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

Srinidhi Ramachandra[1], Federico Polo[2], Fabio Edafe [3], Klaus C. Schuermann[2], Christian A. Nijhuis[4], Peter Belser[3] William F. Reus[4], George M. Whitesides[4], Luisa De Cola* [1,2]

[1]*Laboratory of Supramolecular Chemistry and Technology, University of Twente, P.O. box 217, 7500 AE Enschede, The Netherlands*

[2]*Westfälische Wilhelms-Universität Münster, Physikalisches Institut, Mendelstraße 7, 48149 Münster, Germany*

[3]*Department of Chemistry, University of Fribourg, chemin du musée 9, 1700 Fribourg, Switzerland*

[4]*Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford street, Cambridge, MA 02138, USA*

## 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 ($\mu$) and standard deviation ($\sigma$) 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 $\mu_{\log} / \sigma_{\log}$ and $\mu_{\log} \times \sigma_{\log}$. The average trace in figure 9 is a plot of $\mu_{\log}$ vs. voltage; the lower error bars of this trace represent $\mu_{\log} / \sigma_{\log}$ and the upper error bars represent $\mu_{\log} \times \sigma_{\log}$.

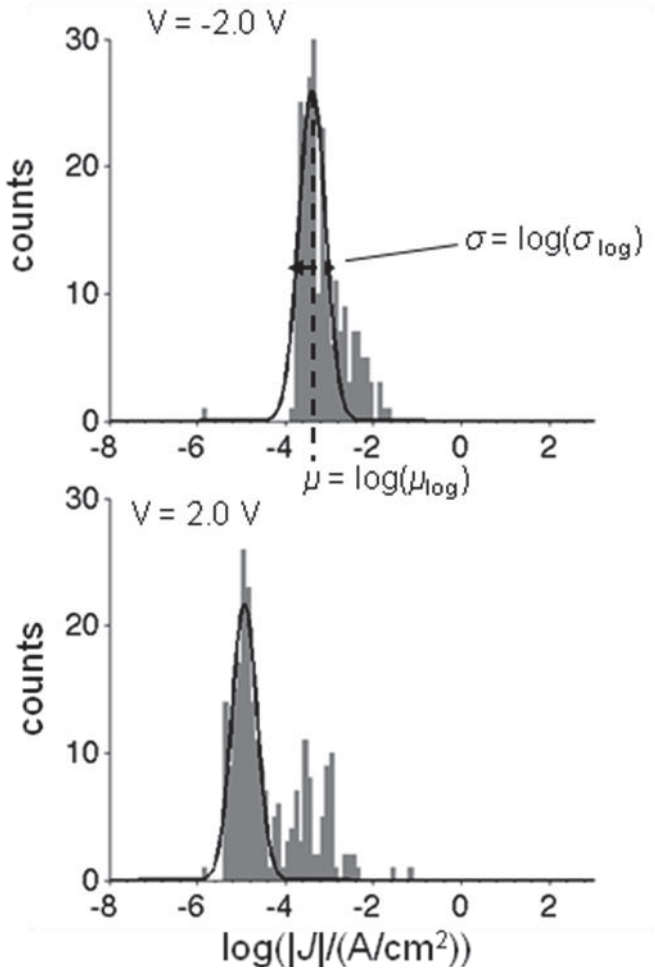

**Figure S1.** Fitted histograms of log(|$J$|), where $J$ has units of A/cm$^2$. The histograms (gray) of log(|$J$|) for applied voltages of -2.0 V (top) and 2.0 V (bottom) are fitted with Gaussians (black). The Gaussian fit gives the log-mean ($\mu_{\log} = 10^{\mu}$) and log-standard deviation ($\sigma_{\log}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

**Comparison of solution vs. SAM cyclic voltammograms**

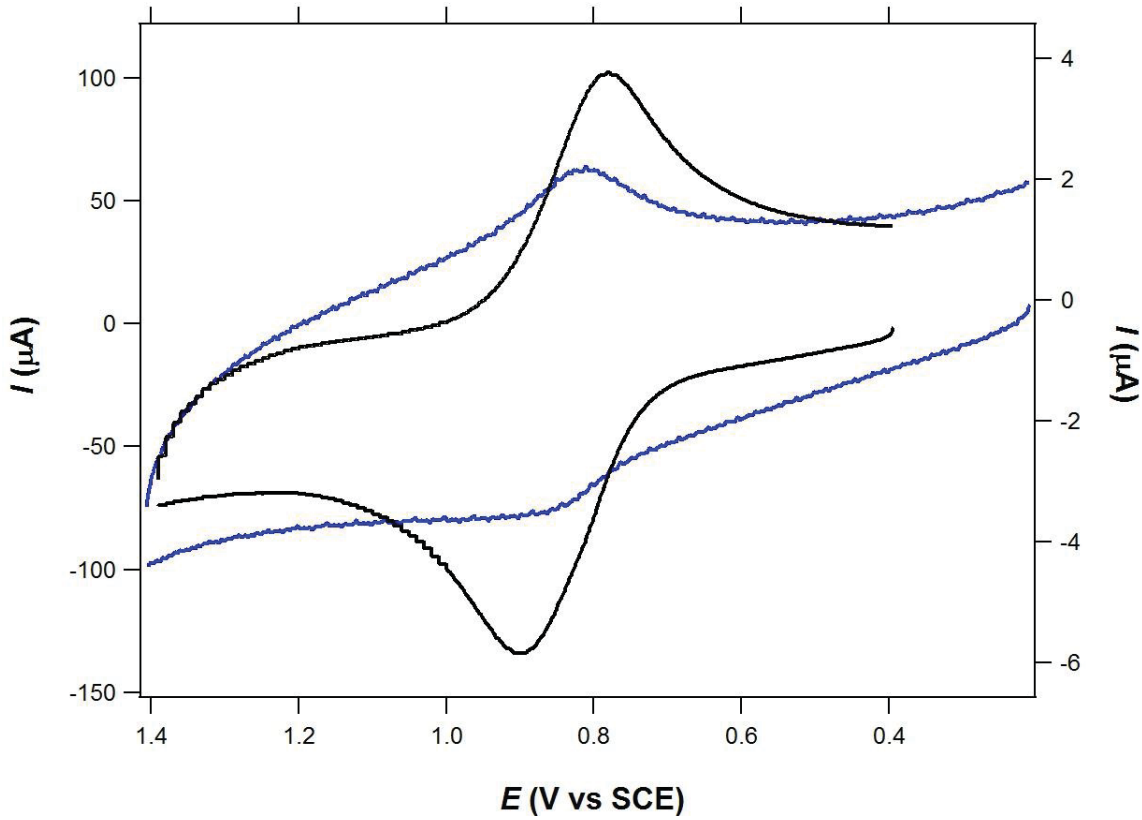

**Figure S2.** Comparison of cyclic voltammograms of Os-SAc in solution (black) and Os-SAC SAM (blue).