Electrogenerated chemiluminescence of Bis [4-(dimethylamino) phenyl] squaraine

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Experimental section

Reagents: The BDPSQ was prepared in excellent yield by the previously reported method.[S1] Precursor (the squaric acid and N, N-Dimethyaniline) were of analytical reagent grade. TBAP (tetrabutylammonium perchlorate), $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) were of electrochemistry reagent grade obtained from Alfa Aesar China Co.,Ltd, All other reagents (DMF, $CHCl_3$) were of analytical reagent grade and were used before further purification.

ECL measurement: ECL and electrochemical measurements were performed at an electrochemical working station V-MP3 (Princeton Applied Research Co. Ltd., USA). ECL signals were recorded by an Ultra-weak Chemiluminescence Analyzer (BPCL-K, Institute of Biophysics, Academia Silica, Beijing, China) controlled by a personal computer with 0.1 s sample interval. While collecting ECL signals, the cell was placed directly in front of the photomultiplier (PMT operated at 800V) and the PMT window was opened towards the working electrode only. Equipped with a three-electrode ECL cell, the working electrode was Pt electrode (3.0mm in diameter), the reference electrode was an Ag/AgCl (3M KCl) electrode, and the counter electrode was a Pt wire electrode. ECL spectra were measured by a series of filters of 535, 555, 575, 620, 640, 680, 705 and 750 nm (provided by Beijing Institute of Biophysics, Academia Sinica, China) before the photomultiplier tube (PMT) window and detecting the intensities of ECL passing through these filters respectively under same experimental conditions.
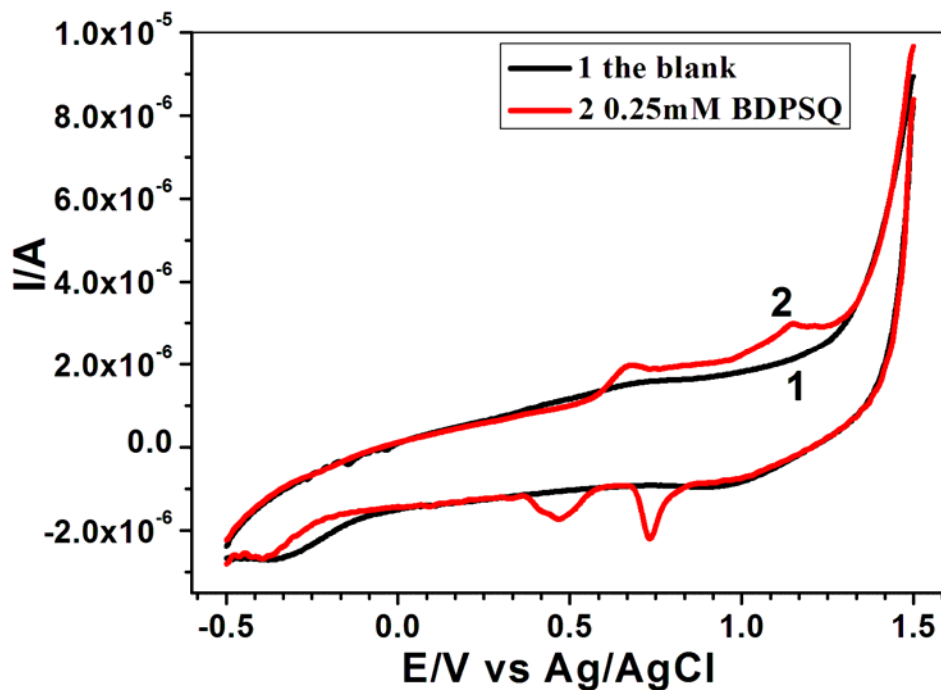
Fig. S1 Cyclic voltammogram of 0.25mM BDPSQ, in CH_2Cl_2 with 0.1M TBAP as the supporting electrolyte at Pt electrode(3.0mm), Scan rate at 60mV/s, the curve 1 is the CV of the blank.
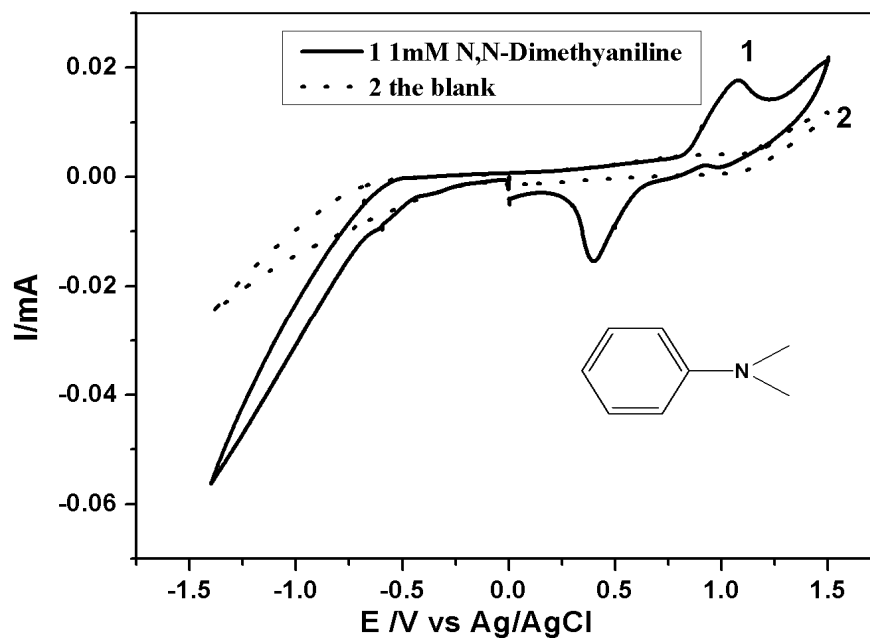

Fig. S2 Cyclic voltammogram of 1mM N, N-dimethyaniline, in $CHCl_3$ with 0.1M TBAP as the supporting electrolyte at Pt electrode, Scan rate at 50mV/s. the curve 2 is the CV of the blank.
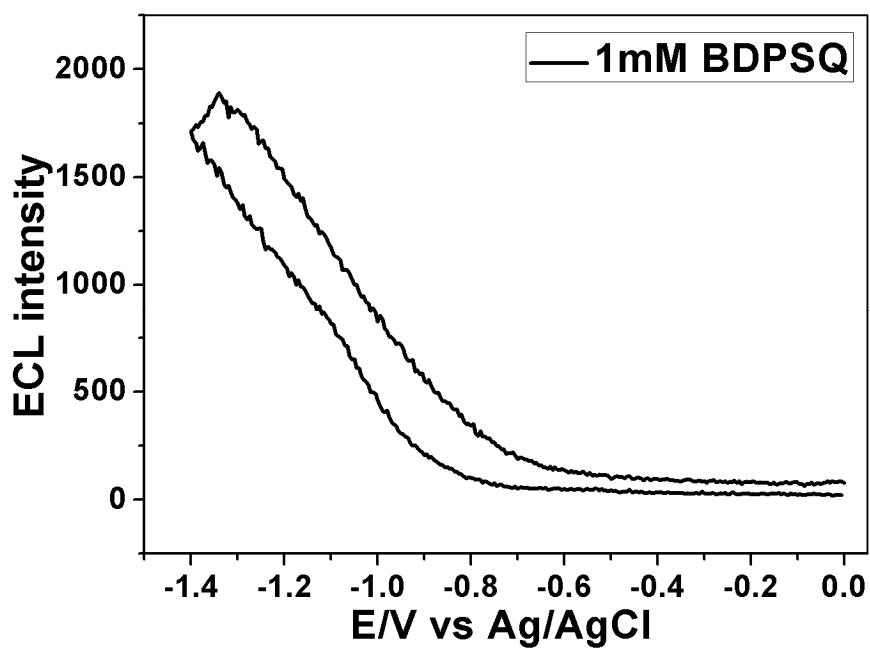
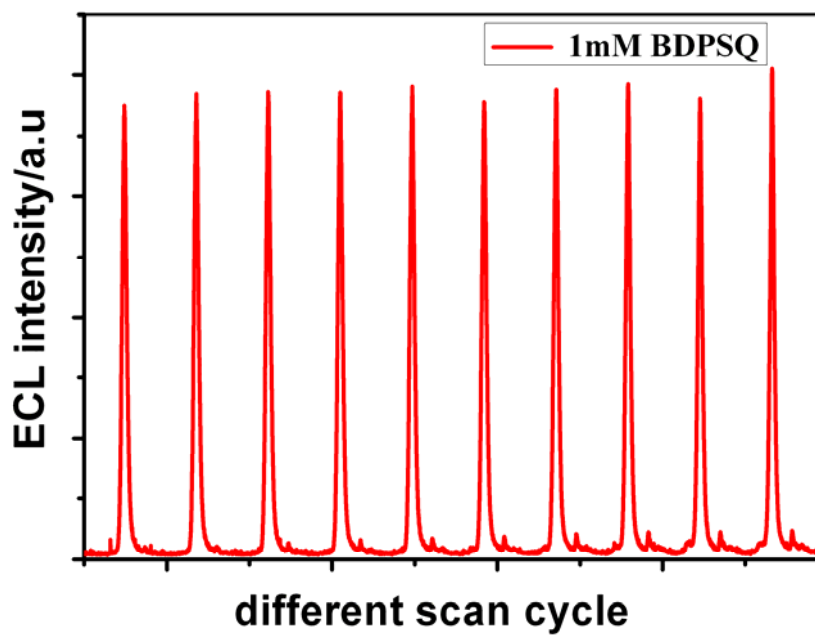**Fig. S3** ECL potential curve of BDPSQ from 0 to -1.4V at Pt electrode (φ=3.0mm) in CHCl$_3$

Fig. S4 The stability of ECL intensity scan at negative potential (-1.4-0V) with different cycles at the same electrode Pt (φ=3mm)
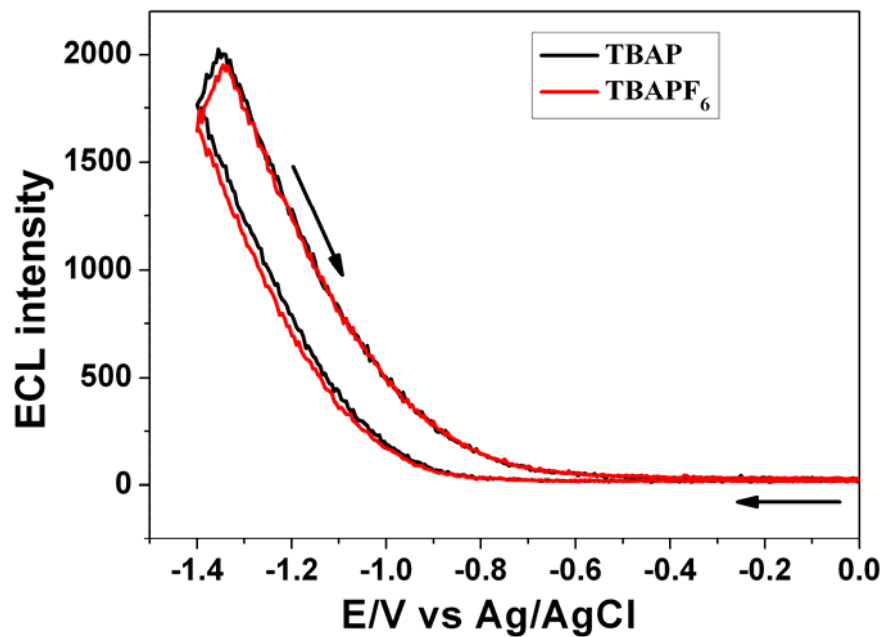
Fig. S5 The influence of different supporting electrolytes (TBAP and TAPF$_6$) to the ECL of 1mM BDPSQ.
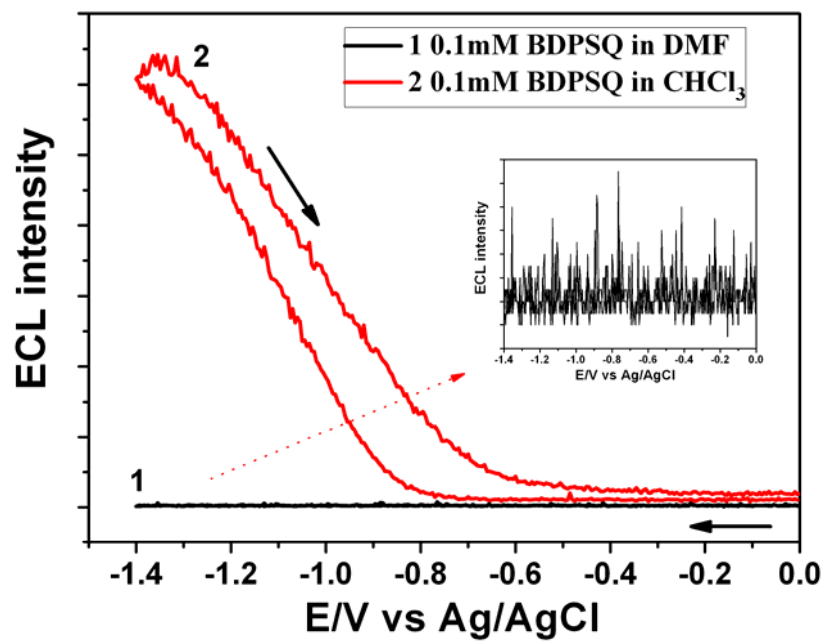

Fig. S6 The influence of different solvents (DMF and CHCl$_3$) on the ECL of 1mM BDPSQ Inset: amplified ECL of the BDPSQ in DMF solvent
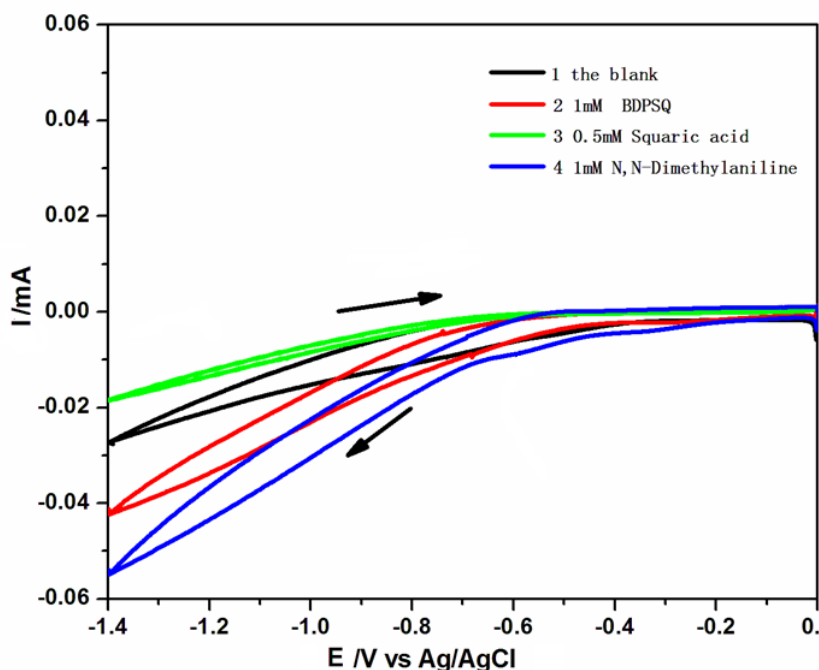
Fig. S7 Cyclic voltammograms of the blank(1) ,the BDPSQ(2) and the different precursors (the squaric acid (3) and N, N-dimethyaniline(4)) on the same condition (0.1M TBAP in CHCl$_3$ solution with scan rate 50mV/s at a Pt working electrode(3.0mm))

Discussion on the dynamics process of ECL

The detailed ECL dynamics is not easy to clarified as there's no obvious reduction peak observed due to the significant reduction current from the solvent. Therefore, it is difficult to determinate if BDPSQ is reduced by the directly electrochemical reduction (heterogeneous) or the catalytic reduction by the solvent (homogeneous).Therefore, both routes are possible here. It is also difficult to calculate the quantum yield of ECL and reation rate constant for the reduction of BDPSQ.

BDPSQ$^-$ seems to be an instable intermediate compared with BDPSQ$^+$, because of the observation of higher ECL in the a wider potential region(-1.4~1.4V), as the BDPSQ$^+$ is stable enough to annihilation with BDPSQ$^-$ in despite of the fact that most of the BDPSQ$^+$ can be electrochemical reduced as can be seen in Figure S1, while, in the positive region, no ECL is observed, suggesting that the BDPSQ$^-$ is not stable enough for the annihilation in the positive region.

For the catalytic reduction of BDPSQ, which involves the homogeneous reaction of BDPSQ and

CHCl$_3 \cdot ^-$,although the reaction CHCl$_3^-$ with BDPSQ is only occurring at an appreciable rate,

the substantial amount of CHCl$_3$(slovent) that can be significantly reduced at the electrode is likely to trigger the reaction to produce more BDPSQ$^-$ for ECL.

The formal potential of BDPSQ$^{0/-}$ and CHCl$_3^{0/-}$ is also difficult to determine, because there is no well-defined redox peaks from the CVs. Even though, there is an ECL peak observed at ca. -1.3V, it doesn't necessarily mean that is corresponding to the electrochemical reduction of BDPSQ, because the ECL process involves the homogeneous reaction, which is determined by

both the concentration of BDPSQ$^-$ by CHCl$_2$•, and some other pre- or post- reactions at the electrode.

Reference：S1. (a) A. H. Schmidt. *Synthesis*, 1980. 961; (b)G. Maahs and P. Hegenberg. *Angew. Chem. Int. Ed. Engl.*, 1966 (**5**), 888; (c) K.Y .Law and F. C Bailey. *Can. J. Chem.* 1986 (**64**), 2267.