

## SPECTROSCOPIC AND PHOTOLUMINESCENT PROPERTIES OF NANOSTRUCTURED POLYFLUORENES/TiO<sub>2</sub> COMPOSITE FILMS USED FOR OLEDs

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**Abstract.** *In this work we present spectroscopic and photoluminescent properties of nanostructured polymeric composite films of nanocrystalline TiO<sub>2</sub> and polyfluorenes (PF+nc-TiO<sub>2</sub>). The films were deposited onto glass and KBr substrates by spin-coating PF-in-toluene solution with embedding of 5-nm thick nc-TiO<sub>2</sub> particles. The nc-TiO<sub>2</sub> wt concentration embedded in PF was chosen as 1%, 2% and 4%. The FTIR, FTR, UV-VIS-NIR and photoluminescence characterization were carried-out to study the influence of oxide nanoparticles on the absorption spectra, molecular structures and emissive luminescence of the composites. It was shown that the presence of TiO<sub>2</sub> nanoparticles results in improvement of charge separation of carriers generated by light excitation. Under a short wavelength excitation, in some samples a PL enhancement was observed. Under normal or long wavelength excitation, PF fluorescence quenching occurred for all the composites. Aging process of the composites was also investigated.*

### I. INTRODUCTION

Conducting polymers and polymer-based devices have been increasingly investigated due to their many potential applications such as optoelectronics, OLED displays, solar flexible cells, etc [1-2]. For OLED, it is very important to improve the luminescence efficiency of the emission layer. Efficient device operation requires optimization of three factors: (i) equalization of injection rates of positive (hole) and negative (electron) charge carriers (ii) recombination of the charge carriers to form singlet exciton and (iii) radiative decay of the excitons. Of the two carriers, electrons have the lower mobility and hence limit the current conduction process. By adding a hole transport layer (HTL) to the three-layer device one can improve the equalization of injection rates of hole and electron, consequently to obtain a higher electroluminescent efficiency of the OLED. Recently, among the nanostructured materials there are polymeric nanocomposites have been studied strongly day-by-day, because these materials can change the properties of the devices built-up from them. By embedding inorganic nanocrystalline oxides into polymer matrices one can enhance the efficiency and service duration of the devices. Being in nanoparticle form, the oxides can substantially influence both the electrical and optical properties of the polymer in which they are embedded. For instance, TiO<sub>2</sub> nanocrystals were embedded in conjugate polymer MEH-PPV to form a composite thin film that was studied as photoactive material in [3].

It has been shown that MEH-PPV luminescence quenching was much strongly with rod-like  $\text{TiO}_2$  in comparison with dot-like one. It is seen that polyfluorines (PF) with different additives can emit blue or red light, they are also a good candidate for OLED because of their high chemical stability and the versatile chemical structures, which make them ideal for chemical modifications [4]. By embedding oxide nanoparticles into PF, one can expect enhancement in the emission property of this polymer. The aim of this paper is thus to study spectroscopic properties such as FTIR spectra, absorption and photoluminescence of PF+nc- $\text{TiO}_2$  nanocomposites films, which are used for preparation of both the OLEDs and the polymeric solar cells.

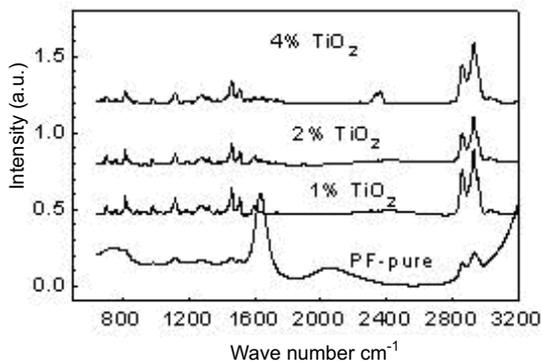
## II. EXPERIMENTS

The glass substrates used for spin coating nanocomposite films were ultrasonically cleaned in distilled water, followed in ethanol and acetone. KBr crystalline substrates were used for characterization of photoluminescence (PL) properties. To deposit the composites layers onto glass, PF solution was prepared by dissolving PF powder in toluene with a ratio as 10 mg of PF in 1 ml of toluene. Then,  $\text{TiO}_2$  nanoparticles were embedded in these solutions according to the weight ratio of  $\text{TiO}_2$ /PF (wt) as 0, 0.01 and 0.04 (i. e. PF alone, PF+1% $\text{TiO}_2$ , PF+2% $\text{TiO}_2$  and PF+4% $\text{TiO}_2$ , further called shortly PF00, PF01 and PF04, respectively). To obtain homogenously dispersion of  $\text{TiO}_2$  in polymer, the solutions were mixed for 12 hours by using magnetic stirring. These liquid composites further used for spin-coating and casting. The conditions for spin coating are following: delay time is 120 s, rest spin time is 30 s, spin speed is 1500 rpm and accelerate is 500 rpm. Finally, the waiting time for drying is 2 min. The films used for PL characterization have been deposited by casting onto KBr tablets with diameter of 10 mm, using 50  $\mu\text{l}$  of the PF solution. To dry the films, the samples were put in a flow of dried gaseous nitrogen for 12 hours. All the samples were put in a fore vacuum box until the measurements. FTIR data were obtained by the measurements on a "Vertex-70 FTIR system in IMN (Institut de Matriaux de Nantes), Nantes, France. UV-VIS absorption and PL spectra were carried-out, respectively on a "Cary-5G and a FL3-2 spectrophotometer using a Xe-lamp as excitation source.

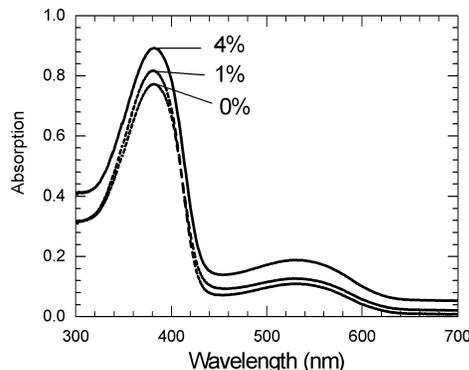
## III. RESULTS AND DISCUSSIONS

The IR absorption spectra of PF composites films are shown in Fig. 1. As reported in [5, 6] the IR bands of the PF can be grouped into three main regions; the region around 3000  $\text{cm}^{-1}$  which is associated with CH stretching vibrations, the region of CH scissoring vibrations below 1600  $\text{cm}^{-1}$ , and the region between 1600 and 1800  $\text{cm}^{-1}$  where two features evolve by heating in air. In our samples of PF and composites there are also three groups of the bands, two end regions (below 1600  $\text{cm}^{-1}$  and around 3000  $\text{cm}^{-1}$ ) have strong bands, in the range of 1600 to 2800  $\text{cm}^{-1}$  there are not any band for PF0, PF01 and PF02, but for PF04 (4%  $\text{TiO}_2$ ) there is one rather strong band at 2360  $\text{cm}^{-1}$  (Fig. 1). The band at 1630  $\text{cm}^{-1}$  of PF is relative with oxygen atom in PF, this feature disappeared in the spectra of composite films, and instead, the other features were grown up. This difference in IR of the two types of the samples can be attributed to the presence of nc- $\text{TiO}_2$ ; the

last can bond with oxygen atoms of PF. As depicted in Fig. 2 (absorption spectra), all



**Fig. 1.** FTIR absorption spectra of PF composites vs. TiO<sub>2</sub> content.



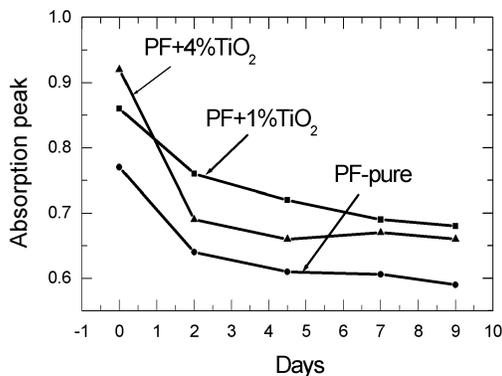
**Fig. 2.** Absorption spectra of PF composite films vs. content of nc-TiO<sub>2</sub>.

the PF00, PF01 and PF04 samples exhibit an absorption peak at wavelength of 380 nm, corresponding to 3.26 eV, which is known that this absorption was attributed to the first vibronic  $\pi - \pi^*$  transition. A very broad peak at 540 nm (2.30 eV) corresponding to the second vibronic  $\pi\pi^*$  transition was also observed. This is related to emission phenomenon of the PF composites, as observed during the heating cycles while the emission near 380 nm is reduced, a second broad emission band around 530–550 nm evolves [7].

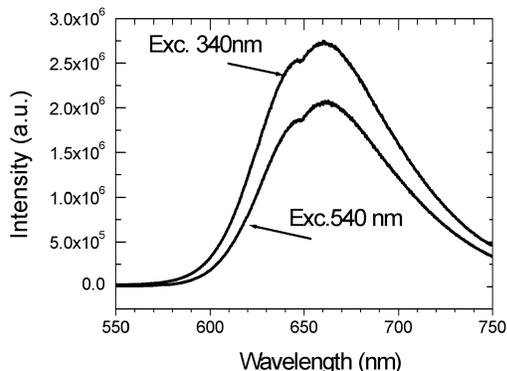
The last transition is strongly For as-prepared samples, absorption coefficient of PF-alone (0.76) is smaller than that of PF01 (0.82) and of PF04 (0.92) composites. The PF04 is strongest absorbed. It is seen that TiO<sub>2</sub> nanoparticles have enabled PF be much better absorbed.

Figure 3 presents aging processes of the composites which shows the decrease of absorption maxima for three composites samples: PF00, PF01 and PF04. From this figure one can see that for the first day the PF04 composite aged faster compared with the pure polymeric PF and PF01. But from the fourth day on, the process seemed to be opposite: the sample with 1%TiO<sub>2</sub> ages slowly, the sample with 4%TiO<sub>2</sub> exhibits stabilized state at a value as high as 0.67. Comparing with the pure polymeric PF, nanocomposites exhibit slower aging process. Indeed, this is a typical advantage of composite materials, for nanocomposites in particular. Using nanocomposites of PF for OLEDs one can prolong their displaying time.

From the absorption spectra, it is seen that for both the pure PF and composites there have been revealed two peaks, one strong at 380 nm and another weak at 540 nm. Thus, in the study of photoluminescence properties, we used two excitation regions nearly above mentioned wavelengths. Fig. 4 shows the PL spectra of a PF04 composite obtained with excitation light sources at 340 nm and 540 nm wavelengths (Xe lamp). This figure shows that the larger energy of excitation photon (shorter wavelength), the larger PL intensity of the composites was obtained. From the emission curve of the Xe lamp, it is seen that the ratio between intensities of light at 540 nm and 340 nm is about 1.5. So the difference in PL intensities can not be attributed due to excitation powers, but it can be



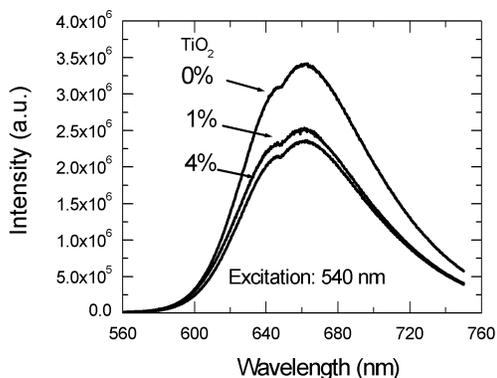
**Fig. 3.** Aging of PF vs.  $\text{TiO}_2$  content in composites.



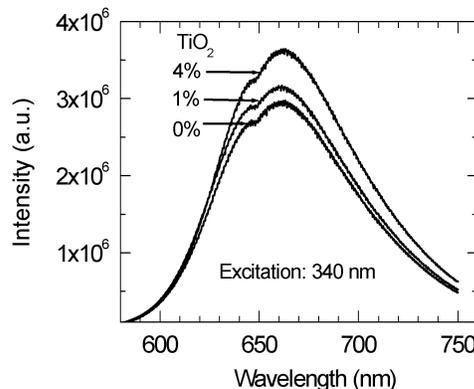
**Fig. 4.** PL spectra of PF04 sample with different excitation wavelengths.

explained by stronger absorption of the PF and PF-composites at 340 nm. PL emission spectra having maxima at ca. 662 nm, corresponding to 1.87 eV and a shoulder near 648 nm (1.91 eV) showed that all the samples emitted intense red light upon photo-excitation at the corresponding absorption maximum. The photoluminescence spectral features of the polymer are not significantly changed when embedded with  $\text{TiO}_2$  nanocrystals. In Fig. 5, the relative PL quenching of polyfluorene films emission is shown as a function of  $\text{TiO}_2$  nanoparticle concentration in the precursor solution. In this spectral region, the  $\text{TiO}_2$  does not show any detectable absorption. All deposited films exhibit PF absorption feature (with a maximum peak at approx. 648 nm) which is similar to that reported for the polymer in solution. As reported in [8], for MEH-PPV composites with the rod-like  $\text{TiO}_2$  nanocrystals, the quenching of fluorescence is significantly higher than in the case of spherical  $\text{TiO}_2$  nanoparticles. In our samples,  $\text{TiO}_2$  particles with 5 nm size are so small, that can be seen as inorganic oxide dots. Presence of these dots in PF has results in the fluorescence quenching clearly as observed for the rod-like nano  $\text{TiO}_2$  in MEH-PPV. This phenomenon is currently attributed to the transfer of the photogenerated electrons to the inorganic semiconductor [9]. As in dot-like nanocrystals, the surface-to-volume ratio is higher than in spheres, the occurrence of enhanced emission quenching can be explained by an increased probability of charge transfer at the PF/ $\text{TiO}_2$  interface. In addition, the higher delocalization of carriers in dots may help in preventing the back recombination of the electrons transferred on  $\text{TiO}_2$  with holes in the polymer.

With an excitation of a short wavelength light the photoluminescence for the composites exhibits an opposite feature. Instead of the PL quenching of the luminescence of PF, an enhancement in PL intensities was observed (Fig. 6). The largest increase of the PL was obtained for the PF04 composite. Although, the PL enhancement has been rarely mentioned, one can suggest that the increase PL intensity for such a PF04 film can be attributed to the large absorption coefficient for  $\text{TiO}_2$  dots. This phenomenon was explained due to the non-radiative Frster resonant energy transfer (FRET) [10] from  $\text{TiO}_2$  nanorods to polymer with excitation of wavelength less 350 nm. From Fig. 5 and

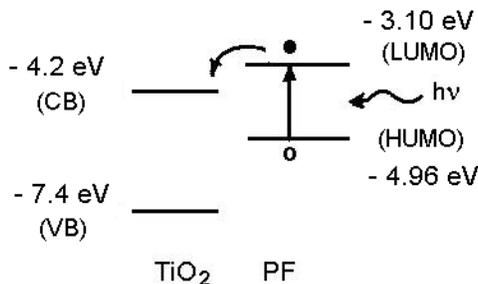


**Fig. 5.** Fluorescence quenching of PF composites with excitation at 540 nm wavelength.



**Fig. 6.** Enhancement in the PL intensity of PF composite films when excited at 340 nm wavelength.

Fig. 6 one can see that in these samples the larger enhancement in PL intensity (under short wavelength excitation), the stronger fluorescence quenching (under normal excitation) occurred. It is known [11] that the fluorescence quenching of polymeric composites such as MEH-PPV+nc-TiO<sub>2</sub> results in a charge-separation at interfaces of nanocrystalline oxide/polymer, consequently reducing the barrier height at the last. Figure 7 exhibits schematically the mechanism of charge transfer at the PF/TiO<sub>2</sub>-nanoparticle interfaces. Under excitation by photons of energy larger than the gap between HOMO and LUMO levels, in the polymer electrons from the HOMO jumped to the LUMO level. As the LUMO level is higher than the conducting band of TiO<sub>2</sub>, these electrons transfer to the last, creating such a called charge-separation zone. This phenomenon indicates that, besides being used for OLEDs, PF composite films can be served as a good material for a photovoltaic solar cell.



**Fig. 7.** Schematic representation of charge transfer at the PF/TiO<sub>2</sub>-dot interfaces. The vacuum level is defined at 0 eV.

#### IV. CONCLUSIONS

Nanostructured polyfluorene + nc-TiO<sub>2</sub> composite films were prepared by spin-coating. Spectroscopic properties such as absorption and photoluminescence spectra vs. the TiO<sub>2</sub> concentration were investigated. Exciting by a short wavelength of 340 nm, the enhancement in PL intensity was obtained the best for the composite film with 4%TiO<sub>2</sub> embedded in PF and with an excitation of a 540 nm wavelength, PF fluorescence quenching occurred strongest also in this sample. From the characterization, it is seen that PF composites films can be suggested as a candidate for both OLEDs and photovoltaic solar cell applications.

#### ACKNOWLEDGMENT

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