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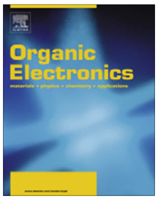

Letter

Electrochemical control of amplified spontaneous emission in conjugated polymers

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ABSTRACT

We present a method of electrochemically tuning the threshold intensity of the amplified spontaneous emission (ASE) of a semiconducting polymer thin film. This can be achieved in close contact with a conducting polymer electrode (PEDOT:PSS), if the latter is electrochemically tuned to an optically transparent redox state for the emitted wavelength of interest. This electrical switch between ASE and fluorescence hints that a new route to achieve electrically pumped laser is by combining an electrochemical device with a lasing conjugated polymer.

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1. Introduction

Semiconducting polymers possess several interesting combined (opto-) electronic properties. One combination is that these materials can exhibit amplified spontaneous emission (ASE) and fast charge transport; a prerequisite for optically pumped solid state lasers [1,2]. The low-threshold energy for ASE demonstrated for conjugated polymers makes them as good as any other dye commonly used in liquid or solid-state laser systems [3]. Various concepts have been explored to increase the efficiency of polymer light emitting devices and their inherent current density in order to create an electrically-pumped organic solid state laser [4]. To achieve lasing in diode architectures one of the greatest challenges is to obtain ASE close to the charge injecting and transparent electrode, while retaining an efficient waveguide of the optical mode [1]. Poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT:PSS) is a conducting polymer that is transparent at blue optical wavelengths and has sufficient conductivity to serve as the electrode in light emitting diodes with low turn-on voltage [5]. However due to its high absorption in the visible region (in the pristine form) and having refractive index similar to the emitting polymer, PEDOT:PSS has not been considered as an electrode in electrically pumped diode lasers.

In this letter, we report optically pumped ASE of a polyfluorene derivative that is sandwiched between a PEDOT-PSS electrode and a glass substrate. The oxidation level of PEDOT:PSS is electrochemically controlled by including the sandwich stack in an electrochemical cell including an aqueous salt. First, by increasing the oxidation level of PEDOT we find that the threshold for ASE decreases. Secondly, we demonstrate that lasing can be achieved in aqueous gel media. The results suggest the suitability of PEDOT:PSS as an electrode in electrically pumped organic lasers and may pave the way for exploring organic lasers as sensor transducers in aqueous sensing applications.

2. Results and discussion

The emitting conjugated polymer used is a alkoxyphenyl-substituted polyfluorene [6], characterized by a little overlap between the absorption and emission spectra, which is desired for low threshold ASE and long optical

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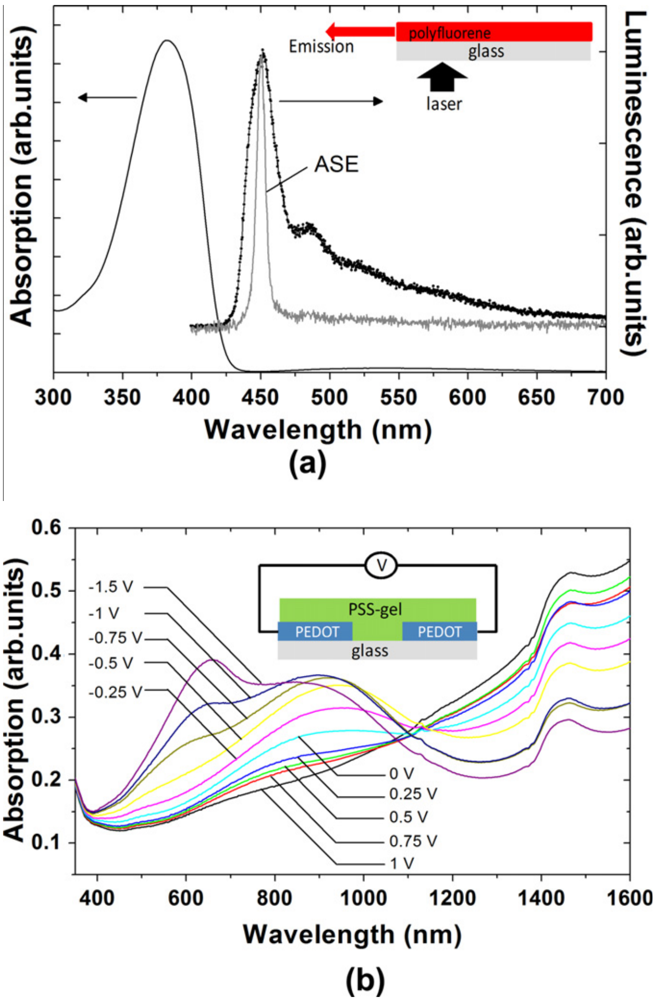

Fig. 1. (a) The absorption and the emission spectra of the LL20 spun on glass. The emission spectra are normalized at the same maxima and they correspond to pumping intensities of 3.3 kW/cm^2 and 10 kW/cm^2. (b) The absorption spectra of PEDOT-PSS at different applied biases in the electrochromic device sketched in the inset. (The shoulder at 1400 nm is an artefact in the measurement).

gain lengths. Fig. 1a displays the striking difference in broadening between the photoluminescence emission (26 nm broad) and the ASE spectrum centered at 452 nm with a width of only 7 nm. The pumping laser is an optical parameter oscillator – OPO-coupled to Nd:YAG laser with a 5 ns pulse and a 10 Hz repetition rate, emitting at 330 nm. The duration of the laser pump pulse is longer than the lifetime of the excited singlet state usually reported for polyfluorenes (0.5 ns) [7]. Therefore the measurements can be considered as quasi-steady state with the excitation density as a function of pump intensity rather than of pump energy [1]. The 150 nm-thick polymer layer deposited on glass is irradiated by a 10 mm long beam stripe. Fig. 2 plots the emission spectra at pump intensities ranging from 1.9 kW cm^{-2} to 10 kW cm^{-2}. There is a noticeable narrowing of the emission peak as the pumping intensity increases. The threshold intensity for the ASE is identified by plotting the output intensity, recorded along the plane of the film, as a function of the pump intensity (Fig. 2, inset) [8–10]. The threshold intensity is 3.7 kW/cm^2 (or 17 μJ/cm^2 per pulse), a value similar to what has been measured in other polymers of the polyfluorene family [3].

The conducting polymer electrode used is made from PEDOT:PSS. Diethyleneglycol is used as a secondary dopant in order to reach pristine conductivity values up to 10 S/cm [5]. A silane-coupling agent (Silquest) is used to cross-link the conducting layer making it insoluble in water electrolytes. Two PEDOT:PSS electrodes on the substrate are connected via a polyelectrolyte gel (33 wt.% PSS, 8 wt.% glycerol, 8 wt.% D-sorbitol in DI water) to form a simple electrochromic device setup (inset Fig. 1b) [11]. The modulation of the absorption spectrum of PEDOT, in the electrochromic device, is given in Fig. 1b, where the data are collected for a device excluding the emitting layer. In its pristine conducting state ($V = 0$ V), the conducting polymer appears as semi-transparent (light blue) and absorbs mostly in the red to near infra-red (NIR) region, a specific feature of the absorption of the polaronic and bipolaronic bands [12]. Interestingly, further oxidation, from 0 V to +1 V, leads to a decrease of the optical absorption at the

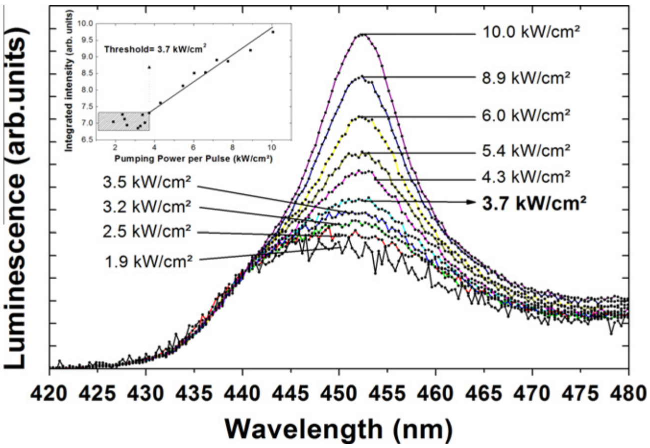

Fig. 2. The emission spectra of LL20 as a function of the pumping intensity. The spectra were normalized to common background intensity. The inset plots the integrated emission intensity for all the wavelengths as a function of the pumping power per pulse.

luminescence emission wavelength of PPF-1. Conversely, reduction of PEDOT-PSS, achieved by applying from a negative voltage to the PEDOT electrode (0 V to -1.5 V), is accompanied with an enhancement of a broad visible absorption feature peaking at around 630 nm. This absorption band originates from neutral PEDOT segments. Hence, it is expected that PEDOT:PSS in its “fully” oxidized state absorbs the luminescent wavelengths from PPF-1 to a very low degree. This should enable long optical gain lengths in a PPF-1 film coated by a “fully” oxidized PEDOT:PSS film.

The conjugated polymer PPF-1 film (150 nm thick) on glass is covered by a PEDOT-PSS (50 nm thick) film in a sandwich device configuration, illustrated in the inset of Fig. 3a. This simple stacked device combines an electrochromic layer and a luminescent emitting layer. The role of the electrochemical layer is to provide a tool to control the oxidation level and the absorption spectrum of the PEDOT:PSS electrode. Another PEDOT:PSS electrode adjacent to the electrochromic pixel to serves as the counter electrode for the electrochromic switching experiments. The two PEDOT:PSS films are connected via a polyelectrolyte gel. Since, the refractive index of PEDOT:PSS at 450 nm is 1.73, which is close to 1.76 measured for LL20, those two polymer layers together form a slab optical waveguide with glass ($n = 1.45$) and the polyelectrolyte gel ($n = 1.3$) as the cladding. The PPF-1 layer is optically pumped through the glass substrate at a power intensity of 50 kW cm^{-2} (stripe length of 10 mm), i.e. well above its ASE threshold intensity for LL20 films on glass excluding the PEDOT:PSS film on top. The emission spectrum is controlled by the electric potential applied to the electrochromic PEDOT:PSS layer (Fig. 3a). When PEDOT is reduced (negative bias), it efficiently absorbs the luminescence emission generated in the wavelength region around 450 nm. The optical loss, as the emission is guided along the PPF-1-PEDOT:PSS waveguide, overwhelms the optical gain and no amplification is thus possible: the emission spectrum corresponds to the photoluminescence spectrum of PPF-1 when excited below the ASE threshold. Upon oxidizing the polymer, by applying a positive bias voltage, the emission spectrum becomes gradually narrower, i.e. the gain becomes larger than the optical loss of the PEDOT:PSS film. At 1 V bias, the width is 7 nm, similar to the ASE spectrum found from PPF-1 films on glass, compare with the data given in Fig. 1a. The emission amplification is made possible despite the fact that light propagates inside the PEDOT:PSS film because PEDOT:PSS turns transparent enough at 450 nm when it is in its oxidized state. This is the first demonstration of ASE of conjugated polymers for films in close proximity to a highly conducting polymer ($\sigma = 10$ S/cm) and an electrolyte. Additionally, this optical device appears as a ASE potentiometer, switching from spontaneous photoluminescence emission to ASE by increasing the applied potential on PEDOT:PSS.

The experiment is repeated using aqueous electrolyte (0.1 M NaCl) as the outer cladding layer. Again, switching between the ASE and photoluminescence is observed (Fig. 3b). Long optical gain length inside the electroactive polymer films combined with electrochromic activity can be used as a sensible probe in electrochemical sensor experiments. This concept may have a potential impact for biological sensing since the rate of the electrochromism can be related to the recognition event of enzymes located along the surface of the conducting polymer within a cell medium.

3. Conclusion

In summary, we report ASE from a conjugated polymer thin film in close contact with a layer of the conducting polymer PEDOT:PSS. As the electrochemical state of PEDOT is switched in situ, using an electrochemical cell configuration, the ASE characteristics are tuned. As PEDOT is oxidized beyond its pristine oxidation level the ASE peak grows, thus demonstrating that the lasing threshold can be decreased by further oxidizing PEDOT. Our findings provide new insights regarding combining charge-injecting electrodes with lasing polymers towards a technology of electrically pumped lasers. The emitting organic layer would be sandwiched between the electrochemically tunable PEDOT electrode and another electron injecting electrode patterned on the

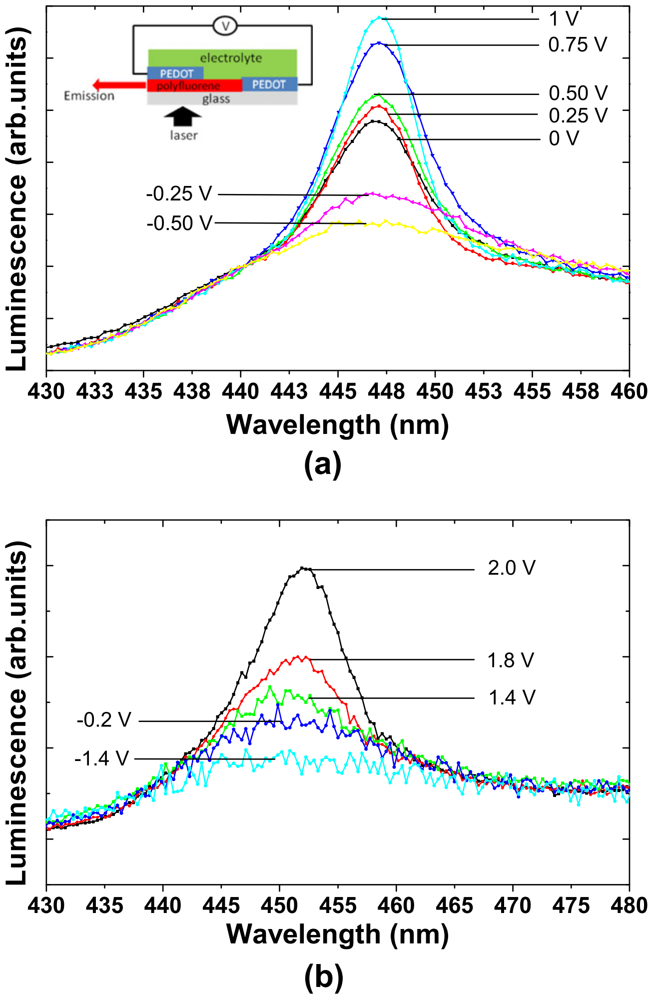

Fig. 3. (a) The inset shows a sketch of the electro-photonic device. The electric potential is applied between the two PEDOT:PSS electrodes, while the emitting layer LL20 is pumped optically through the glass substrate. The emission spectra is plotted at different electric potentials applied between the PEDOT-PSS electrodes. (b) The emission spectra at different potentials of a glass/LL20/PEDOT:PSS device in water. The spectra are normalized at the same background intensity and the pumping intensity is 50 kW/cm^2.

substrate. The electron injecting contact would be placed on the other side of the emitting polymer Moreover, an aqueous electrolyte solution can be used as the cladding layer on top of the electrochemically active and conducting polymer electrode. This may open for novel opto-electrochemical sensors for applications in biology and diagnostics.

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