Supporting Information

Electrogenerated chemiluminescence of the tris(2,2′-bipyridine)ruthenium(II)/aliphatic amine system: an universal effect of perchlorate salts

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EXPERIMENTAL

Chemicals. Tris(2,2'-bipyridyl)ruthenium(II) dichloride hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$, min 98%), tri-*n*-ethylamine (TEtA, 99.5%), tri-*n*-propylamine (TPrA, 98%), and tri-*n*-butylamine (TBuA, 98.5%), sodium perchlorate monohydrate ($NaClO_4 \bullet H_2O$ ≥99.0%), sodium phosphate monobasic (NaH_2PO_4, ≥99.0%), and Zonyl® FSO-100 ($F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_{0-15}H$) were purchased from Sigma-Aldrich. Other chemicals were analytical reagent graded and used as received. All solutions were prepared with deionized water (Milli Q, Millipore). The pH of the phosphate buffer solution (0.15 M) containing different amine coreactants was adjusted with concentrated NaOH or phosphoric acid.

Apparatus. The three-electrode system consisted of a working electrode, a coiled Pt wire counter electrode, and a saturated calomel electrode (SCE). Cyclic voltammetry and ECL measurements were conducted with a MPI-EII device (Xi´an Remex Analytical Instrument Co., LTD, China). For fluorescence measurements, a Hitachi Fluorescence Spectrophotometer F-7000 was used.

Procedures. A glassy carbon electrode of 3-mm-diameter and a gold electrode of 2-mm-diameter were polished mechanically with alumina slurry from 1.0 □m down to 0.05 □m, followed by sonication in distilled water for 1 min to remove debris, and were thoroughly rinsed with Milli-Q water. Before each measurement, the gold working electrode was subjected to repeated scanning in a potential range from –0.5 to 1.4 V in 0.15 M PBS (pH 7.5) until reproducible voltammograms were obtained. The modification of the gold electrode with FSO-100 was conducted by immersing the electrochemically cleaned gold electrode in 5 wt.% FSO aqueous solution for 5 min, followed by thoroughly rinsing with Milli-Q water. Solutions were deaerated by bubbling Ar of high purity (99.995%), and a constant flow of Ar was maintained over the solution during ECL measurements. Scan rates for the cyclic voltammetry measurements were all set to 100 mV/s. Reported values for the amine oxidation currents and ECL intensities were based upon the average of at least three scans with a relative standard deviation (RSD) of ±10%. All potentials reported in this paper were referred to the SCE. All experiments were performed at 20 ± 2 °C.

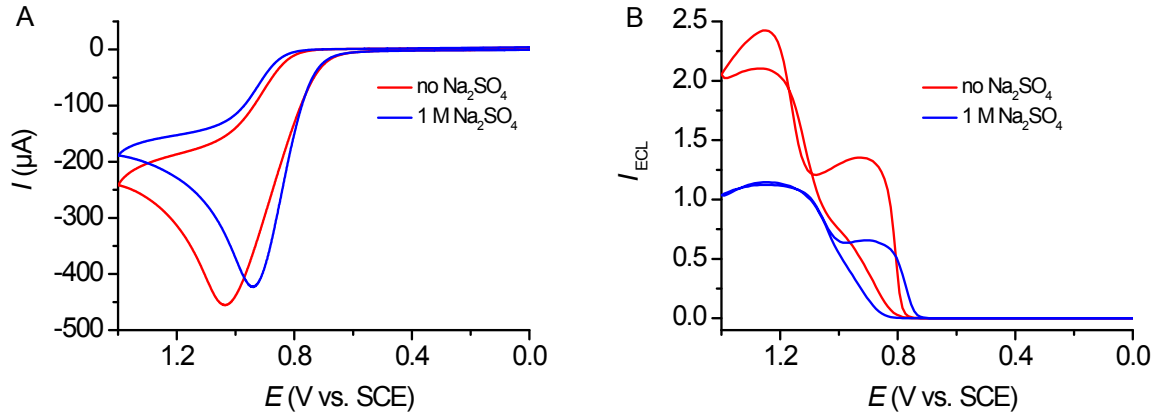

Figure S1. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 100 mM TPrA in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M Na_2SO_4. Electrode, glass carbon.

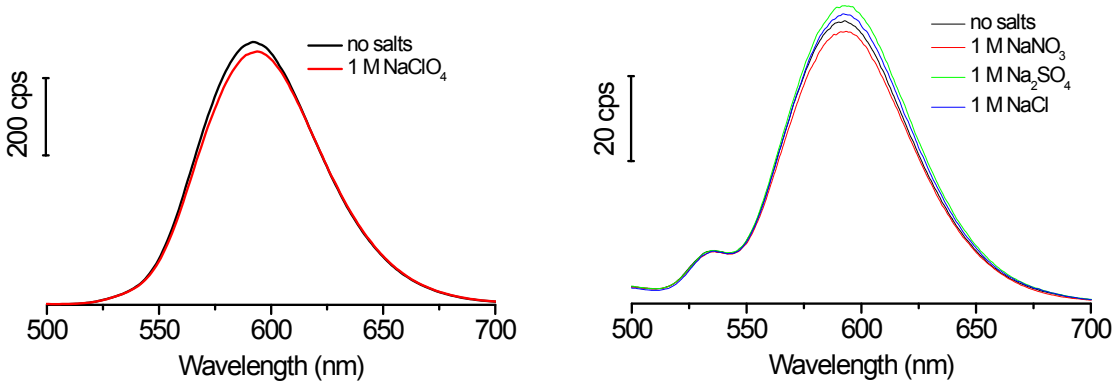

Figure S2. (A) Fluorescence spectra of 10 μM $Ru(bpy)_3^{2+}$ without and with 1 M added $NaClO_4$ in 0.15 M phosphate buffer at pH 7.5. (B) Fluorescence spectra of 1 μM $Ru(bpy)_3^{2+}$ without and with 1 M added $NaNO_3$, Na_2SO_4 and NaCl in 0.15 M phosphate buffer at pH 7.5. Similar phenomena were observed in phosphate buffer solution of different pH, or with further addition of TPrA.

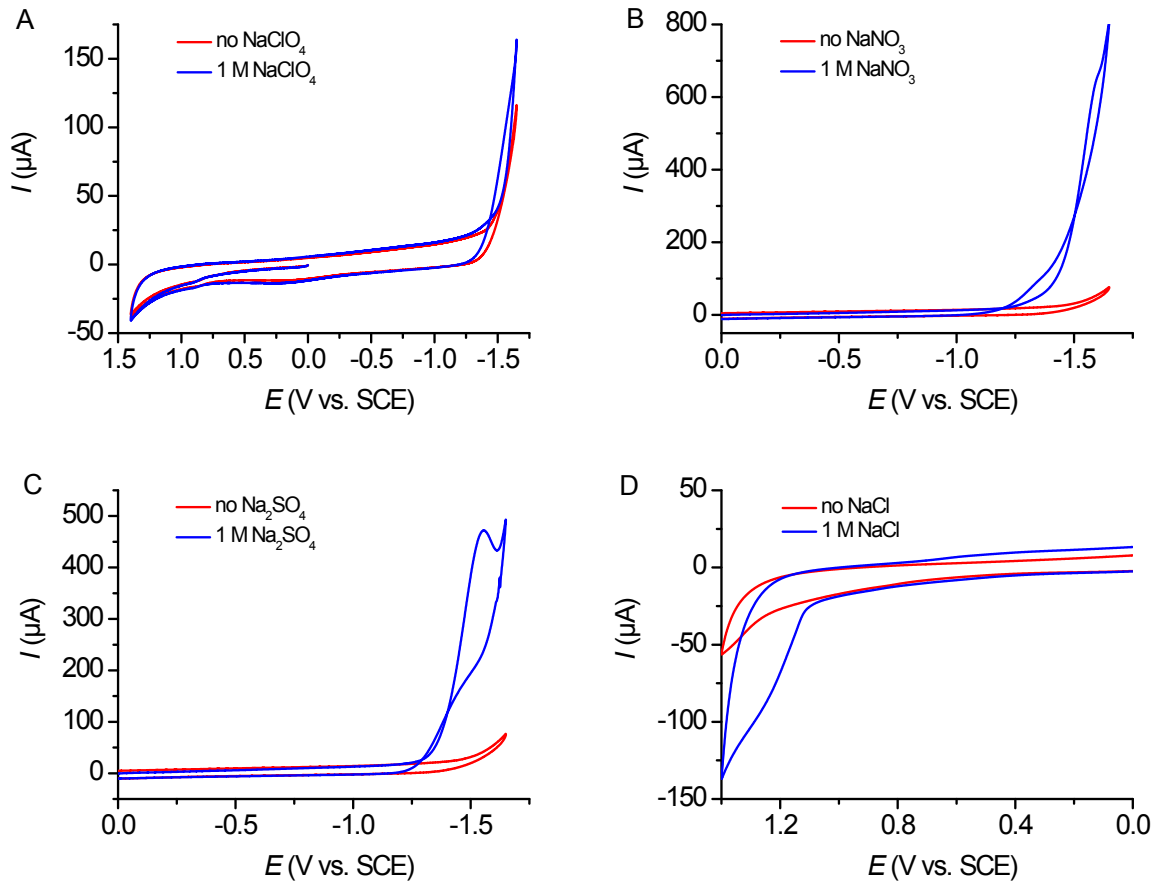

Figure S3. CVs of a glassy carbon electrode in 0.15 M phosphate buffer at pH 7.5 without (red) and with (blue) 1 M added $NaClO_4$, $NaNO_3$, Na_2SO_4 and NaCl. Scan rate, 100 mV/s. The solution was degassed to remove oxygen prior to CV measurements.

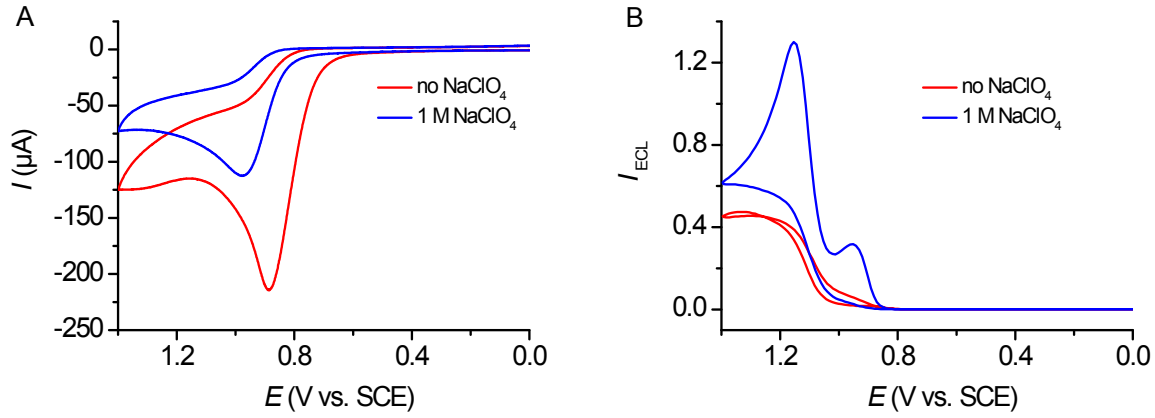

Figure S4. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 10 mM TBuA in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M $NaClO_4$. Electrode, glass carbon.

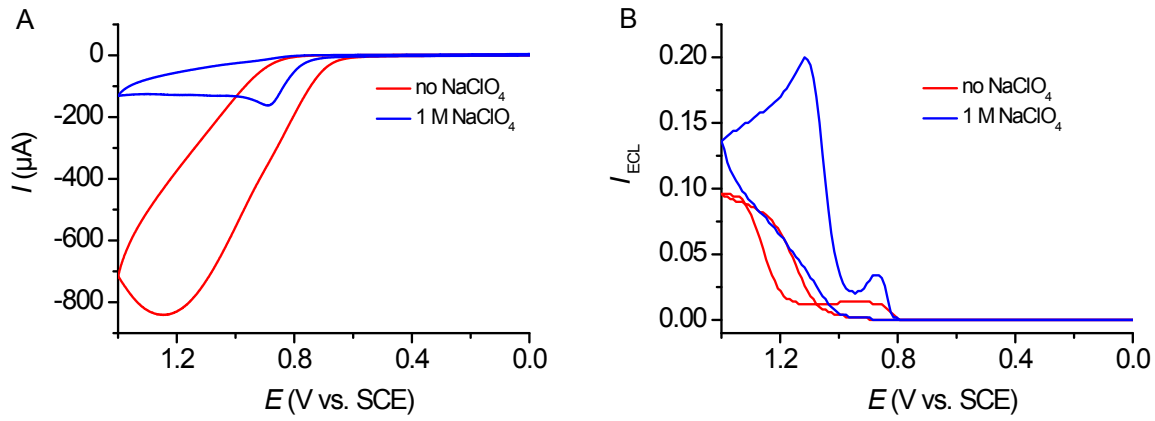

Figure S5. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 100 mM 2-(dibutylamino)ethanol in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M $NaClO_4$. Electrode, glass carbon.

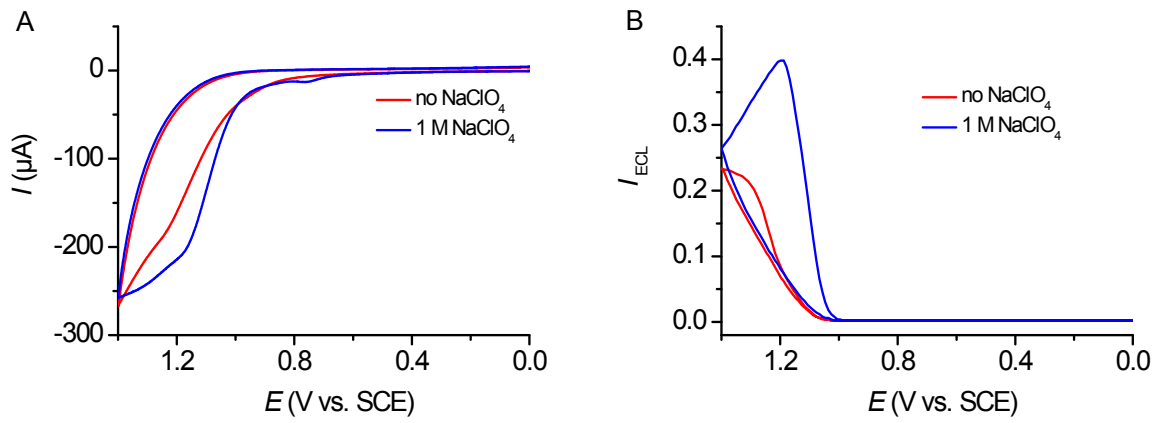

Figure S6. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 100 mM butyl(ethanol)amine in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M $NaClO_4$. Electrode, glass carbon.

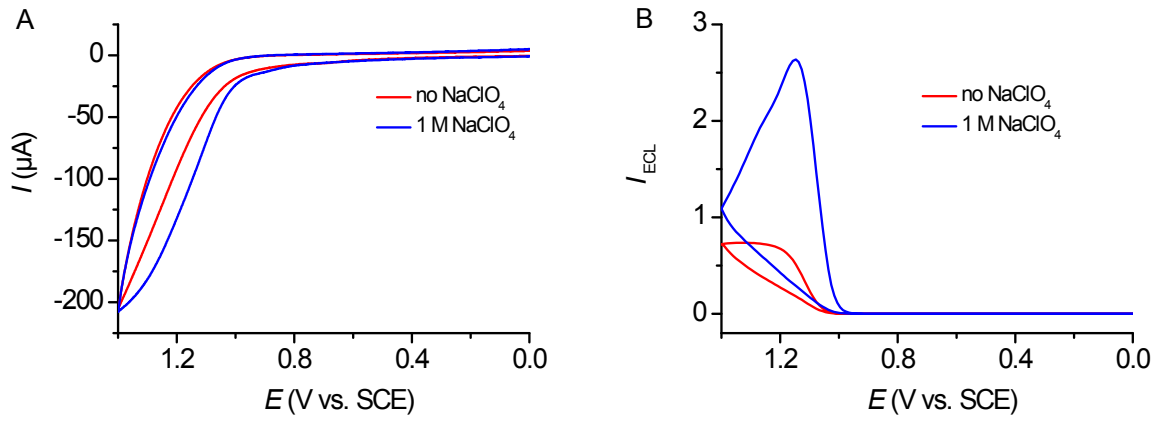

Figure S7. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 100 mM dipropylamine in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M $NaClO_4$. Electrode, glass carbon.

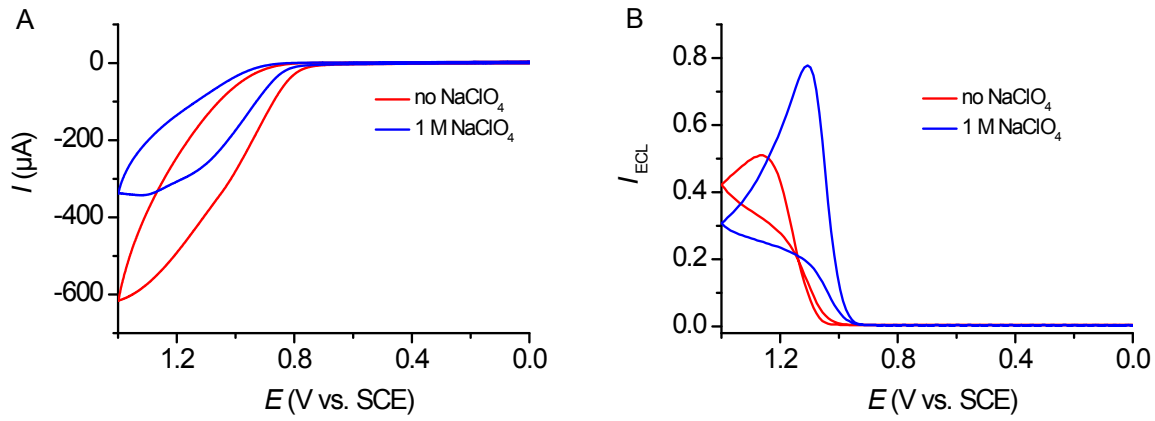

Figure S8. (A) CV and (B) ECL curves for 1 μM $Ru(bpy)_3^{2+}$ and 100 mM tri-*n*-methylamine in 0.15 M PBS at pH 7.5 without (red) and with (blue) 1 M $NaClO_4$. Electrode, glass carbon.