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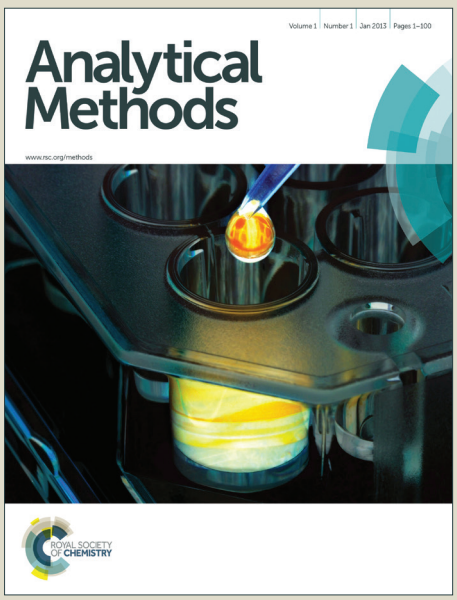

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ARTICLE TYPE

Electrochemiluminescence detection of chlorpromazine hydrochloride at bare and graphene oxide modified glassy carbon electrodes

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The electrochemiluminescence (ECL) of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridyl) and $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline) at bare and graphene oxide (GO) modified glassy carbon (GC) electrodes has been employed for the determination of chlorpromazine hydrochloride (CPZ). The ECL intensity was gradually increased with the increasing concentration of CPZ under optimal condition. For $Ru(bpy)_3^{2+}$, a linear response was obtained over CPZ concentration range of 1.0×10^{-6}~1.0×10^{-4} mol•L^{-1}, with a detection limit of 1.0×10^{-8} mol•L^{-1} at a bare GC electrode in phosphate buffer (pH = 7). The detection limit can be further down to 1.0×10^{-10} mol•L^{-1} after modification of the GC electrode with GO. In the case of $Ru(phen)_3^{2+}$, the linear response was acquired over a CPZ concentration range of 1.0×10^{-11}~1.0×10^{-7} mol•L^{-1}, and the detection limit can be reduced further to 1.0×10^{-11} mol•L^{-1} on the GO modified GC electrode. All these are much lower compared to other detection methods. The proposed method was applied to the determination of spiked CPZ in human serum; the recovery was quite satisfactory with good reproducibility and stability, providing the possibility of developing an ECL detection method for CPZ.

Introduction

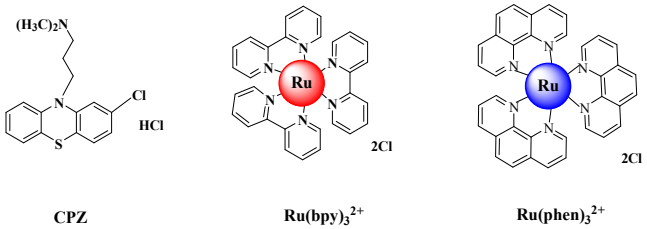
Antipsychotic drugs are widely used as therapeutic agents for treating various mental and personality disorders.[1] Chlorpromazine hydrochloride (CPZ, Scheme 1) is such a compound and belongs to the phenothiazine neuroleptic group. The discovery of antipsychotic agent CPZ in the early 1950s and the advent of even more powerful phenothaizinic psychopharmacological agent represented a landmark in the history of the medical and psychiatric science.[2] CPZ is used for the control of psychoses including schizophrenia, mania and several disturbed or agitated behavior, it is also used for the relief of nausea, vomiting, preoperative anxiety and intractable hiccups.[3,4] However, excess CPZ has inhibiting effect on neural system, respirometric system and circulative system. Generally, oral lethal dose is 15-150 mg CPZ kg^{-1}, and lethal blood concentration is 5-10 mg CPZ L^{-1}.[5] Therefore, the determination of residual CPZ in human serum is of great significance in the clinical detection.

Many methods have been reported for the individual determination of CPZ, such as spectrophotometry,[6,7] colorimetry,[8] HPLC,[9] titrimetry,[10] and spectrofluorimetry.[11] However, it is still a great challenge to develop a simple but reliable detection method for the rapid and sensitive determination of CPZ. A potential approach is to utilize an electrochemiluminescence (ECL) method,[12-15] which can produce light at an electrode without involving any light source. Considering that CPZ has two N atoms in the structure, it can be detected by using of a ruthenium complex/CPZ ECL system. In our previous works,[16-18] melamine, malachite green, leucomalachite green and hydrazine hydrate were detected using ECL, where the determinand was employed to be an amine additive candidate of ruthenium complexes, providing strong evidence for the proposed ECL method.

To improve detecting efficiency, graphene oxide (GO) was immobilized on the glassy carbon (GC) electrodes, because GO has high Young's modulus and hardness, excellent flexibility, and low cost compared with carbon nanotubes, which make it an effective reinforcement for electrode composites.[19] In particular, GO is negatively charged and has many π-conjugated aromatic domain in its basal plane,[20] thus it is a remarkable material for strongly immobilizing substances that are positively charged and have aromatic structure through both electrostatic interaction and π–π stacking interaction.[21] PVA (polyvinyl alcohol) has been chosen as a membrane material and solvent for GO, due to the reason that there are a large number of hydrophilic groups on GO surface, such as hydroxyl, carboxyl, and epoxy,[22] which can form hydrogen bonds with the PVA chains that contain even more hydrophilic groups, enhancing the interfacial adhesion ability and the mechanical performance of the resulting PVA/GO composite.[23]

To make a comparison, $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridyl, Scheme 1) and its derivative $Ru(phen)_3^{2+}$ (phen = 1,10-phenanthroline, Scheme 1) were chosen here. The later has better adsorptive ability on the GO modified GC electrode because phen is a tricyclic aromatic ligand while bpy is a bidentate aromatic ligand.[24-28] Attributed to both the π–π stacking interaction and the electrostatic interaction, immobilization of the ruthenium complexes can be achieved easily by immersing GO modified GC electrodes into the corresponding solution of the

ruthenium complex, and the interaction may accelerate the electron transfer and amplify ECL signals even at a lower concentration of CPZ. The results demonstrated that the logarithmic concentration of CPZ was linear over a CPZ concentration ranges of 1.0×10^{-10}~1.0×10^{-6} mol•L^{-1} for $Ru(bpy)_3^{2+}$ and 1.0×10^{-11}~1.0×10^{-7} mol•L^{-1} for $Ru(phen)_3^{2+}$ at GO modified GC electrode surface. All of these can provide the possibility of developing an ECL method for accurate determination of CPZ.



CPZ $Ru(bpy)_3^{2+}$ $Ru(phen)_3^{2+}$

Scheme 1 Structures of chlorpromazine hydrochloride (CPZ), $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$.

Experimental

Materials and reagents

The Cl^- salt of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ were samples left in our previous work.[29,30] GO was bought from Nanjing XFNANO Materials Tech Co., Ltd, China. CPZ was bought from Beijing century audiocodes biological technology Co., Ltd, China. PVA (average M_w 17 000, 99% hydrolyzed) was bought from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. Other chemicals and solvents were all of reagent grade and used as received. All experiments were performed in compliance with the relevant laws and institutional guidelines, and were approved by Dalian University of Technology. Informed consent was obtained for all human subjects. Blood samples were collected from healthy volunteers of appropriate age and sex.

Modified electrode preparation

GC working electrodes (3.0 mm in diameter) were first polished with a slurry of 0.05 mm alumina, then sonicated, and rinsed with deionized water. Then the electrode was successively sonicated in 1 : 1 nitric acid and doubly distilled water, and allowed to dry at room temperature. An amount of 0.75 mg of the treated GO[31] was dispersed with the aid of ultrasonic agitation in 5 mL deionized water, then 1 mL was taken to mix with 2 mL 5% PVA aqueous solution, to obtain a homogeneous, well-distributed suspension, then 10 μL of this suspension was dropped onto the surface of the pretreated GC electrode, and the solvent was allowed to evaporate at room temperature in the air. Fig. 1 shows the SEM images of the fracture surface of PVA and PVA/GO films.

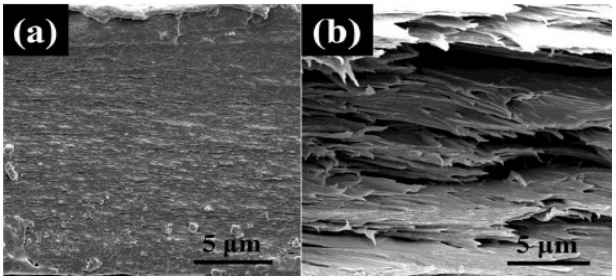


Fig. 1 SEM images of the fracture surface of PVA/GO films, (a) PVA alone, (b) PVA with GO.

ECL measurement

ECL measurements were performed on an MPI-B multifunctional ECL system from Xi'an Remex Analyse Instrument Co., Ltd., and the detecting method has been described elsewhere.[32-34] All experiments were carried out at room temperature. The ruthenium complex and corresponding CPZ additive were added into 0.1 mol•L^{-1} phosphate buffer (pH = 7), and then the mixture was transferred to an ECL detection cell. A KCl-saturated Ag/AgCl electrode and a platinum wire electrode were used as the reference and the auxiliary electrode, respectively. Cyclic potential sweep experiments were carried out in the potential region from 0 to 1.8 V and then back to 0 at a scan rate of 100 mV•s^{-1}, the ECL signals and CV vs. time were measured repeatedly for at least 5 times, and the averaged readings were used for the creation of plots.

Results and discussion

Effect of pH on ECL

As is known that pH of the buffer solution has an important effect on aqueous ECL reactions,[35] 0.1 mol•L^{-1} phosphate buffer was employed and the pH of the solution was adjusted with phosphate acid and NaOH solution to the required pH value at first, then ECL performance for 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ and 1.0×10^{-5} mol•L^{-1} CPZ under different pH from 5 to 9 was studied at a GC electrode. As shown in Fig. S1, both the highest ECL signal and the highest signal-to-noise ratio can be reached at pH = 7. And the measurements were repeated several times with a relative standard deviation (RSD) of less than 4.5%, suggesting good stability and reproducibility under this condition, so 0.1 M phosphate buffer (pH = 7) was chosen for all the ECL measurements in this study.

Effect of scan rate on ECL

According to the literature,[25,36] the scan rate could affect the ECL over a wide range, because the ECL efficiency significantly depended on the rate of generation/annihilation of the excited state $^*Ru(bpy)_3^{2+}$. To investigate the effect of different scan rate on ECL intensity, ECL performance for 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ and 1.0×10^{-5} mol•L^{-1} CPZ under different scan rate were also performed. The results are shown in Fig. S2. It is noted that the scan rate affected the ECL dramatically at GC electrode in 0.1 mol•L^{-1} phosphate buffer. The best reproducibility and stability was reached when scan rate was 100 mV•s^{-1}. Therefore, 100 mV•s^{-1} was employed for all the detections below.

ECL performance after addition of CPZ

Two obvious oxidation peaks can be observed in 0.84 V and 1.09 V from Fig. S3, because there are two amine groups in CPZ, so the two peak current can be determined to be the first step oxidation (0.84 V) and the second step oxidation (1.09V) of CPZ. After the addition of a certain amount of CPZ into 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ phosphate buffer (pH = 7) solution, cyclic voltammograms and the corresponding ECL performance for the system at the GC electrode under different potentials is shown in Fig. 2. When the electrode potential was scanned positively close to 1.25 V, upon the oxidation of Ru^{2+}, an ECL signal was observed.[37,38] It is noted that the anodic current increased along with the increasing of the oxidation potential, and significant

enhancement can be observed when the electrode potential was close to 1.25 V, demonstrating that CPZ can be a candidate as an amine additive reductant, to build a $Ru(bpy)_3^{2+}$/CPZ ECL system. In the presence of CPZ, the original anode current increased around 0.84 V and 1.09 V. This indicates that CPZ has sensibilization effect on $Ru(bpy)_3^{2+}$ oxidation current. However, the CPZ oxidation peak at 1.09 V could't be observed, due to the overlap of the $Ru(bpy)_3^{2+}$ oxidation peak at 1.25 V.

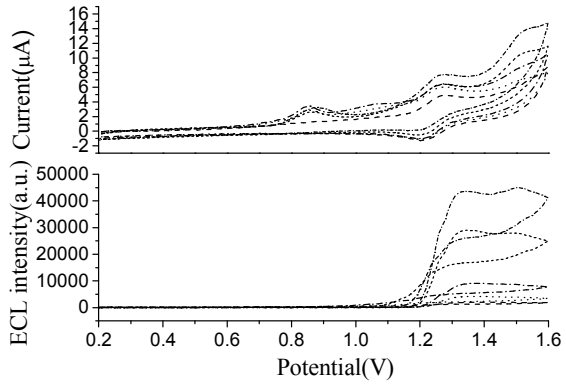


Fig. 2 Cyclic ECL and voltammetric curves in 0.1 mol•L^{-1} phosphate buffer (pH = 7) at a GC electrode: 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ alone (dash), addition of 1.0×10^{-6} mol•L^{-1} CPZ (dot), addition of 1.0×10^{-5} mol•L^{-1} CPZ (dash dot), addition of 5.0×10^{-5} mol•L^{-1} CPZ (short dash), 1.0×10^{-4} mol•L^{-1} CPZ (short dash dot), respectively; scan rate: 100 mV•s^{-1}.

Similar to the mechanism of the ECL of the $Ru(bpy)_3^{2+}$/TPrA system, CPZ undergoes oxidation at proper positive potential at the electrode surface, which leads to the formation of a radical cation intermediate. Then it reacts with the oxidized $Ru(bpy)_3^{3+}$ to form the excited state $Ru(bpy)_3^{2+}$* and light will be obtained when the excited $Ru(bpy)_3^{2+}$* releases energy[25] to return to $Ru(bpy)_3^{2+}$. The ECL sensing mechanism for CPZ can be proposed as follows:

$$Ru(bpy)_3^{2+} \longrightarrow Ru(bpy)_3^{3+} + e^-$$

$$CPZ \longrightarrow {}^{\bullet+}CPZ + e^-$$

$${}^{\bullet+}CPZ \longrightarrow {}^{\bullet}CPZ + H^+$$

$$Ru(bpy)_3^{3+} + {}^{\bullet}CPZ \longrightarrow Ru(bpy)_3^{2+*} + {}^{+}CPZ$$

$$Ru(bpy)_3^{2+*} \longrightarrow Ru(bpy)_3^{2+} + h\nu$$

Scheme 2 Proposed ruthenium/CPZ ECL mechanism.

Both the pH value and the scan rate on the ECL result were studied in detail following the above mentioned procedure, and the same trend can be observed compared with those of before the addition of CPZ, so pH = 7 and 100 mV•s^{-1} were employed for the detections. For 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 7) at the GC electrode, the ECL intensity of $Ru(bpy)_3^{2+}$ was observed to increase along with the increasing concentration of CPZ, and the logarithmic ECL increase [$lg\Delta ECL = lg(ECL_{after\ addition\ of\ CPZ} - ECL_{before\ addition\ of\ CPZ})$] versus the logarithmic concentration of CPZ was linear over a CPZ concentration range 1.0×10^{-6}~1.0×10^{-4} mol•L^{-1} (Fig. 3, slope = 0.8018; intercept = 7.8662; correlation coefficient = 0.9965; n = 7), the CPZ detection limit was 1.0×10^{-6} mol•L^{-1}.

However, for 2.0×10^{-4} mol•L^{-1} $Ru(phen)_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 7) at the GC electrode, the ECL intensity of $Ru(phen)_3^{2+}$ was increased with the increasing concentration of CPZ. The logarithmic ECL increase [$lg\Delta ECL = lg(ECL_{after\ addition\ of\ CPZ} - ECL_{before\ addition\ of\ CPZ})$] versus the logarithmic concentration of CPZ is linear over a CPZ concentration range 1.0×10^{-8}~1.0×10^{-4} mol•L^{-1} in Fig. S4 (slope = 0.717; intercept = 8.146; correlationcoefficient = 0.99587; n = 8). The CPZ detection limit is 1.0×10^{-8} mol•L^{-1}, which is lower than the above-mentioned method for detecting CPZ based on $Ru(bpy)_3^{2+}$.

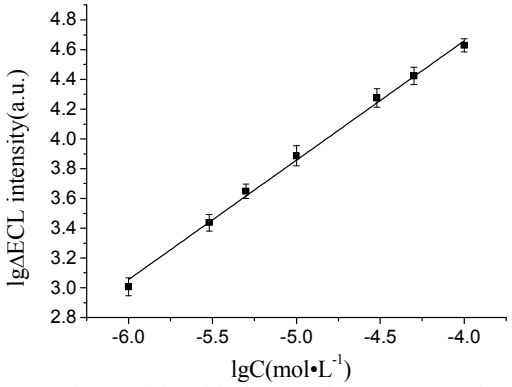


Fig. 3 Dependence of logarithmic ECL increase versus logarithmic concentration of CPZ in 0.1 mol•L^{-1} phosphate buffer (pH=7) at GC electrode.

Detection of CPZ on GO modified electrode

In order to make a comparison with that of the bare GC electrode, the same conditions as above mentioned were employed for the control experiment on the GO modified GC electrode, and good reproducibility and stability can be achieved when utilizing 0.15 mg•mL^{-1} GO and 3.4% PVA to modify the GC Electrode.

After addition of a certain amount of CPZ into 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ and 2.0×10^{-4} mol•L^{-1} $Ru(phen)_3^{2+}$ phosphate buffer (pH = 7) solution, cyclic voltammograms and the corresponding ECL performance at the GO modified GC electrode were performed at different potentials. For 2.0×10^{-4} mol•L^{-1} $Ru(bpy)_3^{2+}$ and 2.0×10^{-4} mol•L^{-1} $Ru(phen)_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 7) at the GO modified GC electrode, the ECL intensity of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ increased with an increase in the amount of CPZ. The ECL increase ($\Delta ECL = ECL_{after\ addition\ of\ CPZ} - ECL_{before\ addition\ of\ CPZ}$) versus the logarithmic concentration of CPZ is linear over a certain range of the concentration of CPZ. A linear regression equation (ΔI_{ECL}=134.698lg[CPZ] + 1502.99, R = 0.99656, n = 5) was obtained in the range of 1.0×10^{-10}~1.0×10^{-6} mol•L^{-1} and CPZ detection limit was 1.0×10^{-10} mol•L^{-1} at a signal to noise ratio of three (Fig. S5). $Ru(phen)_3^{2+}$ as an alternative luminophore at GO modified GC electrode, by contrast, demonstrated better quantitative examination for CPZ. The ECL increase ($\Delta ECL = ECL_{after\ addition\ of\ CPZ} - ECL_{before\ addition\ of\ CPZ}$) versus the logarithmic concentration of CPZ was linear over a CPZ concentration range of 1.0×10^{-11}~1.0×10^{-7} mol•L^{-1} (ΔI_{ECL}= 369.556lg[CPZ] + 5803.07, R = 0.9968, n = 5), and the detection limit can be reduced further to 1.0×10^{-11} mol•L^{-1} (Fig. S6).

Stability of the ECL measurement on the GO modified GC electrode

Fig. 4 shows the ECL performance by immersing the GO modified GC electrode in 0.1 mol•L^{-1} phosphate buffered solution (pH = 7) containing 2.0×10^{-4} mol•L^{-1} Ru(bpy)$_3^{2+}$ and 3.0×10^{-6} mol•L^{-1} CPZ, then continuously cyclic potential scanning for ten times at the scan rate of 100 mV•s^{-1}. No significant change for the ECL intensity can be observed in the detection process, suggesting good reproducibility and stability of the ECL measurement on the GO modified GC electrode. Under the same condition, the GO modified GC electrode immersed into 2.0×10^{-4} mol•L^{-1} Ru(phen)$_3^{2+}$ and 3.0×10^{-6} mol•L^{-1} CPZ in 0.1 mol•L^{-1} phosphate buffered solution (pH = 7), the experimental result that almost no change for the ECL intensity can be obtained also shows excellent reproducibility and stability of the GO modified GC electrode.

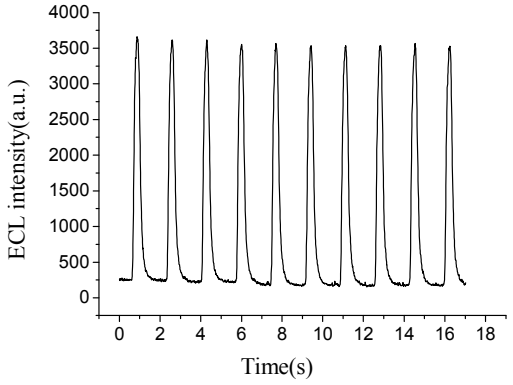


Fig. 4 Continuous cyclic scan of GO modified GC electrode for 10 cycles in pH = 7 phosphate buffer containing 2.0×10^{-4} mol•L^{-1} Ru(bpy)$_3^{2+}$ and 3.0 ×10^{-6} mol•L^{-1} CPZ ; the scan rate was 100 mV•s^{-1}.

Interference study

Several potential interferences were investigated in the determination of 1.0×10^{-4} mol•L^{-1} CPZ by using 2.0×10^{-4} mol•L^{-1} Ru(bpy)$_3^{2+}$ in 0.1 mol•L^{-1} phosphate buffer (pH = 7) at a GC electrode. A species did not make much interference if it caused a relative error of no more than ±5% in the measurement of 1.0×10^{-4} mol•L^{-1} CPZ. So, not much interference could be observed[39] when up to a 1000-fold was included of Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}, HSO_3^-, NH_4^+, maltose and glucose; a 400-fold of SO_4^{2-}; a 100-fold of Fe^{3+}; a 50-fold of Na^+; a 10-fold of ascorbic acid; respectively.

Application

To further assess the accuracy of the proposed method, it was applied to the determination of CPZ in human blood. To collect serum,[40] the blood was drawn without anticoagulant and then put in a serum tube at room temperature for 15 to 30 minutes until the blood clots. Then, the tube was centrifuged at 4000g for 5 minutes. Transfer the serum to a glass test tube capped with a rubber stopper for use. Different concentrations of CPZ dissolved in serum solution was added into 2.0×10^{-4} mol•L^{-1} Ru(phen)$_3^{2+}$. The analytical results are shown in Table 1. It is noted that the recovery was satisfactory at a GC electrode. RSDs of less than 3.5% for CPZ was obtained thus confirming the accuracy of the method and suggesting the absence of any interfering species on the ECL measurement, further demonstrated the applicability of this method.

Table 1 Recovery of CPZ determined by proposed method[a].

Spiked (mol•L^{-1})	Detected (mol•L^{-1})	Average (mol•L^{-1})	Recovery	RSD[b]
1.00×10^{-6}	1.02×10^{-6} 0.98×10^{-6} 1.01×10^{-6}	1.00×10^{-6}	100%	2.1%
1.00×10^{-5}	0.98×10^{-5} 1.02×10^{-5} 1.05×10^{-5}	1.02×10^{-5}	102%	3.5%
1.00×10^{-4}	0.99×10^{-4} 1.00×10^{-4} 0.98×10^{-4}	0.99×10^{-4}	99%	1.6%

[a] Average of three measurements and the averaged readings were used. Applied potential: 0-1.8 V (vs. Ag/AgCl); Scan rate: 100 mV•s^{-1}.
[b] RSD, relative standard deviation.

Conclusions

In conclusion, the ECL of Ru(bpy)$_3^{2+}$/Ru(phen)$_3^{2+}$ at GO modified GC electrodes has been successfully employed for the determination of CPZ. The proposed method was applied to the determination of CPZ and the recovery is quite satisfactory with good reproducibility and stability. All of these results provide the possibility of developing a novel ECL detection method for CPZ.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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