Highly Efficient Quenching of Coreactant Electrogenerated Chemiluminescence by Phenolic Compounds

Huzhi Zheng and Yanbing Zu*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China
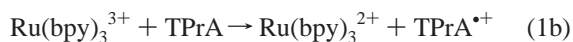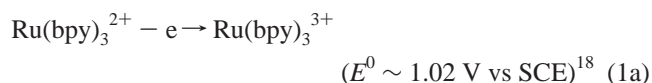
Received: May 30, 2005; In Final Form: July 8, 2005

We describe the quenching effects of phenolic compounds on the electrogenerated chemiluminescence (ECL) of the $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine)/tri-*n*-propylamine (TPrA) system in aqueous solution. First, the emissions via different ECL routes were examined in the presence of 1,4-benzoquinone. It was found that the interception of the ECL intermediate radicals by the quencher molecules significantly influenced the light emission, especially when the direct coreactant oxidation played a predominant role in producing ECL. The most efficient quenching was observed for the low-oxidation-potential (LOP) ECL at a low concentration of TPrA (<5 mM). The Stern−Volmer constant (K_{SV}) of the LOP ECL quenching could be as high as 1.3×10^6 M^{-1}, ~700 times larger than that of the photoluminescence quenching. Other phenolic compounds, such as phenol, hydroquinone, catechol, and dopamine, would be oxidized at the potential where the ECL was generated, and the benzoquinone-containing products exhibited ECL quenching effects similar to that of 1,4-benzoquinone. The highly efficient quenching of the LOP ECL by the phenolic compounds may provide a new approach for the determination of these pharmaceutically and environmentally important molecules.

Introduction

Excited-state quenching of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) photoluminescence via energy-transfer or electro-transfer routes has been intensively studied,[1,2] which can be employed as a sensitive method for determining specific quencher species, such as molecular oxygen.[2] $Ru(bpy)_3^{2+}$ excited state can also be produced by coreactant electrogenerated chemiluminescence (ECL) in aqueous solution,[3] and the ECL intensity may be influenced as well by these quenchers.[4,5] To develop ECL-based sensors for the determination of chemical and biochemical important compounds is of great interest. It has been reported that the oxidation products of phenolic molecules could quench the ECL of $Ru(bpy)_3^{2+}$ with tri-*n*-propylamine (TPrA) as the coreactant.[6−8] The ECL intensity decrease was attributed to the excited-state quenching. However, recent studies indicated that the coreactant ECL might be affected by the reactions between the quencher molecules and the ECL intermediate radicals.[9,10] Besides the excited-state quenching, these side reactions could also lead to the reduction of the ECL intensity. To elucidate the quenching effects of phenolic compounds on the coreactant ECL, more detailed investigation is necessary.

Studies on the ECL mechanism of the $Ru(bpy)_3^{2+}$/TPrA system revealed several emission routes.[9,11−17] When $Ru(bpy)_3^{2+}$ concentration is relatively high, the coreactant oxidation mainly proceeds via the catalytic pathway:

$$Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+}$$
$$(E^0 \sim 1.02 \text{ V vs SCE})^{18} \quad (1a)$$

$$Ru(bpy)_3^{3+} + TPrA \rightarrow Ru(bpy)_3^{2+} + TPrA^{\bullet+} \quad (1b)$$

But, in the presence of dilute $Ru(bpy)_3^{2+}$ and concentrated TPrA, the direct oxidation of the coreactant species at electrode

is predominant:

$$TPrA - e \rightarrow TPrA^{\bullet+}(E^0 \sim 0.9 \text{ V vs SCE})^{13,19} \quad (2)$$
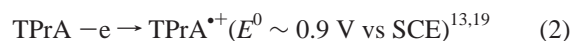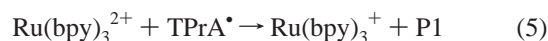
The product of the coreactant oxidation, TPrA cation radical, will undergo a rapid decomposition, which leads to the formation of a highly reducing ECL intermediate, TPrA free radical; and then the excited state is produced by the energetic electron-transfer between $Ru(bpy)_3^{3+}$ and $TPrA^{\bullet}$:

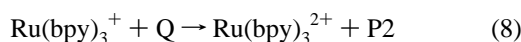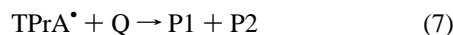$$TPrA^{\bullet+} \rightarrow TPrA^{\bullet} + H^+ \quad (3)$$

$$Ru(bpy)_3^{3+} + TPrA^{\bullet} \rightarrow Ru(bpy)_3^{2+*} + P1 \quad (4)$$

where $TPrA^{\bullet+} = Pr_3N^{\bullet}+$, $TPrA^{\bullet} = Pr_2 NC^{\bullet}HCH_2CH_3$, and P1 $= Pr_2NC^+HCH_2CH_3$.

Recently, evident low-oxidation-potential (LOP) ECL signals were observed at a freshly polished glassy carbon (GC) electrode and at a nonionic fluorosurfactant-modified gold electrode below 1.0 V versus SCE.[12,15,17] Experimental results indicated that, unlike the conventional ECL routes, no oxidation of $Ru(bpy)_3^{2+}$ is required to generate the LOP ECL.[12,15] It has been proposed that the excited state is produced by a new reaction pathway which involves the intermediacy of the TPrA cation radical:[15]

$$Ru(bpy)_3^{2+} + TPrA^{\bullet} \rightarrow Ru(bpy)_3^+ + P1 \quad (5)$$

$$Ru(bpy)_3^+ + TPrA^{\bullet+} \rightarrow Ru(bpy)_3^{2+*} + TPrA \quad (6)$$

In the above ECL routes, the production of the highly reducing intermediates, such as $TPrA^{\bullet}$ and $Ru(bpy)_3^+$, is crucial for the generation of the excited state. In the presence of the reducible quencher species (Q), the intermediate radicals might be consumed by their side reactions with the quencher molecules, resulting in the drop of the ECL intensity:

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* Author to whom correspondence should be addressed.

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$$TPrA^{\bullet} + Q \rightarrow P1 + P2 \qquad (7)$$

$$Ru(bpy)_3^+ + Q \rightarrow Ru(bpy)_3^{2+} + P2 \qquad (8)$$

where P2 represents the reduction product of the quencher molecule. The significance of the intermediate-radical quenching would depend on the competition between the ECL pathways and the side reactions. Our recent study showed that the ECL intensity of the $Ru(bpy)_3^{2+}$/TPrA system could be influenced remarkably by dissolved oxygen molecules.[10]

Here, we report the quenching effect of phenolic compounds on the different ECL routes of the $Ru(bpy)_3^{2+}$/TPrA system in aqueous solution. As indicated in previous studies,[6,7] benzoquinone and benzoquinone moiety-containing molecules generated by the oxidation of phenolic compounds could quench the ECL. Therefore, we first studied the ECL quenching by 1,4-benzoquinone. The results suggested that the interception of the ECL intermediate radicals by the quencher remarkably affected the light emission, especially when the direct oxidation of TPrA played a predominant role in producing ECL. The less efficient LOP ECL route was most greatly influenced at a low TPrA concentration. Similar quenching effects were also observed for other phenolic compounds, such as phenol, catechol, hydroquinone, and dopamine. This may lead to the development of a sensitive method for the determination of the phenolic compounds.

Experimental Section

Chemicals. Tris(2,2′-bipyridyl)ruthenium(II) dichloride hexahydrate ($Ru(bpy)_3Cl_2 \cdot 6H_2O$, min 98%), tri-*n*-propylamine (TPrA, 98%), 1,4-benzoquinone, phenol, catechol, hydroquinone, dopamine, and Zonyl FSO-100 [$F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_x$-H] were purchased from Aldrich. Other chemicals were analytical reagent graded and were used as received. All solutions were prepared with deionized water (Milli Q, Millipore). The pH of the phosphate buffer solution (PBS) containing TPrA was adjusted with concentrated NaOH or phosphoric acid.

Electrochemical and ECL Measurements. Cyclic voltammetry (CV) was performed with the model 600A electrochemical workstation (CH Instruments, Austin, TX). Glassy carbon (GC), platinum, and gold electrodes were polished with 0.05-μm alumina slurry to obtain a mirror surface and then were sonicated and thoroughly rinsed with Milli-Q water. The reference electrode was a saturated calomel electrode (SCE) separated from the working cell by a salt bridge; all potentials reported in this paper are relative to SCE. The counter electrode was a coiled Pt wire. Electrolyte solution was deaerated with Ar via gas bubbling for at least 15 min, and a constant flow of Ar was maintained over the solution during the measurement. Before each experiment, the gold and platinum working electrodes were subjected to repeated scanning in the potential ranges from −0.5 to 1.4 or −0.65 to 1.2 V, respectively, 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 electrode in 0.1 wt % surfactant aqueous solution for 10 min. The ECL signal was measured with a photomultiplier tube (PMT, Hamamatsu R928) installed under the electrochemical cell. A voltage of −800 V (or −600 V when 1 mM $Ru(bpy)_3^{2+}$ was used) was supplied to the PMT with the Sciencetech PMH-02 instrument (Sciencetech Inc., Hamilton, Ontario, Canada). All experiments were performed at room temperature.
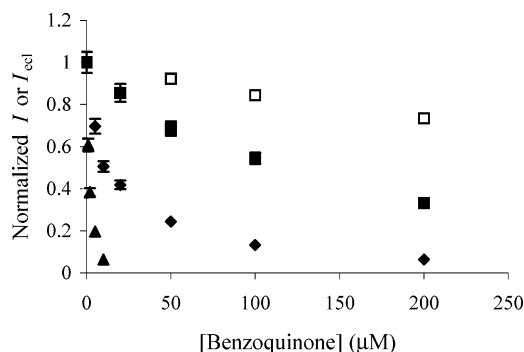

Figure 1. $Ru(bpy)_3^{2+}$ photoluminescence and ECL intensities vs BQ concentration. (□) Photoluminescence, (■) ECL via catalytic route (Pt electrode, 1 mM $Ru(bpy)_3^{2+}$ and 1 mM TPrA), (◆) ECL via direct coreactant oxidation route (GC electrode, 1 μM $Ru(bpy)_3^{2+}$ and 10 mM TPrA), (▲) ECL via LOP route (FSO-modified gold electrode, 1 μM $Ru(bpy)_3^{2+}$ and 2 mM TPrA). Electrolyte solution, 0.15 M PBS (pH 7.5).
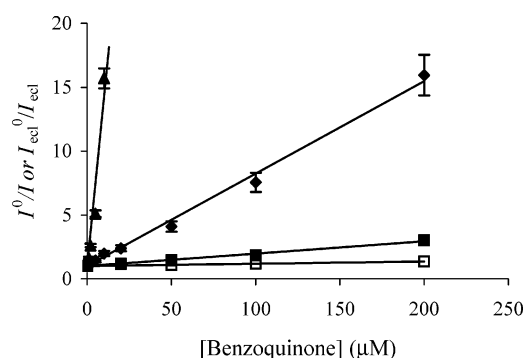

Figure 2. Stern−Volmer quenching plot. (□) Photoluminescence, (■) ECL via catalytic route, (◆) ECL via direct coreactant oxidation route, (▲) ECL via LOP route. Conditions as described for Figure 1.

Results and Discussion

Quenching of Coreactant ECL by 1,4-Benzoquinone. It is known that 1,4-benzoquinone (BQ) can efficiently quench $Ru(bpy)_3^{2+}$ photoluminescence.[1,20] We examined the quenching effect in 0.15 M PBS (pH 7.5) solution. The emission intensity as a function of BQ concentration is shown in Figure 1. The quenching behavior can be described by the Stern−Volmer equation:

$$I^0/I = 1 + K_{SV}[Q] \qquad (9)$$

where I^0 and I represent the emission intensities in the absence and presence of the quencher, respectively. The Stern−Volmer constant K_{SV} defines the efficiency of quenching. From the Stern−Volmer plot shown in Figure 2, the value of K_{SV} for the quenching of $Ru(bpy)_3^{2+}$ photoluminescence by BQ was determined to be ∼1.9×10^3 M^{-1}, close to that obtained previously in aqueous solution (∼2.2×10^3 M^{-1}).[20]

Unlike $Ru(bpy)_3^{2+}$ photoluminescence which occurs under optical excitation, the ECL is preceded by electrochemical reactions. Since the ECL of the $Ru(bpy)_3^{2+}$/TPrA system can be produced via different reaction routes, we investigated the influence of BQ on each route by changing the solution conditions and the electrode material. First, a platinum electrode was used as the working electrode in the presence of relatively concentrated $Ru(bpy)_3^{2+}$ (1 mM). In this case, the ECL would mainly be generated via the catalytic pathway; the surface oxides formed on the Pt electrode inhibited TPrA direct oxidation, minimizing the contribution of the direct coreactant oxidation route in the light emission.[12,14] As shown in Figure 1, the
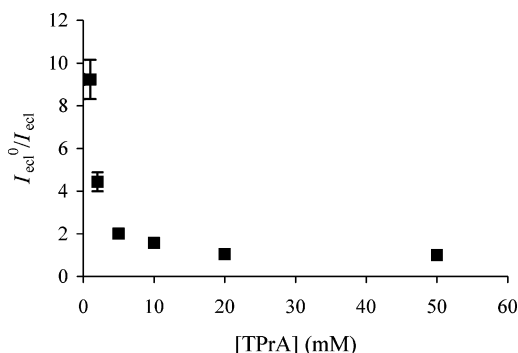
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TABLE 1: The Quenching Effects of BQ and Phenol on Ru(bpy)$_3^{2+}$ Photoluminescence and ECL via Different Routes in 0.15 M PBS (pH 7.5)

emission route	quenching mechanism	K_{SV} (M^{-1})	
		benzoquinone	phenol
photoluminescence	excited-state quenching	1.9×10^3	
ECL-catalytic route (1 mM Ru(bpy)$_3^{2+}$, 1 mM TPrA, Pt electrode)	excited-state quenching + intermediate-radical quenching	9.7×10^3	3.2×10^3
ECL-direct coreactant oxidation route (1 μM Ru(bpy)$_3^{2+}$, 10 mM TPrA, GC electrode)	intermediate-radical quenching (predominant)	7.2×10^4	2.8×10^4
ECL-LOP route (1 μM Ru(bpy)$_3^{2+}$, 2 mM TPrA, FSO-modified gold electrode)	intermediate-radical quenching (predominant)	1.3×10^6	4.2×10^5
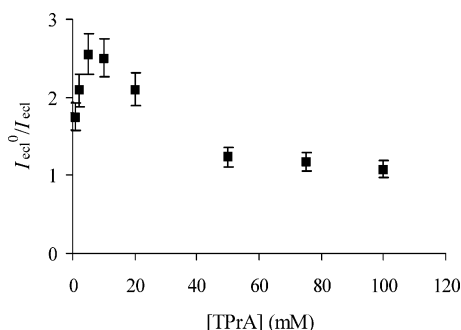
Figure 3. I_{ecl}^0/I_{ecl} as a function of TPrA concentration in the presence of 20 μM BQ. Electrolyte solution, 0.15 M PBS (pH 7.5) containing 1 μM Ru(bpy)$_3^{2+}$. Electrode, GC.

Figure 4. I_{ecl}^0/I_{ecl} for the LOP emission as a function of TPrA concentration in the presence of 5 μM BQ. Electrolyte solution, 0.15 M PBS (pH 7.5) containing 1 μM Ru(bpy)$_3^{2+}$. Electrode, FSO-modified gold electrode.

quenching effect of BQ on the catalytic ECL of the Ru(bpy)$_3^{2+}$/ TPrA system is greater than that on Ru(bpy)$_3^{2+}$ photoluminescence. This suggests the possible interference of the reaction between BQ and the ECL intermediate radical (eq 7) on the ECL process. Because the oxidation potential of TPrA$^\bullet$ has been reported to be ~ -1.7 V versus SCE,[19] BQ ($E^\circ \sim 0.02$ V vs SCE at pH 7.5) is a strong oxidant for the radical species. TPrA$^\bullet$ might be intercepted by BQ before it participated in the ECL route. Therefore, the emission intensity could be reduced not only by the excited-state quenching but also by the intermediate-radical quenching. Despite the complexity of the reaction processes, the relationship between I_{ecl}^0/I_{ecl} (I_{ecl}^0 and I_{ecl} represent the ECL intensities in the absence and presence of the quencher, respectively) and the concentration of BQ was nearly linear (see Figure 2). The Stern−Volmer equation could be applied to describe the quenching behavior.[9] The K_{SV} value of the catalytic ECL quenching is ~ 5 times higher than that of the photoluminescence quenching (see Table 1).

To make TPrA direct oxidation predominant in producing ECL, a GC electrode was used in PBS solutions containing 1 μM Ru(bpy)$_3^{2+}$ and relatively concentrated TPrA (1$\sim$100 mM). Compared with bare noble metal electrodes, the GC electrode facilitates TPrA oxidation because of the more hydrophobic electrode surface.[12,14] Figure 3 shows the value of I_{ecl}^0/I_{ecl} as a function of TPrA concentration in the presence of 20 μM BQ. The quenching effect depended significantly on the coreactant concentration. At low [TPrA], I_{ecl}^0/I_{ecl} could be larger than 2, well beyond the quenching effects on the photoluminescence and the catalytic ECL under the same solution condition. Apparently, the intermediate-radical quenching played a much more important role. When a small amount of TPrA$^\bullet$ was produced at the electrode, a great portion of the intermediate radicals might be scavenged by BQ. A maximum value of I_{ecl}^0/I_{ecl} appeared at [TPrA] ~ 5 mM. The reason for the I_{ecl}^0/I_{ecl} drop at even lower [TPrA] is not clear but might be because the contribution of the catalytic route in the emission was unignorable in these cases. When [TPrA] > 10 mM, the ECL quenching also became less efficient. As a larger amount of TPrA$^\bullet$ was produced following TPrA oxidation at the electrode,

more of these radicals could escape from the interception and participate in the ECL pathway, making the intermediate-radical quenching effect weakened.

The efficient quenching of the ECL produced via the direct TPrA oxidation route at [TPrA] ~ 10 mM is shown in Figure 1. Compared with that of the catalytic ECL quenching, the value of K_{SV} increased by ~ 7-fold (see Table 1).

Next, we examined the quenching effect of BQ on the LOP ECL of the Ru(bpy)$_3^{2+}$/TPrA system. Although the LOP ECL could be produced at the GC electrode, the overlapping of the emission signal with the conventional ECL peak at a higher oxidation potential made it difficult to measure the LOP ECL intensity with high accuracy.[12,15] Therefore, a nonionic fluoro-surfactant-modified gold electrode was used here to generate the LOP ECL signal. As demonstrated in our previous study,[17] the adsorption of the fluorosurfactant molecules (Zonyl FSO was used here) at the gold electrode would facilitate TPrA oxidation by rendering the electrode surface more hydrophobic and inhibiting the growth of the surface oxides in the potential region below 1.0 V. When the electrode potential was scanned to more positive values, the desorption of the surfactant species occurred, following which gold surface oxide formed rapidly and TPrA oxidation was suppressed. As a result, an evident LOP ECL peak appeared in the potential range from 0.8 to 1.0 V.[17] It was found that the efficiency of the LOP ECL quenching by BQ also depended on coreactant concentration, as shown in Figure 4. Highly efficient quenching was observed at low [TPrA] (<5 mM). With [TPrA] increasing, I_{ecl}^0/I_{ecl} dropped rapidly. As discussed above, the significant dependence of I_{ecl}^0/I_{ecl} on [TPrA] can be interpreted by the intermediate-radical quenching mechanism. Unlike that shown in Figure 3, no maximum value of I_{ecl}^0/I_{ecl} appeared in Figure 4, suggesting little contribution of the catalytic ECL pathway in the light emission. This is consistent with the LOP ECL mechanism proposed recently,[15] where the oxidation of Ru(bpy)$_3^{2+}$ is not involved. In the LOP ECL process, both of the crucial intermediate radicals, that is, TPrA$^\bullet$ and Ru(bpy)$_3^+$ ($E^\circ \sim -$
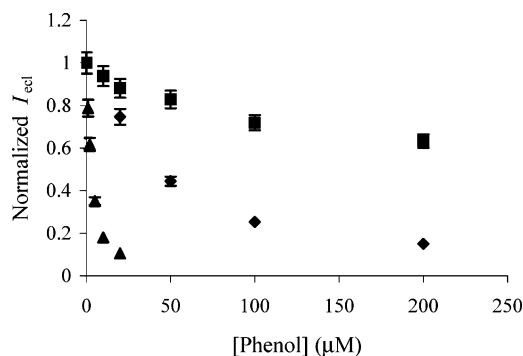
Figure 5. $Ru(bpy)_3^{2+}$ ECL intensities vs phenol concentration. (■) ECL via catalytic route (Pt electrode, 1 mM $Ru(bpy)_3^{2+}$ and 1 mM TPrA), (◆) ECL via direct coreactant oxidation route (GC electrode, 1 μM $Ru(bpy)_3^{2+}$ and 10 mM TPrA), (▲) ECL via LOP route (FSO-modified gold electrode, 1 μM $Ru(bpy)_3^{2+}$ and 2 mM TPrA). Electrolyte solution, 0.15 M PBS (pH 7.5).

1.52 vs SCE),[18] would be able to react with BQ. In other words, the LOP ECL reactions 5 and 6 had to compete with the side reactions 7 and 8, respectively. As suggested by previous studies,[9,13,21] reactions 5 and 6 were less efficient than reaction 4. Therefore, compared with the conventional ECL, the LOP ECL route might be less favorable in competing with the side reactions, resulting in the more significant intermediate-radical quenching effect at low [TPrA]. A highly efficient quenching effect on the LOP ECL has also been observed when dissolved oxygen molecules behaved as the ECL quencher.[10] The influence of BQ on the LOP ECL almost disappeared at [TPrA] > 20 mM, indicating that the intermediate-radical quenching effect may become small when a large excess of ECL intermediate radicals was produced.[10]

As shown in Figure 1, the most efficient quenching has been observed in the LOP ECL case. In the presence of 2 mM TPrA, the value of K_{SV} for the LOP ECL quenching could be as high as $\sim 1.3 \times 10^6$ M^{-1}. At even lower TPrA concentrations, the accurate measurement became difficult because of the weak light emission.

Quenching of Coreactant ECL by Other Phenolic Compounds. Most phenolic compounds with one hydroxyl-substituted aromatic ring system do not effectively quench $Ru(bpy)_3^{2+}$ photoluminescence.[6,22] However, the oxidation products of these compounds containing BQ moiety would exhibit more efficient quenching effect on $Ru(bpy)_3^{2+}$ excited state.[6] As the ECL of the $Ru(bpy)_3^{2+}$/TPrA system is produced in a potential region where the oxidation of the phenolic compounds occurs, the emission can be quenched obviously by these species.[6,7] We examined the influences of the phenolic compounds on the ECL produced via different emission routes.

Figure 5 shows the quenching effects of phenol. Similar to BQ, phenol exhibited various quenching efficiency on each ECL route. The catalytic ECL generated at the Pt electrode was least affected. Linear relationship between the value of I_{ecl}^0/I_{ecl} and phenol concentration was obtained, as shown in Figure 6. For the ECL produced at low [$Ru(bpy)_3^{2+}$] and relatively high [TPrA] by using the GC electrode or for the LOP ECL produced by using the FSO-modified gold electrode, the quenching effects were [TPrA]-dependent, as shown in Figures 7 and 8. The behavior suggests the important role of the intermediate-radical quenching mechanism. As expected, the most efficient quenching was observed in the LOP ECL case. These results indicate that the oxidation products of phenol, o- or p-benzoquinone,[6] behaved like BQ species in quenching the coreactant ECL,
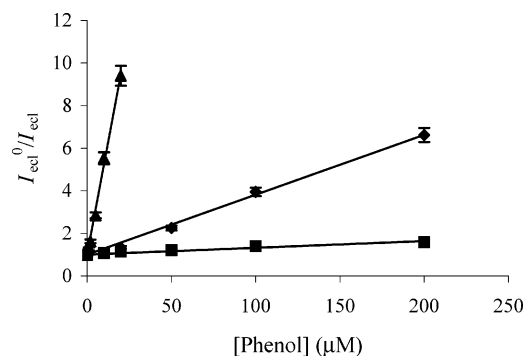

Figure 6. Stern−Volmer quenching plot. (■) ECL via catalytic route, (◆) ECL via direct coreactant oxidation route, (▲) ECL via LOP route. Conditions as described for Figure 5.
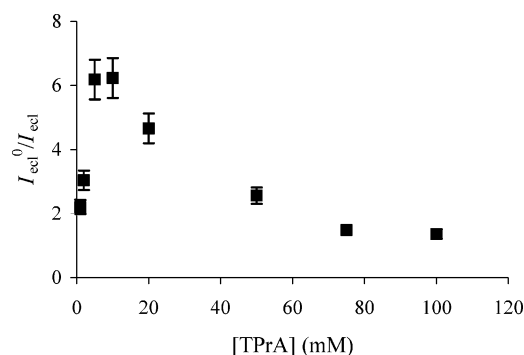

Figure 7. I_{ecl}^0/I_{ecl} as a function of TPrA concentration in the presence of 200 μM phenol. Electrolyte solution, 0.15 M PBS (pH 7.5) containing 1 μM $Ru(bpy)_3^{2+}$. Electrode, GC.
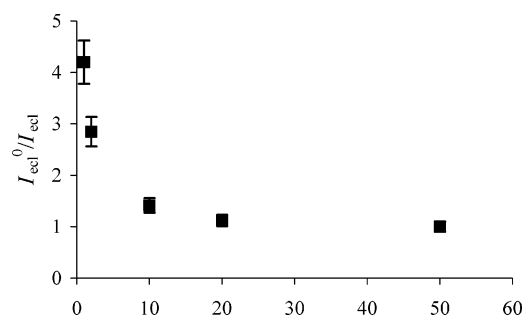

Figure 8. I_{ecl}^0/I_{ecl} for the LOP ECL as a function of TPrA concentration in the presence of 5 μM phenol. Electrolyte solution, 0.15 M PBS (pH 7.5) containing 1 μM $Ru(bpy)_3^{2+}$. Electrode, FSO-modified gold electrode.

TABLE 2: The Quenching Effects of Some Phenolic Compounds on the LOP ECL of the $Ru(bpy)_3^{2+}$/TPrA System[a]

compound	hydroquinone	catechol	dopamine
K_{SV} (10^6 M^{-1})	1.1	0.74	0.61

[a] Electrolyte solution, 0.15 M PBS (pH 7.5) containing 1 μM $Ru(bpy)_3^{2+}$ and 2 mM TPrA.

although the values of K_{SV} obtained in the different ECL routes are generally smaller than those of BQ (Table 1).

Other phenolic compounds, including hydroquinone, catechol, and dopamine, have also been investigated as quenchers for the coreactant ECL. Generally, the quenching behavior was similar to that of phenol. The values of K_{SV} for the quenching of the LOP ECL by these compounds are listed in Table 2.

In previous studies,[6−8] the ECL quenching has been proposed as a possible method for the determination of phenolic compounds, a class of pharmaceutically and environmentally

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important molecules; however, the reported quenching efficiency is much lower than that obtained in this work. Under the experimental conditions mentioned therein (Pt working electrode was generally used), the ECL signal was mainly produced via the catalytic route although the direct coreactant oxidation route could not be completely ruled out. When all of the ECL routes contribute to the emission significantly, the ECL quenching processes become more complicated and it would be difficult to determine what fraction of the ECL quenching occurs via different routes.

Conclusions

Phenolic compounds or their oxidation products can quench the ECL of the $Ru(bpy)_3^{2+}$/TPrA system generated via different reaction pathways. The quenching efficiency depends greatly on the ECL route and the experimental condition. Besides the excited-state quenching, the reactions of the ECL intermediate radicals with the quencher molecules or their oxidation products obviously influenced the emission intensity. When TPrA direct oxidation played a predominant role in producing ECL, the intermediate-radical quenching effect was TPrA concentration-dependent and was more significant at low [TPrA]. The less efficient LOP ECL was most greatly quenched. This may lead to the development of a sensitive method for the determination of the phenolic compounds.

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