Pure Appl. Chem.; doi:10.1351/PAC-CON-10-11-07

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 → 2 V → -2 V → 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 $\mu_{log} \times \sigma_{log}$.

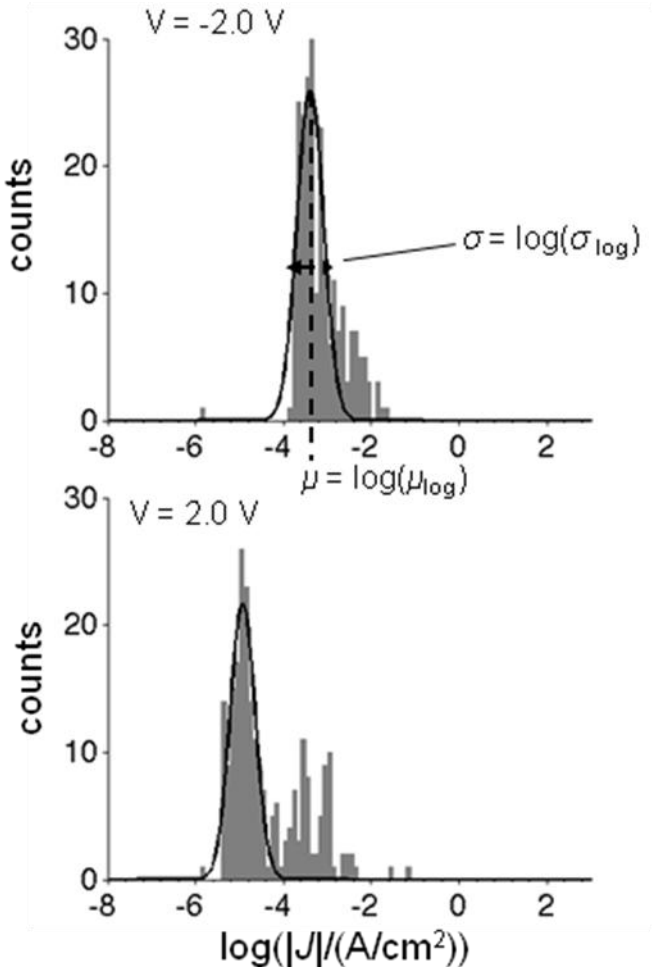

Figure S1. Fitted histograms of log(|*J*|), where *J* has units of A/cm^2. The histograms (gray) of log(|*J*|) for applied voltages of -2.0 V (top) and 2.0 V (bottom) are fitted with Gaussians (black). The Gaussian fit gives the log-mean ($\mu_{log} = 10^{\mu}$) and log-standard deviation ($\sigma_{log} = 10^{\sigma}$) 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

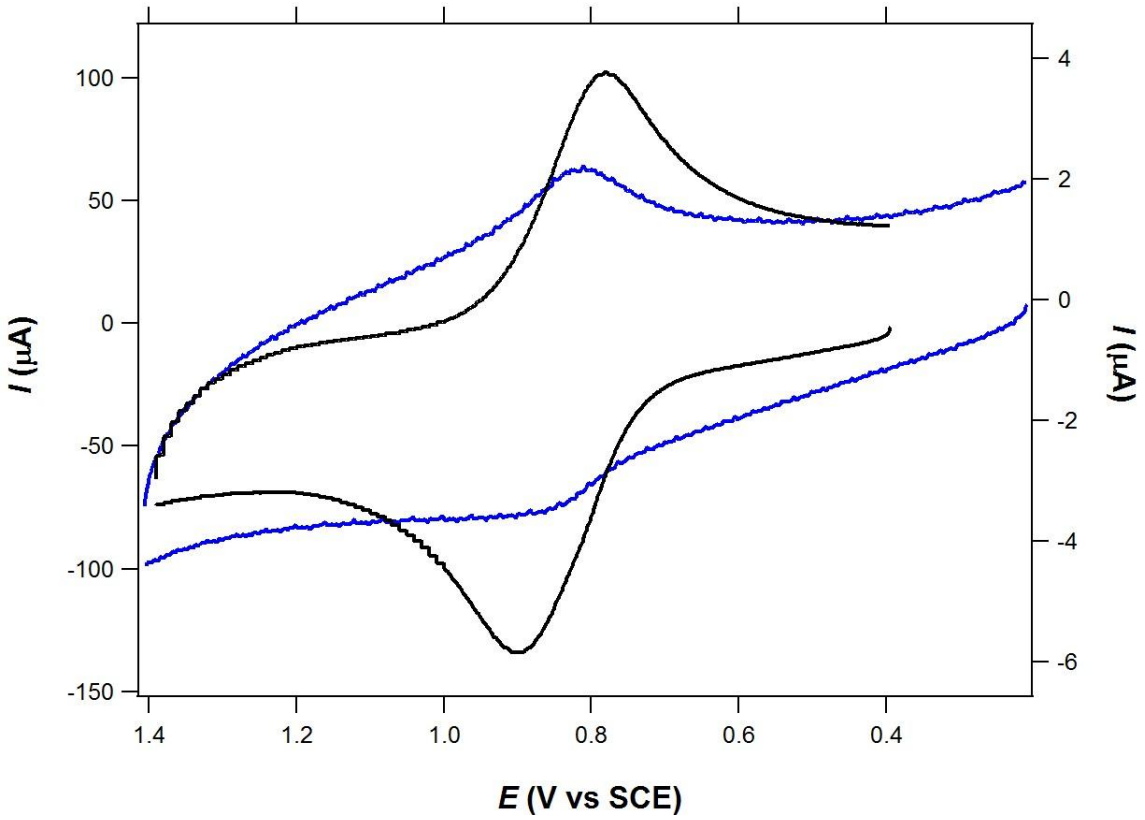

Figure S2. Comparison of cyclic voltammograms of Os-SAc in solution (black) and Os-SAC SAM (blue).