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Synthesis and properties of a novel redox driven chemiluminescent material built on a terthienyl system

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ABSTRACT

A novel redox driven chemiluminescent material built on a terthienyl system, namely 5,7-di-ethylenedioxythiophen-2-yl-2,3-dihydro-thieno[3,4-*d*]pyridazine-1,4-dione (ETE-Lum), which is soluble in both organic media and basic aqueous solution was synthesized and characterized. Furthermore, its polymer, PETE-Lum, which is one of the most rare examples of chemiluminescent polymeric materials bearing a pyridazine unit, was obtained successfully by electrochemical means. Both of the materials give chemiluminescence either by treatment with oxidants (H_2O_2 and/or $KMnO_4$) or by the application of a potential pulse.

1. Introduction

Chemiluminescence (CL), generation of light by a chemical reaction, has received much attention in the field of analytical and material sciences due to its high sensitivity, high luminescence efficiency, and simple instrumentation.[1,2] For example, 3-aminophthalhydrazide (luminol)[3] (Fig. 1) and its derivatives, a vibrant class of chemiluminescent compounds, have been mostly used in (electro)CL detection in immunoassays with flow injection and liquid chromatography.[1–4] Furthermore, investigators in forensic science used luminol effectively to detect trace amounts of blood left at crime scenes, since it emits blue-green light (at 425–450 nm) in the dark when it is sprayed on the suspicious area, if there are any bloodstains.[5]

Recently, we have disclosed a program aimed at the design and synthesis of novel electroluminescent materials where the chemiluminescent pyridazine unit and the electro active terthienyl system were combined (TTT-Lum, Fig. 1).[6] We envisaged that such a unique combination of chemiluminescent pyridazine unit on one side and the electro active terthienyl system on the other would result in CL under an external stimulus. Furthermore, considering the fact that there are disadvantages of luminol and its derivatives (e.g., solubility, destruction of chemiluminescent unit, indistinct reaction mechanism, etc.),[7,8] which restrict their use to some extent in material science, this rational design where the electropolymerizable terthienyl system was included would not only eliminate these problems, but also allow polymerization of the material.

Herein we wish to report the synthesis, characterization, and properties of a novel redox driven chemiluminescent material built on the terthienyl system, namely 5,7-di-ethylenedioxythiophen-2-yl-2,3-dihydro-thieno[3,4-*d*]pyridazine-1,4-dione (ETE-Lum, Fig. 1). It is thought that the presence of ethylenedioxythiophene side groups would not only lower the oxidation potential of the monomer due to its electronic nature but also assure the formation of linear polymer chains by leaving only one position (C-5) for polymer chain growth. Furthermore, the electropolymerization of ETE-Lum at relatively low oxidation potential provided the corresponding polymer, PETE-Lum, which also exhibited (electro)CL. The chemiluminescent, electrochemical, and optical properties of both

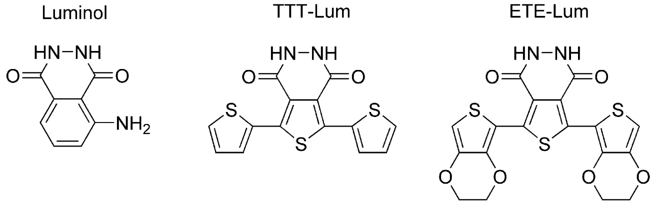

Figure 1. Chemical structures of luminol, TTT-Lum, and ETE-Lum.

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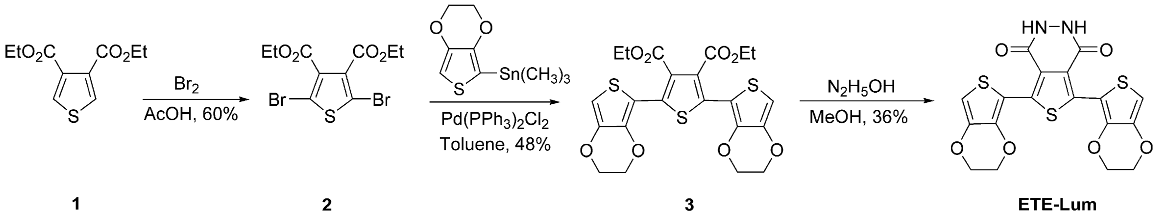

Scheme 1. The synthesis of ETE-Lum.

ETE-Lum and PETE-Lum were elaborated in comparison with TTT-Lum, luminol, and their polymers, respectively. The versatility of these compounds in analytical and forensic science applications is also presented.

2. Results and discussion

The synthesis of ETE-Lum was carried out through a three-step reaction sequence (Scheme 1). Bromination of diester **1** was followed by Stille coupling reaction of dibromo ester **2** with 2-(trimethylstannyl)-3,4-ethylenedioxythiophene to give terthienylester **3**. The treatment of **3** with hydrazine gave ETE-Lum after precipitation with HCl. ETE-Lum was soluble in both organic media (acetonitrile, DMSO) and basic aqueous solution.

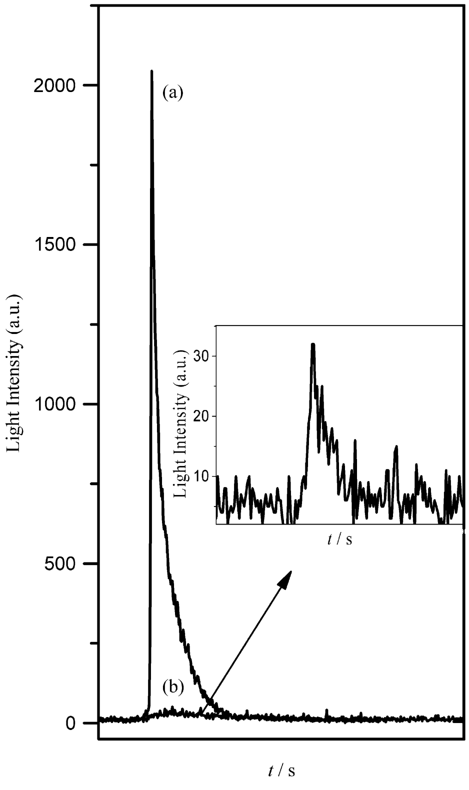

Figure 2. The intensity of the light obtained from the CL reaction of ETE-Lum (10^{-5} M) dissolved in 0.1 M NaOH solution with (a) 10^{-4} M $KMnO_4$ and (b) 10^{-4} M H_2O_2.

The characterization of the compound was based on ^1H and ^{13}C NMR spectroscopy, FTIR data, and the mass analysis. The ^1H NMR spectrum of ETE-Lum revealed two singlets at 8.00 and 5.90 ppm corresponding to the pyridazine and α-protons of the EDOT units, respectively, along with a triplet at 4.30 ppm. A nine-line ^{13}C NMR spectrum was also consistent with the structure, which gave the correct mass analysis.

After characterization, the chemiluminescent properties of ETE-Lum were investigated and compared to those of luminol and TTT-Lum, since all possess the same chemiluminescent group. We were delighted to note that CL was observed from the reaction of ETE-Lum with H_2O_2 as oxidant, when dissolved in 0.1 M NaOH aqueous solution (Fig. 2). ETE-Lum and TTT-Lum emitted a bright green light (λ_{em}=496 nm for ETE-Lum and λ_{em}=492 nm for TTT-Lum) whereas the emission of blue light (λ_{em}=410 nm) was observed in the case of luminol (Fig. S1). Fortunately, this glow can easily be sensed by the naked eye in the dark (Fig. 3). Under the light of the CL reaction of luminol,[5] a proposed mechanism for the CL reaction of ETE-Lum and TTT-Lum is given in Scheme 2.

The CL reaction can also be initiated with $KMnO_4$ (Figs. 2 and 4). However, the CL reaction of ETE-Lum or TTT-Lum with $KMnO_4$ follows a slightly different path when compared to H_2O_2: the permanganate ion (MnO_4^-) was reduced to manganate (MnO_4^{2-}) when ETE-Lum or TTT-Lum was oxidized to the excited state (first CL step) and light is generated on falling to the ground state. Furthermore, the CL reaction of ETE-Lum with MnO_4^{2-} is very slow; however, it can be sped up by adding a proper catalyst. Therefore, in the presence of Fe^{3+}, light emission was observed by the oxidation of the tested compound when the manganate ion was reduced to mangane(IV)oxide (MnO_2) (second CL step, see Scheme S2).

The CL reaction has attracted much attention in analytical chemistry for the detection of biologically active materials and/or toxic metals.[9] In the case of luminol, the metallic ions play important roles as catalyst: speeding up the CL reaction, increasing the light intensity, etc.[1] In order to reveal the effect of the metal ion on the CL reactions of ETE-Lum and TTT-Lum, and to investigate the sensitivity of these novel materials to the metal ions, a variety of metal cations (Ag^+, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Cr^{2+}, and Fe^{3+}) were tested. It was found that ETE-Lum, like TTT-Lum, was highly sensitive to Fe^{3+}, which could catalyze the CL reaction (Figs. 5 and 6).

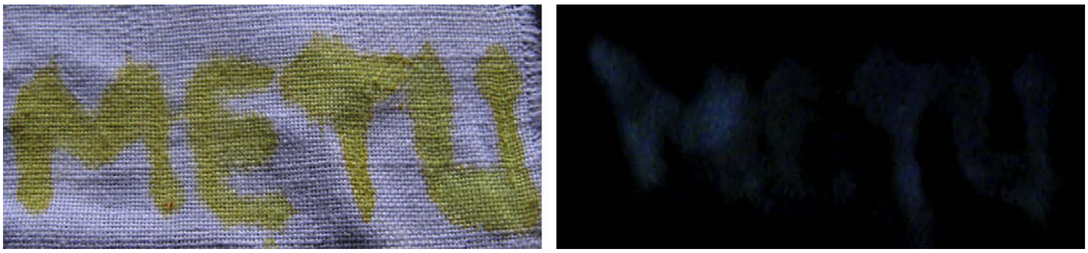

Figure 3. The image of writings with $K_3[Fe(CN)_6]$ (aq) solution: under ambient light (left) and after spraying basic ETE-Lum/H_2O_2 solution in the dark (right).