

Luminescent acetylthiol derivative tripodal Osmium(II) and Iridium(III) complexes. Spectroscopy in solution and on surfaces

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Supplementary Information

Experimental procedure for measuring and analyzing $J(V)$ data:

A wire soldered to the syringe needle made electrical contact between the EGaIn and a Keithley 6430 sub-femtoamp electrometer. Using a tungsten needle, we grounded the Au substrate. We collected each $J(V)$ trace by applying a sweep of voltages (1 trace = 0 V \rightarrow 2 V \rightarrow -2 V \rightarrow 0 V in steps of 0.1 V) and measuring current with the electrometer. To obtain current density, J , we measured the diameter of the footprint of the conical tip of EGaIn on the surface of the SAM, calculated the area of the footprint by assuming a circular cross section, and divided the measured current by the calculated area. We imaged the junction using a CCD camera fitted with a 450x magnifying lens and situated in the plane of the Au surface (to afford a side view).

We measured a total of 264 $J(V)$ traces by forming a total of 11 individual contacts between EGaIn and the SAM. These measurements were distributed over two separate, SAM-covered, Au substrates. Each trace yielded two values of current density for each applied voltage (one value for the forward arm of the trace, another for the reverse); thus, a total of 528 values of

J were collected for each of the 41 discrete values of V . For each applied voltage, we constructed a histogram (see figure S1), having 10 bins/decade, of $\log(|J|)$, where J has units of A/cm^2 . We found that, for each applied voltage, the values of $\log(|J|)$ were normally distributed (i.e. $|J|$ was log-normally distributed). Using the nonlinear least-squares, trust-region fitting algorithm in MATLAB 7.8.0, we fit the distribution of $\log(|J|)$ with a Gaussian and determined the mean (μ) and standard deviation (σ) of $\log(|J|)$. The log-mean and log-standard deviation of $|J|$ are given by $\mu_{\log} = 10^\mu$ and $\sigma_{\log} = 10^\sigma$, respectively. Thus, 68% of the distribution of $|J|$ at a given voltage lies between $10^{\mu-\sigma}$ and $10^{\mu+\sigma}$, or equivalently, between μ_{\log}/σ_{\log} and $\mu_{\log} \times \sigma_{\log}$. The average trace in figure 9 is a plot of μ_{\log} vs. voltage; the lower error bars of this trace represent μ_{\log}/σ_{\log} and the upper error bars represent $\mu_{\log} \times \sigma_{\log}$.

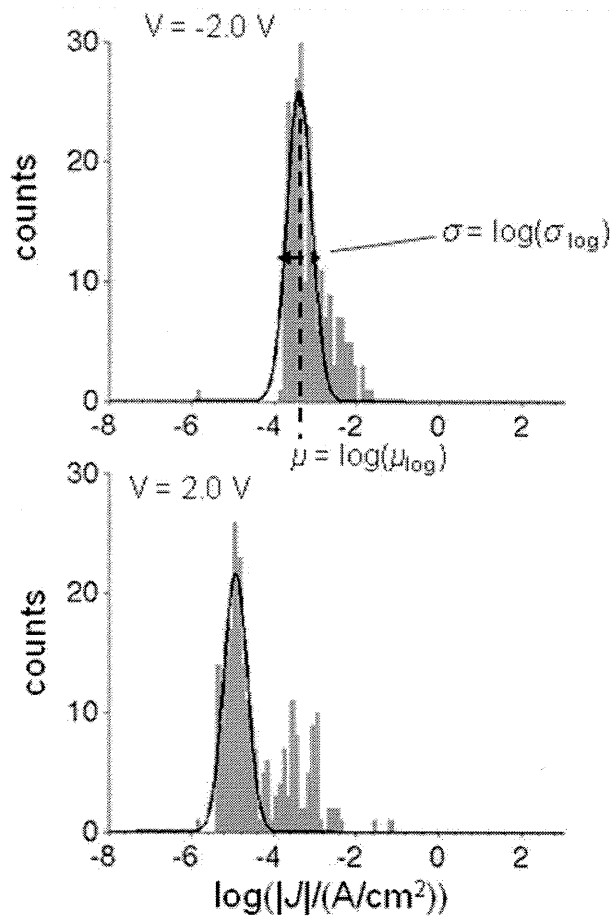


Figure S1. Fitted histograms of $\log(|J|)$, where J has units of A/cm^2 . The histograms (gray) of $\log(|J|)$ for applied voltages of -2.0 V (top) and 2.0 V (bottom) are fitted with Gaussians (black). The Gaussian fit gives the log-mean ($\mu_{\log} = 10^{\mu}$) and log-standard deviation ($\sigma_{\log} = 10^{\sigma}$) at a given applied voltage. Values for μ_{\log} and σ_{\log} at each voltage are used to construct the average trace in figure 9.

Comparison of solution vs. SAM cyclic voltammograms

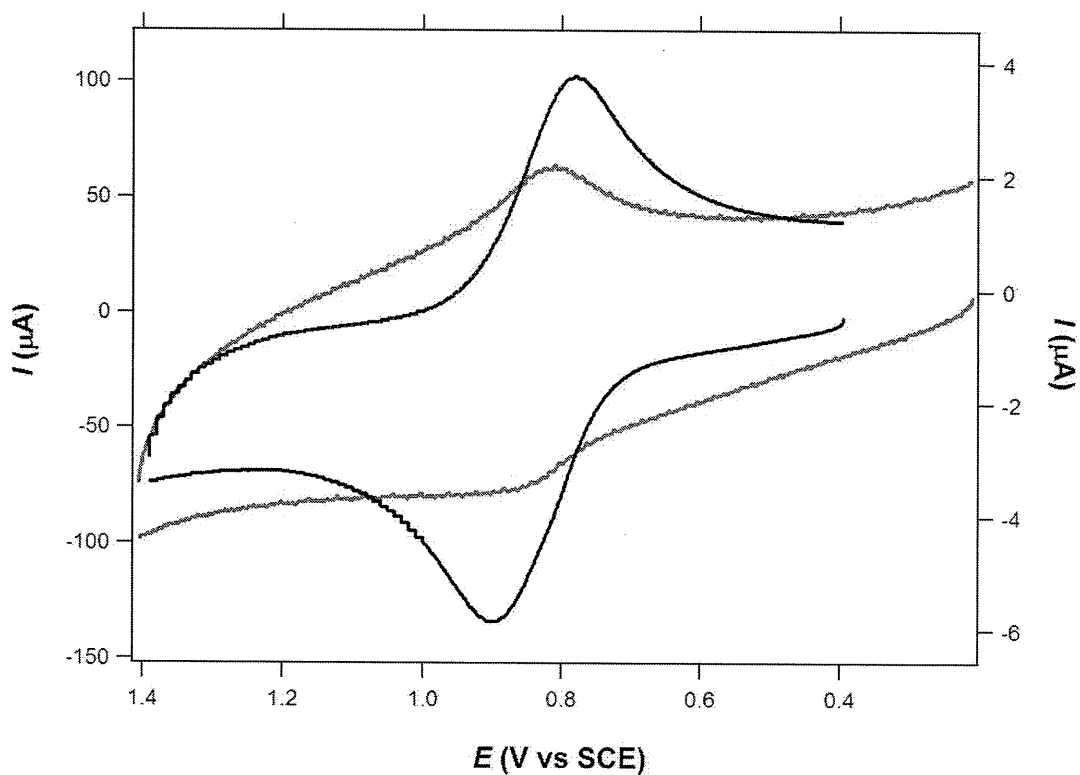


Figure S2. Comparison of cyclic voltammograms of Os-SAc in solution (black) and Os-SAC SAM (blue).