## Supplementary Information

# pH-Dependent Rectification in Self-Assembled Monolayers Based on Electrostatic Interactions

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## 1. Synthesis of 1-(12-mercaptododecyl)imidazole and preparation & characterization of the self-assembled monolayer of 1-(12-mercaptododecyl)imidazole on gold

All organic solvents were dried under standard purification conditions. Thioacetic acid *S*-(12-bromododecyl) ester was prepared according to a previously reported procedure (S. Yokokawa, K. Tamada, E. Ito, M. Hara, *J. Phys. Chem. B* **2003**, *107*, 3544).

**1-(12-acetylthiododecyl)imidazole.** To a solution of imidazole (0.5 g, 7.3 mmol) in anhydrous THF (10 mL) was added NaH (0.19 g, 7.9 mmol) at 0 °C. After stirring for 10 min at 0 °C, thioacetic acid *S*-(12-bromododecyl) ester (3.56 g, 11.0 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of water (10 mL), and the organic materials were extracted with dichloromethane (2×30 mL). The combined organic layer was dried with $Na_2SO_4$, and concentrated. The residue was purified by silica column chromatography ($CH_2Cl_2$/MeOH = 20/1) to give 1-(12-acetylthiododecyl)imidazole (2.0 g, 88%). mp. 48°C, $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.34-1.25 (m, 16H), 1.56 (m, 2H), 1.76 (m, 2H), 2.32 (s, 3H), 2.86 (t, $J$ = 7.4 Hz, 2H), 3.92 (t, $J$ = 7.1 Hz, 2H), 6.91 (s, 1H), 7.27 (s, 1H), 7.47 (s, 1H); $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 26.5, 28.7, 29.0, 29.1, 29.3, 29.4, 30.6, 31.0, 47.0, 118.7, 129.3, 137.0, 196.0 ppm. HRMS(FAB) Calcd for $C_{17}H_{31}N_2OS$ [$(M+H)^+$]: 311.2157. Found: 311.3162.

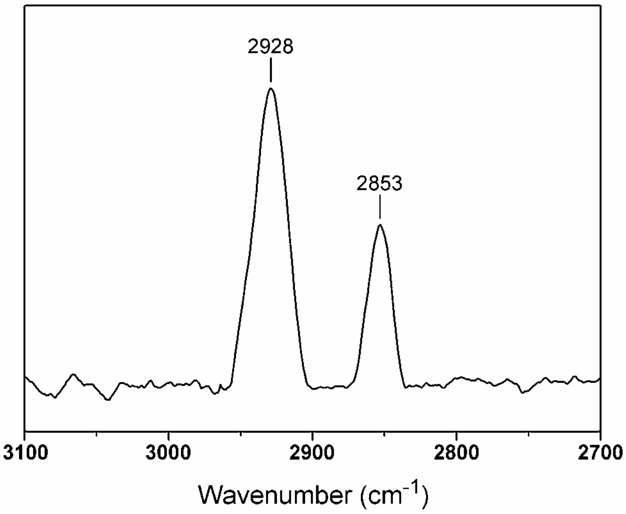
**1-(12-mercaptododecyl)imidazole.** To a solution of 1-(12-acetylthiododecyl)imidazole (100 mg, 0.32 mmol) in EtOH (3 mL) was added a solution of NaOH (0.79 mmol, 1M) in $H_2O$ at 0 °C. The reaction mixture was stirred at room temperature for 1 h. After evaporation of EtOH, the organic materials were extracted with $CH_2Cl_2$, dried with $Na_2SO_4$, and the solvent was evaporated. Purification of the residue by flash column chromatography on silica ($CH_2Cl_2$/MeOH = 20/1) afforded 1-(12-mercaptododecyl)imidazole (71 mg, 82%). mp. 35 °C, $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.25-1.37 (m, 17H), 1.60 (m, 2H), 1.76 (m, 2H), 2.52 (q, 7.3 Hz, 2H), 3.91 (t, $J$ = 7.1 Hz, 2H), 6.90 (s, 1H), 7.05 (s, 1H), 7.46 (s, 1H); $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 24.6, 26.4, 28.3, 28.9, 29.0, 29.3, 29.4, 30.9, 33.9, 46.9, 118.7, 129.2, 136.9 ppm. HRMS(FAB) Calcd for $C_{15}H_{29}N_2S$ [$(M+H)^+$]: 269.2051. Found: 269.2302.

**Preparation of Self-Assembled Monolayers.** The gold substrates were prepared by thermal evaporation of 5 nm of titanium and 100 nm of gold onto silicon wafers. Prior to use, gold substrates were cleaned for 1 min in piranha solution (3:7 by volume of 30% $H_2O_2$ and $H_2SO_4$, *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*), rinsed with $H_2O$ and ethanol, and dried under a stream of argon. The SAMs of 1-(12-mercaptododecyl)imidazole were prepared by immersing the gold substrates in a 1 mM solution of ethanol overnight. After the formation of SAMs, the substrates were rinsed with ethanol several times and then dried under a stream of argon.

**Grazing Angle FT-IR Spectroscopy.** IR spectra were obtained in a single reflection mode using a dry $N_2$-purged Thermo Nicolet Nexus FT-IR spectrophotometer equipped with the smart SAGA (Smart Apertured Grazing Angle) accessory. The *p*-polarized light was incident at $80^o$ relative to the surface normal of the substrate and a narrow band mercury-cadmium-telluride (MCT) detector cooled with liquid nitrogen was used to detect the reflected light. We averaged 2000 scans to yield the spectra at a resolution of 2 $cm^{-1}$ and all the spectra were reported in the absorption mode relative to a clean gold surface.

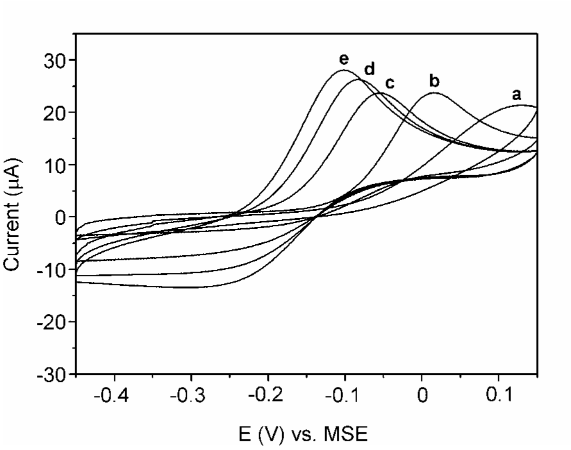
**Ellipsometry.** The thicknesses of the monolayer films were measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corporation, IL) equipped with a He-Ne Laser (632.8 nm) at a $70^o$ angle of incidence. A refractive index of 1.46 was used.

- SAMs of 1-(12-mercaptododecyl)imidazole were characterized by grazing angle FT-IR spectroscopy and ellipsometric measurement. The $CH_2$ stretching vibrations of the alkyl chain are very sensitive to the lateral packing density and to the presence of gauche defects, which makes these vibration modes ideally suited as probes to determine the crystallinity of SAMs. In the IR spectra of the SAMs, the $CH_2$ stretching vibration peaks were observed around at 2853 $cm^{-1}$ (symmetric $CH_2$ stretching) and 2928 $cm^{-1}$ (asymmetric $CH_2$ stretching). The peak positions of the $CH_2$ stretching vibration mean that SAMs has the relatively disorganized "liquid-like" structure. (R. G. Synder, H. L. Strauss, and C. A. Elliger, *J. Phys. Chem.*, 1982, **124**, 5145) Such disorganization might be caused by relatively bulky head group and short alkyl chain. In previous reports, SAM presenting carboxylic acid head groups has disorganized structure in the case of $C_{10}$ carboxylic acid (11-mercaptoundecanoic acid) in contrast to orderedness in the case of $C_{15}$ carboxylic acid and alkane or alcohol monolayers of the similar chain length ($C_{11}$) have well-ordered structure. (R. V. Duevel and R. M. Corn, *Anal. Chem.*, 1992, **64**, 337 and references therein) The thicknesses of the SAMs were measured to be about 17 Å supporting the formation of monomolecular film.



**S1.** IR spectrum of $CH_2$ stretching region obtained from the SAMs of 1-(12-mercaptododecyl)imidazole.

## 2. Activation of the 1-(12-mercaptododecyl)imidazole-modified gold electrode



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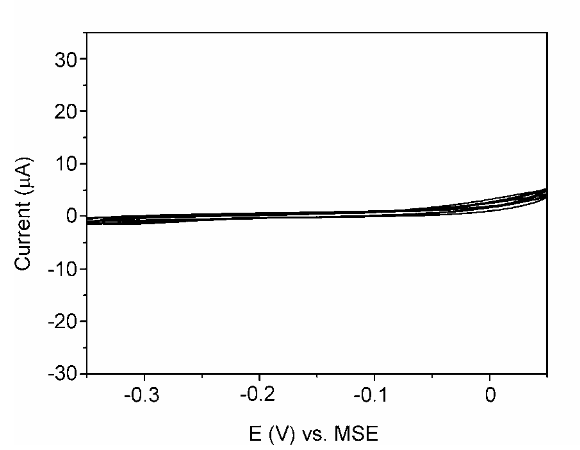
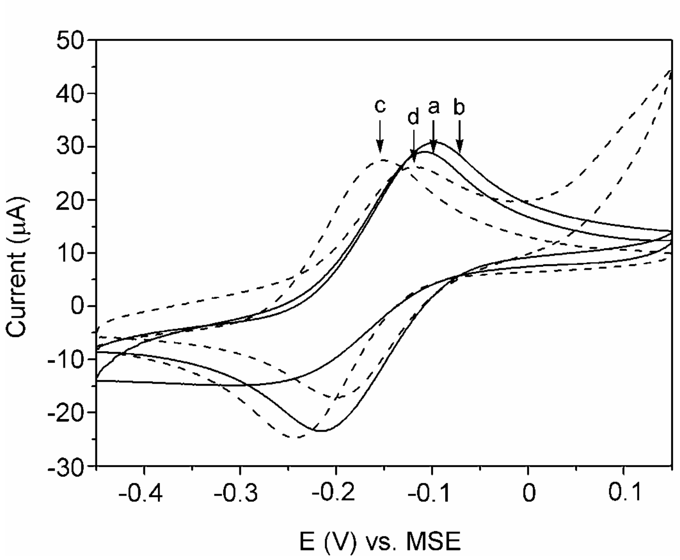
**S2.** CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr at pH 2 during the repeated potential scans. During the first scan, the hindrance of electron transfer is evident in the CV (line a). The lines b, c, d, and e are the CVs of the 2nd, 3rd, 4th, and 5th scans, respectively.



**S3.** CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr at pH 12 during the repeated potential scans.

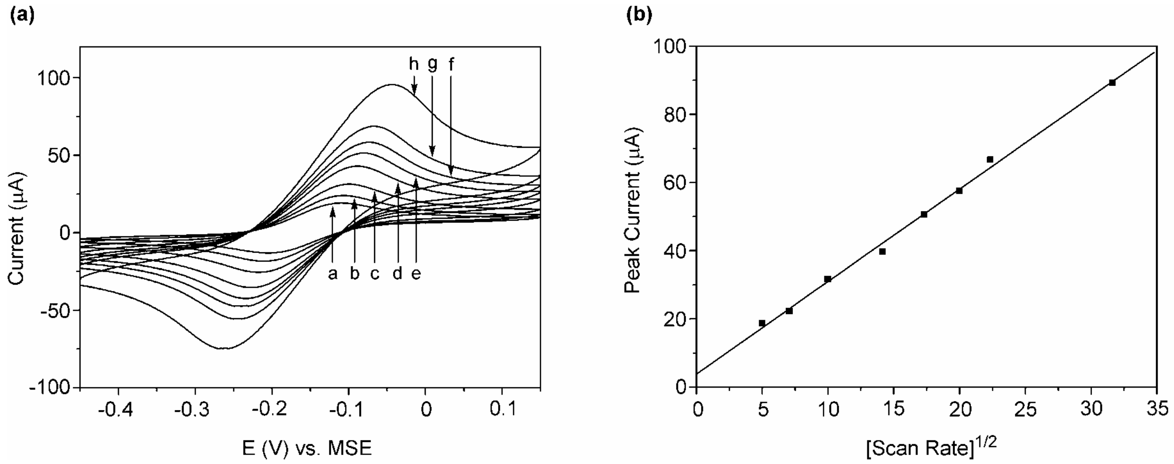
## 3. Comparison of CVs between on the naked bare gold and the SAM-modified gold at different pHs



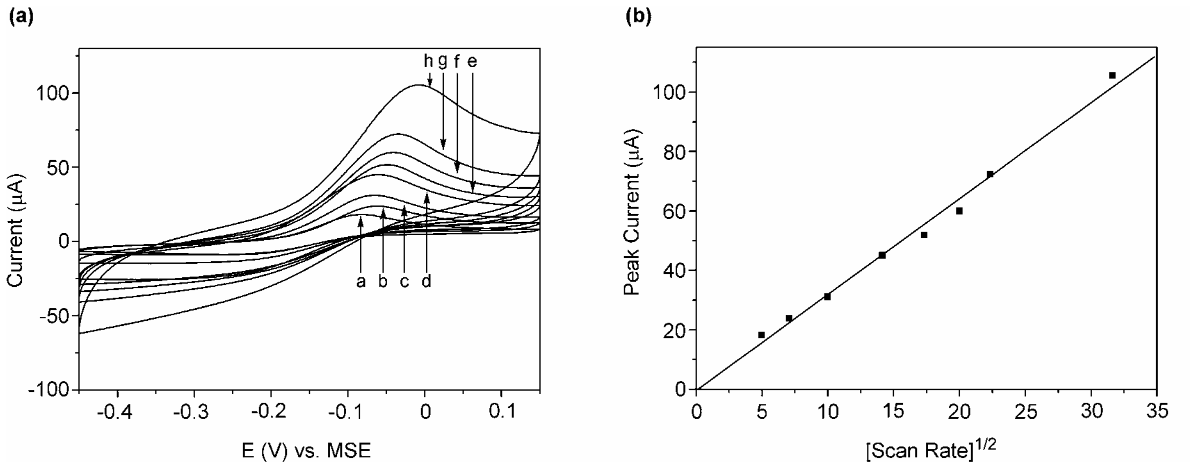
**S4.** CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr (a) at pH 2 and (b) at pH 12. CVs of the naked bare Au in the same solution (c) at pH 2 and (d) at pH 12.

## 4. CVs of the SAM-modified Au on scan rate from 25 mV/s to 1000 mV/s

- Cyclic voltammograms are obtained as a function of the scan rate both at pH 2 and at pH 12. In basic electrolyte, a well-defined voltammetric response (Figure S4(a)) is observed with a peak potential separation of 96 mV (scan rate = 25 mV/s). The anodic peak current varied linearly with the square root of the scan rate between 25 mV/s and 1000 mV/s, as shown in Figure S.4(b). This indicates the ferrocene oxidation reaction is limited by semi-infinite linear diffusion of the reactant. The increased separation between the peak potentials over this range of scan rate demonstrates quasi-reversible electrochemical reaction. In acidic electrolyte, the anodic peak current increased linearly with the square root of the scan rate and the anodic peak potentials over this range of scan rate are shifted positively (shown in Figure S.5), indicating the semi-infinite linear diffusion and the quasi-reversible reaction. Although the modified electrode experiences the activation step, the SAM on the electrode may affect the kinetics of electron-transfer leading to the quasi-reversible redox reaction. These results show that the kinetics of the oxidation of ferrocene is the nearly same in both acidic and basic electrolyte, in contrast to the very reduced kinetics of the reduction of $FcOH^+$.

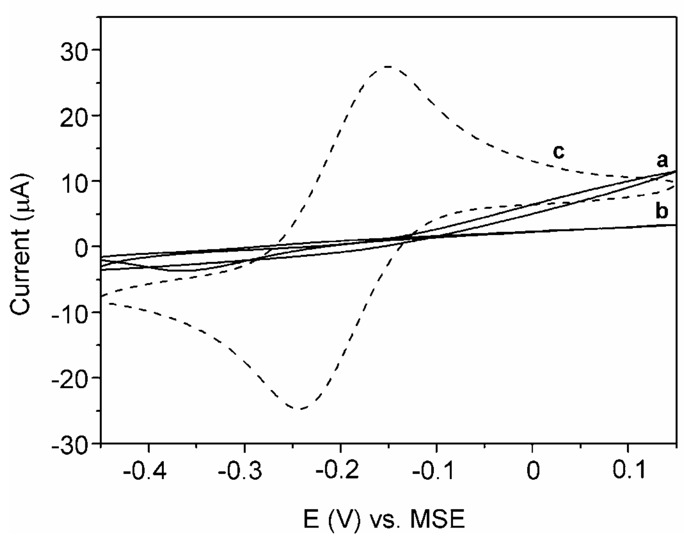


**S5.** (a) CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr at pH 12 on scan rate of (a) 25 mV/s, (b) 50 mV/s, (c) 100 mV/s, (d) 200 mV/s, (e) 300 mV/s, (f) 400 mV/s, (g) 500 mV/s and (h) 1000 mV/s. (b) Plot of anodic peak currents to potential sweep rate.



**S6.** (a) CVs of the SAM-modified Au in a solution containing 0.5 mM ferrocenemethanol and 10 mM KBr at pH 2 on scan rate of (a) 25 mV/s, (b) 50 mV/s, (c) 100 mV/s, (d) 200 mV/s, (e) 300 mV/s, (f) 400 mV/s, (g) 500 mV/s and (h) 1000 mV/s. (b) Plot of anodic peak currents to potential sweep rate.

## 5. Effect of the terminal imidazole group



**S7.** CVs of the SAM of 11-amino-1-undecanethiol on Au in 0.5 mM ferrocenemethanol and 10 mM KBr at (a) pH 2 and (b) pH 12. (c) The CV of the bare Au in the same solution at pH 2 (dashed line). The blocking effect of the SAM is obvious in both (a) and (b). Scan rate = 50 mV/s.