



Electrically excited polymers for the detection of dinitrobenzene



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ABSTRACT

In this paper, we present an organic light emitting diode (OLED) used as a sensor for the detection of 1,4-dinitrobenzene (1,4-DNB). The detection method relies on the attenuation of the emitted light due to interactions between the 1,4-DNB and the active organic layer. The mechanism responsible for this attenuation involves an electron transfer from the electron donating organic layer to the electron deficient nitroaromatic 1,4-DNB. Devices were fabricated and tested against various concentrations of 1,4-DNB to determine if a dependence on concentration exists and to reveal more detail about the internal quenching mechanism.

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1. Introduction

There is a pressing need for lightweight, low cost, highly effective, and rapidly responding sensors for explosive compounds. Explosive devices can be put into many forms, which can then be camouflaged to further complicate their ability to be safely detected. A method to defeat explosive hazards is the direct detection of the chemicals associated with them such as 2,4,6-trinitrotoluene (TNT) and other nitroaromatics [1]. Methods of direct chemical detection of explosive hazards are extensive in the literature, and include gas and liquid chromatography [2,3], capillary electrophoresis [4], cavity ringdown spectroscopy [5], ion mobility spectrometry [6], surface acoustic wave devices [7], infrared spectroscopy [8], Raman spectroscopy [9], small molecules [10], and fluorescent polymers [11,12]. Of particular relevance to the work discussed herein is the use of fluorescent polymers whose emitted radiation is changed by an oxidative quenching mechanism when they are in contact with electron withdrawing nitroaromatic compounds [13,14]. Traditional fluorescence-based sensors that utilize this sensing scheme excite the fluorescent polymer with an independent light source to induce photoluminescence (PL), and the resulting steady-state fluorescence is monitored for changes indicating the presence of target analytes.

Herein we detail a novel sensing scheme in which a fluorescent polymer is fabricated into an organic light emitting diode (OLED) to act as a sensing device. It has been shown that the PL spectral output from a given conjugated or fluorescent polymer matches that of its electroluminescence (EL) spectrum. This indicates that emission from EL and PL originate from the same excited states [15]. This leads to the possibility that both EL and PL are susceptible to the same quenching mechanisms. To test this hypothesis we constructed a sensor device that excites a polymer by passing electrical current through it, generating electroluminescence, and then subjecting the polymer to 1,4-dinitrobenzene (1,4-DNB), an electron withdrawing nitroaromatic compound. The light generation is achieved in the same manner as in simple OLED devices: electrons are injected from a low work function cathode into the LUMO of the polymer and holes are injected from a high work function anode into the HOMO of the polymer, leading to radiative recombination in the polymer [16]. The emitted radiation from the sensing light emitting diode (SLED) is monitored for attenuations that indicate the presence of target nitroaromatic compounds, in this case 1,4-DNB vapor, a surrogate for the high explosive TNT. This paper describes the response of our SLED device to 1,4-DNB vapor. Stern–Volmer (SV) experiments were carried out to test the concentration dependent response of the SLED and gain insight into the quenching mechanism. Additionally, measurements were performed on test structures similar to the SLED device to investigate how the 1,4-DNB was diffusing into the active polymer layer. Finally, the effect of cathode morphology and degradation is related to device response and performance.

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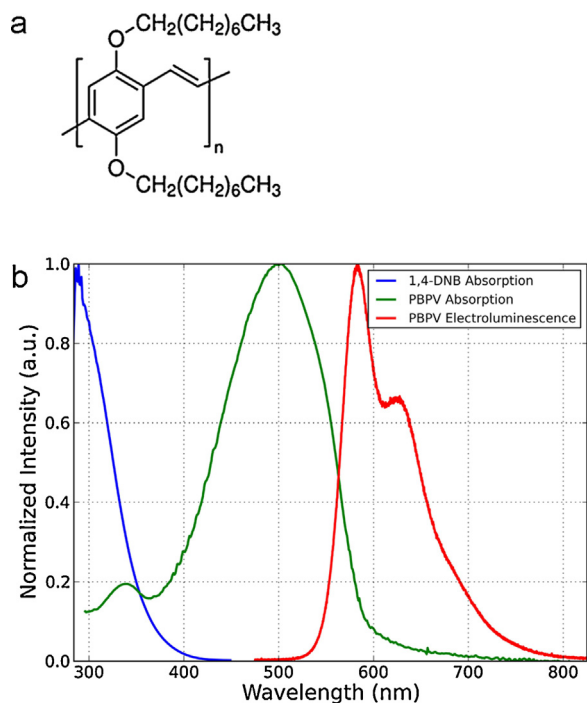


Fig. 1. (a) PBPV structure and (b) optical comparison of PBPV absorption, PBPV electroluminescence, and 1,4-DNB absorption.

2. Materials and methods

2.1. Polymer sensor material

Polyphenylene vinylenes (PPV) are well studied, light emitting, conjugated polymers offering good mechanical and processing properties, with high luminescence and permeability to small molecules [17]. Substitutions on the PPV backbone with an alkyl and alkoxy substituent improve the solubility and can modify the optical band gap [18]. Poly[2,5-bis(octyloxy)-1,4-phenylenevinylene] (PBPV) (Sigma–Aldrich) was dissolved in chloroform at a concentration of 3.5 mg/mL and placed in a heated ultrasonic water bath for 30 min. Fig. 1a shows the structure of PBPV, which contains substituted alkoxy groups providing improved solubility. The plots shown in Fig. 1b compare the optical absorption and electroluminescent emission of PBPV. The maximum absorption and emission of the PBPV occur at approximately 500 nm and 583 nm, indicating a Stokes shift of 83 nm. The emission spectrum was observed to be independent of the applied voltage.

2.2. Device structure

OLEDs are electroluminescent devices which operate under electron and hole injection from a cathode and anode respectively. Additional layers may be used at each of these interfaces to promote electron injection at the cathode, hole injection at the anode, and carrier transportation to the emissive layer. Heterojunction devices have become widely used because transition layers of different materials provide a better energy level match between the anode and the polymer HOMO, and the cathode and polymer LUMO. Experimentation was performed on the device shown in Fig. 2a, a heterojunction OLED device with a 60 nm PBPV emitting/sensing layer. The substrate consists of glass coated with indium tin oxide (ITO), providing a transparent anode. A 60 nm layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), a polymer complex solution with a high work function was used as a hole transport layer. The cathode consists of an

8 nm tris(8-hydroxyquinolino) aluminum (Alq_3), 0.8 nm lithium fluoride (LiF), and 50 nm aluminum (Al). The LiF and Alq_3 are used together to provide a low work function interface between the polymer and Al for better electron injection [19]. A fully fabricated device is shown in Fig. 2b without a voltage applied and in Fig. 2c with a voltage of 19 V.

2.3. Sensor fabrication

The overall fabrication process can be separated into cleaning and preparation, polymer deposition, and cathode deposition. First, the ITO substrate is patterned using a thick negative permanent photoresist to define active areas on the ITO surface. Next, the polymers are deposited with common spin coating techniques to generate thin uniform polymer films. Finally, the cathode is deposited by thermal evaporation under vacuum.

ITO coated glass slides (Sigma–Aldrich) with a 15–25 Ω/sq surface resistivity were used as the substrate and anode. Glass slides were degreased with a solvent cleaning method consisting of successive soaking in organic solvents followed by deionized water rinsing. The cleaned substrates were coated with SU-8 2005 (Microchem) by spin casting. The substrates were then soft baked to remove remaining solvents. The photoresist was then exposed to a UV source using an AOI mask aligner while using a photo mask. Following exposure, substrates were post baked for and then developed in 100% propylene glycol methyl ether acetate. A final hard bake was used to make the photoresist permanent and resistive to further processing. The final thickness of the SU-8 film was measured to be approximately 5 μm with a profilometer (Veeco Dektak 8). This step leaves certain parts of the ITO exposed where it can be in contact with the polymer.

The SU-8 coated substrates were again solvent cleaned as previously described, and then loaded in an oxygen plasma treatment system (Nordson March PM-100). Treating the surface of ITO with oxygen plasma has shown to create a smoother surface, lower sheet resistance, increase the work function, and increase surface energy and polarity of the ITO substrate [20]. The work function of ITO can be raised in an oxygen plasma to create a lower barrier for hole injection at the ITO/PEDOT:PSS/PPV interface [21]. Finally, this treatment creates a hydrophilic surface by increasing the surface energy, reducing the contact angle between the ITO and water based PEDOT:PSS [22], and ultimately creating a more uniform spin deposited film. The hole transport layer PEDOT:PSS (Sigma–Aldrich) was filtered and deposited by spin casting. A dehydration bake was then performed to remove moisture. The emissive and sensing PBPV (Sigma–Aldrich) was dissolved in chloroform and placed in a heated ultrasonic water bath. The PBPV solution was then deposited by spin casting, and a solvent bake was performed to remove remaining chloroform. A cotton swipe dipped in acetone was used to expose part of the ITO substrate to provide an anode connection. The polymer coated substrates were then loaded into a thermal evaporation system for thin film deposition. The evaporator sources contained the following materials: 99.9% pure LiF powder (Cerac Specialty Inorganics), 99.999% Al pellets (Kurt J. Lesker), and Alq_3 powder (Sigma–Aldrich). Deposition was initiated when a base pressure of approximately 5.0×10^{-7} Torr was achieved. Alq_3 was deposited until a final thickness of 8 nm was reached. Lithium fluoride was deposited until a final thickness of 0.8 nm was reached. Aluminum was deposited until a final thickness of ~ 50 nm was reached. Following cathode deposition the finished device was thermally annealed under vacuum.

2.4. Data collection and measurement setup

A customized Labview program was created to automate the testing of the SLED devices. The emission of the SLED was collected

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