

## Supplementary Information

### **A Self-Assembly Net Structure Film for Immobilization of Tris(2,2'-bipyridyl) Ruthenium(II) and Its Ultrasensitive Electrogenerated Chemiluminescent Sensing for Phenol**

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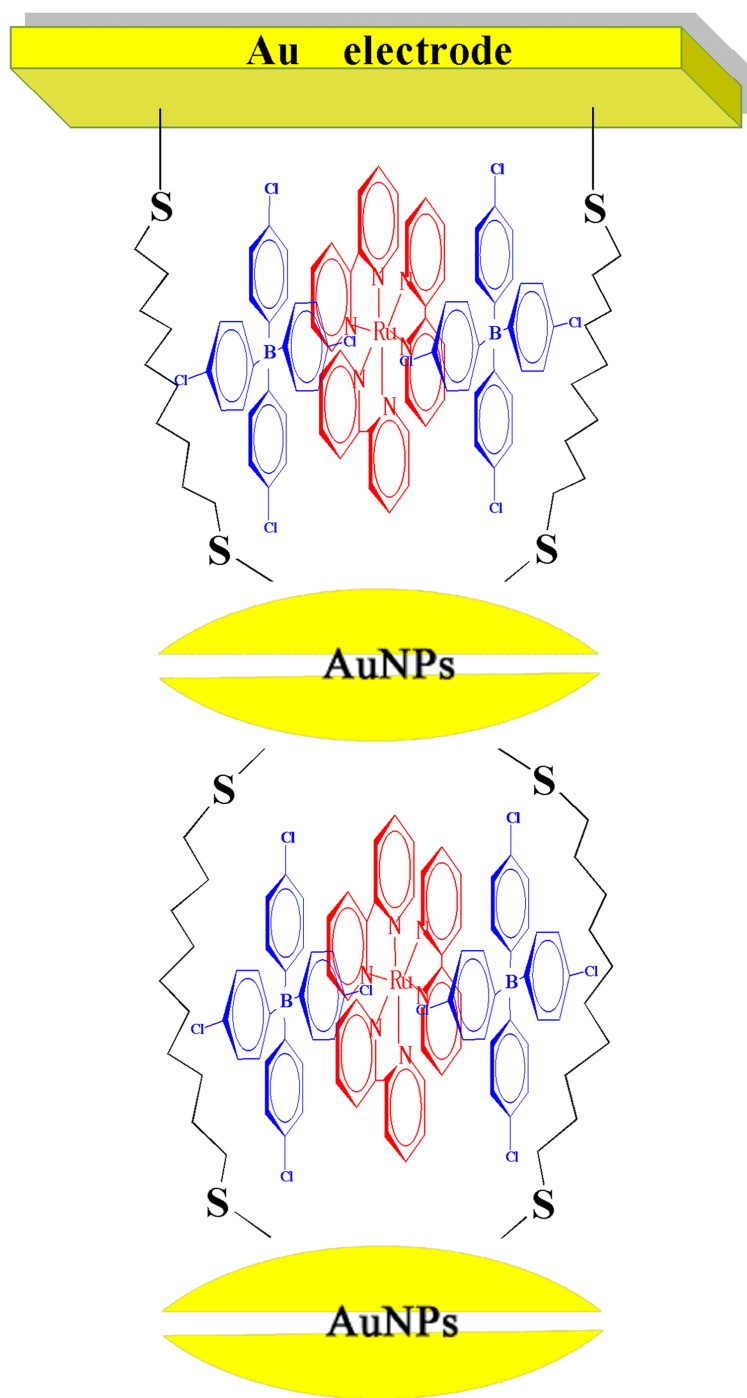
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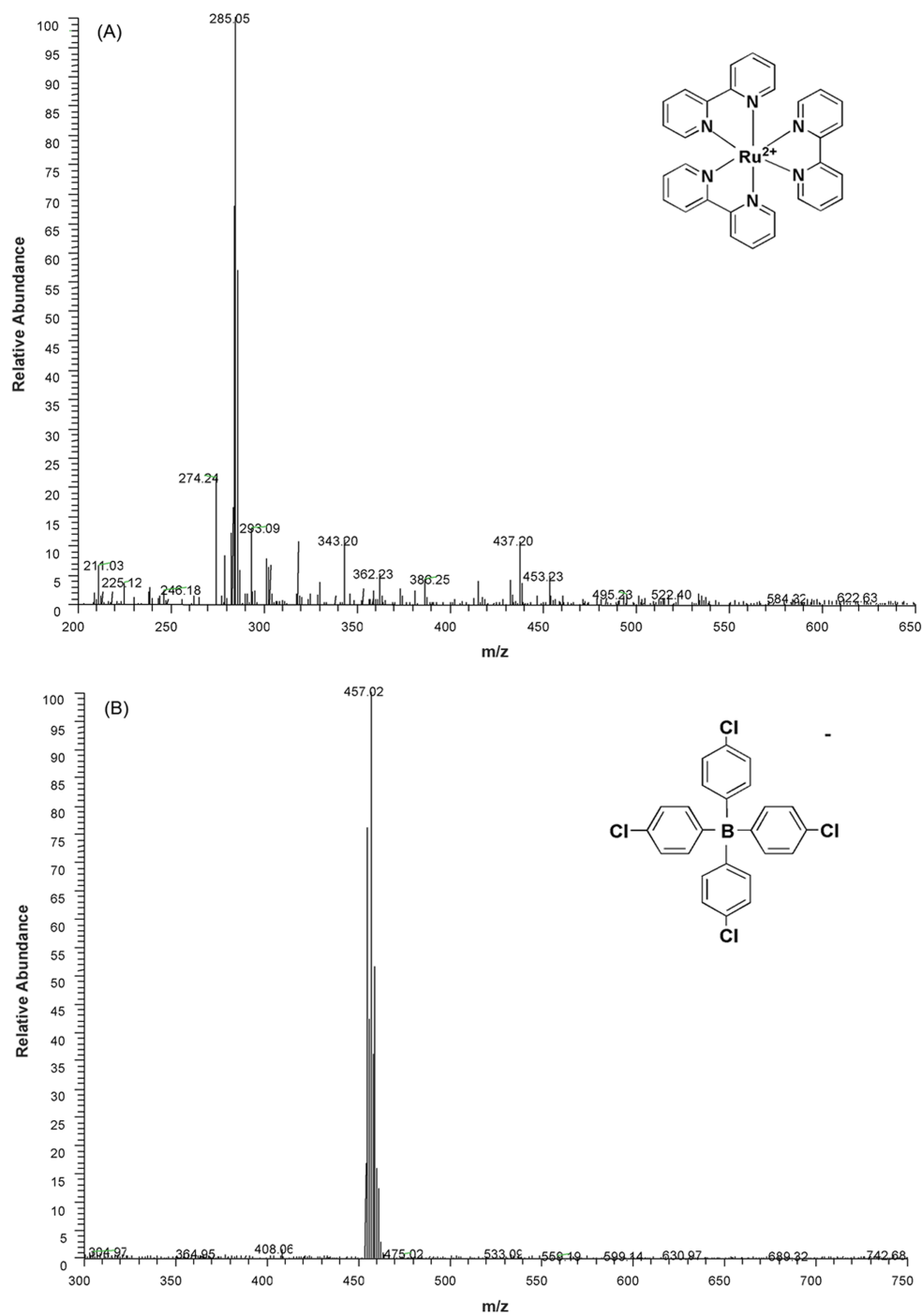


Scheme S1. The schematic illustration of DDT/Ru-AuNPs double layers on gold electrode surface. (For convenience of drawing the second DDT/Ru-AuNPs layer, only the two opposite interfaces of spherical AuNPs were depicted in Scheme S1.)

## 2. Synthetic procedure of RuDB

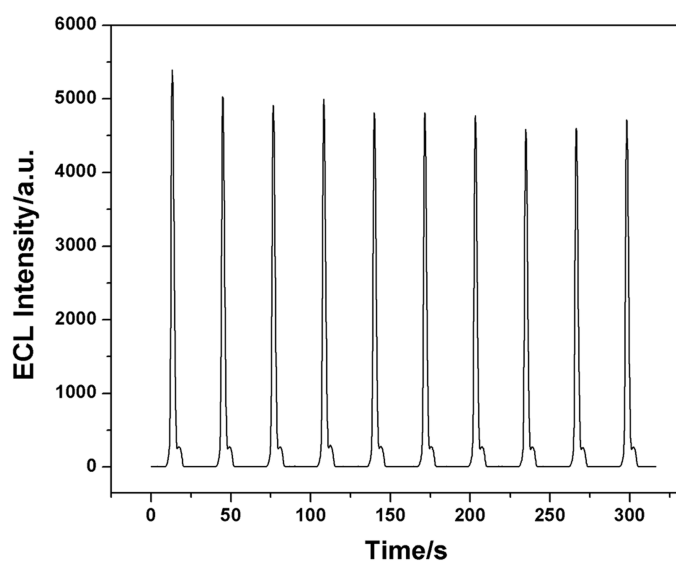
Synthesis of RuDB was a double decomposition reaction in which the water-soluble  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  was transformed into the hydrophobic RuDB. The synthetic procedure was as follows. 0.1239 g  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 mL doubly distilled water thoroughly, while 0.1424 g  $\text{K}[4-(\text{Clph})_4\text{B}]$  in anhydrous ethyl alcohol. After adding  $\text{K}[4-(\text{Clph})_4\text{B}]$  solution into the  $\text{Ru}(\text{bpy})_3^{2+}$  aqueous solution dropwise under stirring, precipitation was observed and subsequently obtained from filtration, followed by rinse, drying under infrared lamp. Finally, the obtained solid was dissolved in acetone to prepare a stock solution of 0.5 g/L RuDB.

### 3. Mass spectrum of RuDB



**Fig. S1** Positive mass spectrum (A) and negative mass spectrum (B) of RuDB. The  $m/z = 285.05$  ion in (A) corresponds to  $Ru(bpy)_3^{2+}$  (molecular weight 569.62,  $z=2$ ), while the  $m/z = 457.02$  ion in (B) corresponds to  $(4-Clph)_4B^-$  (molecular weight 457.01).

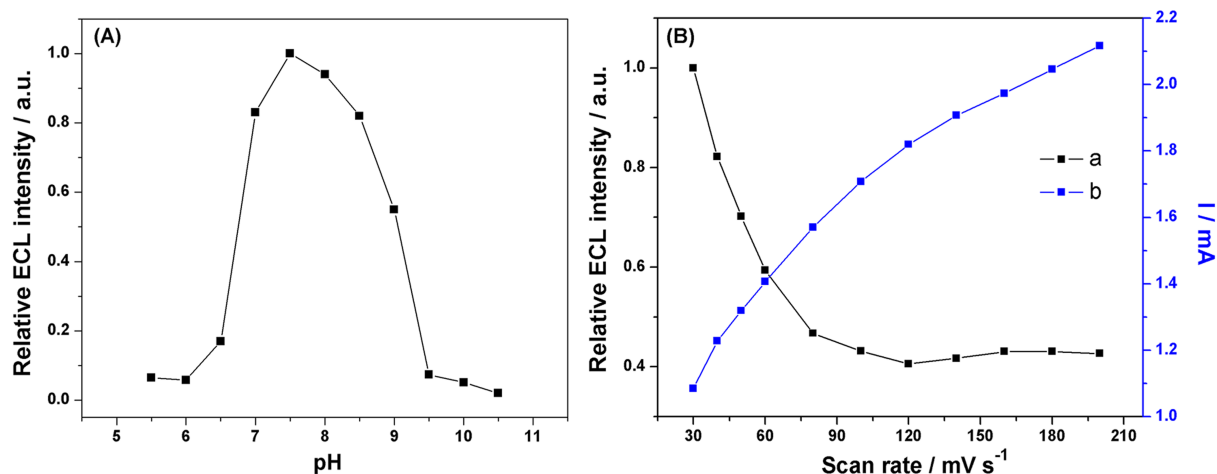
#### 4. Investigation of the ECL activity of RuDB



**Fig. S2** ECL intensity-time curves of ITO coated with RuDB with 25 mM TPrA in pH 7.5 PBS (0.2 M) under ten continuous cycles of CV scan. The voltage of the PMT was set at 800 V. Scan rate: 100 mV s<sup>-1</sup>.

Herein, our purpose of transforming the water-soluble Ru(bpy)<sub>3</sub>Cl<sub>2</sub> to the hydrophobic complex RuDB is to ensure the stability of the ECL reagent in aqueous solution and the convenience of its immobilization. Actually, this type of ruthenium complexes has been widely studied as the important ECL reagents in our previous work.<sup>1,2</sup> As shown in Fig. S2, the high-intensity ECL signal of RuDB was obtained when the ITO coated with RuDB was employed as the work electrode, implying that it possesses high ECL activity. The detailed modification process is that the ITO electrode was coated with 10  $\mu$ L RuDB acetone solution (0.5 g/L) and then dried with N<sub>2</sub> until all acetone volatilized.

## 5. Effect of pH and scan rate on ECL intensity of the DDT/Ru-AuNPs double layers modified gold electrode



**Fig. S3** (A) Effect of pH on ECL intensity of DDT/Ru-AuNPs double layers in 0.2 M PBS. The scan rate was 100 mV/s. (B) Effect of scan rate on (a) ECL intensity and (b) electric current of DDT/Ru-AuNPs double layers in 0.2 M PBS (pH 7.5).

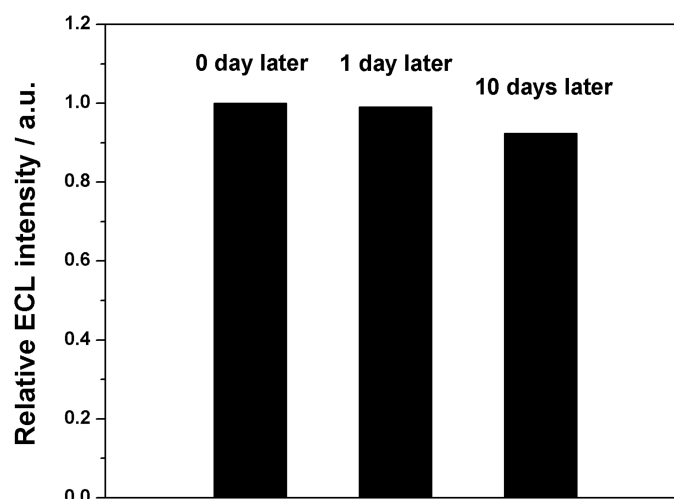
The pH value of electrolyte and the scan rate are two major influencing factors on the ECL intensity of  $\text{Ru}(\text{bpy})_3^{2+}$ -TPrA system. The strong dependence of ECL response of the  $\text{Ru}(\text{bpy})_3^{2+}$ -TPrA system on the pH of the electrolyte has been confirmed.<sup>3</sup> Fig. S3(A) shows the suitable pH value of the PBS to the ECL analysis of DDT/Ru-AuNPs double layers modified gold electrode is 7.5. According to previous works,<sup>4</sup> the strong pH dependence of ECL may mainly result from pH dependence of deprotonation of TPrA ( $\text{p}K_a = 10.7$ ) and its radical cation, and pH dependence of stability of electrogenerated  $\text{Ru}(\text{bpy})_3^{3+}$ .

The effect of the scan rate on the ECL intensity of DDT/Ru-AuNPs double layers in pH 7.5 PBS was also investigated. The ECL intensity at different scan rates of the range from 30 to 200 mV/s is shown in Fig. S3(B). It can be observed that the ECL intensity decreases sharply with the increase

of scan rate over the range of 30-100 mV/s and then remains almost constant from 100 to 200 mV/s. The higher the scan rate, the larger the electric current<sup>5</sup> and the much higher the depletion rate of TPrA, leading to a lower concentration of TPrA in the vicinity of the gold electrode surface. In addition, it has been well confirmed that the ECL intensity is linearly proportional to the concentration of TPrA.<sup>5</sup> Consequently, we can account for the decreased ECL intensity with the reason that the concentration of TPrA in the vicinity of the gold electrode surface decreased with increasing of the scan rate. In other words, ECL might be under diffusion control since the firm net structures were built on the gold electrode surface.

Based on the above investigations, the PBS solution of pH 7.5 and the scan rate of 100 mV s<sup>-1</sup> were the optimal conditions and resultantly employed for the ECL investigation in the following experiments.

## 6. Stability of the DDT/Ru-AuNPs double layers on gold electrode surface



**Fig. S4** The ECL peak intensity of the DDT/Ru-AuNPs double layers modified gold electrode 0, 1 and 10 days later.

As shown in Fig. S4, 99.1% of the ECL intensity was observed on the next day and 92.4% remained ten days later, indicating that the DDT/Ru-AuNPs double layers modified gold electrode exhibited good stability. Coupled with the simple operation and the enhanced ECL signal, the ECL sensor possesses good performance.

### Reference:

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