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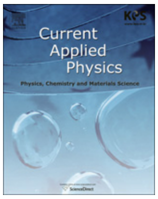

# Thickness effects on the optical properties of layer-by-layer poly(*p*-phenylene vinylene) thin films and their use in energy-modulated structures

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## ABSTRACT

Poly(*p*-phenylene vinylene) (PPV) thin films were produced by layer-by-layer (LbL) method, using soluble PPV-precursor and dodecylbenzenesulfonate salt (DBS). The amount of deposited layers strongly influences the optical properties of the thermally converted PPV film. The absorbance and luminescence spectra of ultra-thin films (consisting of only two or three PPV layers) are shifted to smaller wavelengths with respect to spectra of thicker films. This is related to the smaller average conjugation length of polymer chains, resulting in a higher HOMO–LUMO gap energy of the material. However, if a thick film is produced by repeating the deposition process and thermal conversion of ultra-thin layers, the optical spectra are still displaced to higher energies in comparison with those of thicker films produced by the conventional continuous deposition of layers. This result enabled the production of multilayered polymeric films with modulated energy profile, taking the number of deposited layers as the only variable in the manufacturing process of the structure. The aim is to guide the excitation to specific regions of the material through the Förster-type energy transfer processes. Such systems can be used at interfaces electrode/polymer and/or electrode/polymeric active layers in order to improve the performance of organic optoelectronic devices.

## 1. Introduction

Conjugated polymers have great potential to be applied as active layer in organic semiconductor devices [1]. In particular, thin films of the poly(*p*-phenylene vinylene) (PPV) family are currently investigated and widely used in polymer light emitting diodes (PLEDs) [2,3] and organic photovoltaic cells [4–6]. However, there are several issues related to optimizing the performance of these devices such as the balance of charges due to different diffusion lengths of carriers in the active region [7], and the emission quenching at the region near the polymer/electrode interfaces [8,9]. Several studies report on the use of an interlayer inserted between the injection layer (usually a film of poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate), PEDOT:PSS [10,11]) and the light emitting layer, whose properties are tuned to improve the device performance [12–16]. This interlayer plays two main roles: to prevent electrons and excitons from moving from the PEDOT:PSS layer to the emissive polymer (back transfer process), and to separate the active layer from the injection layer, so as to minimize chemical reactions between them and thereby reduce the emission quenching at the interface [15,16]. However, the interlayer must possess specific properties that meet these requirements, such as work function and appropriate HOMO–LUMO gap energy, as well as properties for the efficient transport of charge carriers.

Favarim et al. in particular, proposed to make multilayered thin films with modulated energy profile [17], to guide the excitation to specific and functional sites of the device. The energy profile is determined by differences in HOMO–LUMO gap energy between the layers containing polymer chains with different conjugation lengths. The excitation is driven by the energy profile through the Förster-type energy transfer between the chains [18]. In this sense, the layer-by-layer method is very appropriate to deposition of the thin films [19–21], since it allows the manipulation of the multilayers in a molecular scale. The authors of ref. 17 were able to vary the HOMO–LUMO gap of PPV through the incorporation of different amounts of dodecylbenzenesulfonate (DBS) into the PPV-precursor poly(xylylidene tetrahydro-thiophenium chloride) (PTHT) solution. A bilayer in the LbL film was completed through deposition of a polyanionic PSS layer, forming a PTHT:DBS/PSS bilayer which was converted to PPV after thermal treatment. Then, heterostructures with variable HOMO–LUMO gap could be formed along the deposition direction by changing the DBS concentration. However, the

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use of electronically inert materials as the PSS [16,17,22] or poly(styrene-4-sulfonate) [23] in the LbL composition of PPV layers can interrupt the carrier transport in these films, affecting negatively the performance of the resultant thin film device, as reported by Ogawa et al. for PPV-based photovoltaic cells [24].

In this work, we report that the HOMO–LUMO gap of PPV is dependent not only the DBS concentration, but also the number of layers of PTHT/DBS. After thermal conversion, films consisting of 3 layers of PTHT/DBS had higher HOMO–LUMO gap than films with 10 layers of PTHT/DBS. The maximum intensity of absorbance for 3 layers PPV film was around 400 nm, whereas for 10 layers PPV film was around 450 nm. Furthermore, with deposition and thermal conversion of 3 layers of PTHT/DBS in addition to the 3 layers already deposited and thermally converted, the intensity of absorbance increased due to the increased thickness of the material, but the maximum absorbance at 400 nm was maintained. Repeating this process again, there was a further increase in absorbance intensity, but the position of its maximum is not changed. These results opened the possibility to construct multilayered films with modulated energy profile by combining the overlap of multiple depositions of a PPV film with few layers (to produce a layer with higher bandgap) with the continuous deposition of several layers (to produce a layer with lower bandgap), resulting differences in energy gap larger than 0.3 eV. The energy transfer processes through the single step structure was verified by photoluminescence (PL) measurements, showing this structure is able to promote directional migration of the excitation into the sample.

## 2. Experimental details

For the production of the LbL–PPV films, we followed the procedure proposed by Marletta et al. [25], using the alternating adsorption of the precursor polymer, PTHT, and DBS in aqueous solution. The materials were purchased from Aldrich and were used without further purification. The concentration was $10^{-2}$ M for both solutions. The method used in the deposition of the layers is depicted in Fig. 1: the cleaned and hydrophylized substrate (BK7 glass) is immersed in the PTHT solution for 30 s (process indicated by number 1 in Fig. 1). It is then washed with ultrapure water (resistivity 18.2 MΩ/cm) and dried for 5 min. by spinning. This process is indicated by number 2 in Fig. 1. After, it is immersed in the solution of DBS also for 30 s (number 3 in Fig. 1), and then the process of washing and drying is repeated (number 4 in Fig. 1). At the end of this cycle, we obtain a PTHT/DBS layer. The thermal treatment of the film was conducted for 30 min in a home-made oven maintained at 100 °C, at ambient conditions. The result of this process is the thermal conversion of the PTHT/DBS layer in a PPV conjugated polymer layer, through the elimination of the sulfonate lateral group [25].

The absorbance measurements were made with a USB-4000 minispectrometer (Ocean Optics) using a DT-Mini-2-GS model UV–vis lamp. The same spectrometer was used in the photoluminescence (PL) measurements, during which the films were kept in a cryostat at $10^{-2}$ Torr to reduce the photodegradation effects [26]. As excitation we used a 473 nm solid-state laser, with intensity ca. 1 mW $cm^{-2}$. For polarized measurements were used linear polarizers from Edmund Optics with high extinction ratio. All measurements were performed at room temperature.

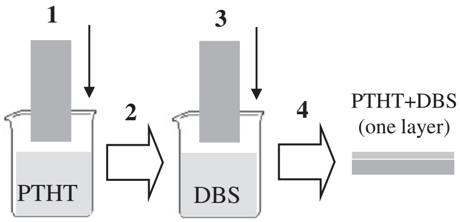

**Fig. 1.** Scheme of the sequence for deposition of PTHT/DBS layers, where 1 and 3 indicate the substrate dipping in aqueous solutions of PTHT and DBS, respectively, and 2 and 4 relate to the washing and drying processes.

## 3. Results and discussion

Fig. 2 shows the absorbance and PL spectra of a PPV converted film made by continuous deposition of 10 layers of PTHT/DBS. These spectra are typical of LbL–PPV films with a high conjugation length [25], showing maximum absorbance around 450 nm and purely electronic emission peak around 510 nm. It also shows that the vibronic structure is well defined, with relatively narrow bands, indicating the good optical quality of the film [27]. There is some overlap between the spectra in the region around 500 nm, which can result in a slight distortion of the PL spectrum due to self-absorption [28]. However, such effects do not affect the analysis of the results discussed here, so the correction due to self-absorption was not performed on the spectra presented in this paper.

The Fig. 3 shows the absorbance curves of LbL–PPV films. The curves in solid line refer to the absorbance spectra obtained from a film deposited as follows: initially, 3 layers of PTHT/DBS were deposited (according to the procedure reported in the experimental section), and then a thermal treatment was carried out for conversion to PPV. The absorbance of this film is the curve with lowest intensity (maximum intensity of around 0.05) in Fig. 3. After, 3 PTHT/DBS layers were deposited on these 3 layers of PPV, the thermal conversion process was done again, and the absorbance curve was extracted (spectrum with maximum intensity around 0.07 in Fig. 3). A diagram of this deposition procedure is showed in Fig. 4(a). This same procedure was repeated in the sequence,

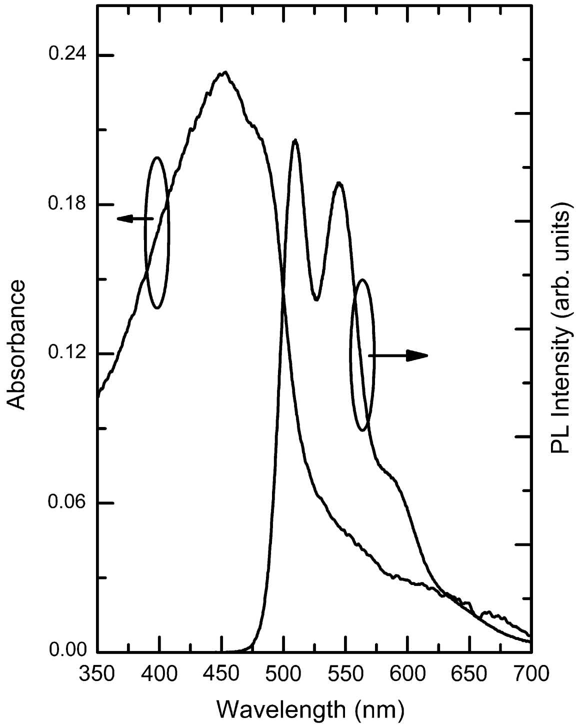

**Fig. 2.** Absorbance (left panel) and PL (right panel) spectra of the PPV film with 10 layers.