Electronic Supplementary Information (ESI) for

NIR Electrochemiluminescence from Au_{25}^- Nanoclusters Facilitated by Highly Oxidizing and Reducing Co-reactant Radicals

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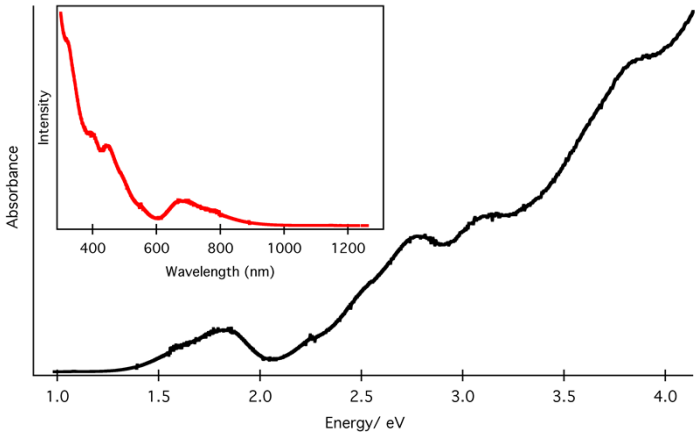

Figure S1. UV-vis-NIR spectrum (in the energy scale) of the Au_{25}^- in dichloromethane. The inset shows the same spectrum in the wavelength scale.

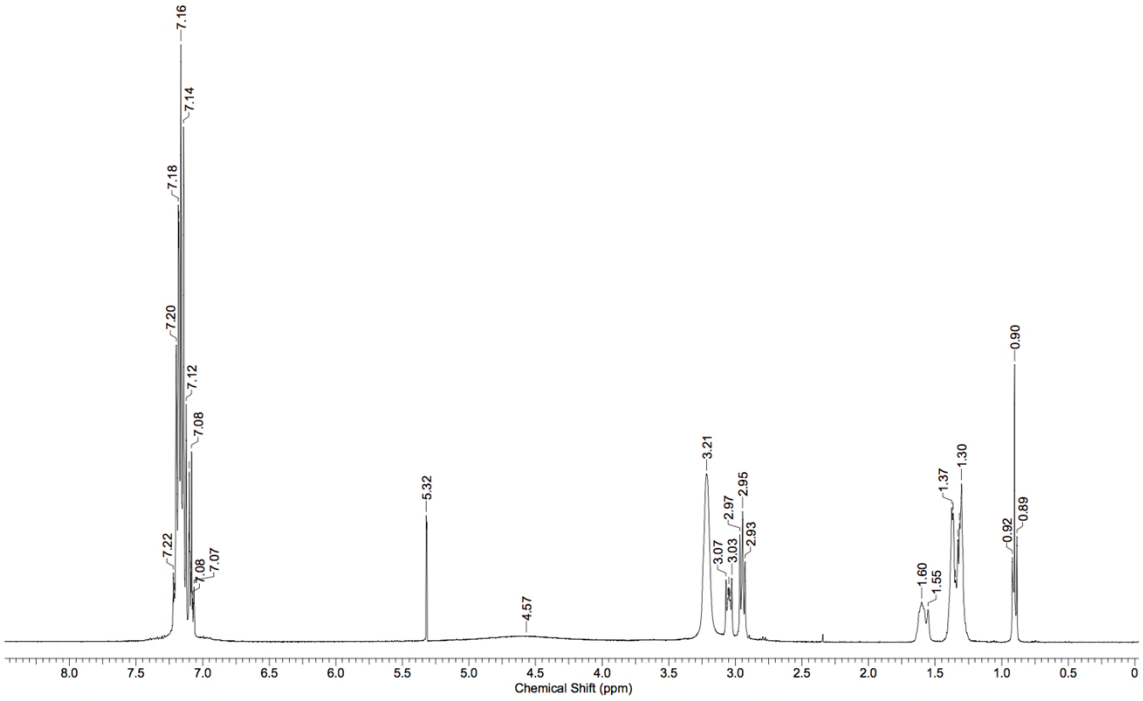

Figure S2. ^{1}HNMR of the crystallized Au_{25}^{-} in d_2-dichloromethane.

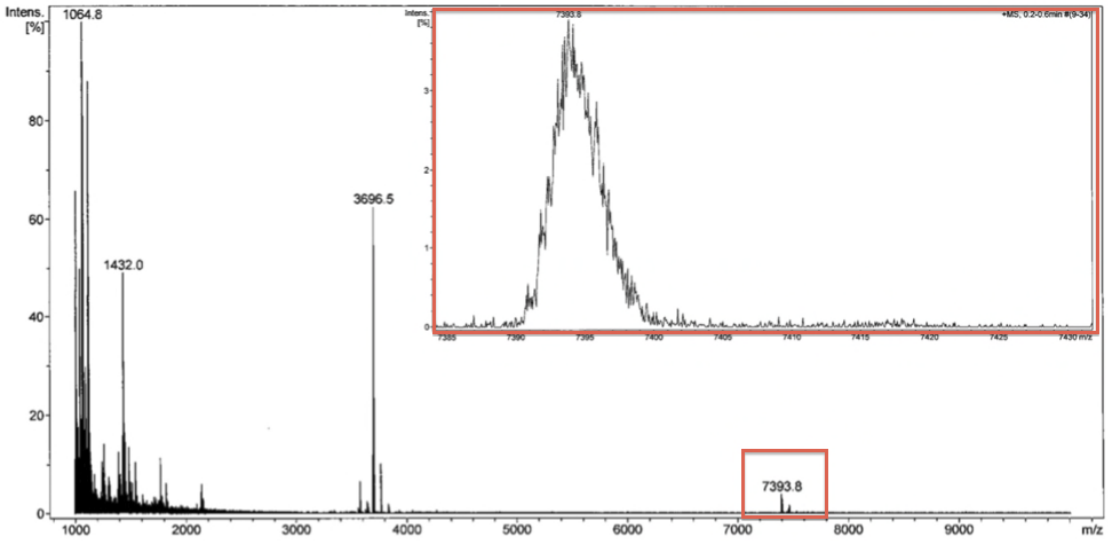

Figure S3. ESI mass spectrum of the $Au_{25}(SC_2H_4Ph)_{18}$.TOA, obtained in CH_2Cl_2/Methanol mixture.

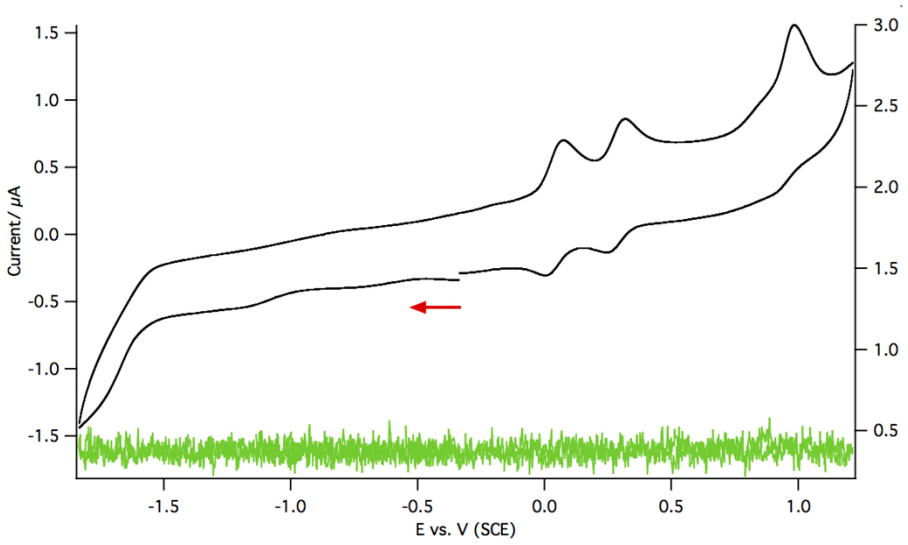

Figure S4. ECL-Voltage curve and cyclic voltammogram of 0.1 mM Au_{25}^- in in 1:1 acetonitrile:benzene containing 0.1 M TBAP. Scan rate was at 100 mVs^{-1}. The arrow indicates the starting potential.

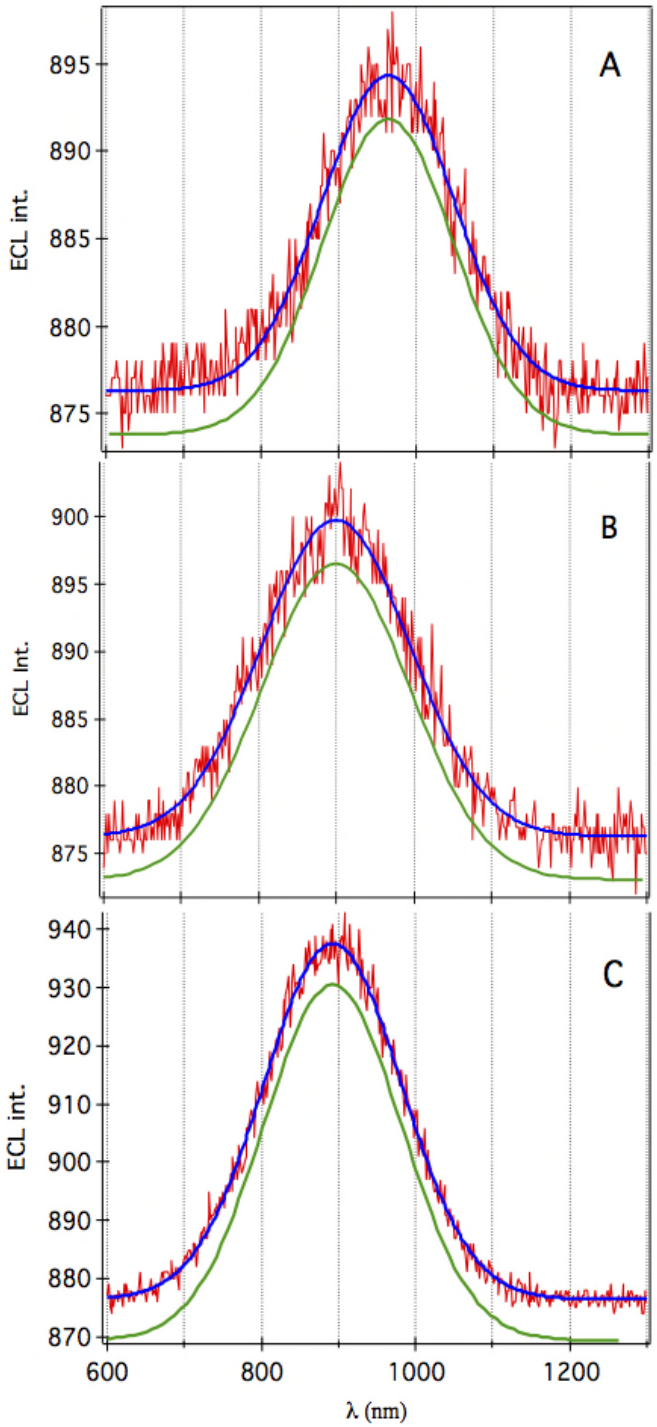

Figure S5. Curve-fitted ECL spectra acquired at (A) 1.76 V, (B) 1.276 V, (C) 1.174 V.

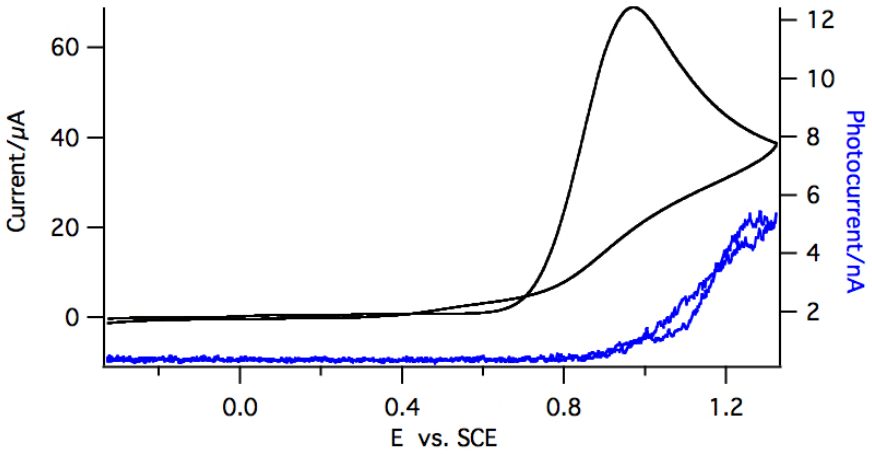

Figure S6. ECL-Voltage curve of 0.1 mM Au_{25}^- in the presence of 12.5 mM TPrA in 1:1 acetonitrile: benzene containing 0.1 M TBAP. Scan rate was at 100 mVs^{-1}.

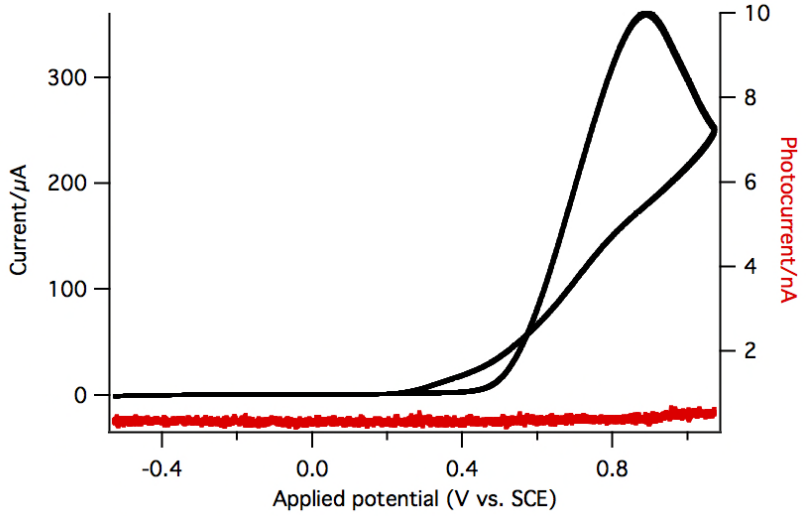

Figure 7. ECL-Voltage curve of 50 mM tri-*n*-propylamine (TPrA) in 1:1 acetonitrile: benzene mixture containing 0.1 M tetra-*n*-buthylammonium perchlorate. Scan rate was at 100 mVs^{-1}.

ECL spectroscopy was conducted on an Acton 2300i spectrograph with two gratings (50 l/mm blazed at 600 nm and 300 l/mm blazed at 700 nm) and an Andor iDUS CCD camera (Model DU401 BR-DD-352).

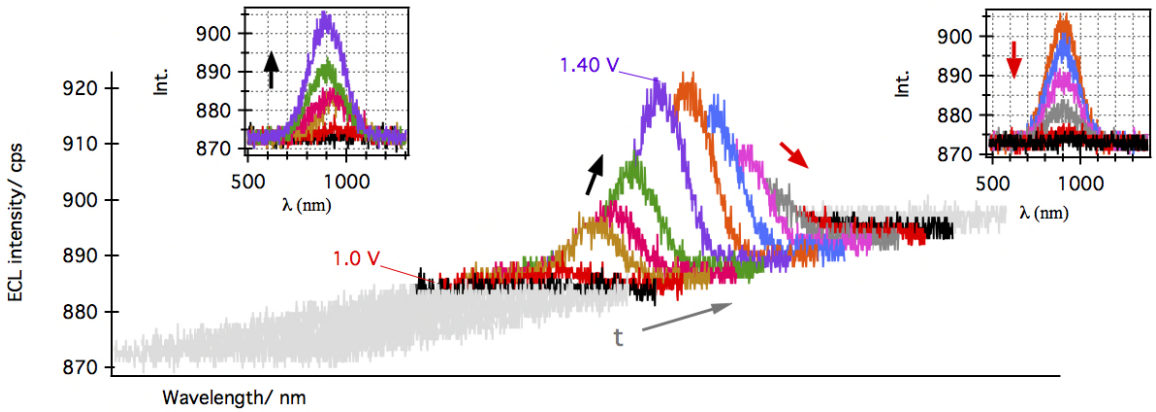

Figure S8. Spooling ECL spectra and stacked spectra for 0.1 mM Au_{25}^- in the presence of 6.3 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}, and an Andor BR-DD CCD camera (cooled at -65 ^oC) was used.

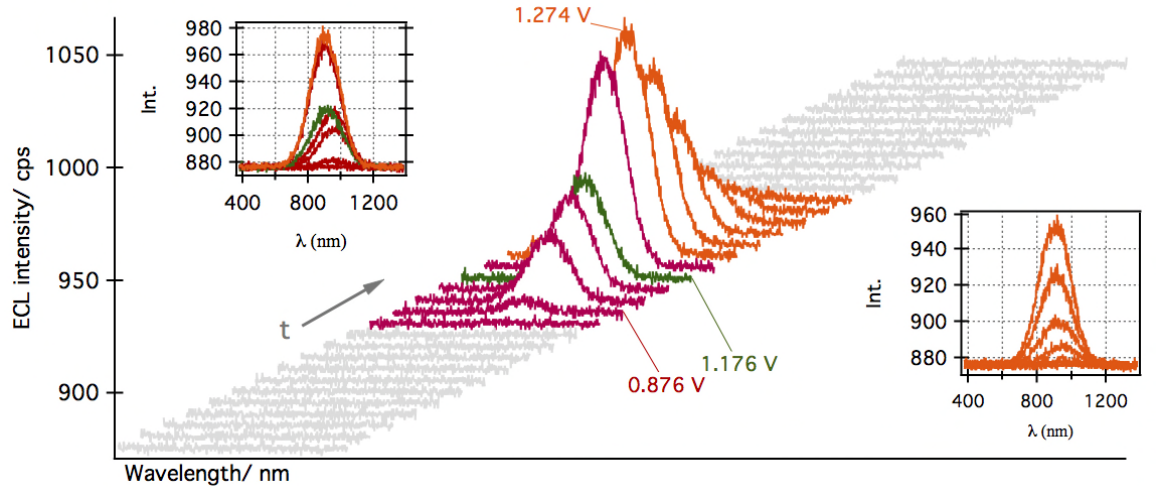

Figure S9. Spooling ECL spectra and stacked spectra for 0.1 mM Au_{25}^- in the presence of 25 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}, and an Andor BR-DD CCD camera (cooled at -65 ^oC) was used.

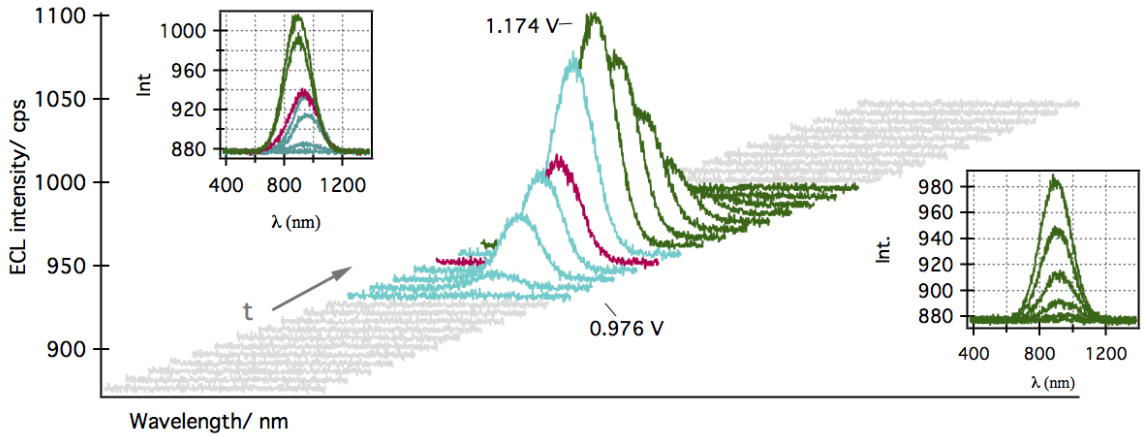

Figure S10. Spooling ECL spectra and stacked spectra for 0.1 mM Au_{25}^- in the presence of 50 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}, and an Andor BR-DD CCD camera (cooled at -65 ^oC) was used.

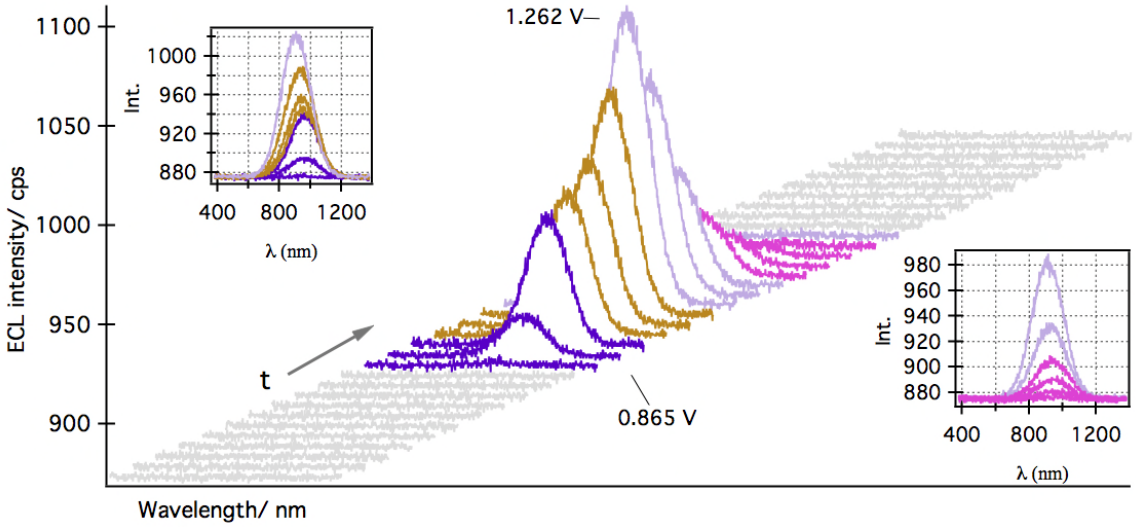

Figure S11. Spooling ECL spectra and stacked spectra for 0.1 mM Au_{25}^- in the presence of 100 mM TPrA, recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}, and an Andor BR-DD CCD camera (cooled at -65 ^oC) was used.

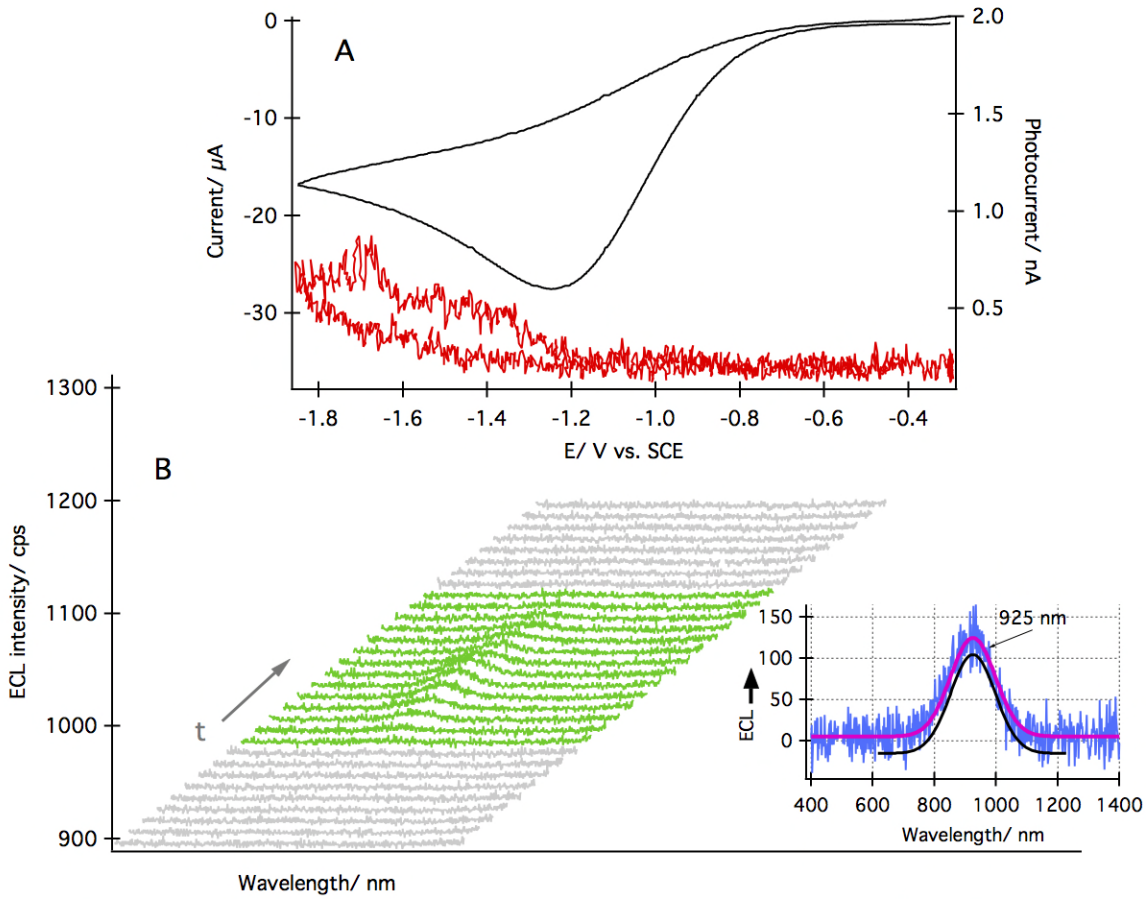

Figure S12. (A) ECL-voltage curve for 0.1 mM Au_{25}^- in the presence of 2.5 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.

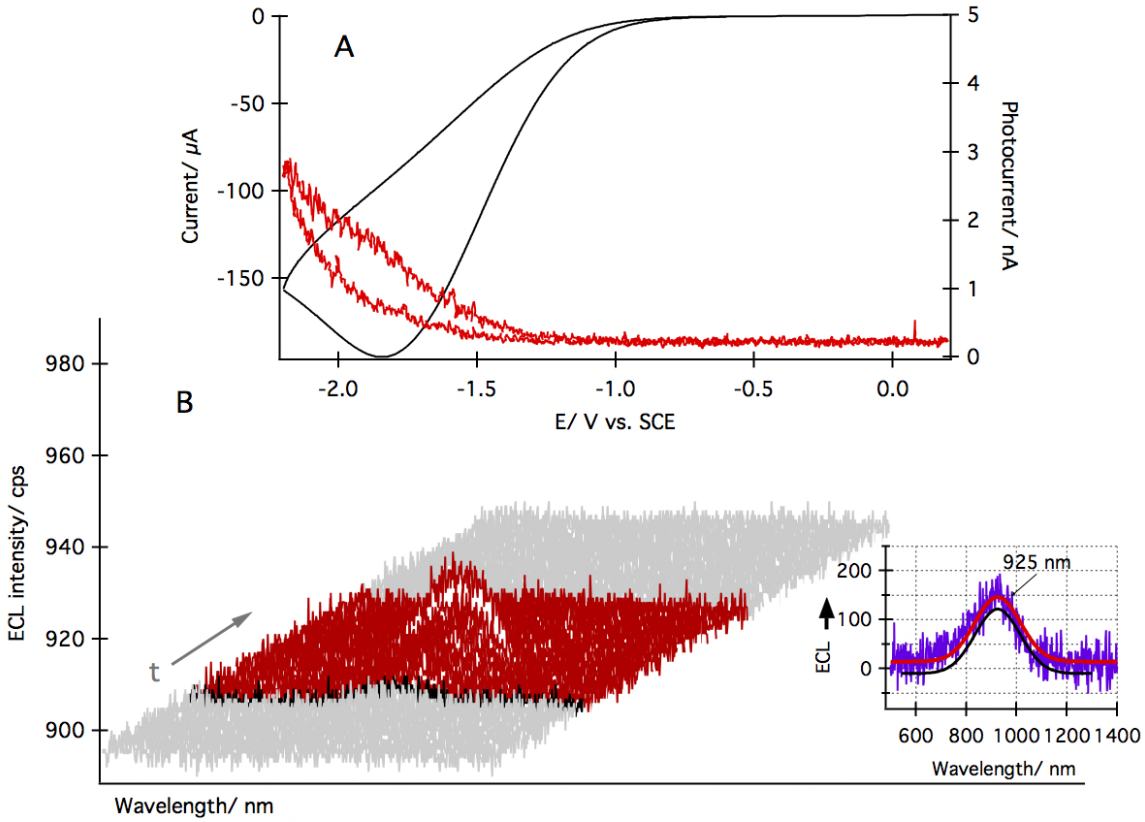

Figure S13. (A) ECL-voltage curve for 0.1 mM Au_{25}^- in the presence of 25 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.

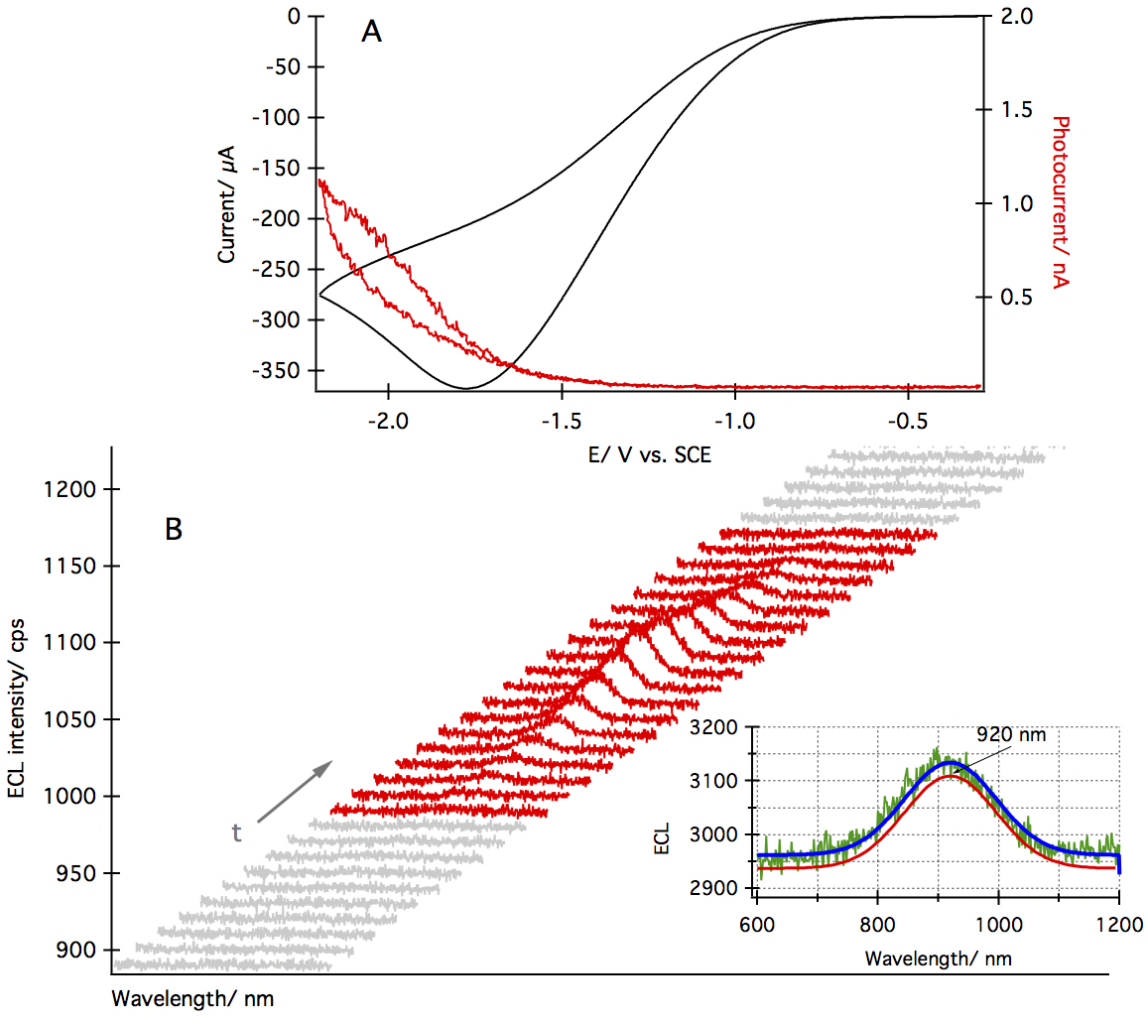

Figure S14. (A) ECL-voltage curve for 0.1 mM Au_{25}^- in the presence of 50 mM benzoyl peroxide (BPO), recorded in 1:1 acetonitrile: benzene, containing 0.1 M TBAP. The scan rate was at 0.1 Vs^{-1}. (B) Spooling ECL spectra of the same solution mixture during 62 s as the potential scanning. The inset shows accumulated spectrum. An Andor BR-DD CCD camera (cooled at -65°C) was used.

Table S1. ECL efficiencies of the Au_{25}^-/TPrA system with various TPrA concentrations relative to those of the $Ru(bpy)_3^{2+}$/TPrA with the corresponding TPrA concentrations.[1]

[TPrA]/ mM	eff. by PMT / %	eff. by camera/ %
6.3	0.0013	2.9
12.5	0.0005	4.0
25	0.0045	7.4
50	0.0156	68.3
100	0.0203	111
200	1.8601	114

Table S2. ECL efficiencies of the Au_{25}^{-}/BPO system with various BPO concentrations relative to those of the $Ru(bpy)_3^{2+}$/BPO with the corresponding BPO concentrations.

[BPO]/ mM	eff. by PMT/ %	Eff. by Camera/%
2.5	0.0019	3.8
5	0.03	32.0
25	0.000010	0.022
50	0.0012	0.5

As an example, ECL efficiency values were calculated by integrating ECL-voltage curves and the corresponding cyclic voltammogram, and comparing the integrated ECL intensities (equivalent to the number photons) and the current values (charges) of the Au_{25}^{-}/TPrA samples with those of the reference $Ru(bpy)_3^{2+}$/TPrA during the ECL experiments. The quantum yield was calculated using the below equation:

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

where Φ is the quantum yield (%) relative to the $Ru(bpy)^{2+}$/TPrA, ECL is the ECL intensity, current is the electrochemical current value, St is the standard (the $Ru(bpy)^{2+}$/TPrA) and x is the sample (the Au_{25}^{-}/TPrA). Table S1 shows calculated values for each TPrA concentration.[1]

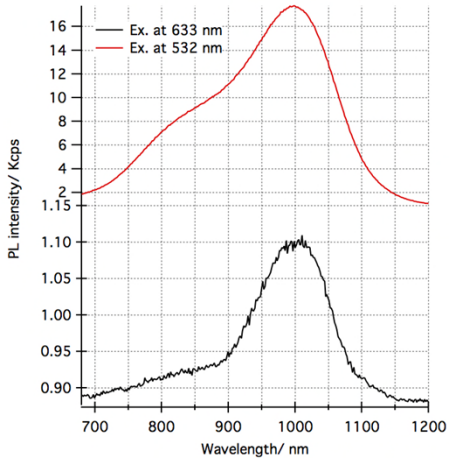

Figure S15. Photoluminescence spectra of 0.1 mM solution of Au_{25}^{-} in acetonitrile: benzene excite with 532 nm (red curve) and 633 nm (black curve) laser sources. The spectra clearly show the effect of the excitation wavelength on the photoluminescence intensity, while the peak wavelength remained the same.

The R980 PMT detector does not respond well after 830 nm (less than 0.1% in QE, Figure S15) for the Au clusters, while it has a high QE of 7.5% for $Ru(bpy)_3^{2+}$ emission at 650 nm. The ECL efficiency for the Au_{25}^-/TPrA co-reactant system relative to that for the $Ru(bpy)_3^{2+}$/TPrA is then underestimated.

It is fortunate to see that the Andor iDUS BR-DD CCD camera has very similar response for both the $Ru(bpy)_3^{2+}$ (emission at 650 nm) and Au_{25}^- (emission at 900-950 nm) (red in Figure 16). The ECL quantum yields measured by the camera and Acton spectrograph set are more reliable.

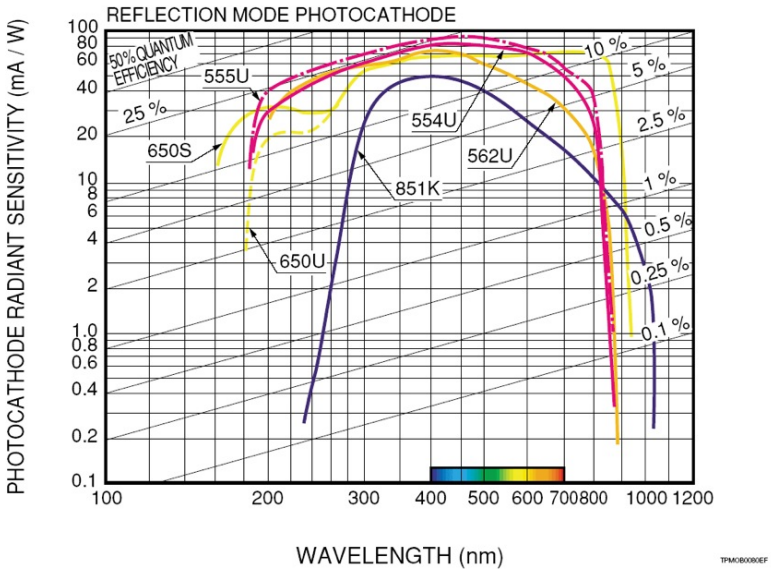

Figure S16. The spectral response curve, 562U for Hamamatsu R928 PMT used in our PL spectrometer.

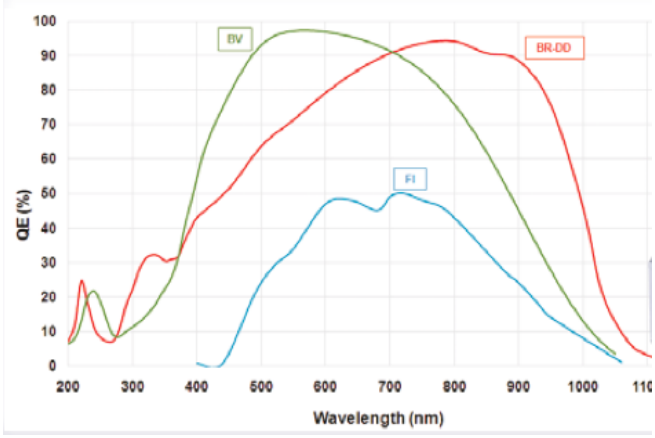

Figure S17. The iDus CCD camera response curve (BR-DD, red).

1. K. N. Swanick, M. Hesari, M. S. Workentin and Z. Ding, *J. Am. Chem. Soc.*, 2012, **134**, 15205-15208.