

SUPPORTING INFORMATION

A Glow in the Dark: Synthesis and Electropolymerization of A Novel Chemiluminescent Terthienyl System

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Experimental

All chemicals were purchased from Aldrich Chemical. 0.1 M LiClO₄ dissolved in freshly distilled (over CaH₂ under N₂ atmosphere) acetonitrile (ACN) containing 5% of BF₃-etherate by volume or neat BF₃-etherate solution was used as electrolyte solution. An indium-tin oxide (ITO, Delta Tech. 8–12 Ω, 0.7x5 cm) and a platinum wire were used as working and counter electrodes, respectively, as well as Ag/AgCl in 3 M NaCl(aq) solution as a reference. Repetitive cycling or constant potential electrolysis was used to obtain the polymer films. Spectroelectrochemical properties were investigated by using an ITO electrode as well as a platinum wire as counter electrode and an Ag wire as a pseudo-reference electrode (calibrated externally using 5 mM solution of ferrocene/ferrocenium couple). In order to equilibrate the redox behavior of the polymer film and to obtain repeated results, the coated polymer film were switched between its neutral and oxidized states several times before electroanalytical and optical studies.

FT-IR spectra were performed with a Bruker Vertex 70 Spectrophotometer assembled by an Attenuated Total Reflectance (ATR) unit. NMR spectra were recorded on a Bruker NMR Spectrometer (DPX-400) in CDCl₃. Electroanalytical measurements were performed using a

Gamry PCI4/300 potentiostat-galvanostat. The electro-optical spectra were monitored on a Hewlett–Packard 8453A diode array spectrometer. Fluorescence measurements were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. Photographs and videos of chemiluminescence reactions were taken by using a Canon (Power Shot A720IS.) digital camera. Chemiluminescent emission was monitored by using an Electron Tubes photomultiplier tube (PMT) assembled by a RX2000 Rapid Kinetics Spectrometer Accessory. Electroluminescent emission was also recorded using the PMT assembled by a UV cell under a potential scanning or a potential pulse.

Synthesis of 5,7-di-thiophen-2-yl-2,3-dihydro-thieno[3,4-d]pyridazine-1,4-dione (TTT-Lum)

The synthesis of monomer TTT-Lum is described in Fig. S1. To a solution of diethyl thiophene-3,4-dicarboxylate **1** in acetic acid was added bromine to give a dibrominated compound **2** in 60% yield. Then, the Stille coupling reaction of compound **2** with trimethyl(thien-2-yl)stannane in the presence of catalytic bis[triphenylphosphine)dichloropalladium] gave a terthienyl compound **3** in 40 % yield. Reaction of hydrazine with compound **3** produced dihydroxypyridazine TTT-Lum in 85-90 % yield.

TTT-Lum.

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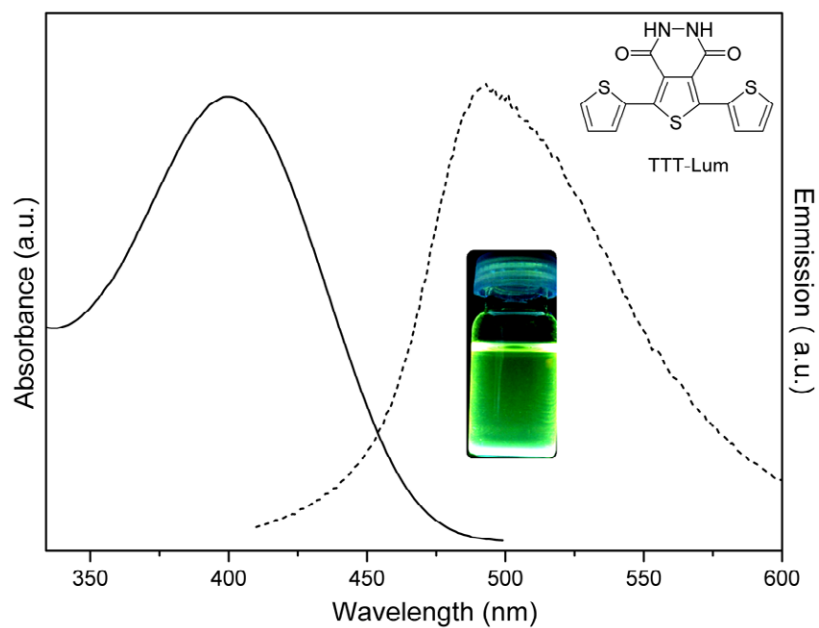


Fig. S2 The absorption and emission (excited at 400 nm) spectra of TTT-Lum in DMSO.

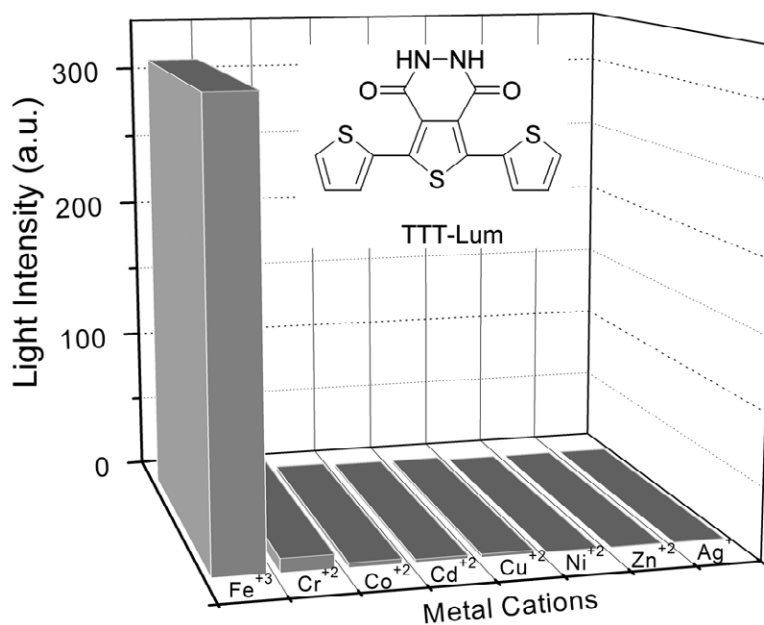


Fig. S3 The intensity of the light obtained from the chemiluminescence reaction between 1.0×10^{-5} M TTT-Lum dissolved in 0.1 M NaOH solution with 1.0×10^{-4} M H₂O₂ in the presence of different metal cations (0.1 M).

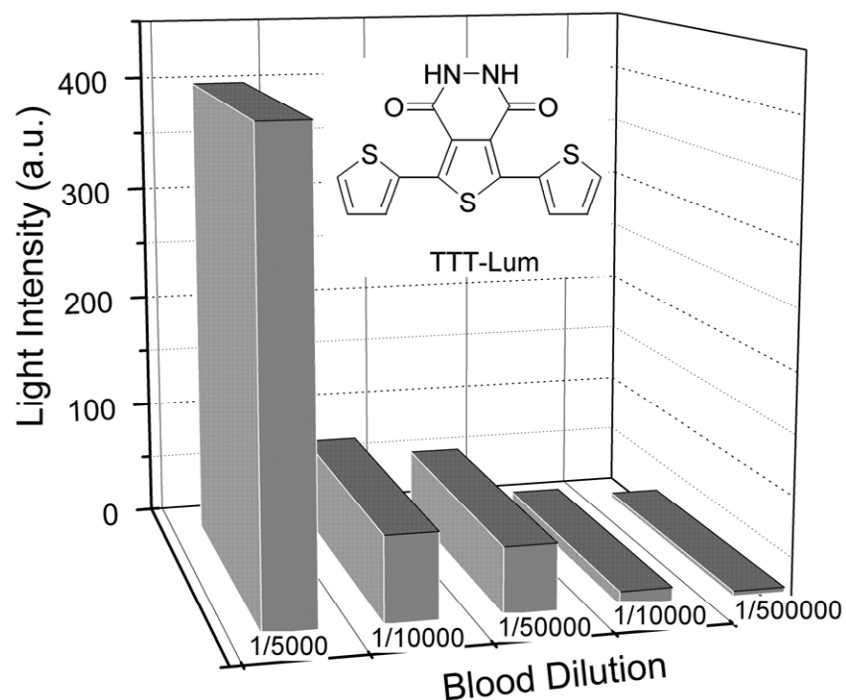


Fig. S4 The intensity of the light obtained from the chemiluminescent reaction between 1.0×10^{-5} M TTT-Lum dissolved in 0.1 M NaOH solution with 1.0×10^{-4} M H_2O_2 in the presence of different dilution ratio of blood with water.

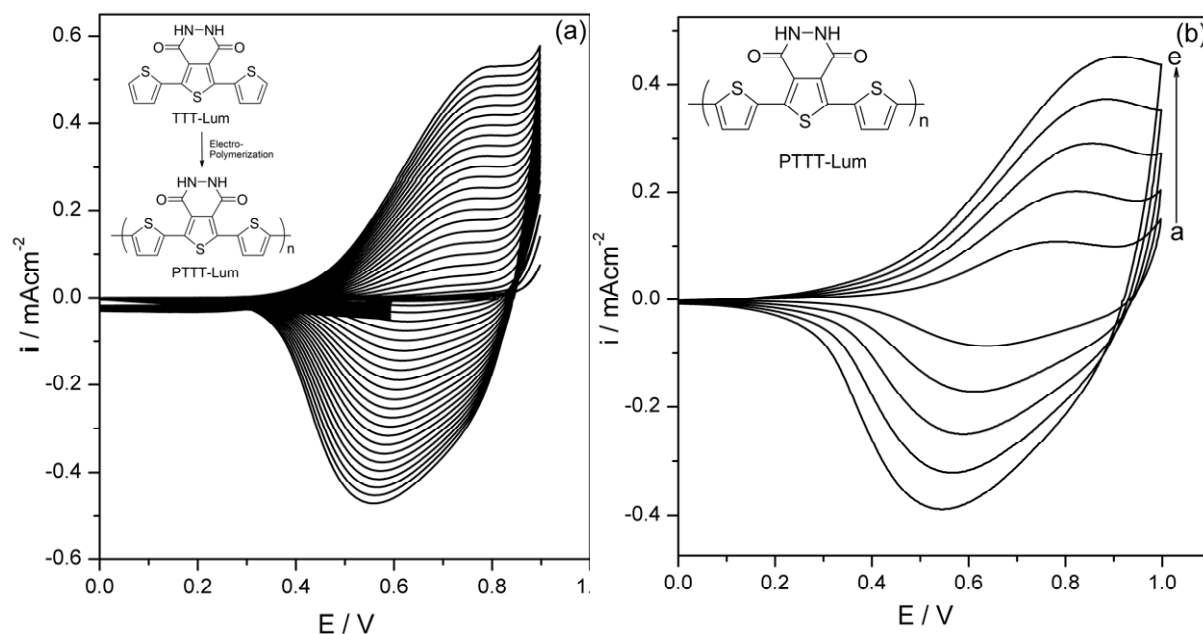


Fig. S5 (a) Repeated scan electropolymerization of 1.0×10^{-3} M TTT-Lum on an ITO electrode in BF_3 -etherate solution at a scan rate of 100 mV/s and (b) Scan rate dependence of PTTT-Lum film in BF_3 -etherate at different scan rates: (a) 20; (b) 40; (c) 60; (d) 80 and (e) 100 mV/s.

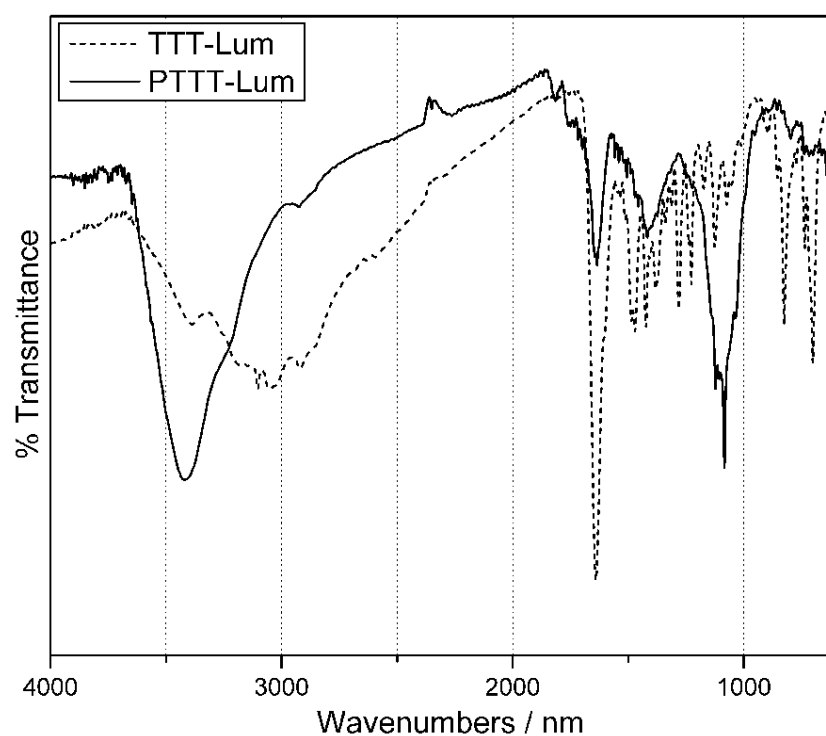


Fig. S6 FT-IR spectra of TTT-Lum and its corresponding polymer, PTTT-Lum.

The peaks at 700 cm^{-1} (α -H of thiophene rings) and 824 cm^{-1} (β/β' -H of thiophene rings) are the characteristics of TTT system.¹ It was clear that the absence of the peak at 700 cm^{-1} in the polymer spectrum confirmed the α -coupling between the external thiophene rings. However, the other peaks (i.e., 1636 cm^{-1} (C=O groups), 3404 cm^{-1} (N-H groups)) in the spectrum of PTTT-Lum were remained unchanged upon polymerization.² Moreover, the presence of ClO_4^- dopant was confirmed by the peaks at 1085 cm^{-1} and 627 cm^{-1} in the polymer spectrum.

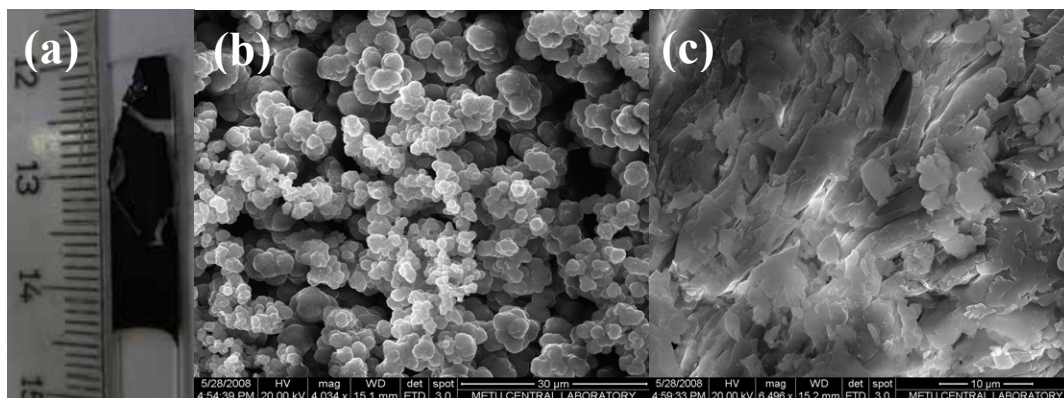


Fig. S7 (a) Electrochemically obtained PTTT-Lum on ITO. SEM photographs of PTTT-Lum synthesized via constant potential electrolysis at **(b)** 1.1 V and **(c)** 1.3 V.

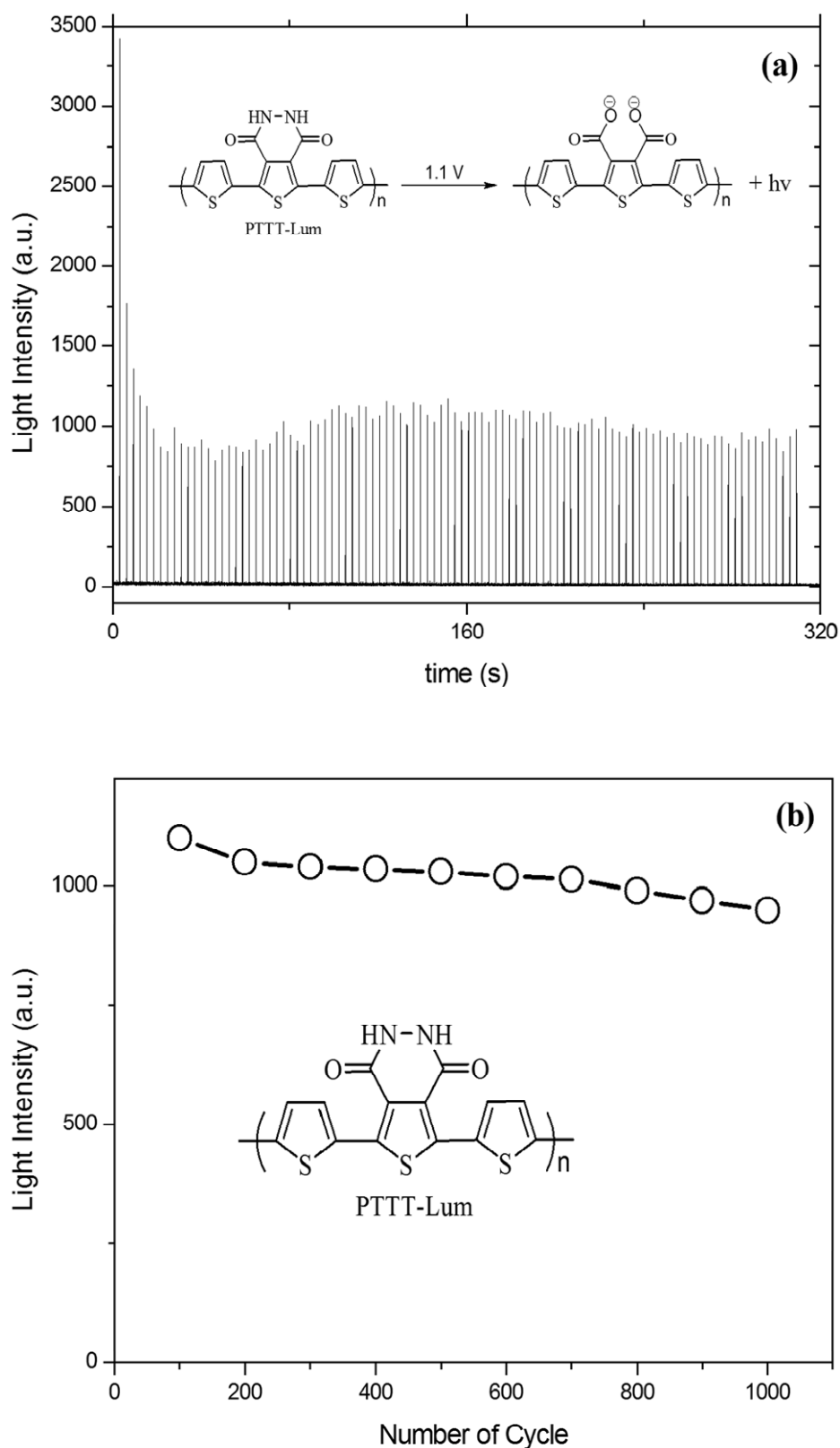


Fig. S8 (a) ECL of PTTT-Lum in monomer-free $\text{BF}_3\text{-Et}_2\text{O}$ medium. Square wave potential experiment, applied voltages were set as 1.1 V (0.1 s) and 0.0 V (3.0 s). **(b)** Representation of ECL activity over 1000 cycles.

References

1. J.P. Ferraris, T.R. Hanlon, *Polymer*, 1989, **30**, 1319
2. E.P. Koval'chuk, I.V. Grynchyshyn, O.V. Reshetnyak, R.Y. Gladyshevs'kyj, J. Błażejowski, *Eur. Polym. J.*, 2005, **41**, 1315.