OPTICAL STUDY OF PURE AND DOPED CONJUGATED POLYMERS WITH ZnO NANOPARTICLES

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The aim of this work was to study, the optical characteristics of two mixed solutions of poly [2-methoxy-5-(2'-ethylhexyloxy) -1, 4-phenylene vinylene] (MEH-PPV) and Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N, N'-diphenyl)-N, N'-di(pbutylphenyl)-1,4-diamino-benzene)] (PFO-co-DBP) conjugated polymers with zinc oxide (ZnO) nanoparticles. Benzene was used as the solvent. Different concentrations of solutions based on MEH-PPV were prepared varied from 0.50 to 3.0125μM. While for the PFO-co-DBP the concentrations were from 1.725 to 14 μM. The zinc oxide ZnO nanoparticles were dispersed in benzene from 1.25 mg to 10 mg. These solutions were characterized for optical characteristics such as absorption and fluorescence in the visible region 300-800 nm. Similar experiments were conducted to find the optical properties for pure PFO-co-DBP, ZnO and then the blended solutions (MEH-PPV + PFO-co-DBP, and MEH-PPV + PFO-co-DBP + ZnO). A systematic study is presented to find the optimum solution concentration of MEH-PPV: PFO-co-DBP with ZnO nanoparticles. Fluorescence of the blends has increased dramatically upon adding ZnO. Maximum intensity of fluorescence was observed with three peaks at 480, 520 and 570 nm, for the blend of (MEH-PPV: PFO-co-DBP: ZnO) with concentrations 3.0125 μM: 4 μM:10 mg respectively. The fluorescence and absorption properties were dependent on the concentrations of solution used.

1. Introduction

Recently, conjugated polymers have attracted considerable attention for applications in electronics and optoelectronics, including organic solar cells [1-4], transistors [5-7], light emitting diodes [8-15] and lasers [16].Since the report in 1990 by Burroughs et al on the electroluminescence from light emitting diodes based on conjugated polymers [8], many researchers have focused on the study of spin coated conjugated polymers, especially their physical, optical and photoelectric properties [10-11,17-21]. Shortly afterwards, the scientists have concentrated on improving the electrical conductivity, absorption and the photoluminescence of the polymers used in thin film forms for light-emitting diode (LED) applications [21-22].

Nowadays, many researchers are involved in trying different kinds of electrodes, or inserting more layers between electrodes and blending of more than one polymer to optimize the efficiency and reliability of the optoelectronic devices, by focusing on modifying the morphology and the physical properties of the device's nanostructured layers [3,5]. Sometimes, the blend can be designed to incorporate distinctive aspects of both conjugated polymers, and occasionally new properties may occur in the blend's nano- structure not present in either polymer. Using a blended solution of conjugated polymers to fabricate the active layer either for a light-emitting diode

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(LED) or solar cell, is a promising method to optimize the performance, efficiency and lifetime of such devices [1].

Incorporating emissive materials to the active layer of polymeric solar cells, such as nanoparticles, have resulted in enhancement of power efficiency and up-grade the performance of these devices [23-24].

Alyamani et al, reported that the photoconductivity of light emitting diodes based on conjugated polymers is severely limited by low charge mobilities between the electrodes [24], so by doping the polymeric blend with n-type or p-type electronic materials, the performance of light emitting diodes can be improved [25].

Most of the polymers studied were spin coated in thin film form used in organic solar cells and light emitting diodes. Due to its various advantages over other polymers, the poly [2-methoxy-5- (2'-ethyl hexyloxy)-1, 4-phenylene vinylene (MEH-PPV) received extensive attention due to its good solubility in solvents, simple processing, in the deposition of the active layer of various optoelectronic devices [15-19, 21].

Many efforts were made to manipulate the morphology of MEH-PPV films by using various solvents, spin speeds and concentrations, and thereby to alter the optical and electrical properties of the polymeric films. It is well known that the performance of the Polymeric Light Emitting Diodes PLED's or solar cells, is greatly influenced by the movement of charge carrier's in the active layer made from pure or blended conjugated polymer [10-11,25].

However, the published work did not include analysis, for solution blending of (MEH-PPV) and Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N, N'-diphenyl)-N, N'-di(pbutylphenyl)-1,4-diamino-benzene)] (PFO-co-DBP) with ZnO nanoparticles, which can be used to spin coat the blend layer in light emitting diodes [25].

In this paper, using benzene as the solvent, a MEH-PPV: PFO-co-DBP blend under certain concentration was made. The optical characteristics of MEH-PPV and PFO-co-DBP polymeric solutions and with various concentrations were investigated. The results of the absorption and fluorescence spectra for the MEH-PPV and PFO-co-DBP are presented. The optical characterizations made on the conducting polymer MEH-PPV and the roles of blending the two polymers with ZnO nanoparticles are reported. The behavior of both pure polymers/ blends are discussed and the possibility of using them as nanostructured thin films for optoelectronic devices.

2. Experimental

2.1 Polymer synthesis

The Poly[2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-phenylenevinylene] (MEH-PPV) and Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N,N'-diphenyl)-N,N'-di(pbutylphenyl)-1,4-diamino-benzene)] (PFO-co-DBP) conjugated co-polymers were obtained from American Dye Source with molecular weight of 70000 and 100000 respectively. The molecular structures of the two polymers are given in figure 1(a) and 1(b). The purity of the conjugated polymer samples is more than 98%, so the polymer materials were used in experiments without further purification.

(a)   *(b)*
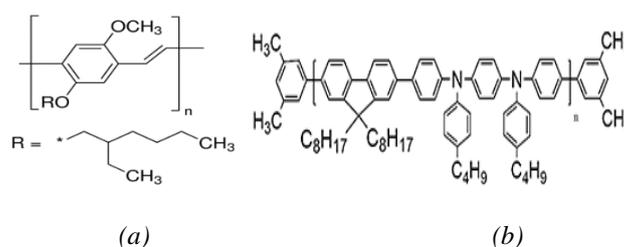
Fig. 1. The Molecular structures of: (a) Poly[2-methoxy-5-(3,7-dimethyl-octyloxy)-1,4-phenylenevinylene]: ADS108RE and (b) Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N,N'-diphenyl)-N,N'-di(pbutylphenyl)-1,4-diamino-benzene)]: ADS232GE

2.2 Polymer blend: ZnO nanoparticles synthesis

Prior to preparing the blends, pure MEH-PPV and PFO-co-DBP were dissolved in benzene, stirred on a magnetic stirrer and filtered thoroughly at room temperature, and kept away from light to avoid any photo degradation process.

Solutions of the two polymers were then used to prepare the various concentrations. The blends were prepared by mixing 1.0 μM, 2.0 μM and 3.0125 μM of MEH-PPV separately with 3.5 μM, 7 μM and 14μM of the PFO-co-DBP. ZnO nanoparticles were dispersed in benzene with various concentrations from 1.25 mg to 10 mg / 5ml.

A spectrofluorometer (Perkin Elmer LS-55) was used to record the fluorescence spectra of the pure and blended solutions, at room temperature. The optical properties such as absorption were measured in the visible range wavelength (340-700 nm) using a Perkin Elmer lambda 40 UV-VIS spectrophotometer.

3. Results and discussions

The absorption spectra for a wide range of concentrations of MEH-PPV (ADS108RE) concentrations ranging   from 0.5 to 3.0125 μM were recorded. As shown in figure 2, there were three main peaks found along the spectra: one around 300 nm, next around 330 nm and the last one around 490 nm; while the shape of absorption spectra remained the same irrespective of the concentration. The optical density was greatly increased with increasing MEH-PPV (ADS108RE) concentration.
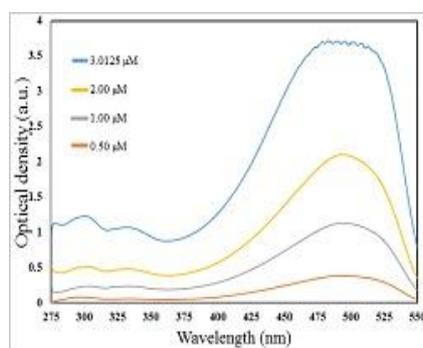

Fig. 2. The absorption spectra versus wavelength of for MEH-PPV (ADS108RE) with various concentrations in benzene

Hence, for Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(N, N'-diphenyl)-N, N'-di(pbutylphenyl)-1,4-diamino-benzene)] (PFO-co-DBP), the absorption spectra showed only one peak at 376 nm, recorded for a wide range of concentrations from 1.725 to 14 μM.

Meanwhile, as shown in figure 3, the observed peak shape of absorption spectra remained the same irrespective of the concentration. While, the optical density was greatly increased with increasing (PFO-co-DBP) concentration.
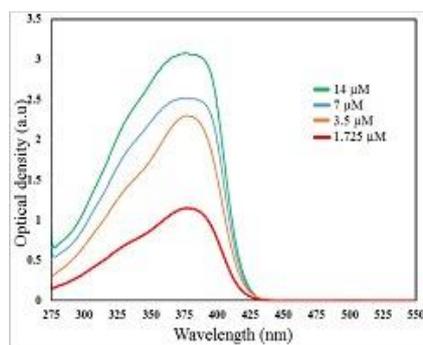
Fig. 3. Absorption spectra of (PFO-co-DBP) in benzene recorded for a wide range of concentrations

The results of the fluorescence spectra of MEH-PPV (ADS108RE), are represented in Fig. 4 for various concentrations ranging from (0.5 to 3.0125 µM). One peak for the low concentration (0.5 µM) showed around 550 nm, the shape of the fluorescence spectra did not change for different wavelengths of excitation, indicating that there was only one emitting species for MEH-PPV (ADS108RE) in benzene at low concentrations.
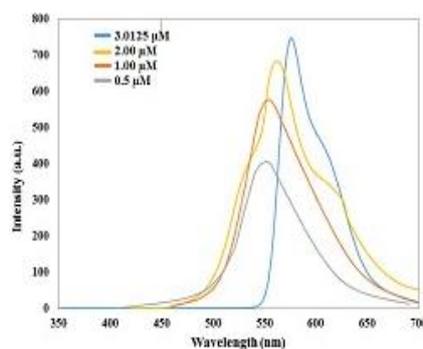

Fig. 4. The fluorescence spectra of MEH-PPV (ADS108RE) dissolved in benzene
at various concentrations

For higher concentrations from 1 to 3.0125 µM of MEH-PPV in benzene, a shift towards higher wave number was recognized in the fluorescence spectra. Fig. 4 showed that when the concentration increased up to 1 µM, the peak was around 555 nm. While for the 2 µM concentration, the spectrum had a peak around 560 nm with a hump around 610 nm. Again at 3.0125 µM the primary peak was shifted to 590 nm with shoulder at 615 nm.

As can be seen in Fig. 5, Only one dominant peak is shown at 465 nm in the fluorescence spectra of (PFO-co-DBP) for all concentrations from 1.725 to 14 µM. The peak's shape remained unaltered throughout the range of the concentration investigated. While fluorescence's peak intensity was enhanced with increasing PFO-co-DBP concentration. +

The fluorescence spectra of ZnO dispersed in benzene at 1.25 mg/ 5 ml to 10 mg/5 ml were obtained. The spectra showed there were three peaks at 400 nm was primary, next at 445 nm and last at 472 nm. The fluorescence spectra presented in figure 6 maintained similar shapes throughout the range of ZnO concentration investigated, while fluorescence intensity increased with an increasing concentration of ZnO. According to Jayabharathi et al, the two peaks at 445 nm and 472 nm may have resulted from defect state fluorescence of ZnO and also due to the ZnO particle size ranged from 8 nm -100 nm investigated under SEM analysis [26].

Similarly, the absorption spectra of ZnO dispersed in benzene at 1.25 mg/5 ml to 10 mg / 5 ml were obtained. The result (not represented here) showed that there was only one band at 302 nm.

According to Ton-that et al, the light emission efficiency was improved by mixing the n-type ZnO which has higher electron mobility than hole mobility with conjugated polymer which shows higher hole mobility than electron mobility [27].
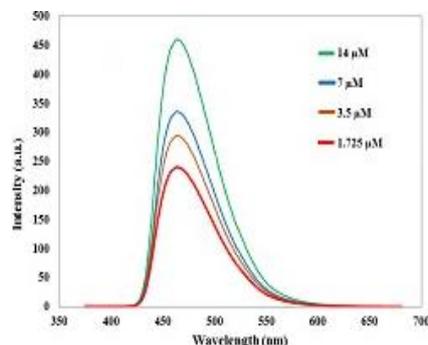

Fig. 5. The fluorescence spectra of PFO-co-DBP at concentrations from 1.725 to 14 µM
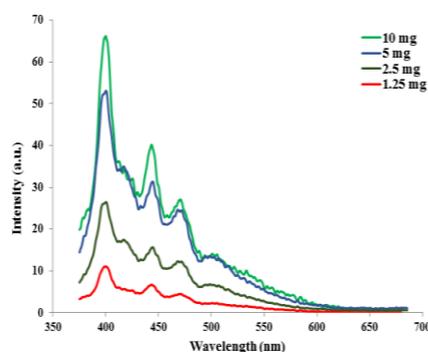

Fig. 6. The fluorescence spectra of ZnO nanoparticles dispersed in Benzene at various concentration (1.25 mg to 10 mg)

Fig. 7 represents the Fluorescence spectra versus wavelength of the various MEH-PPV (ADS108RE) and PFO-co-DBP (ADS232GE) blends. The various concentrations of the blends are listed in Table 1. The best spectral coverage can be recognized for the blend 2.0µM: 7.0µM of the polymers MEH-PPV and PFO-co-DBP respectively within the wavelength range from 440 nm to 600 nm.
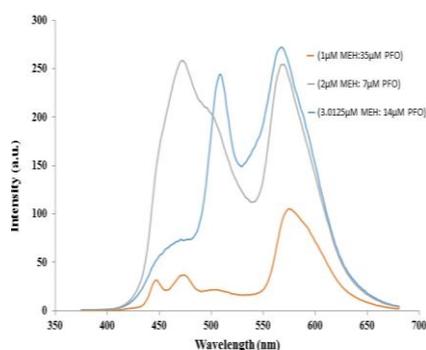

Fig. 7. Fluorescence spectra versus wavelength of the various MEH-PPV (ADS108RE) and PFO-co-DBP blends represented in Table 1.

Table 1. The various concentrations of MEH-PPV (ADS108RE) and PFO-co-DBP blends

MEH-PPV (ADS108RE)	PFO-co-DBP (ADS232GE)
1.0 μM	3.5 μM
2.0 μM	7 μM
3.0125 μM	14 μM

Konoshchuk et al reported that the interaction between the ZnO nanoparticles with the conjugated polymer has resulted in enhanced of the fluorescence characteristics of polymeric blends [28,29].

Additionally, Musa et al reported on the improvement in the photoluminescence emission from conjugated polymers which may be due to the tiny size of ZnO nanoparticles added compared to the large molecules of polymers [30].

Fig. 8 represents the fluorescence spectra of the various MEH-PPV and PFO-co-DBP blends with ZnO nanoparticles for the various concentrations represented in Table 2. The best characteristics can be recognized for the 10 mg ZnO doped blend 3.0125μM: 14μM of the polymers MEH-PPV and PFO-co-DBP respectively.
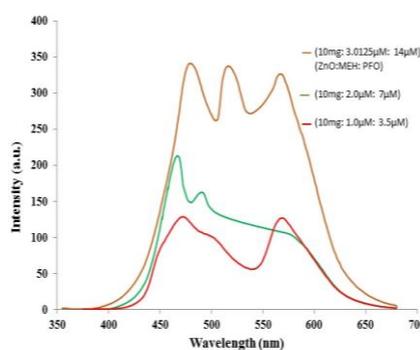

Fig. 8. Fluorescence characteristics of the various blends of polymers with ZnO nanoparticles

Table 2. The various concentrations used of MEH-PPV and PFO-co-DBP blends with ZnO nanoparticles

ZnO	MEH-PPV	PFO-co-DBP
10 mg	1.0 μM	3.5 μM
10 mg	2.0 μM	7 μM
10 mg	3.0125 μM	14 μM

4. Conclusions

Pure and blended conjugated co-polymers with added ZnO nanoparticles have been investigated. At optimal blend concentrations of MEH-PPV/PFO-co-DBP/ZnO, optical properties showed fluorescence covering a spectral range from 455 nm to 610 nm (minimum 50% of peak intensity). The fluorescence was in blue-green region.

The addition of ZnO nanoparticles has greatly improved the fluorescence optical properties. However, the exact mechanism how ZnO nanoparticles interacts and improves the efficiency of conjugated polymer blended is may be the higher mobility of charges due to the n-type ZnO nanoparticles induced into the blended p-type conjugated polymer in solution. Further research work is required to optimize blend composition, processing conditions and using them in

thin film structures to obtain more improved optical properties and further to investigate the possibility of applying them in solution- processed organic light emitting diodes and solar cells.

Acknowledgements

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