Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Redox Mediated Electron Transfer Behaviors at Azobenzene Functionalized Electrode

Yinan Qin [a,b], Lei Xu [b], Jiangtao Ren [a], Yaqing Liu [*a], Erkang Wang [*a]

Experiments: A gold ball electrode was used as working electrode. The gold electrode was first annealed with hydrogen flame and then cooled down to room temperature. The Au/Azb-HDT was prepared by first immersing the fresh gold electrode into 0.1mM 4-Aminoazobenzene (Azb) solution four hours and then into 1mM hexadecane-1-thiol (HDT) solution overnight. The Au/Azb electrode was prepared by immersing gold electrode into 0.1mM 4-Aminoazobenzene solution four hours. The Au/HDT electrode was prepared by immersing gold electrode into 1mM MHDT solution overnight. After taking out, the electrodes were rinsed with plenty of absolute ethanol followed by Milli-Q water. All used glasswares were cleaned by cooking in 25% nitric acid and then in purified water. Cyclic voltammograms were recorded in a classical three electrode system by a CHI 830 (CO. Chenhua, Shanghai). EIS was performed using Autolab PG30/FRA2 instrument (Eco Chemie, Netherlands). Platinum foil and Ag/AgCl electrode worked as counter and reference electrode, respectively. Mixture of Britton-Robinson (B-R) buffer solution (pH 5) and 0.1M sodium perchlorate was used as supporting electrolyte. The BR buffer contains HAc (0.04 M), H_3PO_4(0.04 M) and H_3BO_3 (0.04 M). NaOH (0.2 M) was used to adjust pH value of the solution to five. The solutions were deoxygenated by purging with argon for electrochemical measurement. All used solutions were freshly prepared for each experiment.

Results:

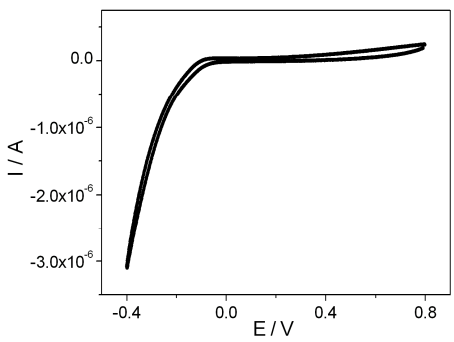

Figure S1. Current response of the Au/Azb-HDT electrode in 1 mM $Ru(NH_3)_6^{3+}$ solution. Scan rate: 100 mV/s.

Figure S1 shows the current response of the Au/Azb-HDT electrode in $Ru(NH_3)_6^{3+}$ solution. No obvious redox peaks are observed. When potential negatively scan the reduction of $Ru(NH_3)_6^{3+}$ by the surface Azb is thermodynamically unfavorable since the redox potential of $Ru(NH_3)_6^{3+/2+}$ (-0.13V) is more negative than the first redox potential of surface Azb (E_1^o, 0.3V) and a little negative than the second redox potential of surface Azb (E_2^o, -0.12V). That is consistent with the results of the Au/Azb-HDT in $Ru(NH_3)_6^{2+}$ system (Figure 4 in the manuscript). No obvious anodic peak is found during reverse potential scan. The possible reason might be that the quantity of $Ru(NH_3)_6^{2+}$ in the system is not enough to be detected for the redox mediation.

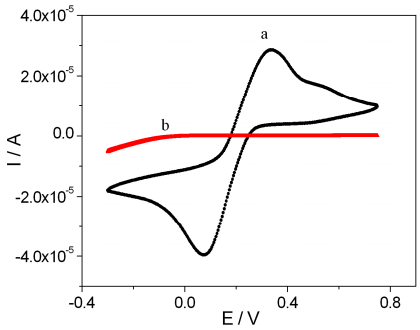

Figure S2. Current responses of the Au/Azb (a) and Au/HDT (b) electrodes in 1 mM BQ solution. Scan rate: 50 mV/s.

Figure S2a shows current response of the Au/Azb electrode in BQ solution. Comparing with current response of the naked Au electrode in BQ solution (Fig. 5a in the manuscript), the peak-to-peak potential difference increases from 100 mV to 260 mV accompanying with decreased current amplitude. While, the potential difference is much smaller than that of Au/Azb-HDT electrode in BQ solution (Fig. 5b in the manuscript). With Au/HDT modified electrode, electron transfer between redox probe and electrode is strongly inhibited (Figure S2b). The different current responses are contributed to the different surface structures. With Au/Azb modified electrode, a loosely adsorbed Azb molecular layer formed on the Au electrode. BQ molecules could penetrate to the underlying electrode surface through defects on the gold electrode, leading the partly blocked current response. With Au/HDT modified electrode, the compact HDT molecular layer acts as inhibitor to block the direct electron transfer between redox probe and the underlying electrode. With Au/Azb-HDT modified electrode, the compact HDT layer acts as inhibitor and redox mediation could only occur at the sites where Azbs are adsorbed, leading to the mediated behavior.