Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information:

Nano-confined Electrochemical Reaction Studied by Electrochemical Surface Forces Apparatus

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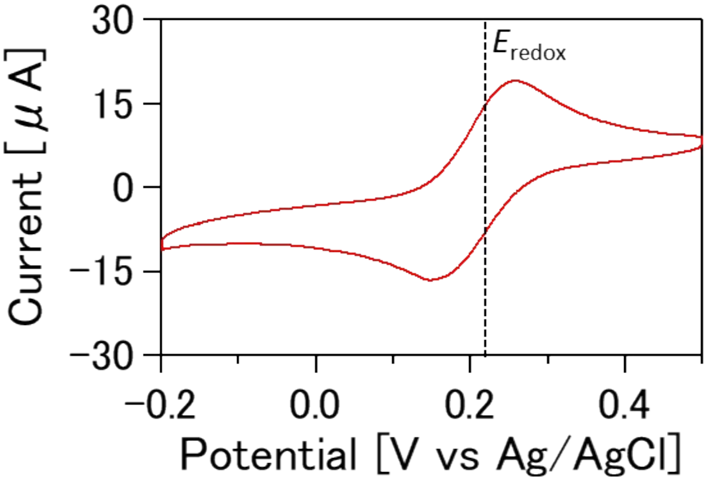

Fig. S1 A cyclic voltammogram of Pt electrode on a SFA disk in the 0.1 mM $Fe(CN)_6^{3-/4-}$ solution.

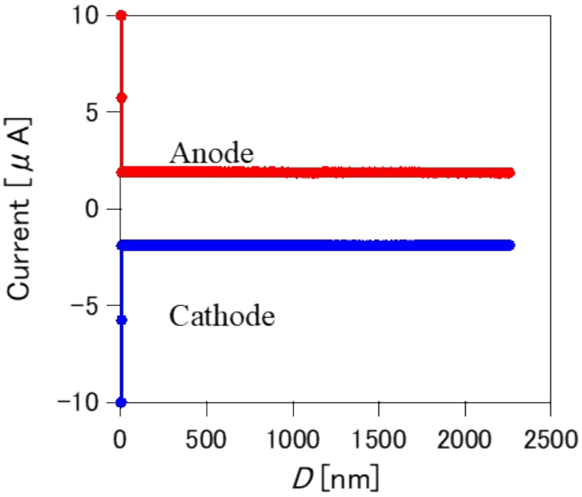

Fig. S2 Current profiles of anode (red) and cathode (blue) in the 0.1 mM $Fe(CN)_6^{3-/4-}$ solution during approach. ΔV =50 mV

Feedback current between anode and cathode.

We attributed the current shown in Fig. S2 to the so-called feedback current, observed when two electrodes in an electrolyte solution of a redox couple were brought closer at given electrochemical potentials (anode: $E_{\mathrm{redox}} + \Delta V$ mV vs. Ag/AgCl, cathode: $E_{\mathrm{redox}} - \Delta V$ mV.). Under such condition, (1) reduced species reacted with the anode, (2) formed oxidized species diffused to the cathode, reacted with the cathode, and (3) resulting reduced species could go back to the anode with diffusion. Such cycled reaction could amplify the current between two electrodes, as illustrated in Fig. 1 (b). The currents at the anode and the cathode should be identical for this mechanism, which agreed with the current profiles shown in Fig. S2. Thus, we attributed the currents in Fig. S2 to the feedback current, and plotted the anode current as the current in the main text.

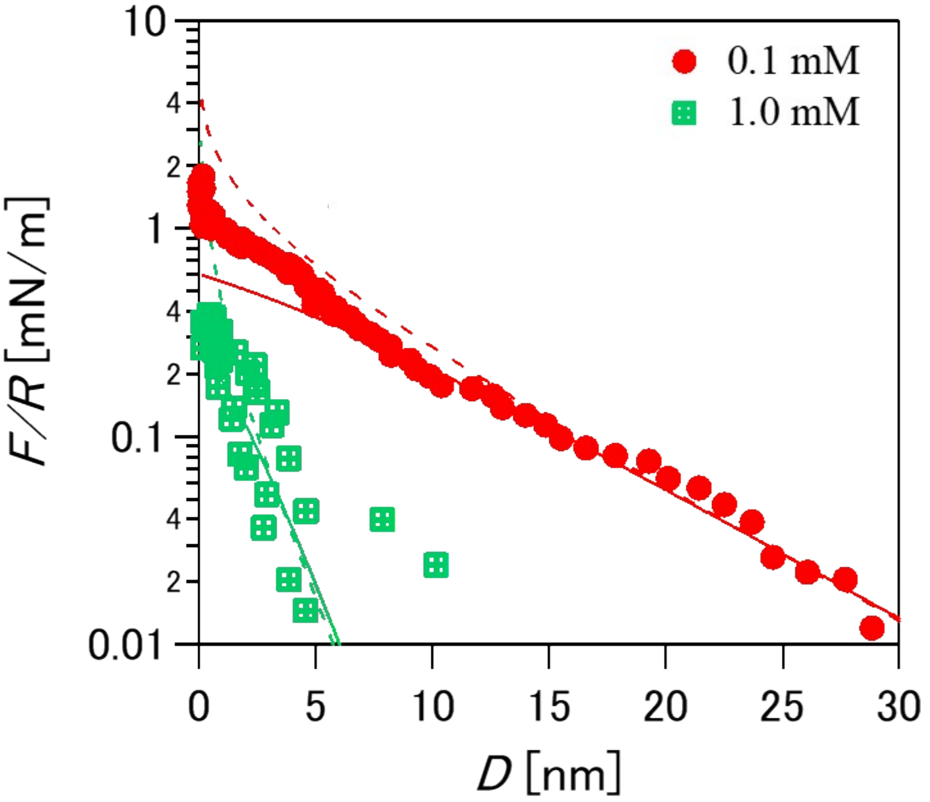

Fig S3 Examples of fitting the force profiles for the Pt electrodes in aqueous $Fe(CN)_6^{3-/4-}$ using the Poisson-Boltzman equation of the electric double layer force for the constant potential (solid line) and constant charge (broken line) model. $\Delta V = 50$ mV, during approach.

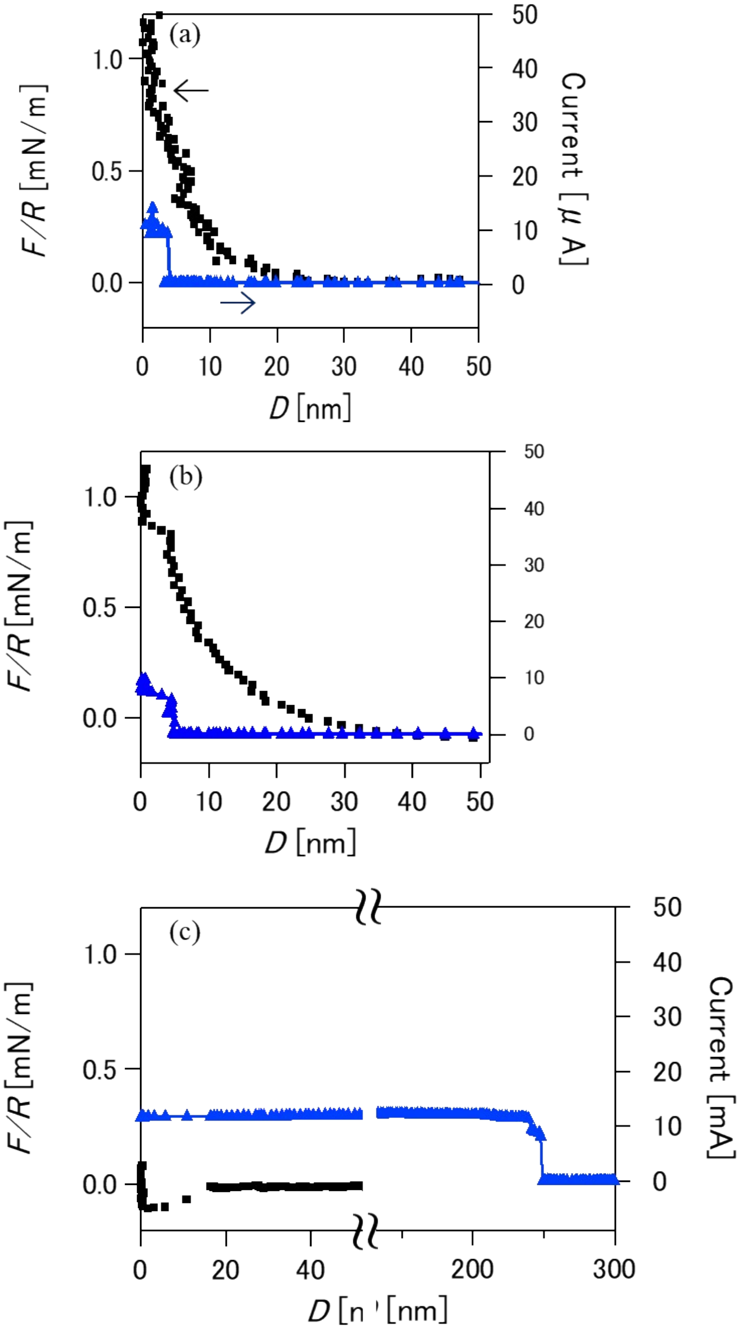

Fig. S4 Profiles of forces between the Pt electrode surfaces in the 0.1 mM $Fe(CN)_6^{3-/4-}$ solution upon separation depending on ΔV (a) 0 mV, (b) 5 mV, (c) 50 mV. Current profiles simultaneously measured are also plotted in the same figure.

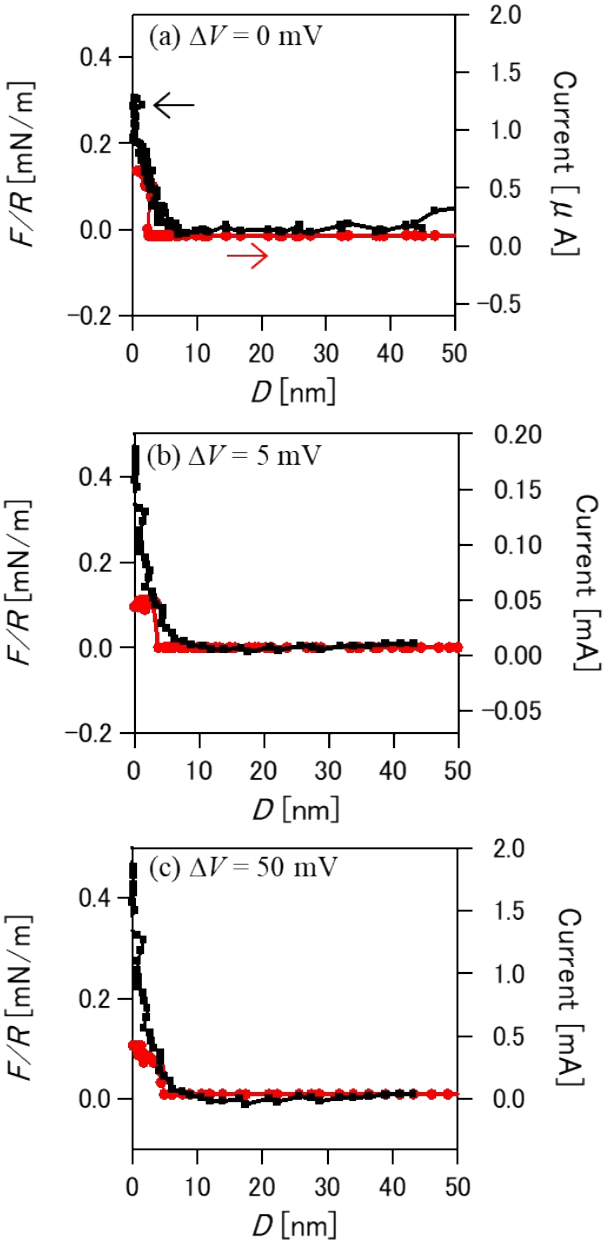

Fig. S5 Profiles of forces between Pt electrode surfaces in 1 mM $Fe(CN)_6^{3-/4-}$ solution upon approach depending on ΔV (a) 0 mV, (b) 5 mV, (c) 50 mV. Current profiles simultaneously measured are also plotted in the same Figure.

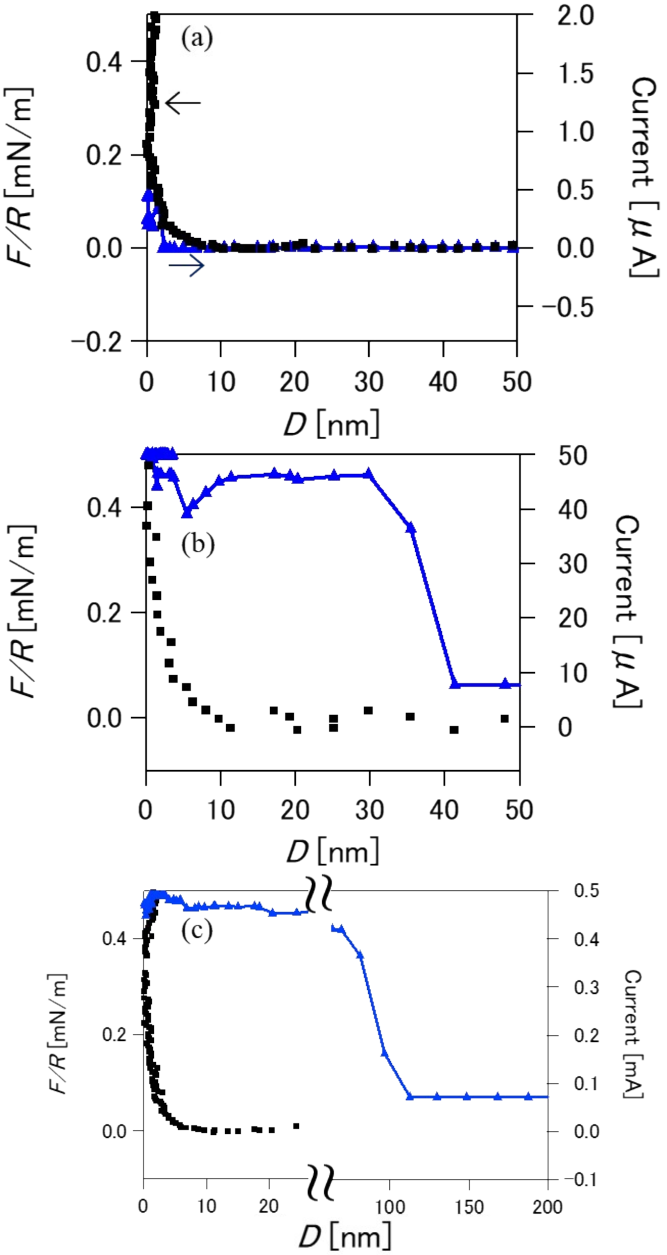

Fig. S6 Profiles of forces between Pt electrode surfaces in 1 mM $Fe(CN)_6^{3-/4-}$ solution upon separation depending on ΔV (a) 0 mV, (b) 5 mV, (c) 50 mV. Current profiles simultaneously measured are also plotted in the same Figure.

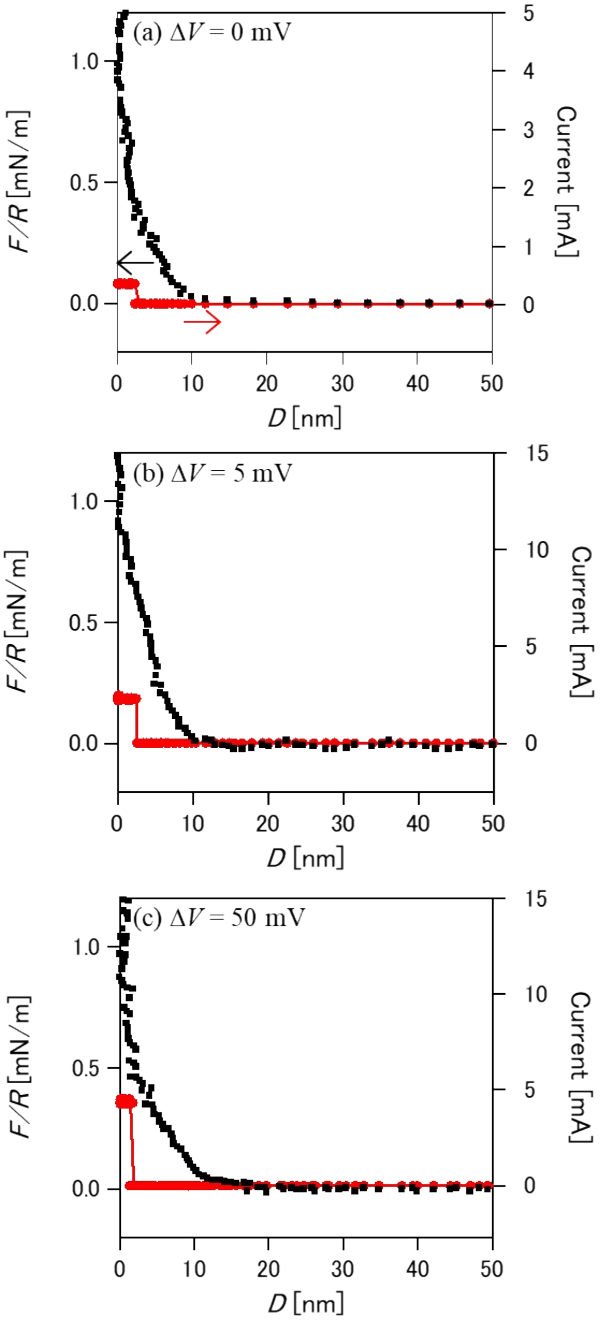

Fig. S7 Profiles of forces between Pt electrode surfaces upon approach in 10 mM $KClO_4$ solution depending on Δ*V* (a) 0 mV, (b) 5 mV, (c) 50 mV. Current profiles simultaneously measured are also plotted in the same Figure.

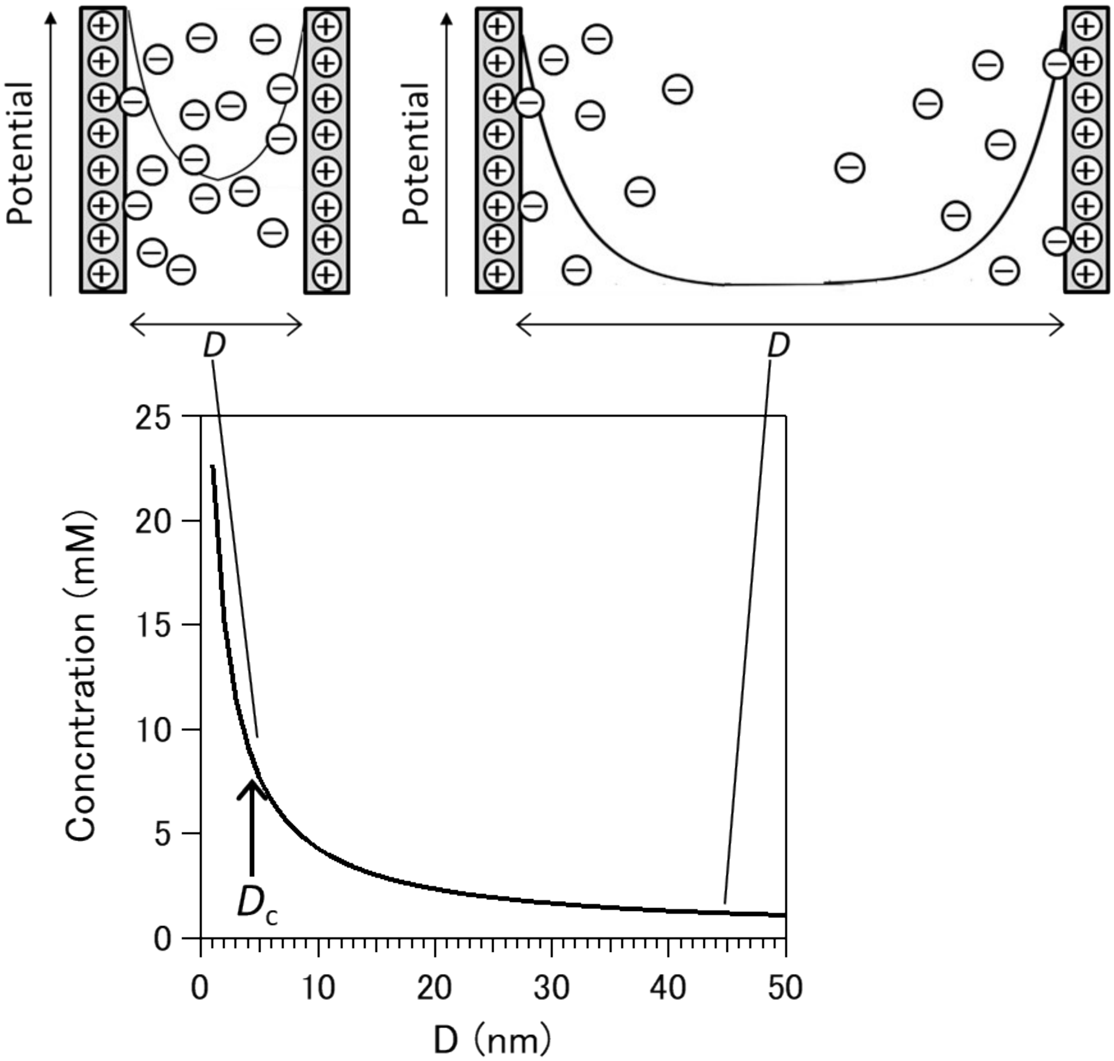
Potential
Potential
D
D
Concntration (mM)
25
20
15
10
5
0
0
10
20
30
40
50
D (nm)
D_c

Fig. S8 Average concentration of $Fe(CN)_6^{3-/4-}$ in 0.1 mM $Fe(CN)_6^{3-/4-}$ solution confined between Pt electrodes at various D. ΔV =50 mV.