

Electronic Supplementary Information for

**Near-infrared electrochemiluminescence from $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}^+$
clusters co-reacted with tri-n-propylamine**

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1. Chemicals

Hydrogen tetrachloroaurate trihydrate (Aldrich, 99.9%), phenylethanethiol (Aldrich, 98%), tetraoctylammonium bromide (Aldrich, 98%), sodium borohydride (Aldrich, 99%), hydrogen peroxide (Caledon, 30%), sodium hydroxide (Caledon, 99%), tetrahydrofuran (Caledon, 99.9%), pentafluorobenzoyl chloride (Alfa Aesar, 99%), methanol (Caledon, 99.8%), dichloromethane (Caledon), chloroform (Caledon, 99.8%), ethanol (Caledon, 99.8%), and acetonitrile (Caledon) were used as received. Deuterated chloroform and dichloromethane was furnished by Cambridge Isotope Laboratories. For the electrochemical experiments benzene (tore seal), acetonitrile (tore seal) and terabutylammonium bromide (99%) were purchased from Aldrich.

2. Synthesis $\text{Au}_{25}(\text{S}(\text{CH}_2)_2\text{Ph})_{18}^+ \cdot \text{C}_6\text{F}_5\text{CO}_2^- (\text{Au}_{25}^+)$

$\text{TOA} \cdot \text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ has been synthesized following published procedures¹. Briefly, 2.54 mmol $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 3.04 mmol tetraoctylammonium bromide (TOABr) were co-dissolved in 100 mL THF. The dark red solution was put in the ice-bath for 30 min and then 15.67 mmol of phenylethane thiol was added one drop at a time over 10 minutes. Meanwhile, the color of mixture turned yellowish while the ice bath was kept for 2 hours. The solution was heated up to room temperature and led to a colorless solution after 3 hours. At this point, the ice bath was put back and 26.69 mmol NaBH_4 ,

dissolved in 20 mL of ice-cold distilled water was added to the mixture quickly under vigorous stirring. A dark solution formed with the addition of the reducing agent. The solution was gravity filtered and the solvent volume was vacuum evaporated. The residual was settled down overnight. The excess of NaBH₄ and phenylethane thiol was removed by washing the crude sample with Water/ethanol mixture. The final product was extracted from -(Au-S-Au-S)-oligomer using acetonitrile to get an oily product, which then recrystallized to obtained a dark-brown needle crystals.

To convert the Au₂₅⁻ to the Au₂₅⁺, bis(pentafluorobenzoyl) peroxide was used as oxidizing agent. Synthesis of bis(pentafluorobenzoyl) peroxide¹ was performed by following Barson's procedure with some modification². Then, the purity of the sample was checked by TLC (15:1 petroleum ether/ ethyl acetate) and ¹⁹FNMR (-133.74, -143.30, -158.15 ppm in CDCl₃). No explosion was observed during the peroxide preparation and the sample was kept in the freezer to prevent decomposition.

Upon addition of the peroxide to the Au₂₅(SC₂H₄Ph)₁₈⁻ an oxidation reaction can happen via electron transfer between the nanocluster and the peroxide¹ which leads to formation Au₂₅(SC₂H₄Ph)₁₈⁺ C₆F₅CO₂⁻ cluster. In our work, the same methodology has been applied to get "1+" monodispersed cluster. Briefly, 1 mmol of crystallized Au₂₅⁻ was prepared in *d*₂-dichloromethane in an NMR tube and ¹HNMR spectrum was recorded. Then 2 mmol of (*d*₂- dichloromethane) was added to the above solution,¹ ¹HNMR (Figure S1) and UV-Vis-NIR (Figure S2) spectra have been taken to monitor the reaction completion and purity of the final product. MALDI-TOF mass spectrum also proved that the original cluster exist over the course of reaction. To run the MALDI experiment, the sample was mixed with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldene]-malononitrile (DCTB), applying 1000/0.2 ratio of matrix/analyte and 7 μ L of the prepared sample was placed on the target plate, dried at room temperature. The laser intensity was kept as low as possible to have a good signal to noise ratio, although some fragmentation observed among the sample analysis.¹

The photoluminescence spectra of different Au₂₅ charge states were obtained in the course of spectroelectrochemistry while a 1 mM Au₂₅⁻ containing 0.1 M TBAP in 1:1

acetonitrile: benzene solution was excited using 532 nm laser, and spectra were recorded with an Andor BR-DD CCD camera (cooled at -65°C) attached to an Acton spectrograph. A long-pass edge filter was placed between the sample and the detector to cut the excitation peak in the PL spectrum. In situ spectroelectrochemical measurements were conducted with a commercially available thin layer quartz cell from BASi connected to a CHI610 potentiostat with a three-electrode configuration. The electrolysis was performed using a nonaqueous reference electrode (Ag/Ag^+ reference electrode (0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile), a Pt mesh and Pt wire as the working and counter electrodes.^{3, 4}

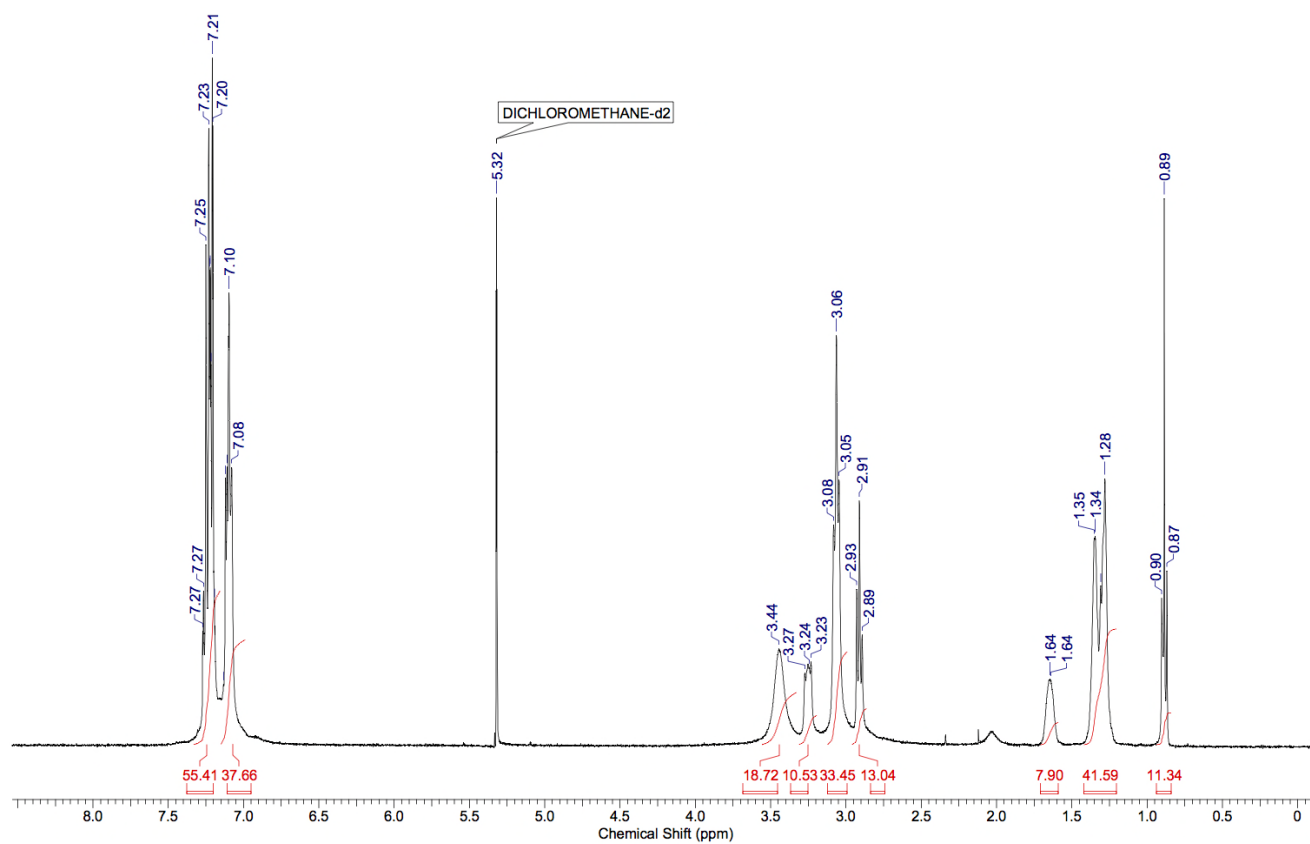


Figure S1. ^1H NMR of synthesized Au_{25}^+ in d_2 -dichloromethane.

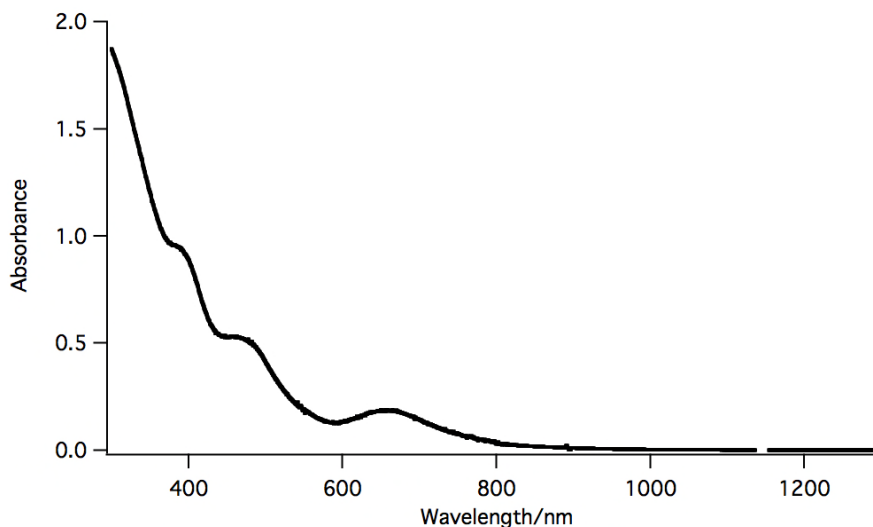


Figure S2. UV-vis-NIR of synthesized Au_{25}^+ in dichloromethane.

3. Electrochemistry and electrogenerated chemiluminescence

Electrochemical analysis has been done in three electrode configuration using CHI610, a Pt disk and two Pt wire have been served as working, reference and counter electrodes in benzene:acetonitrile 1:1 mixture containing 0.1 M tetrabutylammonium bromide (TBAP) supporting electrolyte. The ECL set up details has been reported elsewhere.¹

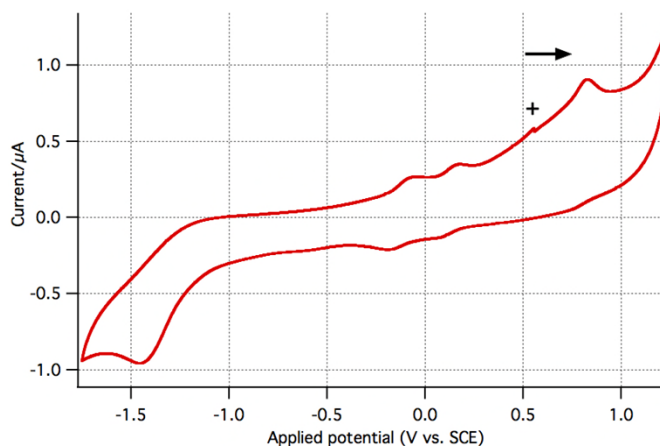


Figure S3. Cyclic voltammogram of 0.1 mM Au_{25}^+ in 1:1 acetonitrile:benzene mixture, containing 0.1 M TBAP as the supporting electrolyte, scan rate: 100 mV/s. The arrow shows potential scanning direction, the cross indicates initial potential.

The formal potentials obtained from DPV¹ data using formula below:⁵

$$E^{0'} = E_{peak} + \frac{\Delta E}{2}$$

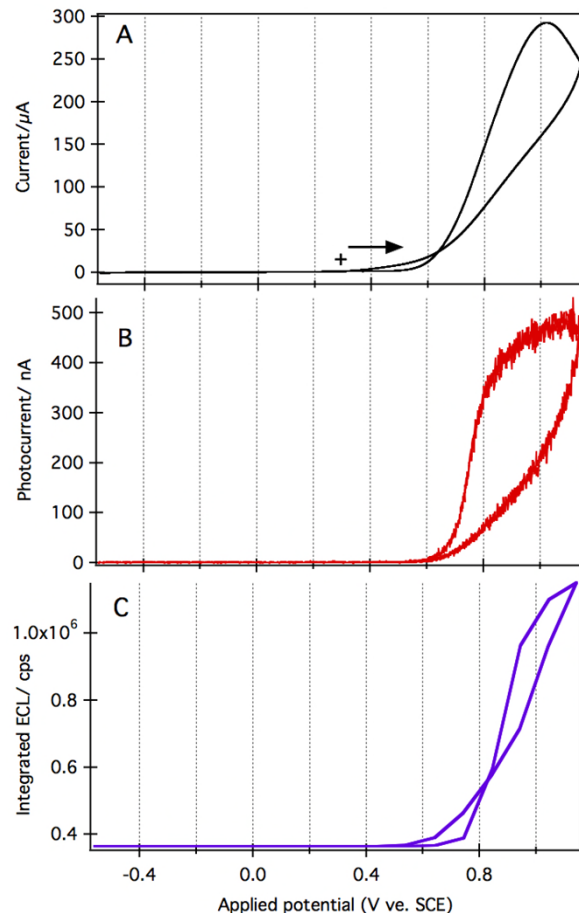


Figure S4. (A) Cyclic voltammogram of 0.1 mM solution of Au₂₅⁺ in 1:1 benzene:acetonitrile mixture containing 0.1 M TBAP in the presence of 50 mM TPrA scanning between -0.482 to 1.216 V, along with (B) ECL-voltage curve recorded by the PMT at a scan rate of 100 mVs⁻¹. (C) ECL Integral of each spooling ECL spectrum in Fig. 1 vs. the applied potential.

While the R928 Hamamatsu photomultiplier tube (PMT) for our routine light emission detection is sensitive below the wavelength of 900 nm, our Andor BRDD camera is able to measure NIR-ECL. Fig. S4 C, the plot of the integration of each spooling ECL spectrum as the total emitted photons vs. the applied potential shows similar trends to that of ECL-voltage curve recorded with the PMT (Fig. S4 B).

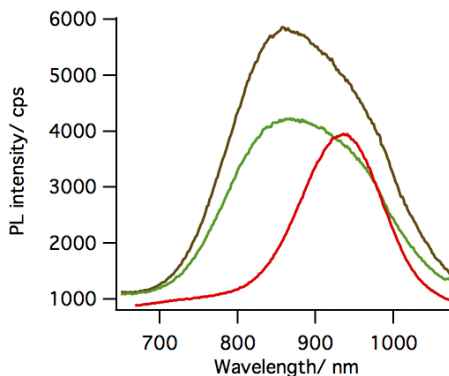


Figure S5. Photoluminescence spectra of 0.1 mM Au_{25}^- (red curve), and Au_{25}^+ (blue curve), Au_{25}^0 (green curve) electrogenerated in the 1:1 acetonitrile:benzene electrolyte solution. The thin layer of the spectroelectrochemical cell was excited using 532 nm laser, and the spectra were recorded with an Andor BR-DD CCD camera (cooled at -65°C) attached to an Acton spectrograph.

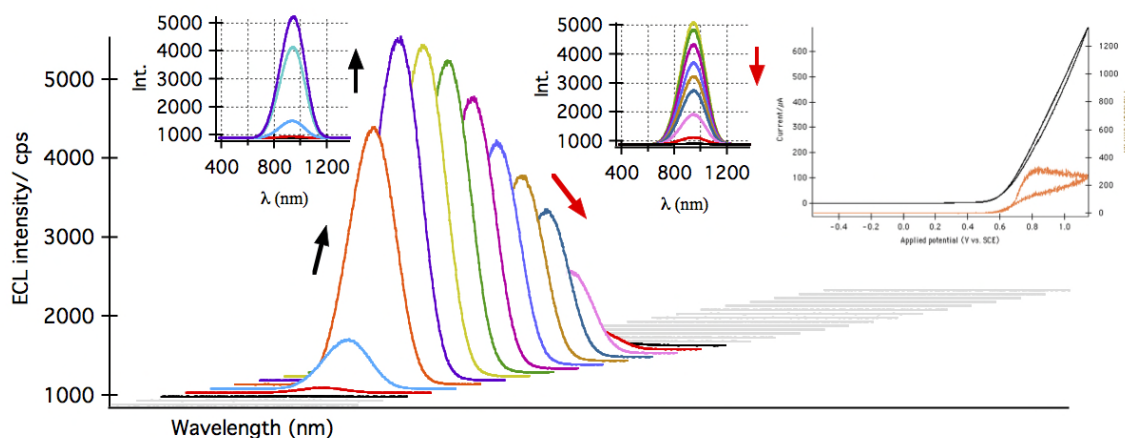


Figure S6: Spooling ECL spectra of $\text{Au}_{25}(\text{S}(\text{CH}_2)_2\text{Ph})_{18} \cdot \text{C}_6\text{F}_5\text{CO}_2$ in the presence of 200 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

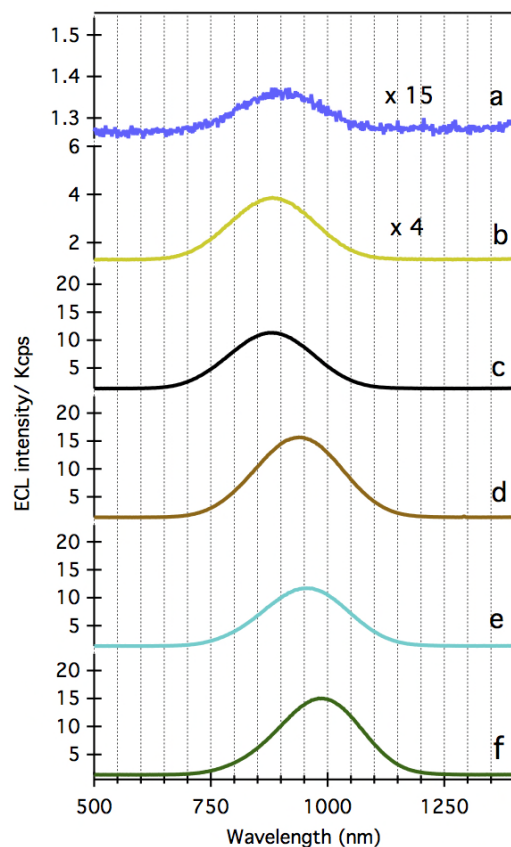


Figure S7. Accumulated ECL spectra of 0.1 mM Au_{25}^+ in 1:1 acetonitrile:benzene mixture containing 0.1 M TBAP and (a) 6.3, (b) 12.5, (c) 25, (d) 50, (e) 100, and (f) 200 mM TPrA. The spectra obtained by cycling potential between -0.545 and 1.145 V.

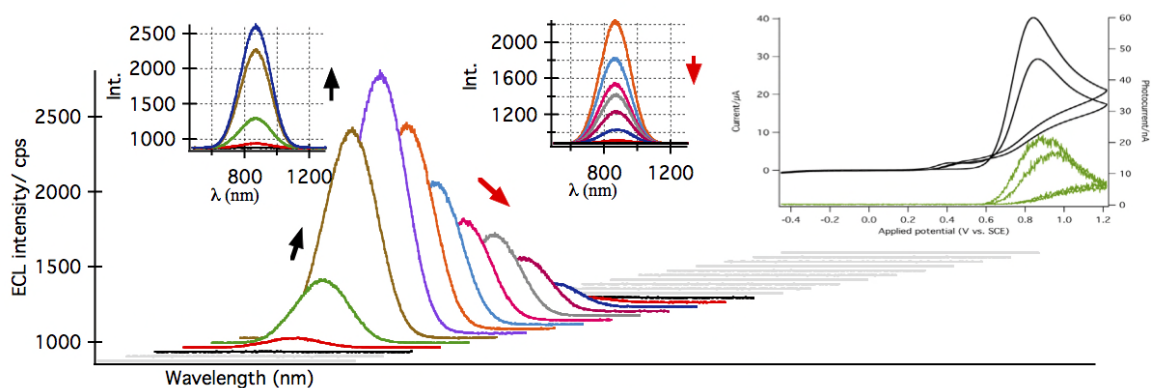


Figure S8. Spooling ECL spectra of $\text{Au}_{25}(\text{S}(\text{CH}_2)_2\text{Ph})_{18} \cdot \text{C}_6\text{F}_5\text{CO}_2$ in the presence of 6.3 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

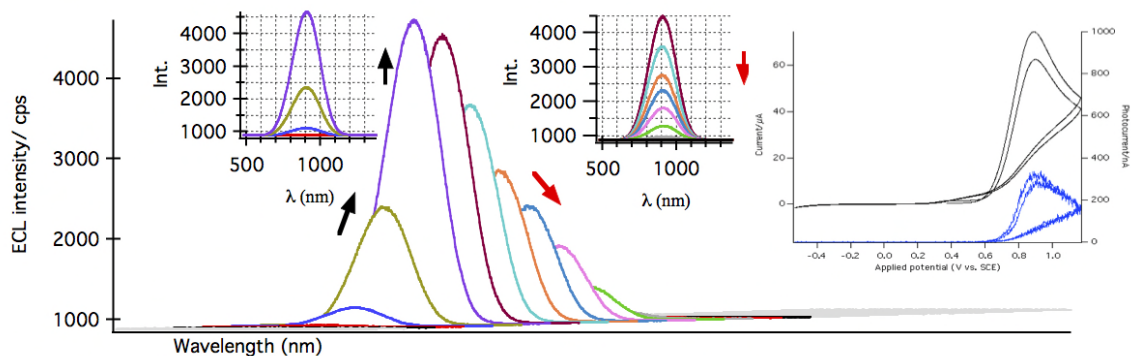


Figure S9. Spooling ECL spectra of $\text{Au}_{25}(\text{S}(\text{CH}_2)_2\text{Ph})_{18}$. $\text{C}_6\text{F}_5\text{CO}_2$ in the presence of 12.5 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

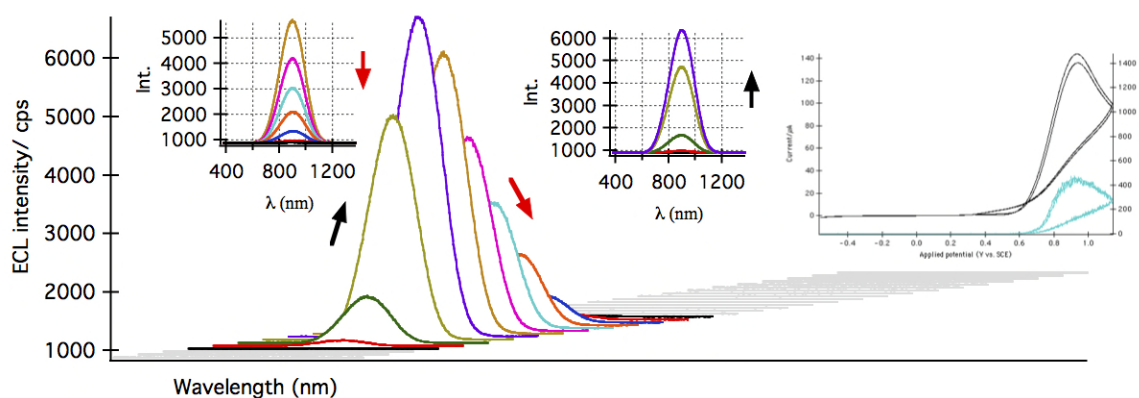


Figure S10. Spooling ECL spectra of $\text{Au}_{25}(\text{S}(\text{CH}_2)_2\text{Ph})_{18}$. $\text{C}_6\text{F}_5\text{CO}_2$ in the presence of 25 mM TPrA. Insets are stacked spectra and ECL-voltage curve measured by the PMT.

Table S1. Relative ECL % for $\text{Au}_{25}^+/\text{TPrA}$ system with various TPrA concentrations.¹

| [TPrA]/mM | Eff. by camera/ % |
|-----------|-------------------|
| 6.3 | 9.6 |
| 12.5 | 20 |
| 25.0 | 116 |
| 50.0 | 88 |
| 100.0 | 544 |
| 200.0 | 735 |

ECL efficiency values were obtained by comparing the integrated ECL intensities (equivalent to the number photons) and the current values (charges) of the $\text{Au}_{25}^0/\text{TPrA}$

samples with those of the Ru(bpy)₃²⁺/TPrA system. The quantum yield was calculated using the below equation:

$$\Phi_x = 100x \left(\frac{\int_a^b ECL dt}{\int_a^b Current dt} \right)_x / \left(\frac{\int_a^b ECL dt}{\int_a^b Current dt} \right)_{St}$$

where Φ is the quantum yield (%) relative to the Ru(bpy)₃²⁺/TPrA system, ECL is the ECL intensity, current is the electrochemical current value, St is the standard (the Ru(bpy)₃²⁺/TPrA) and x is the sample (the Au₂₅⁰/TPrA). Table S1 shows calculated values for each TPrA concentration.¹

Reference:

1. K. N. Swanick, M. Hesari, M. S. Workentin and Z. Ding, *J. Am. Chem. Soc.*, 2012, **134**, 15205-15208.
2. C. A. Barson and R. A. Wisdom, *Eur. Polymer J.*, 1972, **8**, 1139-1144.
3. D. R. Kauffman, D. Alfonso, C. Matranga, G. Li and R. Jin, *J. Phys. Chem. Lett.*, 2012, **4**, 195-202.
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