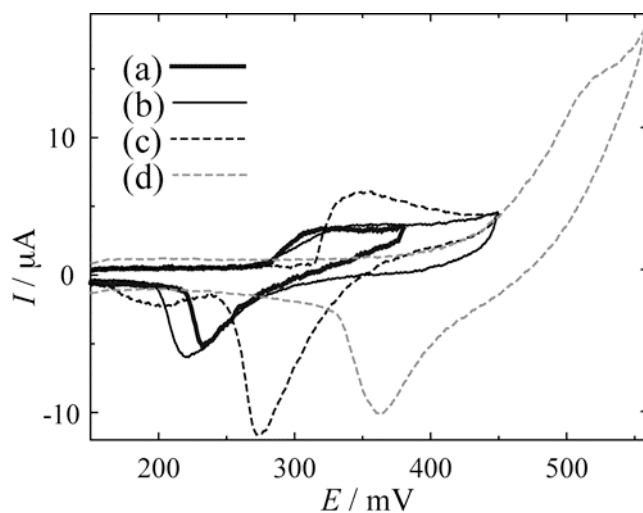


Figure S8. Cyclic voltammograms for 0.1 mM Cyt c at the DCE/W interface in the presence of 1.0 mM (a) DNNS, (b) AOT, (c) BDFHS, and (d) BEHP in DCE. pH = 3.2. Scan rate: 100 mV s⁻¹.

Table S1. Correlation Coefficients of E_{foot} (Table 1) with the Molecular Parameters of the Proteins (Table 2)

		R_{corr}		
		DNNS	AOT	BDFHS
r	($N^a = 5$)	-0.348	-0.556	-0.472
M_r	($N = 7$)	-0.248	-0.514	-0.406
Z	($N = 7$)	-0.369	-0.578	-0.493
E_s	($N = 5$)	-0.231	-0.115	-0.270
H_ϕ	($N = 6$)	-0.713	-0.741	-0.869

^a Number of data.

Table S2. Correlation Coefficients of E_{foot} (Table 1) with the Surface and Volume Parameters of the Proteins (Table 3)

		R_{corr}		
		DNNS	AOT	BDFHS
S_c	($N = 5$)	-0.832	-0.849	-0.793
S_p	($N = 5$)	+0.826	+0.690	+0.775
S_n	($N = 5$)	-0.793	-0.823	-0.777
V_M	($N = 5$)	-0.363	-0.560	-0.486
V_W	($N = 5$)	-0.374	-0.567	-0.475