## Electronic Supplementary Information

# Electrochemilumnescent analysis of tryptophan in aqueous solutions based on its reaction with tetraphenylborate anion

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**Optimization of experimental conditions for tryptophan detection**

The following experimental parameters were optimized to find optimal conditions for ECL detection of Trp in reaction with TPB co-reactant: co-reactant concentration, potential pulse duration, and amplitude. Both peak ECL value and the integral over the pulse period were considered as possible analytical data. Considering the evolution of ECL response from pulse to pulse (Fig.4), we used the average value of light response during the first 5 pulses as a reported value both for peak and integral of ECL emission.

Figure S1 shows the effect of pulse potential applied to the working electrode. The peak of ECL response grows uniformly with the increase of the applied potential while the pulse integral quickly reaches a plateau, i.e. the amplitude of ECL response increases while its duration reduces, so a shorter pulse is observed. At potential as high as 1.4 V, a growth of background emission from TPB itself occurs, as it was shown before.[1, 2] The background emission was attributed to the formation of a fluorescent film on the electrode surface that participates in redox processes (oxidation) and further reacts with TPB in solution. Thus the potential of pulses of 1.3 V was used in further measurements.

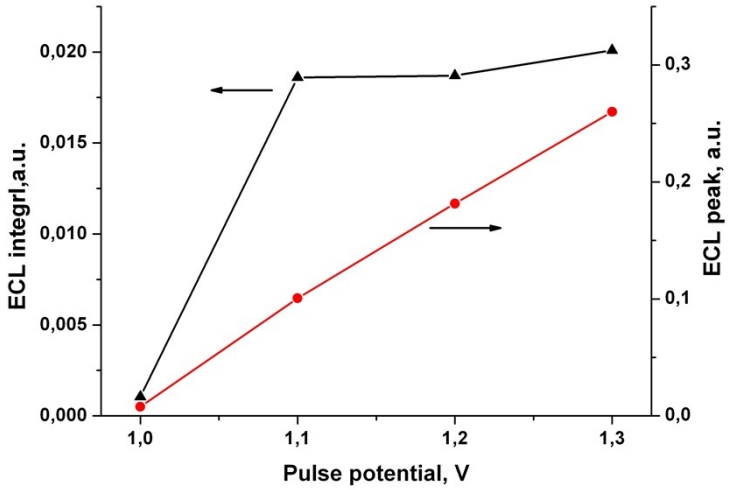


**Figure S1.** Effect of pulse potential on the ECL response. 0.03 mM of Trp, 1 mM of TPB, pulse duration - 0.5 s.

Another important parameter affecting the observed ECL response is the co-reactant concentration (Fig. S2). As it is seen from the figure, both signals (peak and integral values) have a maximum in the range of 1-2 mM. Here we used 2 mM of co-reactant to build a calibration plot.

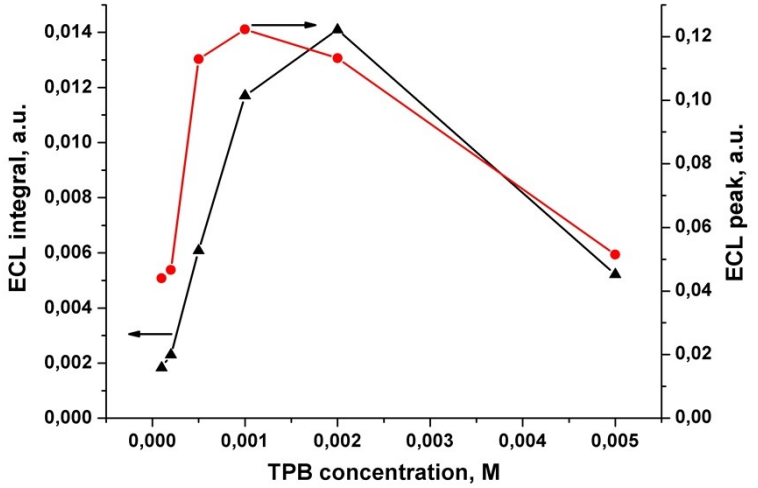


**Figure S2.** Effect of TPB co-reactant concentration on the ECL response. 0.03 mM of Trp, pulse amplitude - 1.3V, pulse duration - 0.5s.

The duration of excitation pulses mostly affects the rate of ECL amplitude decay between the pulses that is likely caused by the electrode fouling. At the same time, the overall amount of ECL emission (the integral) within the pulses remains essentially the same for electrode pulses in the range of 0.1 - 1s (see Fig. S3). It was also found that shorter excitation pulses provide a lower value of the Trp detection limit when Trp concentration is below 1 µM. That is due to a higher signal to noise ratio of the averaged ECL response during the first 5 pulses. Thus 0.1 s pulses were selected for making the calibration plot of Trp determination.

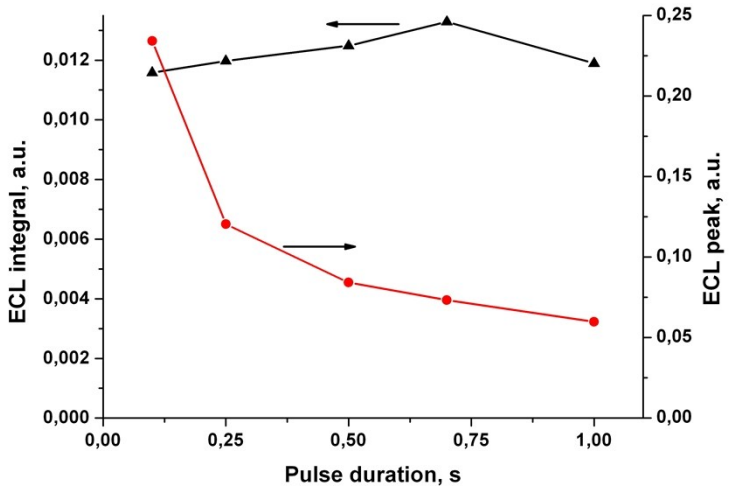


**Figure S3.** Effect of pulse duration on the ECL response. 0.03 mM of Trp, 2 mM of TPB, pulse amplitude - 1.3V.

**Filters used for estimation of tryptophan ECL spectrum**

Spectroscopic study of ECL emission in Trp-TPB system, presented in Fig. 7, was done using a set of colored glass filters (50*50 mm square glass slides). The transmission band for each spectral point was obtained by using either a single glass filter or a combination of a couple of filters (Fig. S4, solid lines). Filters were placed between the bottom of the ECL cell and the PMT window. The result of each ECL measurement was normalized for the integral filter's transmittance and the spectral sensitivity of PMT photocathode at the central wavelength of the appropriate filter (Fig. S4, dash line). The boundaries of spectral bands in Fig. 7 were taken at the wavelengths of intersection between appropriate filters' spectral curves normalized for their integral transmittance.

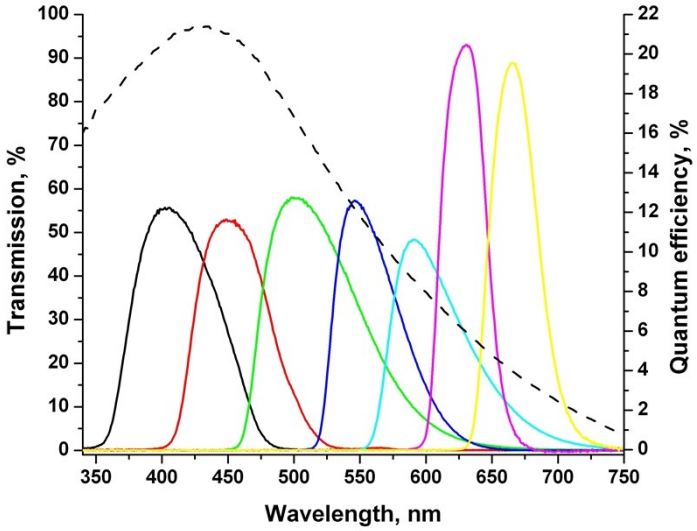


**Figure S4.** Spectral response of applied glass filters (solid lines) and quantum efficiency of PMT photocathode (dash line).

**References**

1. Y. Zholudov, O. Bilash, A. Kukoba and M. Rozhitskii, Electrogenerated Chemiluminescence in Systems with Tetraphenylborate Anion as a Co-reactant. *Analyst* **2011**, *136*, 598–604.
2. Y. Zholudov and G. Xu, Electrogenerated chemiluminescence at a 9,10-diphenylanthracene/polyvinyl butyral film modified electrode with a tetraphenylborate coreactant. *Analyst* **2018**, *143*, 3425-3432.