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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.

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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

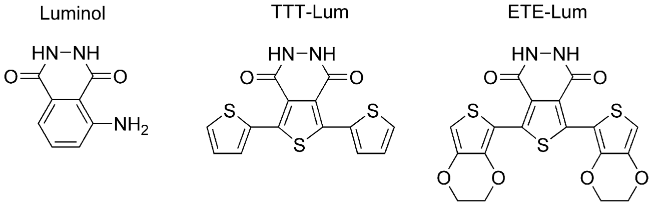

Figure 1. Chemical structures of luminol, TTT-Lum, and ETE-Lum.

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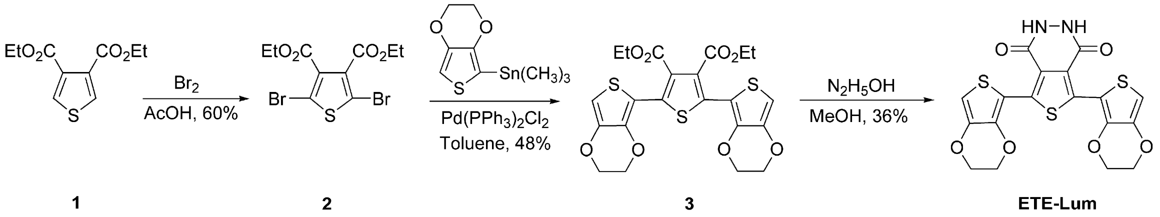


Scheme 1. The synthesis of ETE-Lum.

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.

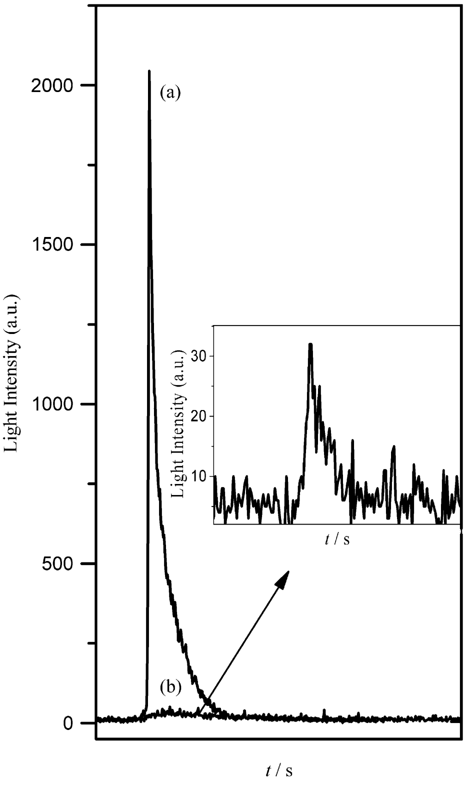


Figure 2. The intensity of the light obtained from the CL reaction of ETE-Lum (10^{-5} M) dissolved in 0.1 M NaOH solution with (a) 10^{-4} M $KMnO_4$ and (b) 10^{-4} M H_2O_2.

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).

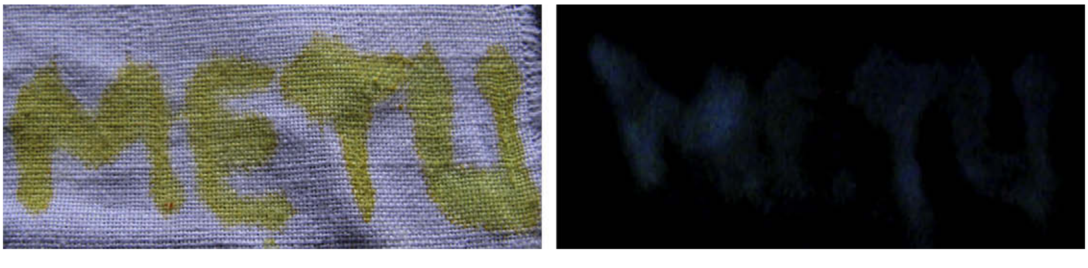
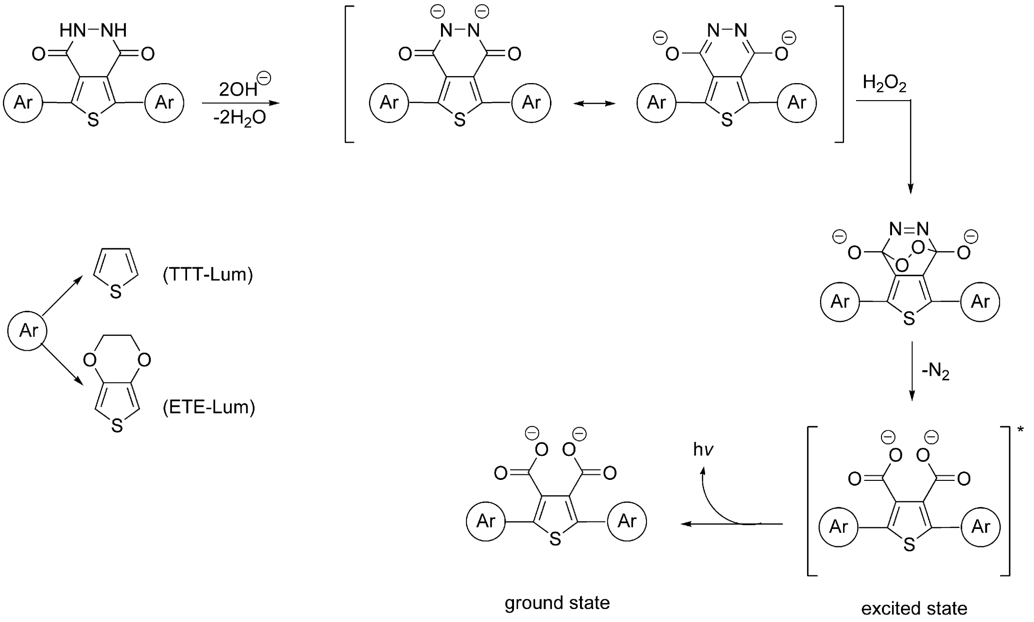


Figure 3. The image of writings with $K_3[Fe(CN)_6]$ (aq) solution: under ambient light (left) and after spraying basic ETE-Lum/H_2O_2 solution in the dark (right).



Scheme 2. CL reaction mechanism for ETE-Lum and TTT-Lum with H_2O_2 in basic solution.

ETE-Lum was so sensitive toward Fe^{3+} ion that the detection was possible even in extremely dilute solutions as well as dilute blood samples (1.0 ppm) (see Figs. S2 and S3). It is noteworthy that both ETE-Lum and TTT-Lum are promising candidates for sensing Fe^{3+} ions. For that reason, it is amenable for use as an Fe^{3+} sensor and/or in forensic applications.

The electrochemical behavior of ETE-Lum and TTT-Lum was investigated in order to elucidate the effect of the external rings in the terthienyl system. Figure 7 depicts the cyclic voltammogram of both systems, which were recorded under the same conditions. During the first anodic scan, both systems have shown three irreversible oxidation peaks (1.10, 1.35, and 1.57 V for TTT-Lum and 0.88, 1.23, and 1.45 V for ETE-Lum). It was found that the first oxidation value of ETE-Lum was lower than that of TTT-Lum where the electronic nature of the external ring determined the oxidation potential of the system, since electron rich EDOT units made oxidation much easier when compared to that of thiophene.

Since the oxidation of the chemiluminescent group can be possible by electrochemical means and this process can be monitored by a photomultiplier tube (PMT), we also examined the electroluminescent properties of the compounds. The application of potential pulse at the onset of the second oxidation peak of TTT-Lum resulted in the generation of light, which could be intensified by further oxidation (see Fig. 8). Based on this observation, it can safely be concluded that the first anodic peak belongs to the oxidation of the external unit whereas the second one is attributed to the chemiluminescent part.

It was also noted that if the anodic scans for ETE-Lum and TTT-Lum were clipped at the first oxidation peak, new reversible peaks, which were intensified after each successive cycle appeared. This

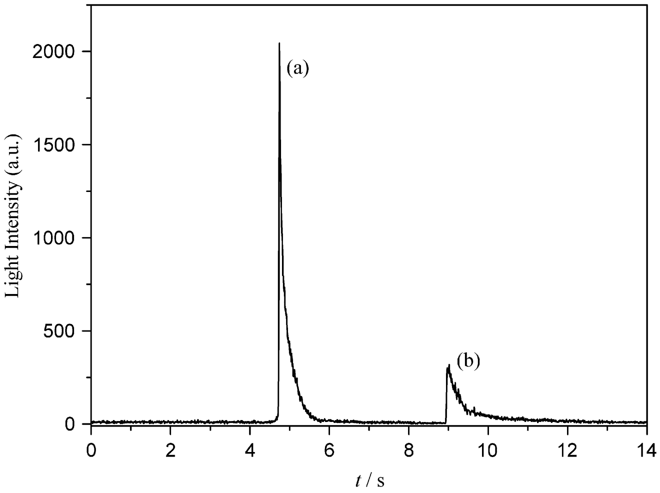


Figure 4. The intensity of the light obtained from the CL reaction of (a) ETE-Lum and $KMnO_4$ and (b) 10^{-2} M Fe^{3+} and a mixture of ETE-Lum and $KMnO_4$.

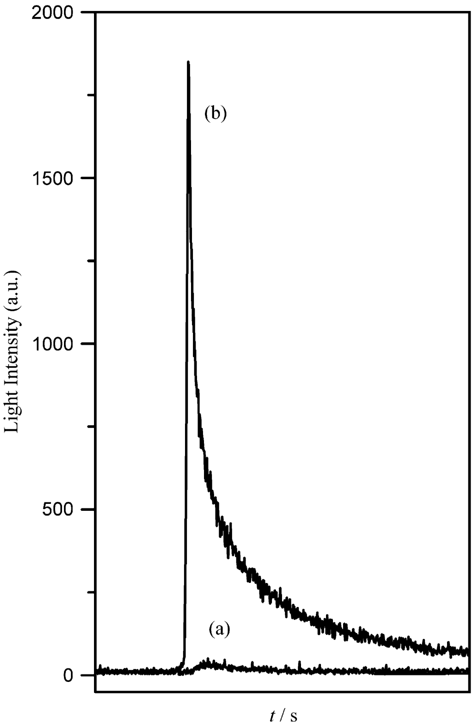


Figure 5. The intensity of the light obtained from the CL reaction of (a) ETE-Lum and H_2O_2 and (b) 10^{-2} M Fe^{3+} and a mixture of ETE-Lum and H_2O_2.

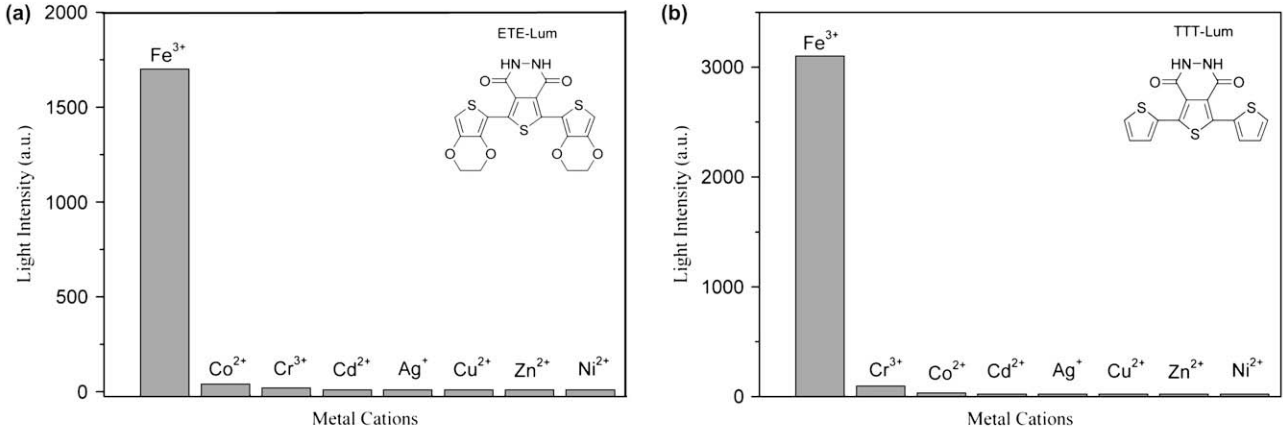


Figure 6. The intensity of the light obtained from the CL reaction of (a) 1.0×10^{-5} M ETE-Lum and (b) 1.0×10^{-5} M TTT-Lum dissolved in 0.1 M NaOH solution with 1.0×10^{-4} M H_2O_2 in the presence of different metal cations (10^{-2} M).

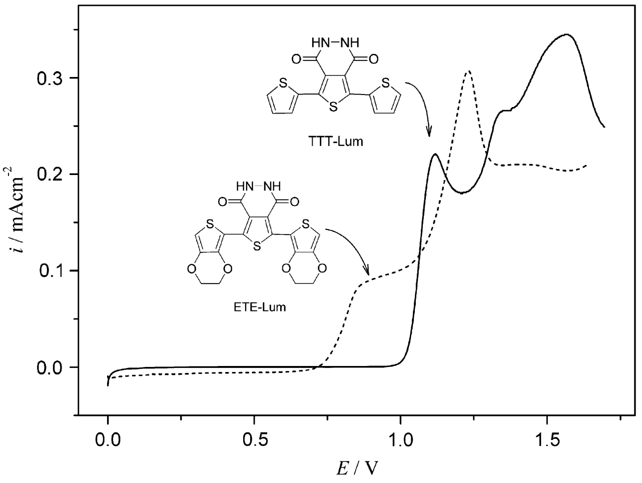


Figure 7. First anodic scans of ETE-Lum and TTT-Lum in 0.1 M TBAP/ACN containing 5% BF_3–Et_2O by volume versus Ag/AgCl at a scan rate of 25 mV/s.

indicated the formation of conducting polymer films (Figs. 9a and S4). The redox behavior of the polymer film of PETE-Lum was also elaborated in monomer-free electrolyte solution and the electrochemical stability of PETE-Lum was tested by cycling the polymer film at a scan rate of 200 mV/s between 0.0 and 0.75 V (see Fig. S5b). It was found that the polymer film was highly robust and environmentally stable, since no appreciable change in its electro activity was observed after 500th cycle.

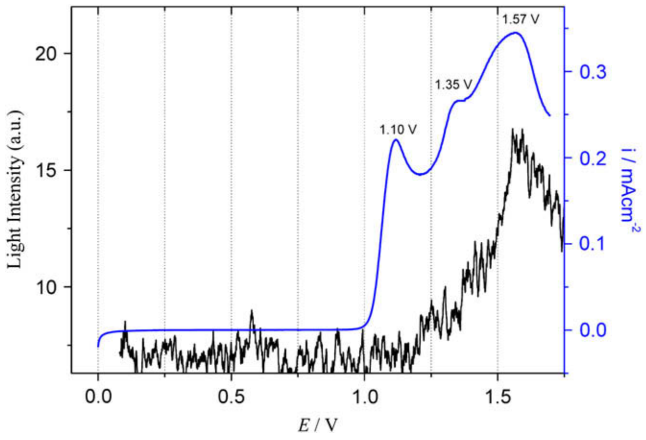


Figure 8. Cyclic voltammogram of 5.0×10^{-4} M TTT-Lum on an ITO electrode in 0.1 M $LiClO_4$/ACN containing BF_3–Et_2O by volume at a scan rate of 25 mV/s as well as the generated light emission during potential scanning.

The spectroelectrochemical properties of a PETE-Lum film deposited on an ITO electrode were investigated by monitoring the changes in electronic absorption spectra upon oxidation. The polymer film in its neutral state exhibited a well defined absorption band at 554 nm, which was attributed to π–π* transition. The electronic band gap (E_g) was defined as the onset energy for the π–π* transition and it was found to be 1.65 eV for PETE-Lum (Fig. 10), which was lower than that of PTTT-Lum (E_g=1.74 eV). Upon oxidation, the intensity of the π–π* transition band of PETE-Lum started to decrease and a new absorption band intensified at 842 nm (polaron formation). Further oxidation caused the disappearance of 554 nm band, which was accompanied by the appearance of a new band at about 1080 nm (bipolaron formation).

PTTT-Lum and PETE-Lum polymer films are (electro)CL as in the case of the corresponding monomers. Light emission was detected by PMT when a potential of 0.9 V (vs Ag wire) was applied to the electrode, which was coated with PETE-Lum (Fig. 11). It is noteworthy that the intensity of light was increased with increasing potential. Furthermore, we have also tested repetitive usage of the PETE-Lum film, which was coated on ITO by applying potential pulses for different time intervals. It was noted that PETE-Lum can be switched a thousand times between 1.1 V (0.1 s) and 0.0 V (3 s) with no appreciable loss in the light intensity (Fig. S7).

3. Conclusion

In conclusion, a novel redox driven chemiluminescent material built on a terthienyl system, ETE-Lum, which is soluble in both organic media and basic aqueous solution was synthesized. ETE-Lum gives CL reactions in the presence of H_2O_2 and/or $KMnO_4$ and it emits bright green light (λ_{max}=496 nm). The reaction can be sped up by the addition of Fe^{3+} to which ETE-Lum is highly sensitive among other metal ions. This feature makes ETE-Lum amenable for use as an Fe^{3+} sensor as well as an alternative candidate for the detection of bloodstains in forensic science. On the other hand, electrochemical polymerization of ETE-Lum provides PETE-Lum as a well-adhered, thick, and highly stable electro active polymer film, which is soluble in basic aqueous solution. The band gap of the PETE-Lum was found to be 1.65 eV, which is lower than that of PTTT-Lum (1.74 eV). Furthermore, PETE-Lum shows electrochemiluminescent properties under very low potentials ($\geq$0.9 V). This study opens the door for the synthesis and engineering of novel (electro)CL materials for the applications in analytical, forensic, and materials sciences through a rational design, which circumvented all of the aforementioned problems with luminol.

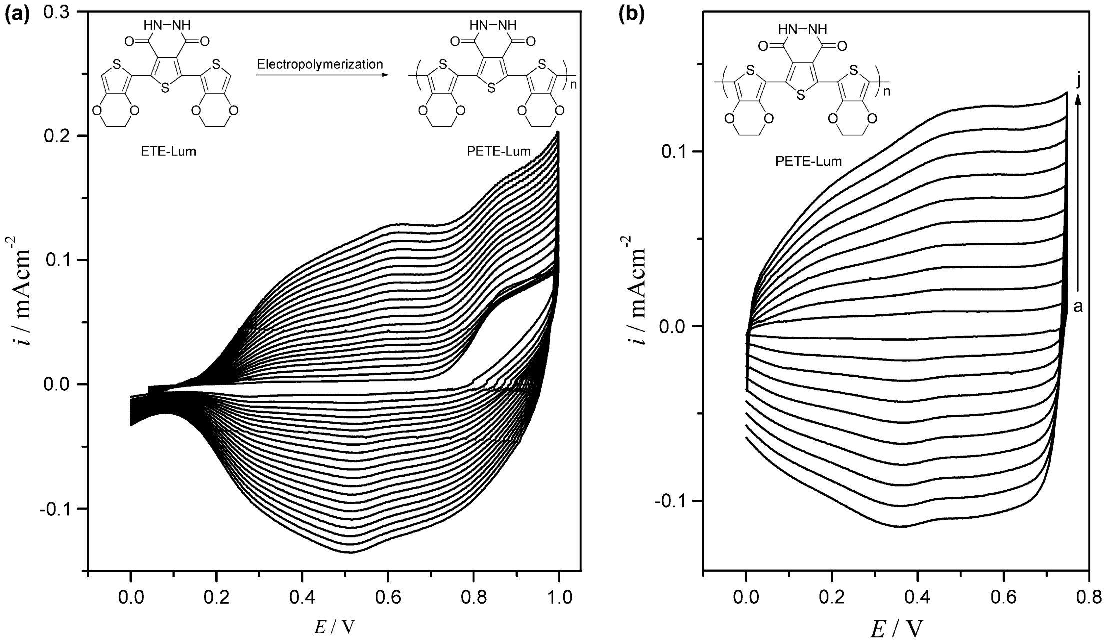


Figure 9. (a) Repeated scan electropolymerization of 1.0×10^{-3} M ETE-Lum on an ITO electrode in 0.1 M TBAP/ACN containing 5% BF_3–Et_2O by volume at a scan rate of 100 mV/s and (b) scan rate dependence of PETE-Lum film in 0.1 M TBAP/ACN at different scan rates: (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 120, (g) 140, (h) 160, (i) 180, and (j) 200 mV/s.

Efforts to combine new streams of thought for further investigation of this field are currently underway in our laboratories and the results will be reported in due course.

4. Experimental section

4.1. Synthesis of ETE-Lum

$N_2H_4 \cdot H_2O$ (6 mmol) was added to a solution of compound **3** (54 mg, 0.19 mmol) in methanol (1 mL) and the mixture was stirred for 2 h at room temperature. Then, it was heated up to 70 °C in a water bath while monitoring with TLC at time intervals (around 3 days). After the completion of reaction, the mixture was concentrated under reduced pressure. The crude solid product was dissolved in a minimum amount of hot water containing 1% NH_4OH (by volume) and precipitated by the addition of concentrated HCl to this solution. The solid was filtered, washed with cold water, and finally dried under vacuum at 70 °C (36% yield):[10] mp 361 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.0 (s, 2H), 5.9 (s, 2H), 4.3 (t, 8H, *J*=4.8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 167.3, 156.1, 152.4, 147.7, 136.9, 114.3, 94.9, 65.3, 65.0; IR (KBr): ν=748, 919, 971, 1100, 1189, 1378, 1424, 1497, 1717, 2856, 2905, 2926, 3467; MS *m/z* 448.50; calcd for $C_{18}H_{12}N_2O_6S_3$ $[M]^+$ 448.59. Anal. Calcd for $C_{18}H_{12}N_2O_6S_3$: C 48.20, H 2.70, N 6.25, O 21.40, S 21.45; found: C 48.32, H 2.78, N 6.18, S 21.32.

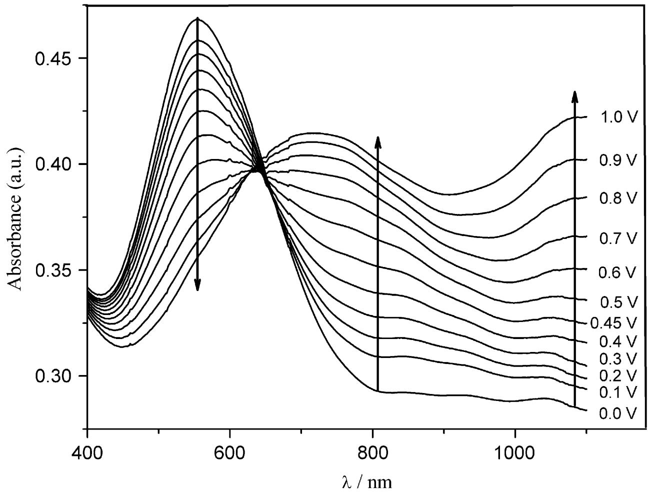


Figure 10. Spectroelectrochemistry of PETE-Lum on ITO in 0.1 M $LiClO_4$/ACN at various applied potentials.

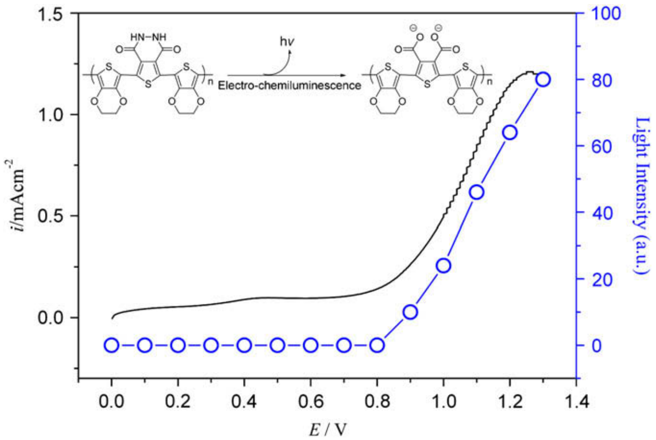


Figure 11. Cyclic voltammogram of PETE-Lum on an ITO electrode in 0.1 M TBAP/ACN containing BF_3–Et_2O at a scan rate of 100 mV/s while the generated light emission during potential scanning.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.019.

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