



## Avoiding trap states in *poly(n-vinylcarbazole)* thin films

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### ABSTRACT

Optical properties of *poly(n-vinylcarbazole)* (PVK) thin films are revisited. Steady-state emission spectra put in evidence a strong red band whose intensity increases with decreasing temperature when the solid state PVK film is excited by a continuous 375 nm laser line. This red band is assigned to the emission from PVK aggregate states which act as trap states for the monomeric PVK triplet high energy (blue) excitons. At the same low temperatures, these trap states can be avoided when the excitation of the PVK film is made by a 355 nm pulsed laser line with 10 Hz repetition rate. The red band was also observed to compete with the emission of guest *poly(3-octadecylthiophene)* (PODT) molecules in a PVK/PODT sequential bilayer structure. Different optical geometries enabled us to show that the exciton energy transfer effect from PVK donor to PODT acceptor states dominates the scenario in the bilayer structure, suppressing almost completely the trap state emissions.

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### 1. Introduction

Since the first polymer light emitting devices (PLEDs) reported in the literature [1], white PLEDs [2–4] have been investigated in order to consecrate conjugated polymers as a prominent, low cost and efficient new class of organic electronic materials. Many strategies have been planned and executed to obtain polymer-based white light-emitting diodes [5–10]. These devices were mainly based on polymer-blend or small-molecule-doped polymer systems [11,12]. However, disadvantages of this approach, such as difficulties in finding polymer components with suitable deep blue or red wavelengths, can happen in the quest to obtain a balanced white-light emission. In this context, *poly(n-vinylcarbazole)* (PVK), a non-conjugated polymer with a luminescent carbazole side group, has been extensively used as a blue phosphorescent host material

[13–16]. However, the use of PVK as a host for the blue phosphorescent component in PLEDs has been put in doubt by Jankus and Monkman [17]. These authors demonstrated the existence of triplet trap species, which were assigned as ground state triplet dimers in PVK with an energy around 2.5 eV. These trap states would likely compete with monomeric triplet states during recombination in the PVK host, thus reducing its deep blue emission. In this work, steady state emissions from PVK films, a green band (507 nm) and a red shoulder (665 nm), were observed at room temperature when the sample was pumped by a continuous 375 nm laser line. With decreasing temperature these two emissions presented an intensity enhancement with a significant reduction of the PVK blue emission. These emissions are assigned, respectively, to recombinations of the ground state triplet dimers [17] and recombinations of aggregate species in the PVK film. However, the enhancement effect of these two species was not observed when excitation of the PVK film was done by a pulsed laser at a low repetition rate. In this case, even at

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low temperatures the PVK film presents only its well known phosphorescent blue emission. In addition, by using a PVK/PODT sequential bilayer at the same pulsed laser excitation and low temperature conditions it is shown that the PVK blue emission survives and contributes effectively to a more balanced white emission.

## 2. Samples and experimental details

The PVK (5.0 mg/mL in chlorophorm) and PODT (5.0 mg/mL in chlorophorm) solutions were produced and left to stir for more than 24 hs. Additional information about the synthesis of the PODT polymer used in this work can be found elsewhere [18]. Thin films of PVK and PODT were fabricated by spin-coating on glass substrates at 1000 rpm. The PODT film was heated at 60 °C in a hot-plate for 30 min to further remove the solvent. The PVK film was left drying inside the glove-box to further remove its solvent. In order to fabricate the PVK/PODT sequential bilayer structure we first spread the PODT solution at 1000 rpm on top of a glass substrate and then heated it at 60 °C for 30 min, as for the pure film. A hexamethyldisilane (HMDS) solution was deposited by spin-coating at 1500 rpm on top of the PODT film prior to the PVK deposition in order to promote its better spreading. The HMDS coated surface becomes neutral, hydrophobic and non-oily. In addition, it offers increased resistivity and is not affected by solvents that are not readily hydrolyzed. The bilayer structure was completed by spreading the PVK solution at 1000 rpm. The bilayer structure was then left drying inside the glove-box to further remove its solvent.

The respective thicknesses and refractive indexes of the samples were measured by ellipsometry using a J.A. Woollan Co., Inc. ellipsometer, model M2000.

The absorption spectra were obtained using a 3600 Shimadzu spectrophotometer. The steady-state emission measurements were performed at different temperatures using a liquid He immersion cryostat and a temperature controller. All films were always in contact with the cold He gas at atmospheric pressure or under vacuum at room temperature to avoid any photo-oxidation effect on them. The detection of the emitted light was made by an Ocean Optics USB2000 mini-spectrometer. For the excitation of the films we have used a CW 375 nm line from a diode laser and a CW 457.9 nm line from an Ar-laser. In this work the detection of the emission signal at an angle of 45° to the normal of the film surface is called 45° geometry. This is the more standard photoluminescence collection geometry. The detection from the edge of the film, with the laser incidence parallel to the normal of the film surface is called 90° geometry. A special experimental set-up was used in order to shine each laser line at the same position on the films, enabling us to compare the respective emission intensities. A pulsed Nd:YAG laser line at 355 nm, with 10 Hz of repetition rate and pulse duration of 4 ns was also used to study the samples.

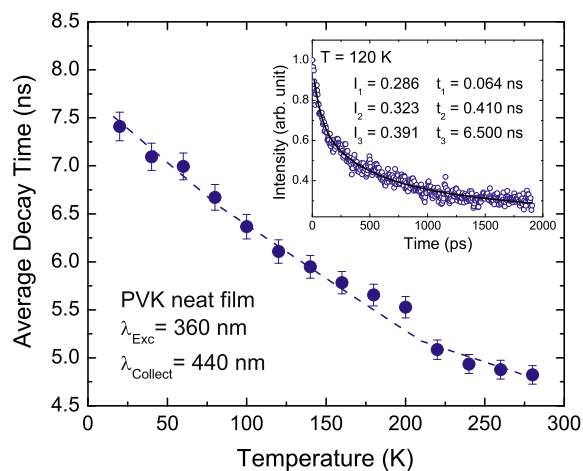
Picosecond time resolved fluorescence measurements were made using a Hamamatsu C5680 streak camera coupled to a monochromator (Acton SpectraPro-2300i). Femtosecond pulses with 80 MHz repetition rate, generated

by a Spectra Physics Tsunami Ti:Sapphire laser coupled to a Spectra Physics GWU-23PS second harmonic generator, were used to produce a vertically polarised excitation source at 360 nm. A time resolution around 7 ps and a spectral resolution of 4 nm can be achieved with this setup, with fluorescence decays obtained by averaging over a 5 nm wide boxed section of the camera image.

## 3. Results and discussions

The average decay time ( $\bar{\tau}$ ) for the PVK film as a function of the temperature is shown in Fig. 1. A decay curve obtained at 120 K is shown in the inset of Fig. 1 as an example. All decay curves have been well fitted with a triple exponential function  $I(t) = \sum_{i=1}^3 I_i e^{-t/\tau_i}$ . The average decay time decreases with increasing temperature.

At room temperature our PVK thin film has the main peak emission at 420 nm, recognized in the literature as a triplet state [17,19]. The molecule conformation of PVK films spin cast from chloroform solution, which is our case, corresponds to a fully eclipsed face to face flat carbazole chromophore stacking [20]. The PVK molecules with more face to face stacked carbazole units have a higher probability of forming triplet excitons. This statement is consistent with previous works [21,22] where the authors reported that the probability of triplet exciton formation depends on the molecular conformation, the film morphology, and increases with decreasing effective conjugation length. The face to face conformation of two carbazole unities, highly ordered with short intermolecular contact, characterizes a polymeric system with short conjugation length. Thus, such shorter conjugation length would favor a higher intersystem crossing rate of singlet excitons to form triplet excitons. A quantum-chemical calculation [23] has confirmed the statements above. In addition, the relatively



**Fig. 1.** Average decay time for the PVK film as a function of the temperature. The dashed line is a guide for the eyes. The excitation of the PVK film was made at  $\lambda_{\text{Exc}} = 360$  nm. All decays have been fitted by a triple exponential function. In the inset it is shown a decay curve obtained at 120 K for a collect wavelength  $\lambda_{\text{Collect}} = 440$  nm, with the corresponding fitting ( $I_i, \tau_i$ ) parameters shown inside the figure. The values of the average decay times were calculated through the expression  $\bar{\tau} = \sum(I_i \tau_i^2) / \sum I_i \tau_i$ .

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