

## Electronic Supplementary Information

### Detection of ozone based on its striking inhibition of tris(1,10-phenanthroline)ruthenium(II)/glyoxal electrochemiluminescence

Wenjing Qi,<sup>a,b</sup> Zhongyuan Liu,<sup>a</sup> Jianping Lai,<sup>a,b</sup> Wenyue Gao,<sup>a,b</sup> Xiaoyun Liu,<sup>a,b</sup> Min Xu,<sup>a,b</sup>  
and Guobao Xu<sup>\*,a</sup>

<sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China. Fax: +86 431 85262747; Tel: +86 431 85262747; E-mail: guobaoxu@ciac.ac.cn

<sup>b</sup> University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, PR China.

\*Corresponding author: Prof. G. B. Xu

### Experimental Section

**Chemicals and materials.** Tris(1,10-phenanthroline)ruthenium(II) ( $\text{Ru}(\text{phen})_3^{2+}$ , 98%) and tripropylamine were purchased from Sigma-Aldrich. Glyoxal and oxalate were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China), respectively. Ozone was obtained by an FMC900 ozone generator (BEYOK ozone, Zhejiang, China). Ozone solutions were prepared in ice water to keep the stability of ozone in solutions, and the concentrations were determined by UV absorption ( $\lambda_{\text{max}} = 258 \text{ nm}$ ;  $\varepsilon \approx 3000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).<sup>1-3</sup> Other chemicals were analytical-reagent grade and used as received. Doubly distilled water was used throughout all experiments. 50 mM phosphate buffer solutions of pH 10.0 were used for ECL detection.

**Apparatus.** Electrochemical experiments were performed with CHI 660C electrochemistry workstation (Shanghai CHI Instruments Co., China). ECL intensities were monitored through the bottom of three-electrode cell with a BPCL ultra-weak luminescence analyzer, which was purchased from the institute of biophysics, Chinese academic of sciences. Unless otherwise noted, the photomultiplier tube voltage is kept

at 1000 V. A glassy carbon working electrode ( $\Phi = 3$  mm), an Ag/AgCl reference electrode (saturated KCl), and a platinum wire counter electrode were used through electrochemical and ECL experiments. The glassy carbon electrode was polished with 0.3  $\mu\text{m}$  alumina and then cleaned with ultrapure water in an ultrasonic bath prior to each use. Fluorescent emission spectra were recorded using a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France) with an excitation wavelength of 450 nm. Excitation and emission slit widths were both 7 nm.

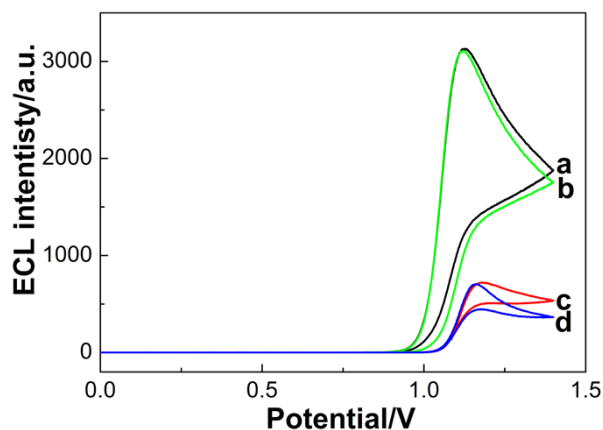
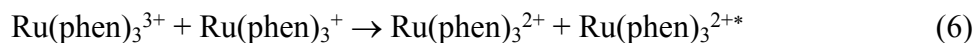
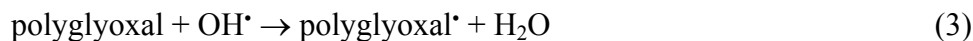
**Procedure of ozone detection.** 50  $\mu\text{L}$  of 100 mM glyoxal, different concentrations of ozone solutions, 500  $\mu\text{L}$  of 0.2 M phosphate buffer solutions (pH 10.0), 100  $\mu\text{L}$  of 5 mM  $\text{Ru}(\text{phen})_3^{2+}$  and an appropriate amount of water were pipetted into a 1.0 mL plastic tube to keep the whole volume of 1 mL. Then the mixture was vortex-mixed and applied for ECL detection after 1 min.

**Ozone detection in indoor air samples.** Firstly, 0.5 mL of 100 mM glyoxal and 5 mL of 0.2 M phosphate buffer solutions (pH 10.0) were injected into a 50 mL plastic tube. Then the plastic tube was put in a ventilated photocopy room containing five multifunctional printers and kept there for eight hours. Finally, the sample was divided into several parts and diluted with water to keep the final concentration of glyoxal at 5 mM. One part was used for ECL measurement of ozone. The other parts were used for the determination of recoveries by adding given amounts of ozone into the sample solutions. All ECL measurements were carried out according to the procedures as mentioned above. The experiment was performed in triplicate.

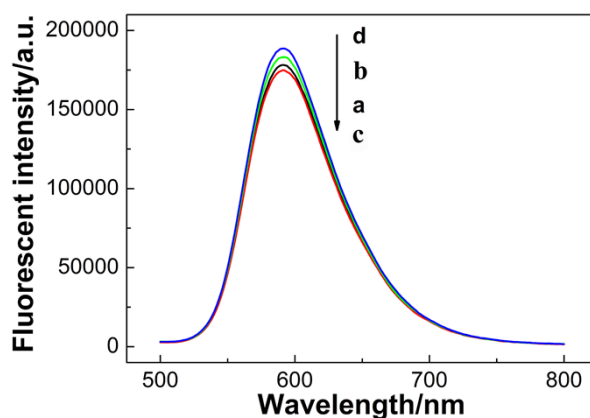
**The proposed ECL mechanism.** During ECL reaction,  $\text{Ru}(\text{phen})_3^{3+}$  and  $\text{OH}^\bullet$  are electrogenerated on electrode surface.  $\text{OH}^\bullet$  can oxidize polyglyoxal to generate polyglyoxal $^\bullet$ . The resulting polyglyoxal $^\bullet$  can react with  $\text{Ru}(\text{phen})_3^{3+}$  to generate  $\text{Ru}(\text{phen})_3^{2+*}$ . It can also react with  $\text{Ru}(\text{phen})_3^{2+}$  to generate  $\text{Ru}(\text{phen})_3^+$ , and then generated  $\text{Ru}(\text{phen})_3^+$  react with  $\text{Ru}(\text{phen})_3^{3+}$  to generate  $\text{Ru}(\text{phen})_3^{2+*}$ . In the presence of ozone, ozone may oxidize polyglyoxal and deactivate polyglyoxal, leading to the dramatic decrease in ECL in the presence of low concentrations of ozone.

Scheme.





**Fig. S1** ECL intensity–potential profiles of  $\text{Ru(phen)}_3^{2+}$ /TPA mixture solutions in the absence (curve a) and presence of ozone (curve b),  $\text{Ru(phen)}_3^{2+}$ /oxalate mixture solutions in the absence (curve c) and presence of ozone (curve d),  $c(\text{Ru(phen)}_3^{2+})$ , 0.5 mM;  $c(\text{ozone})$ , 20  $\mu\text{M}$ ;  $c(\text{TPA})$ , 0.5 mM;  $c(\text{oxalate})$ , 2 mM; Scan rate: 0.1 V/s; photomultiplier tube voltage, 700 V; 50 mM phosphate buffer solutions of pH 7.4 were used for TPA ECL system and 50 mM phosphate buffer solutions of pH 5.9 were used for oxalate ECL system.



**Fig. S2** Fluorescent spectra of  $\text{Ru(phen)}_3^{2+}$  in the absence (curve a) and presence of ozone (curve b),  $\text{Ru(phen)}_3^{2+}$ /glyoxal mixture solutions in the absence (curve c)

and presence of ozone (curve d),  $c(\text{Ru}(\text{phen})_3^{2+})$ , 0.5 mM;  $c(\text{glyoxal})$ , 5 mM;  $c(\text{ozone})$ , 20  $\mu\text{M}$ ;  $\lambda_{\text{ex}}$ , 450 nm;  $\lambda_{\text{em}}$ , 600 nm.

### References:

1. K. Xu, S. Sun, J. Li, L. Li, M. Qiang and B. Tang, *Chem. Commun.*, 2012, **48**, 684-686.
2. C. Prasse, M. Wagner, R. Schulz and T. A. Ternes, *Environ. Sci. Technol.*, 2012, **46**, 2169-2178.
3. N. M. Panich, B. G. Ershov, A. F. Seliverstov and A. G. Basiev, *Russ. J. Appl. Chem.*, 2007, **80**, 1812-1815.