Supporting information

Redox properties of pyrroloquinoline quinone in pyranose dehydrogenase measured by direct electron transfer

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Enzymatic turnover rate of the PQQ domain of CcPDH on the electrode

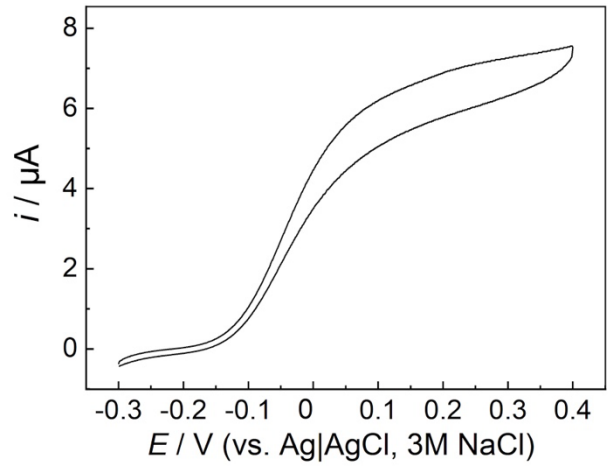

Figure S1. Cyclic voltammogram for L-fucose oxidation of the PQQ domain on ME/AuNPs/AuE in 100 mM L-fucose and 50 mM acetate buffer, pH 6.0, at 30 °C, 1000 rpm, and using the AuNPs casting cycle 3 times electrode. Scan rate = 5 mV s^{-1}. Y-axis is the current, *i*.

A limiting catalytic current (i_{lim}) controlled by an enzymatic turnover rate (k_{cat}) is given by the following equation, with a substrate in excess,

$$i_{lim} = n_s F A \Gamma_E k_{cat}$$

where n_s is the number of electrons of the substrate (2 in this case), F is the Faraday constant, A is electrode surface area, Γ_E is electroactive coverage on the electrode. Γ_E of the PQQ domain was estimated by integrating the observed non-turnover CV curve oxidation peak in Figure 2 using the following equation: $\Gamma_E = Q/nFA$. Q is the charge involved in the reaction, n is the number of electrons involved in the redox process (for PQQ_{red}/PQQ_{semi} oxidation, n = 1). The Γ_E was calculated to be 34 ± 2 pmol/cm^2 (with reference to the geometrical surface area, 0.0201 cm^2). The steady-state limiting current, i_{lim}, for the oxidation of L-fucose was 7.48 μA at 0.4 V (Figure S1). In this condition, i_{lim} would not be the diffusion-controlled catalytic reaction but the rate limiting step of the enzymatic reaction. k_{cat} of the PQQ domain for L-fucose was calculated to be 56.7 s^{-1}, which is accordance with previous reports describing the activity for PMS reduction in solution, approximately 50 s^{-1}. This agreement suggests that the enzymatic activity of the PQQ domain immobilized on the electrode remains is maintained.

Cyclic voltammograms of the PQQ domain of CcPDH at various pH

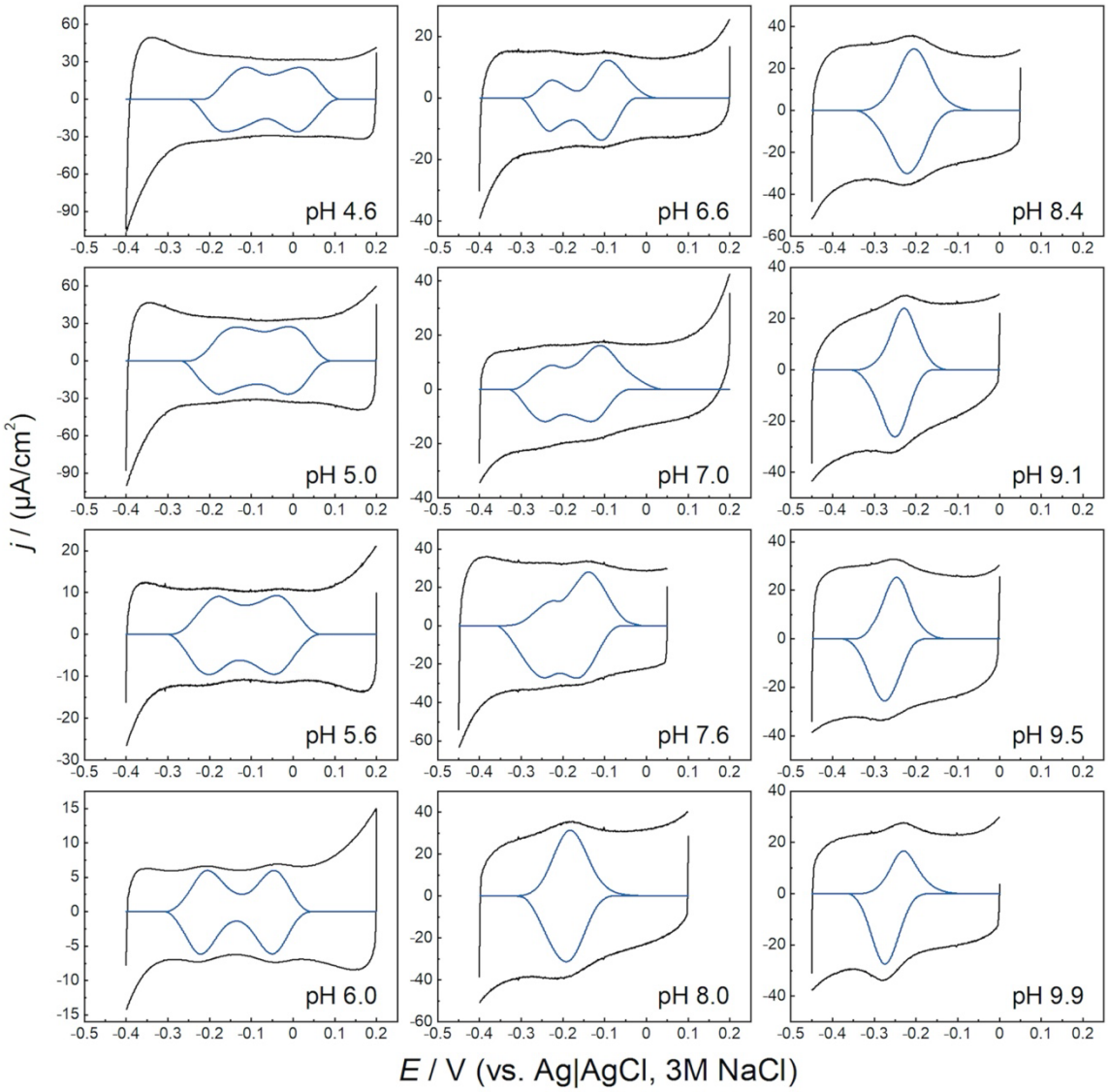

Figure S2. Cyclic voltammograms of the PQQ domain of *Cc*PDH on ME/AuNPs/AuE in 50 mM buffer at various pH. Inset blue line are baseline-subtracted data. The data were used to accurately extract peak potentials. pH 6.0 was at scan rate = 10 mV s^{-1}, the others were at scan rate = 20 mV s^{-1}.

Structure of active site in the PQQ domain of CcPDH

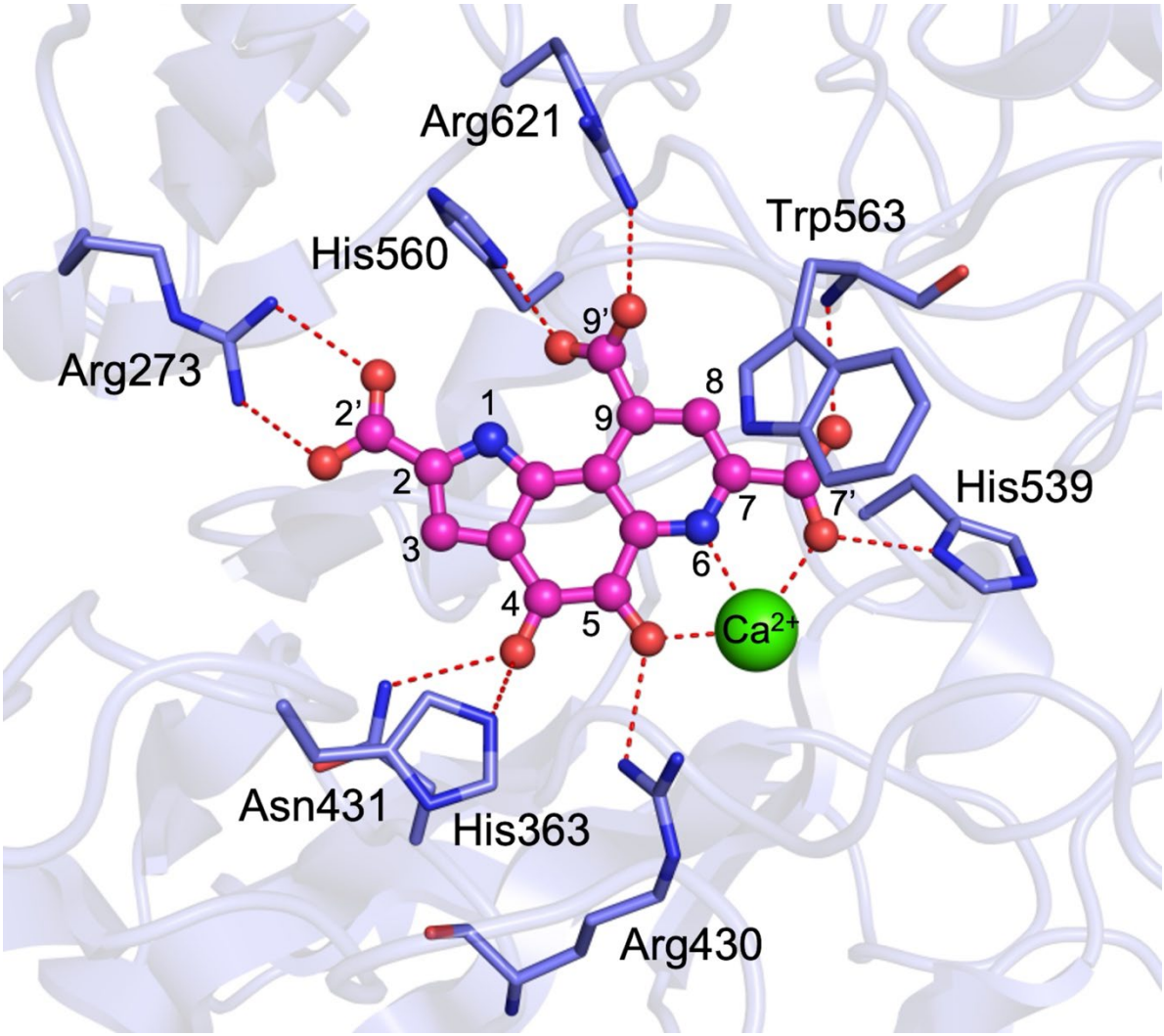

Figure S3. Stick representation of the PQQ-binding site. The dashed red lines interactions within the hydrogen-bonding distance.