# Electronic Supplementary Information

## Electrogenerated Chemiluminescence at 9,10-Diphenylanthracene/ Polyvinyl Butyral Film Modified Electrode with Tetraphenylborate Coreactant

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## Homogeneous ECL of $Ru(bpy)_3^{2+}$/TPB system

Study of ECL in system $Ru(bpy)_3^{2+}$ - $TPB^-$ shows essential influence of fluorophore-coreactant complex formation and its precipitation. Fig. S1.a shows the effect of adding $Ru(bpy)_3^{2+}$ into 30 µM solution of TPB in phosphate buffer (PB, 0.1 M, pH=5) on electrochemical response of the system at glassy carbon disk electrode. As it is seen from the figure, upon addition of $Ru(bpy)_3^{2+}$ the amplitude of TPB oxidation current essentially reduces. When concentration of added $Ru(bpy)_3^{2+}$ corresponds to 0.1 of TPB the peak of TPB oxidation current decreases about 1.6 times suggesting stoichiometry of $Ru(bpy)_3^{2+}$ - $TPB^-$ complex above 1:3 whereas potential of oxidation peak increases about 60 mV.

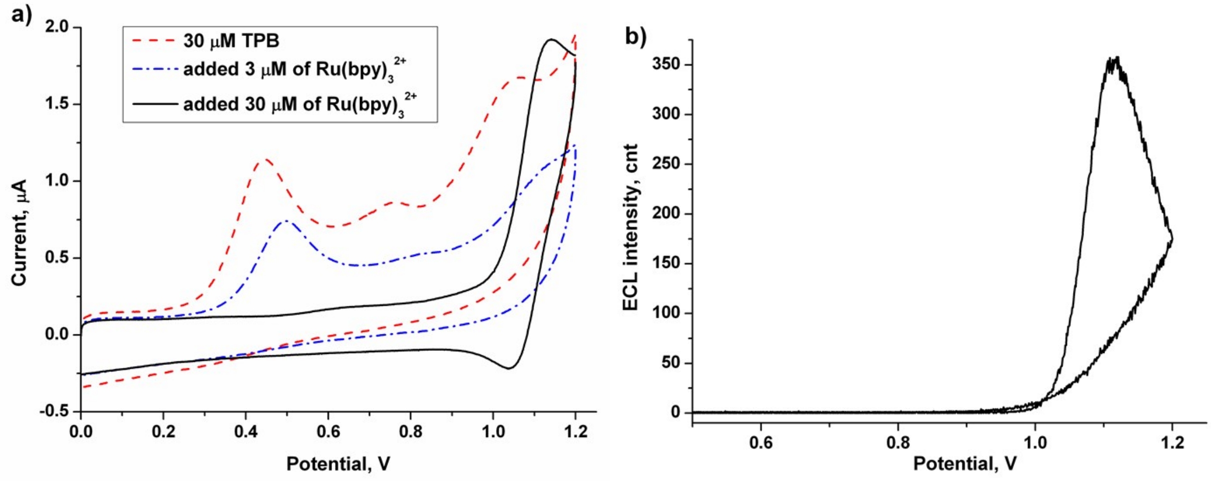

**Figure S1.** a) Effect of $Ru(bpy)_3^{2+}$ addition on cyclic voltammogram of TPB/$Ru(bpy)_3^{2+}$ system: dash line - 30 µM of TPB, dash-dot line - after adding 3 µM of $Ru(bpy)_3^{2+}$; solid line - after adding 30 µM of $Ru(bpy)_3^{2+}$. b) ECL response of system: 30 µM of $Ru(bpy)_3^{2+}$, 30 µM of TPB. Supporting electrolyte - 0.1 M PBS, pH=5, scan rate 100 mV/s.

As it was previously shown, the ECL reaction of $Ru(bpy)_3^{2+}$ with TPB occurs according to oxidative reduction mechanism. The raise of ECL emission corresponds to start of $Ru(bpy)_3^{2+}$ oxidation at the electrode (Fig. S1.b). At the same time due to formation of water insoluble complex the ECL response of this system has saturation at rather low fluorophore and coreactant concentrations (see Fig. S2). The background ECL emission from $Ru(bpy)_3^{2+}$ commonly attributed to reaction with $OH^-$ essentially limits possibility to detect TPB at low concentrations and narrows applicable pH range.[2]

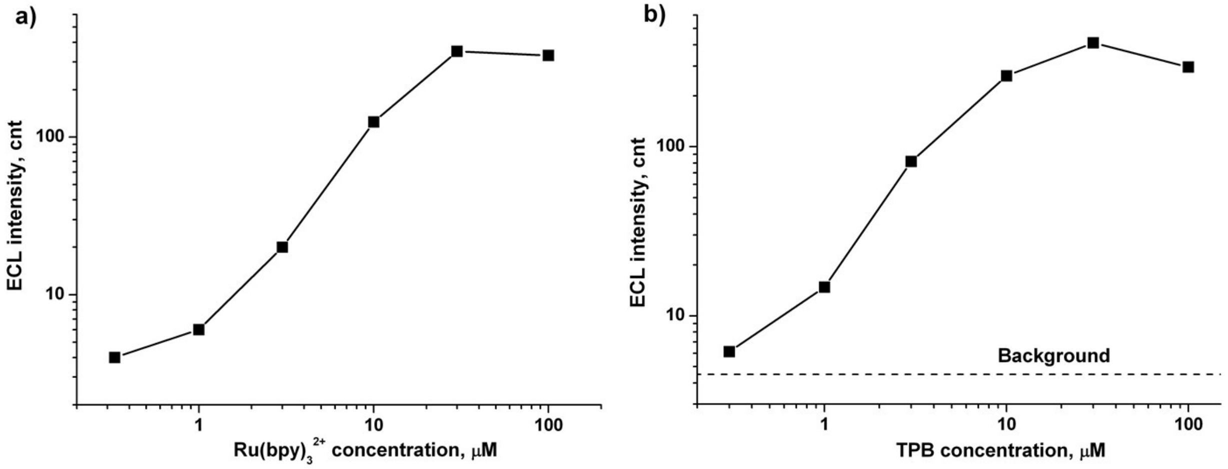

**Figure S2.** Dependence of peak ECL intensity of $Ru(bpy)_3^{2+}$ /TPB system (a) versus $Ru(bpy)_3^{2+}$ concentration when TPB concentration is 30 μM; (b) versus TPB concentration when $Ru(bpy)_3^{2+}$ concentration is 50 μM. Supporting electrolyte 0.1M PB, pH=5, scan rate 100 mV/s.

## ECL in Rubrene/PVB films with TPB coreactant

Experiments with rubrene incorporation into PVB film show that its fluorescence efficiency and redox activity is strongly affected by its environment. While batch solution of rubrene in toluene has saturated orange color and visible fluorescence when illuminated by daylight, its mixing with PVB/Ethanol solution is causing apparent decay of fluorescence ability in comparison to DPA. Further storage of rubrene/PVB mixed solutions was causing much stronger bleaching of rubrene within several days. Background CV curves of rubrene modified electrodes do not show any visible sighs of its electro oxidation in conditions where DPA do (as shown in the inset of Fig. 1). ECL response of 5% rubrene/PVB film (Fig. S3) in comparison with similar DPA containing film is much weaker. Its ECL wave is much broader than the one of DPA while the onset of emission occurs before that of DPA that coincides well with their oxidation potentials in aprotic solvents and poly(methyl methacrylate) films.[3,4] The green-orange spectra of observed emission confirms the emitting species are rebrene molecules (see inset of Fig. S3).

At the same time a distinct peak of ECL emission is present at the same potential as in DPA containing films (about 1.64 V). This potential is too high to be considered as a result of rubrene dication formation.[1] Thus such observation forces us to suggest that the second ECL wave is associated with the third oxidation wave of TPB (apparent peak at about 1.7V) while rubrene and DPA serve as efficient light emitters excited due to energy transfer process from some highly energetic species.

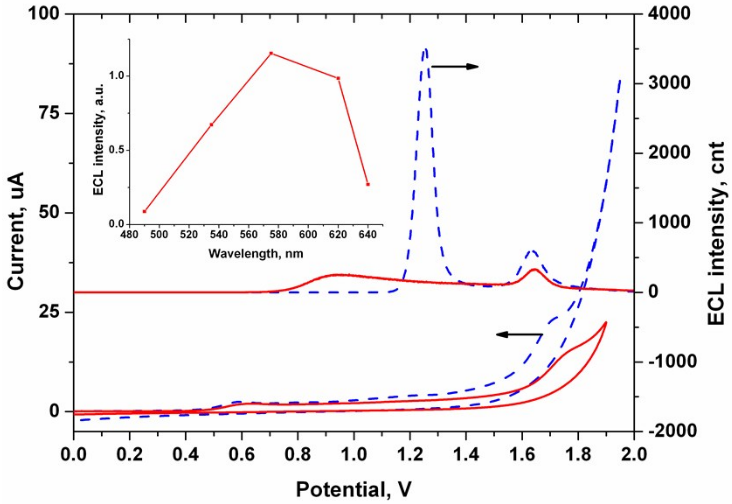

**Figure S3.** Cyclic voltammogram and ECL of 5% DPA/PVB film (blue dashed line) and 5% rubrene/PVB film (red solid line), coreactant - 100 μM TPB. Scan rate - 100 mV/s. Inset: ECL spectra of rubrene/PVB films.

### Electrochemistry of hypochlorite ion and hydrogen peroxide

Comparison of oxidation of hypochlorite ion and hydrogen peroxide (3mM each) on GC and PVB/DPA modified electrodes (Fig.S4) shows that due to essential potential shift of all redox processes in film modified electrodes the oxidation rate of both species is essentially reduced at potential used for pulsed ECL excitation (1.3V). Even higher potential shift will probably occur in the presence of TPB coreactant due to electrode fouling (as observed in Fig.2).

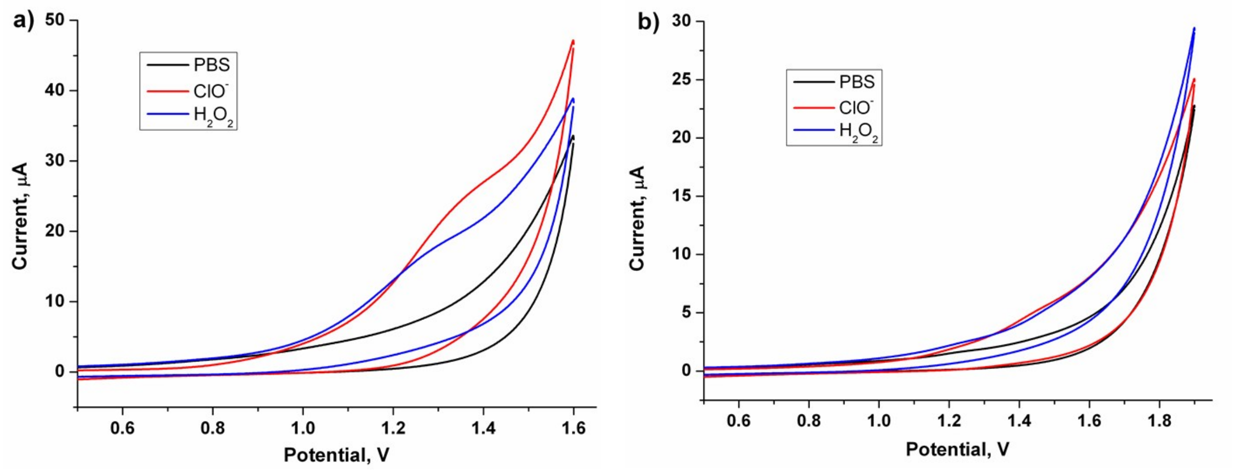

**Figure S4.** Cyclic voltammograms of 3mM hypochlorite ion (red), 3mM hydrogen peroxide (blue) and PBS background (black) on GC electrode (a) and 5% DPA/PVB film modified electrode (b). Scan rate - 100 mV/s.

## References

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