

Research Article

Electrochemiluminescent Detection of Hydrogen Peroxide via Some Luminol Imide Derivatives with Different Substituent Groups

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Some luminol imide derivatives with different substituent groups have been designed and synthesized. Their electrochemiluminescence properties have been measured with a view to developing new biosensors. The ECL response to hydrogen peroxide in the presence of these luminescent derivatives has been investigated taking into account crucial factors such as the applied potential value, injection volume of hydrogen peroxide, and the substituent groups in molecular structures. The experimental data demonstrated that the substituent groups in these imide derivatives can have a profound effect upon the ECL abilities of these studied compounds. The present research work affords new and useful exploration for the design and development of new soft matter for ECL biosensors with luminol functional groups.

1. Introduction

In recent several decades, in the development of biomimetic optoelectronic nanosensors, luminol is considered as an efficient system in chemiluminescence (CL) and electrochemiluminescence (ECL) measurements for the detection of hydrogen peroxide [1–3]. It is well-known that luminol CL in the presence of hydrogen peroxide can be produced through the action of a chemical catalyst like ferricyanide or a biocatalyst such as peroxidase. On the other hand, the application of a potential to oxidize luminol can successfully replace a catalyst to provoke luminol electrogenerated chemiluminescence with inherent high sensitivities and wide linear working ranges [4–8]. For this electrochemical process, as shown in Figure 1, screen-printed electrodes have been demonstrated to trigger luminol ECL as efficiently as glassy carbon macroelectrodes [9–12].

In the previous work, we reported the design and synthesis of functional luminol derivatives with different substituted groups and investigated the interfacial assembly of these compounds with different methods [13–15]. At the same time, their potential for ECL measurement has been demonstrated first [16]. Meanwhile, their interfacial behavior and the morphologies of pure or mixed monolayers used to develop the biomimetic membrane were investigated [17]. The introduction of different substituted groups into those functional compounds can lead to new conjugated structures and new properties are expected. In addition, some luminol imide derivatives with different alkyl substituent chains could form different organogels in various organic solvents [18]. Characterization of the organogels revealed different structures of the aggregates in the gels. We have investigated the effect of the length and number of alkyl substituent chains in gelators

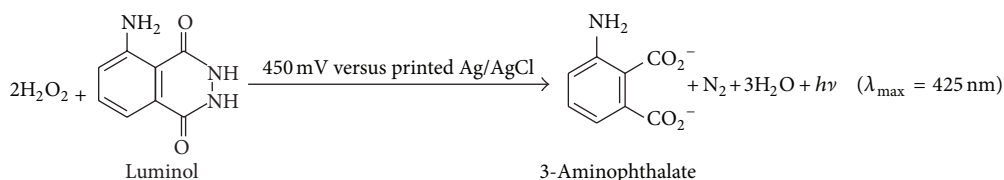


FIGURE 1: Electrochemiluminescence (ECL) reaction of luminol in the presence of hydrogen peroxide.

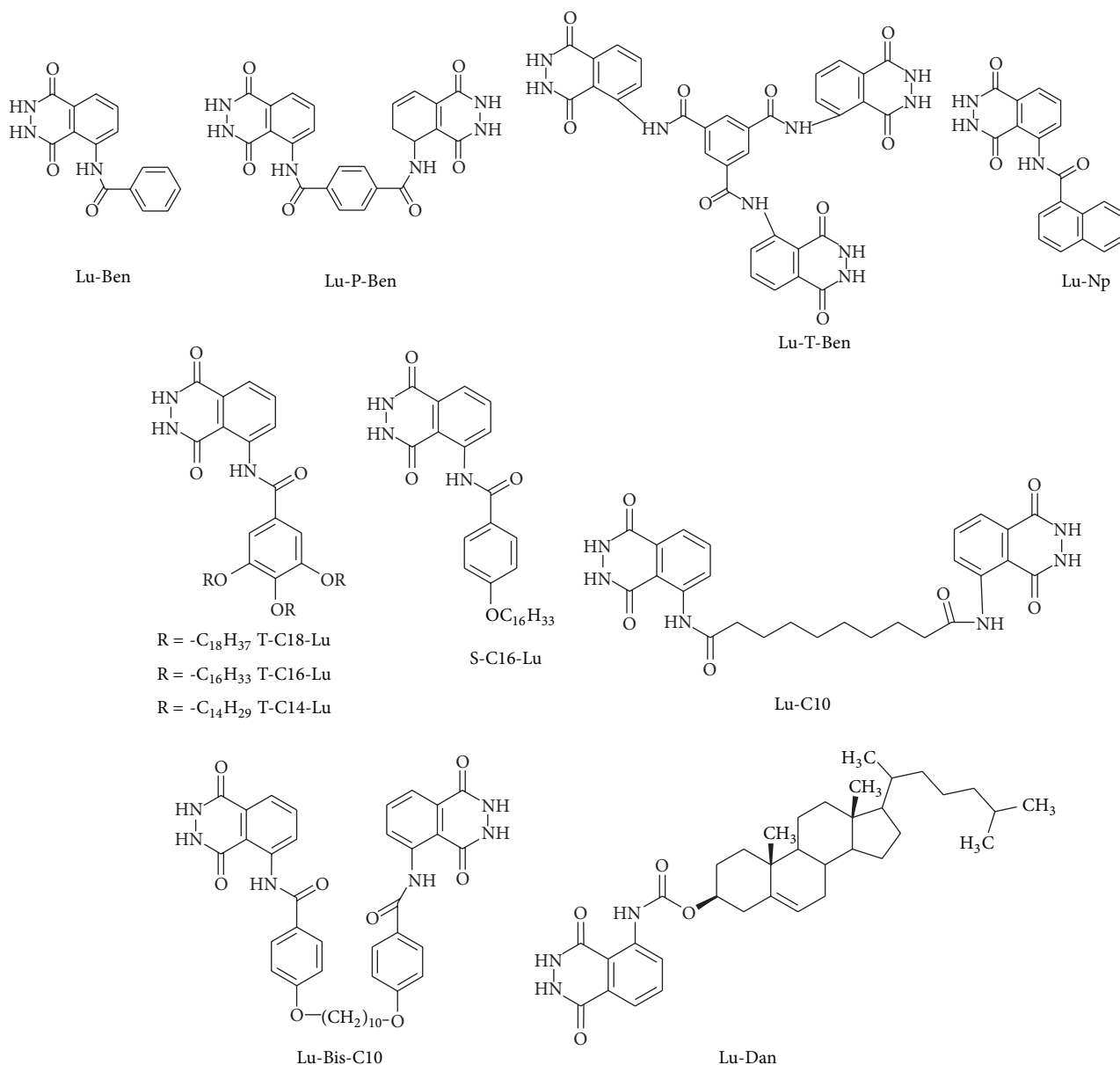


FIGURE 2: Molecular structures and abbreviations of present luminol derivatives with different substituent groups.

on the microstructures of such organogels in detail and found different kinds of hydrogen bond interactions between amide groups.

As an extension work, we reported here the electrochemiluminescence properties of functional luminol derivative containing different substituent groups with a view to developing new biosensors. The ECL response to hydrogen

peroxide in the presence of these luminescent derivatives has been investigated taking into account crucial factors such as the applied potential value, injection volume of hydrogen peroxide, and the substituent groups in molecular structures. The present results may give useful clues for the design and development of new ECL biosensors with luminol functional groups.

2. Experiments

2.1. Reagents. All materials, luminol, cholesteryl chloroformate, benzoyl chloride, 1-naphthoyl chloride, methyl 3,4,5-trihydroxybenzoate, 4-hydroxybenzenecarboxylic acid, and other used reagents were obtained commercially from Alfa Aesar Chemicals, TCI Shanghai Chemicals, Sinopharm Chemical Reagent Co., Ltd (China), and used without further purification. All used solvents were obtained from Beijing Chemicals and were distilled before use. Deionized water was used in all cases. 4-Alkyloxy-benzoic acid and 3,4,5-tris(alkyloxy)benzoic acid with different alkyl substituent chains were synthesized in our laboratory according to our previous report [19] and confirmed by ^1H NMR. These luminol derivatives were synthesized by the reaction of the corresponding chloride precursors with luminol according to slight modifications of procedures already reported in the literature [20, 21]. The final products and their abbreviations are shown in Figure 2, which were confirmed by ^1H NMR.

2.2. Apparatus. The ECL setup was described previously in our reports [17]. The screen-printed sensor (4 cm * 0.6 cm) was comprised of a graphite working electrode (0.19 cm²) and a printed Ag/AgCl reference electrode (0.30 cm²). The screen-printed sensor is connected to a potentiostat. A liquid core optical fiber connected at one end to the photomultiplier tube of a luminometer faced the electrode. Electrochemiluminescence measurements in arbitrary units (a.u.) were recorded with a graphic recorder.

2.3. Characterization. Stock solutions of luminol and present luminol derivatives were dispersed into PBS buffer (pH 8.0) under vigorous stirring prior to use to avoid any precipitation. The screen-printed sensor was immersed in a glass cuvette protected by black paper to avoid light and filled with a PBS buffer (pH 8.0) containing luminol or its derivatives. After the application of a cyclic voltammetry potential (between 450 mV and 850 mV versus printed Ag/AgCl) and stabilization of the luminescent background signal, the ECL reaction was initiated by the injection of hydrogen peroxide solution in the buffer-filled cell. A steady-state light signal was reached after *ca.* 1 min. The working condition (PBS buffer, pH 9.0, 25°C) was optimized for ECL detection to perform below measurements.

3. Results and Discussion

3.1. Effect of Some Factors on ECL Detection. It was reported previously that the screen-printed electrodes can be efficiently used in PBS buffer (pH 8.0). In addition, a cyclic voltammetry potential of $-0.40\text{ V} \sim -0.80\text{ V}$ versus printed Ag/AgCl was described as an optimized value for hydrogen peroxide-detecting optical fiber biosensors based on luminol ECL. In the present work, the best optimal potential value for ECL of luminol derivatives is required to be determined. Consequently, the relationship of ECL intensity as a function of potential was investigated, as shown in Figure 3. For the case of T-C14-Lu, 30 μL (50 μM) hydrogen peroxide solution

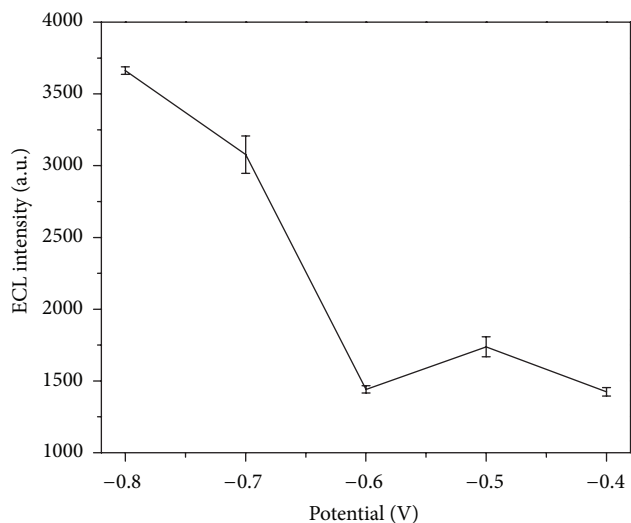


FIGURE 3: ECL intensity as a function of potential for T-C14-Lu. The measurements were performed in PBS buffer (pH 8.0) containing 50 μM of T-C14-Lu. The ECL reaction was initiated by sequential injection of 30 μL hydrogen peroxide solution in the working medium.

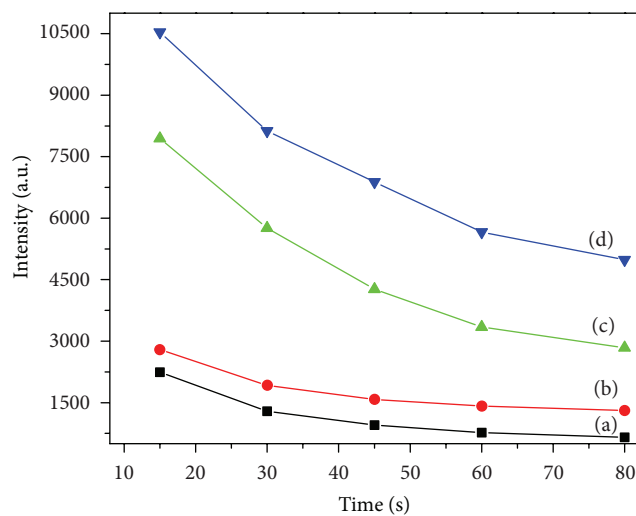


FIGURE 4: Calibration curves for hydrogen peroxide detection. The measurements were performed in PBS buffer (pH 8.0) containing Lu-P-Ben at concentrations of 50 μM . The ECL reaction was initiated by sequential injections of hydrogen peroxide in the working medium at volumes of 10 μL (a), 20 μL (b), 30 μL (c), and 40 μL (d), respectively.

was injected to the working medium. In the same concentration of hydrogen peroxide solution, it can be observed that with the increment of potential value from -0.45 V to -0.80 V , ECL intensity increased. So, the value of -0.80 V was preferred to measure other present systems.

In addition, at a potential value of -0.80 V , the ECL detection with different concentrations of hydrogen peroxide detection was performed for Lu-P-Ben, as shown in Figure 4. The measurements were performed in PBS buffer (pH 8.0)

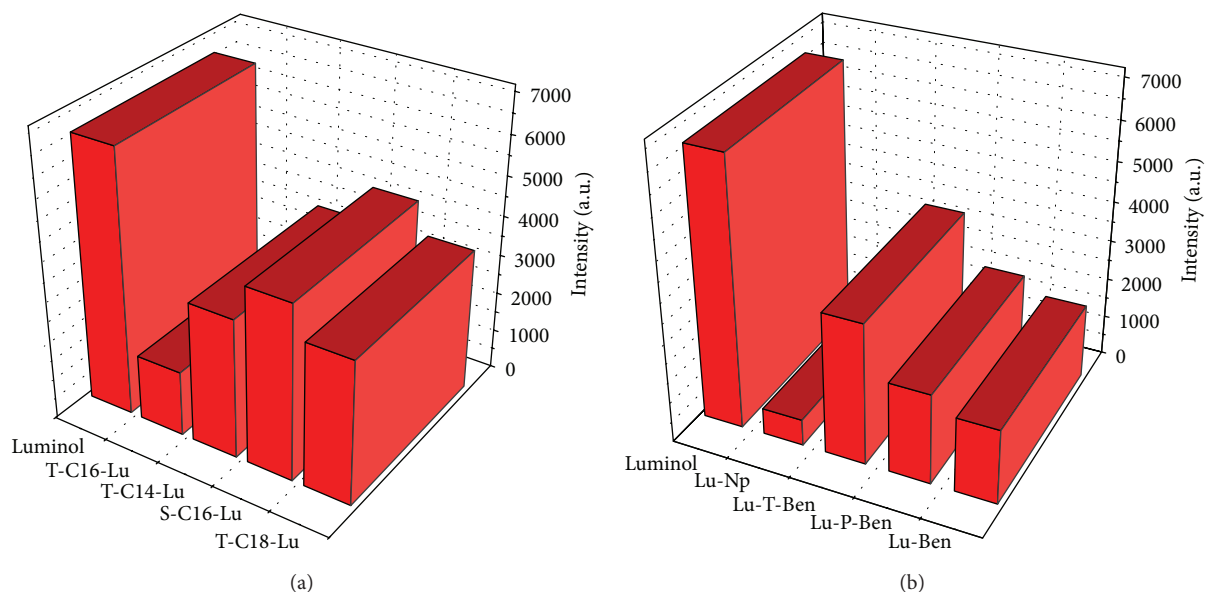


FIGURE 5: Calibration columns for ECL detection of hydrogen peroxide. The measurements were performed in PBS buffer (pH 8.0). The ECL reaction was initiated by sequential injection of 30 μ L hydrogen peroxide in the working medium.

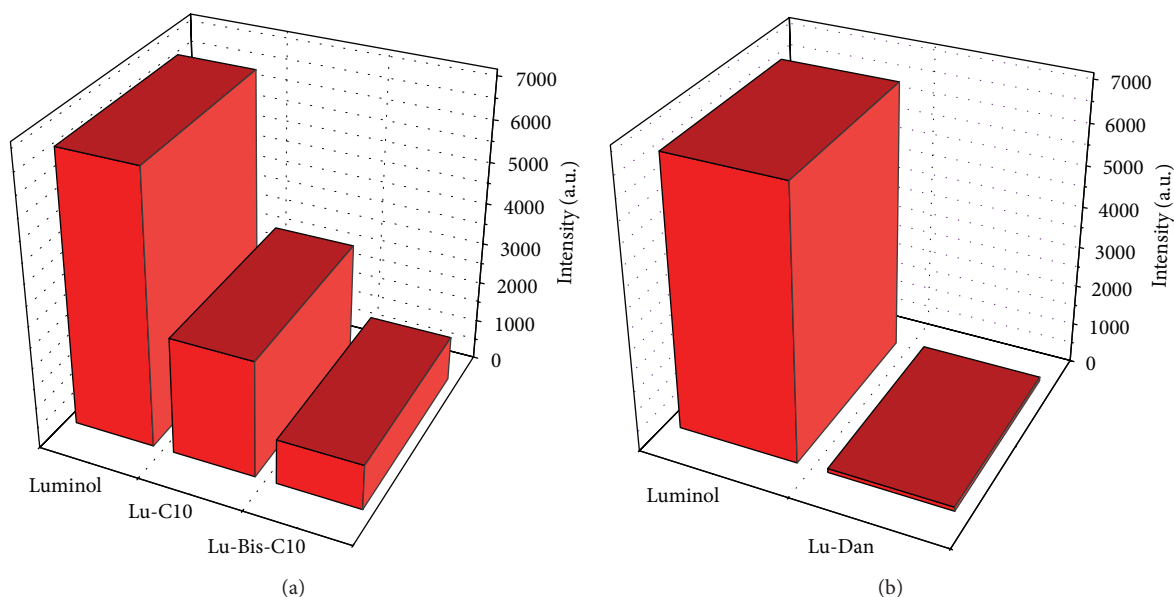


FIGURE 6: Calibration columns for ECL detection of hydrogen peroxide. The measurements were performed in PBS buffer (pH 8.0). The ECL reaction was initiated by sequential injection of 30 μ L hydrogen peroxide in the working medium.

containing Lu-P-Ben at concentrations of 50 μ M. The ECL reaction was initiated by sequential injections of hydrogen peroxide in the working medium at different volumes. It can be observed that with the increment of injection volumes of hydrogen peroxide in the working medium, ECL intensity increased with nonlinear style. The ECL intensity is not strong enough with low injection volumes due to the delay in the dispersion process. So, the injection volume of 30 μ L for hydrogen peroxide was chosen to measure the next research work.

Moreover, ECL measurements of luminol derivatives with different substituted groups were compared, as shown in

Figures 5 and 6, respectively. The measurements were performed in PBS buffer (pH 8.0). The ECL reaction was initiated by sequential injection of 30 μ L hydrogen peroxide in the working medium. Firstly, the ECL intensities of luminol derivatives with single/multi-alkyl chains connected to benzene ring substituted groups were compared. The results showed that among the present four compounds, S-C16-Lu with single alkyl chain showed better ECL property than that of the other compounds with multi-alkyl chains. In addition, as for the present luminol derivatives with aromatic substituted groups, Lu-T-Ben with C3-symmetrical skeleton showed

better ECL behaviors than those of the other compounds with phenyl or naphthyl substituted groups. Interestingly, it should be noted that Lu-Dan with large cholesteryl substituted group showed a weaker ECL property than that of the luminol. For all luminol derivatives, the ECL properties showed a more decrement tendency than that of the luminol, which may be due to the weak solubility, poor dispersion in water, and effect of substituted groups.

3.2. Discussion. In our previous work, we reported the synthesis and characterization of some luminol derivatives containing aromatic/alkyl substituted groups [13, 14]. The introduction of different aromatic substituted groups into the present functional compounds can lead to larger conjugated structures and new properties are expected. At the same time, the size and rigidity/flexibility of functional amphiphiles could regulate the potential properties both in solution and at interface, which demonstrated the advantage of precise molecular design. In addition, we have found that most compounds could form different organogels in various organic solvents [18]. We have investigated the effect of the length and number of alkyl substituent chains in gelators on the microstructures of organogels in detail and found different kinds of hydrogen bond interactions between amide groups. Therein, the alkyl substituent chains in luminol derivatives had played a very important role in regulating the assembly modes and nanostructures in these organogels. Now, the ECL properties generated by the present luminol derivatives in the presence of choline chloride and choline oxidase are under investigation to display the relationship between the molecular structures, as-formed nanostructures, and ECL sensors [22].

4. Conclusions

Some luminol imide derivatives with different substituent groups have been designed and synthesized. Their electrochemiluminescence properties have been measured with a view to developing new biosensors. The ECL response to hydrogen peroxide in the presence of these luminescent derivatives has been investigated taking into account crucial factors such as the applied potential value, injection volume of hydrogen peroxide, and the substituent groups in molecular structures. The experimental data demonstrated that the substituent groups in these imide derivatives can have a profound effect upon the ECL abilities of these studied compounds. The present research work affords new and useful exploration for the design and development of new soft matter for ECL biosensors with luminol functional groups.

Conflict of Interests

The authors declare that they have no direct financial relation with the commercial identities mentioned in this paper that might lead to a conflict of interests for any of them.

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