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Two new dinuclear copper(II) complexes as efficient catalysts of luminol chemiluminescence

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ABSTRACT

The present study, introduces the beneficial catalyze effects of dinuclear copper(II) complexes on the luminol chemiluminescence (CL) reaction. Two new dinuclear copper(II) complexes ($[Cu_2(L)_2(TAE)]X_2$ and $[Cu_2(L')_2(TAE)]X_2$), where TAE = tetraacetylethane; L = N,N′-dibenzyl ethylenediamine and L′ = N,N-dimethyl-N′-benzylethylenediamine; X = ClO_4, have exhibited highly efficient catalytic activity of luminol CL as an artificial peroxidase model at pH as low as 7.5 in water in the presence of H_2O_2 and dissolved O_2 even in the absence of H_2O_2 at elevated pH (~12). The effects of the reactant concentrations and some amino acids on luminol CL were also investigated. Among them, L-cysteine (CySH) containing -SH group was observed to inhibit the CL signal of the luminol-H_2O_2-dinuclear copper(II) complex. A similar phenomenon also was observed for glutathione (GSH), which made CL probe of peroxidase-like dinuclear copper(II) complexes applicable for the determination of such compounds in biological media.

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1. Introduction

Chemiluminescence (CL) is known to be a popular analytical method because of the higher sensitivity, lower detection limit, wider linear range, which can be achieved with simpler instrument. It has been widely applied in many fields such as clinical research, biotechnology, pharmacology, and environmental chemistry [1,2].

One of the most efficient compounds in terms of emitted intensity and probably the most studied is luminol (3-aminophthalhydrazide), whose emission of blue light upon oxidation in alkaline solution. Since CL phenomenon of luminol was first reported by Albrecht [3], investigation of effective catalysts for such CL reactions has been carried out, including metal ions [4–6], metal complexes [7–11], nanomaterials (metal nanoparticles [12], metal oxide nanoparticles [13], magnetic nanoparticles [14], quantum dots (QDs) [15] and carbon-based nanomaterials [16,17]) and enzymes [18,19]. Despite a huge number of studies, the mechanism of the reactions leading to enhancement or inhibition of luminol CL is still not fully understood [20], hampering the development of a new molecular catalyst of CL. The catalyzed luminol CL has been successfully applied in bioanalysis and immunoassay [18,21] or as sensitive detectors for high-performance liquid chromatography (HPLC) [22,23] or capillary electrophoresis (CE) [24–26].

Luminol CL reaction catalyzed by metallic cations (Co^{2+}, Cu^{2+}, Cr^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{4+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Ti^{3+}) and their complexed forms and nanomaterials is known to be optimal at alkaline pH except a few special heterogeneous systems [27,28]. The reasons that luminol/H_2O_2 system could not emit in neutral or weak acidic homogeneous solution could be explained by the fact that H_2O_2 molecule is relatively stable to the metal ion or its complex in a low pH solution [29]. But it is also well-known that the CL systems of luminol were influenced by a lot of substances in the basic solution. Therefore, many luminol CL methods were of high sensitivity but the selectivity of these could not be flattered. Also, when the analytical system is based on biological molecules such as enzymes or binding proteins, the elevated pH becomes an insoluble constraint and the preferred catalyst turns out to be the peroxidase [30]. Due to the importance of luminol in CL research field, to develop a neutral or weak acidic medium luminol CL system in analysis, has high scientific value. However, because of the chemical characters of H_2O_2 and luminol, it is difficult to establish a homogeneous luminol CL system in neutral or weak acidic solution even though many analysts have made a lot of efforts. The consequences are the use of a fragile and expensive molecule, instead of a cost-efficient and stable metallic cation, for analytical applications.

The catalase mimicking properties of homo- and/or hetero binuclear copper(II) complexes have been investigated, but reports on

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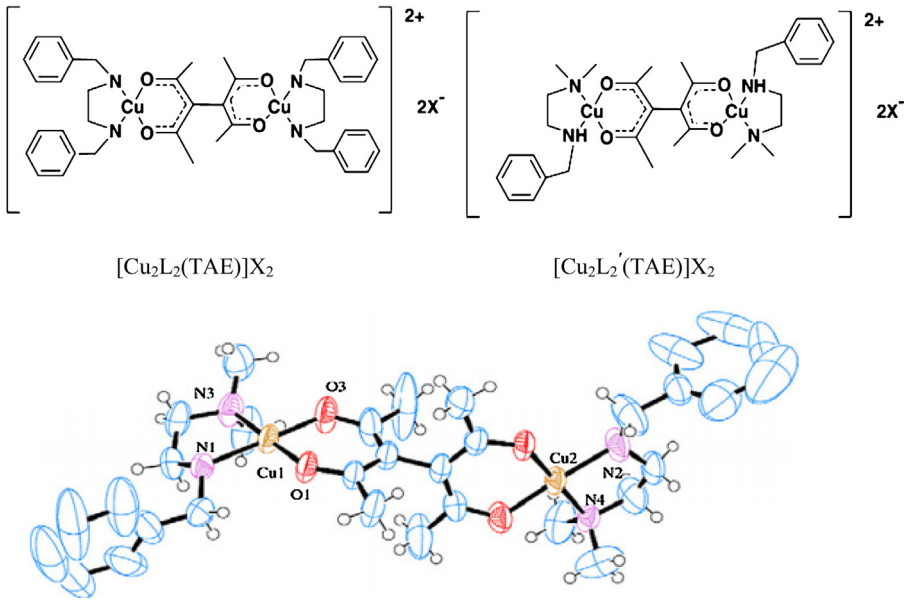

Scheme 1. Structures of two new symmetric mixed-chelate dinuclear copper(II) complexes and X-ray structure of $[Cu_2(L')_2(TAE)]X_2$.

this activity of copper(II)-containing systems are relatively scarce [31,32]. Binuclear copper(II) complexes are generally found to be more reactive than the mononuclear ones. Oishi et al. have reported some binuclear copper(II) complexes showed high catalytic activity for the CL of luminol in the presence of H_2O_2 compared with those of mononuclear copper(II) complexes [33]. Uzu and Sasaki [34] developed a new dicopper complex as a stable artificial peroxidase model, which could produce efficient homogeneous luminol CL with H_2O_2. The main purpose of the current study was to develop the dinuclear copper(II) complexes because of their oxidase-, oxygenase-, and peroxidase-like activity [35] and two of them as new molecular catalysts (Scheme 1), were designed. The present work demonstrates a unique and specific ability of the dinuclear copper(II) complexes to enhance the luminol-H_2O_2 CL emission in the neutral medium as a stable artificial peroxidase model. Analytical application potential for the luminol-H_2O_2-dinuclear copper(II) complex CL assay was also showed. More importantly, the dinuclear copper(II) complexes demonstrated the first example of efficient catalysis for luminol CL using dissolved O_2, even in the absence of H_2O_2 in basic conditions (pH 12). Furthermore, it will find a sensitive sensor for the determination of dissolved oxygen.

2. Experimental

2.1. Reagents and chemicals

All chemical compounds were reagent-grade and purchased from Merck chemical company (Darmstadt, Germany) and used as received without further purification. All dilutions were made in pure water (Milli-Q Plus system, Millipore, 18.2 MΩ cm^{-1}). A 1.0×10^{-2} mol/L stock solution of luminol was prepared by dissolving luminol in 0.01 mol/L sodium hydroxide solutions. Working solution of luminol was prepared by diluting the stock solution with 0.1 mol/L phosphate buffer solution to adjust the pH in the various ranges. A stock solution of H_2O_2 (30%, v/v) was prepared by appropriate dilution of 30% solution with water. Stock solutions 1.0 mmol/L of amino acids and glutathione were prepared by dissolving certain amounts of the reagents in 100 mL water and stored at 4 °C. The mixed-chelate dinuclear copper(II) complexes were synthesized and characterized on the basis of elemental analysis, spectroscopic and conductance measurements, as described before [36]. A 1.0 mmol/L stock standard solution of dinuclear copper(II) complexes were prepared by dissolving 0.1002 g $[Cu_2(L)_2(TAE)]X_2$ and 0.0878 g $[Cu_2(L')_2(TAE)]X_2$ in 100.0 mL of methanol. Working standard solutions were freshly prepared from the stock solution by appropriate dilutions in water before use. A 5.0 mmol/L Cu(II) standard solution was prepared by dissolving $Cu(SO_4)\cdot H_2O$ in pure water.

2.2. Apparatus

The CL signal was monitored using a Sirius Single Tube Luminometer (Berthold, Germany). CL intensity was recorded as a function of time and the time resolution of the apparatus was 1 s. A model 710 Metrum pH meter was used to carry out the pH measurements.

2.3. Procedure

Briefly, glass cells were filled with 300 μL of luminol (various pH in 0.1 mol/L phosphate buffer) at particular concentrations, 50 μL of dinuclear copper(II) complexes (various concentration in methanol) and 50 μL of H_2O_2 (various concentrations in water) as complementary reagent was injected to initiate the light emission. The CL signal kinetics (intensity *versus* times) was recorded soon after mixing of solutions.

3. Results and discussion

3.1. The catalytic property of dinuclear copper(II) complexes

Cu^{2+} catalyzed luminol-H_2O_2 CL reaction is well-known to be optimum at elevated pH (at least 10) [6,10]. Nevertheless, working in biological media inescapably requires the lowering of the pH to more neutral pH values.

Thus, the effect of the presence of dinuclear copper(II) complexes have studied at various pH values from 6.5 to 11. As a control experiment, the same measurements were performed in the absence of catalyst dinuclear copper(II) complexes. Fig. 1 presents the CL signals obtained for different pH values in the presence and in the absence of dinuclear copper(II) complexes. When looking closely to the CL signals obtained, the pH seems

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