

Supporting Information:

S1. HQ reaction density vs. DADOO concentration.

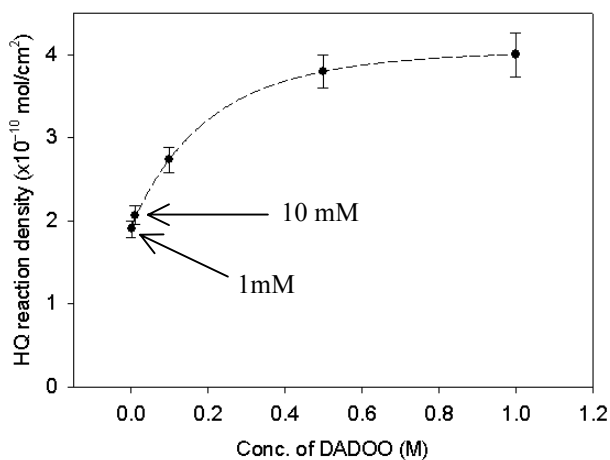


Figure s1. The reaction density from the oxidation peak decreased with lowering DADOO concentration (4.0 and 1.9×10^{-10} mol/cm² at 1 M and 1 mM, respectively).

S2. XPS data of DADOO-reacted SAM I.

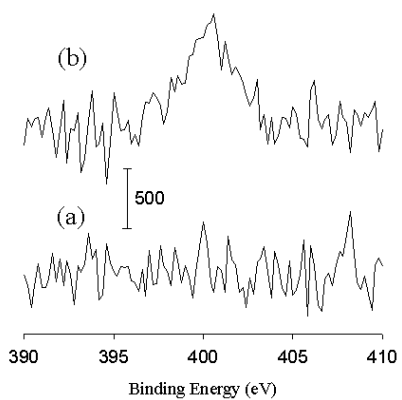


Figure s2. (a) XPS spectra of the N 1s of SAM I after the electrochemical reaction with DADOO and (b) the SAM after simple immersion at open circuit potential for 2 min.

S3. TOF-SIMS data of DADOO-reacted SAM I.

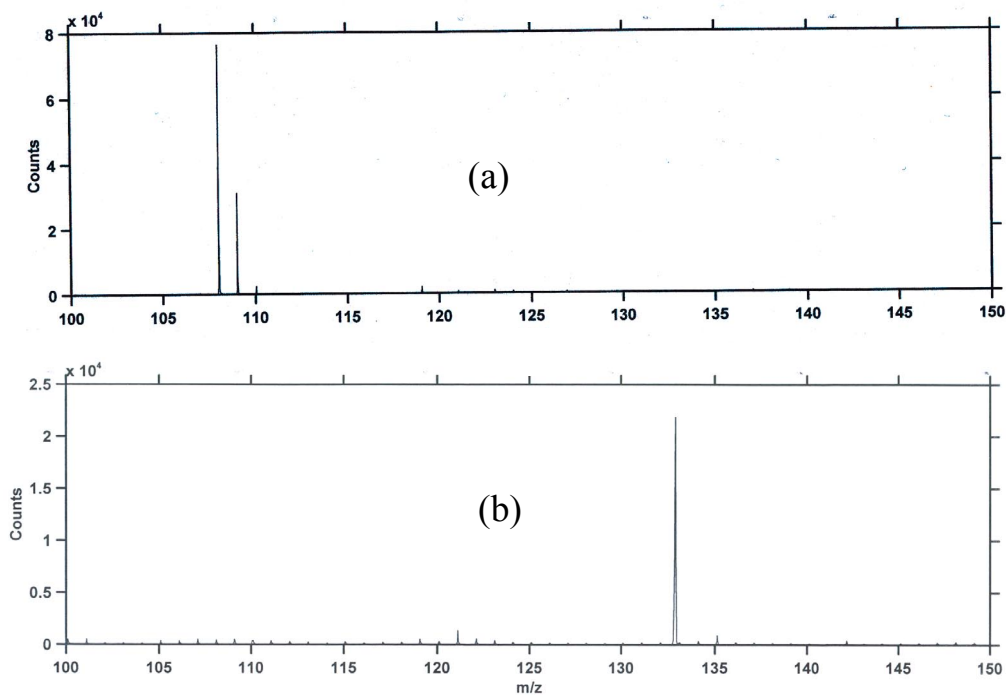


Figure s3. (a) Before and (b) after the electrochemical treatment.

S4. FT-IR data of BPA-reacted SAM I.

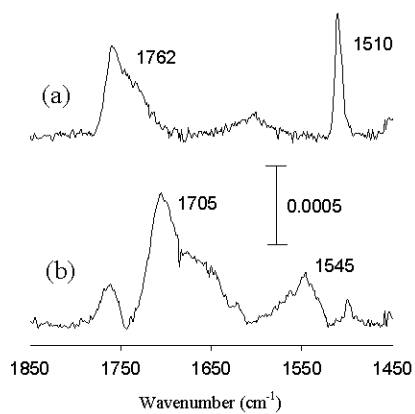


Figure s4. Grazing angle FT-IR spectra obtained for (a) a freshly prepared SAM I and (b) the SAM subjected electrochemical reaction with 1 mM BPA at the post peak potential for 1 min

S5. Detailed experimental for CV, UV, SPR, and micropatterning.

The CV of SAM I was performed with a SAM I/Au working electrode, Pt wire counter electrode, and 'no-leak' Ag/AgCl (Cypress Systems) reference electrode in the acetonitrile solution containing TBAP (0.1 M). Acetonitrile and TBAP were dried before use. The use of butylamine, hexylamine, dodecylamine, and DADDOO gave similar results in CV and FT-IR.

Absolute surface amine concentration was determined by measuring UV absorbance. The DADDOO-reacted substrate (2 cm^2) was immersed into 3 ml of mixed solution with anhydrous ethanol (25 mL), 4-nitrobenzaldehyde (10 mg), and acetic acid (0.002 mL) under argon atmosphere at 50°C for 3 h. After the imine formation by the condensation of free-amine on the surface and 4-nitrobenzaldehyde, the surface was rinsed with anhydrous ethanol and sonicated in absolute ethanol for 1 min. After once repeating these steps, the resulting surface was dried under vacuum and incubated in mixed solution (2 mL) with water (15 mL) and acetic acid (0.02 mL) at 30°C . After the hydrolysis reaction for 1 h, the resulting solution containing the surface was sonicated for 2 min. After removing the surface from the solution, the absorbance of the recovered 4-nitrobenzaldehyde (absorption at near 266 nm) in the hydrolyzed solution was measured by using UV-vis spectrometer. To determine the concentration, $\epsilon_{\text{max}} = 1.45 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$ was used for the solution. Used reference solution was obtained from the hydrolysis of only DADDOO-reacted SAM I surface.

For SPR (Biacore X) experiment, we used streptavidin of 100 g/mL in pH 7.0 PBST carrier solution (0.05% Tween 20). The flow rate of the carrier solution was $4 \mu\text{L}/\text{min}$. An increase of 1000 RU corresponds to a streptavidin density of $1 \text{ ng}/\text{mm}^2$.

For streptavidin **micropatterning**, the biotin array was prepared by the following. In the CV for electrode array, each scan ended at 530 (vs. AgQRE: electrode A) and 630 mV (vs. AgQRE: electrode B), respectively (for comparison, see Figure s5). To estimate reaction density of HQ, CVs were conducted for another electrodes that have known surface area. The reaction density of HQ for each electrode was calculated from the surface-passed charge during CV scans. The charge obtained by integration of the area under the anodic current of the CV. The biotin- modified array was immersed in pH 7.0 PBST (0.05% Tween 20) solution of polyHRP-conjugated streptavidin ($20 \mu\text{g}/\text{mL}$) for 20 min. The resulting array was dipped in a mixed solution of 5 mL pH 7.0 PBS, 1 mL 4-CN ($3 \text{ mg}/\text{mL}$

methanol solution), and 2.5 μL H_2O_2 (30% in H_2O). The resulting pattern was obtained from the biocatalytic precipitation of 4-CN by HRP for 10 min.

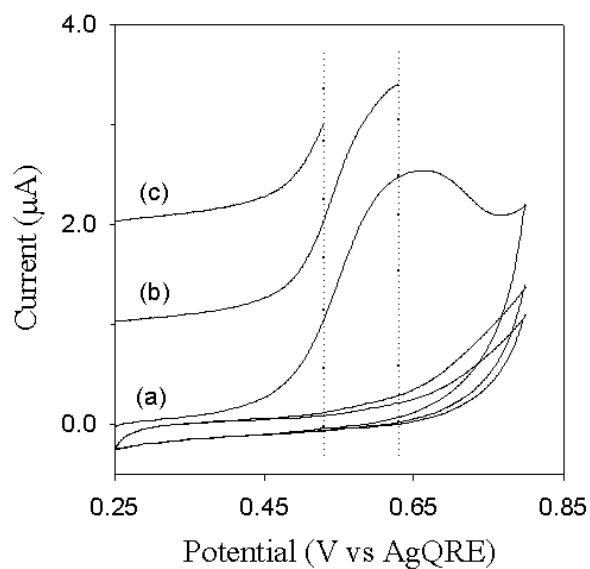


Figure s5. (a) Cyclic voltammogram of SAM I in 1 mM BPA. Scan rate is 50 mV/s. In the CV, potential scan ended at (b) 630 and (c) 530 mV.