

Luminescence Tuning of MEH-PPV for Organic Electronic Applications

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In this report, a doped semiconducting ink consisting of a blended poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with aluminium-tris (8-hydroxyquinolin) (Alq₃) and diluted in toluene is formulated. The intentional doping with the electron transport nanoparticle Alq₃ results in an additional band gap state of the hole transport MEH-PPV polymer and reduction of the switch on voltage of the organic LED display. Doping is probed at room temperature with photoluminescence spectroscopy. Photoluminescence results revealed that as the Alq₃ content increases in blends, characteristic peaks of intensities of MEH-PPV are broadened and reduced. In addition, the emission for Alq₃ concentrations between 30% and 60% are featured by a band at 565 nm (2.19 eV) for the lower concentration and consistently blue shifted to 530 nm (2.33 eV) for the higher concentration. This new band at 565 nm (2.19 eV) neither belongs to pure MEH-PPV nor to Alq₃ and evidences charge transfer from the lowest unoccupied molecular orbital of the Alq₃ to the highest occupied molecular orbital of the MEH-PPV.

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1. Introduction

Organic molecules with π -conjugated structures provide a variety of new materials with metallic and semiconducting properties, attractive for fundamental investigations, engineering applications [1–4], and as a potential bench mark in nanomedicine or life science products at lab-on-a-chip devices [5]. Although several organic based devices, i.e., organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs), have matured for commercial applications, still a long-standing challenge in molecular electronics relays on doping of organic semiconductors [6–10]. Therefore, nanoelectronic engineering by doping of semiconducting materials results from tuned molecules for well-targeted applications. Particularly, OLEDs constitute a novel emission light technology and OPVs is a promising area in the field of green energy generation. Both OLEDs and OPVs structures consist of a stack of organic semiconducting layers sandwiched between a transparent conducting anode and metallic cathode [11–13].

Among the key features of doping organic semiconductors are: (i) precise adjustment of the position of the Fermi level relative to the semiconductor transport levels, (ii) control of energy barriers for charge injection/extraction, and hence (iii) reduction of ohmic losses in transport layers due to increased

conductivity [10, 14–17]. In a previous work, Ahmad et al. found that blending MEH-PPV with Alq₃ in chloroform leads to minor changes in the photoluminescence and favors the photodetection properties [18]. Similarly, Yakuphanoglu et al. observed photovoltaic effects in blends of MEH-PPV with PCBM [19]. In our case, the blending process was carried out in toluene and the MEH-PPV:Alq₃ layers revealed dramatic changes on the photoluminescence spectrum, suitable for OLED devices. Therefore, it is evidenced a charge transfer from the lowest unoccupied molecular orbital (LUMO) of the Alq₃ to highest occupied molecular orbital (HOMO) of the MEH-PPV.

In this investigation, UV-vis absorption and photoluminescence (PL) spectroscopy were used to monitor the molecular doping of MEH-PPV with Alq₃. Optical probes are known as non-invasive methods and give direct information on electronic states.

2. Experimental

The organic molecules MEH-PPV and Alq₃ with a purity > 99% were purchased from Sigma Aldrich and their chemical structures are shown in Fig. 1a and b. The formulated ink (Fig. 1c) consisted of a blended MEH-PPV with Alq₃ diluted in toluene at 1% by weight. Previous to the blending process, MEH-PPV and Alq₃-based inks were bottled separately in an argon atmosphere and kept stirring on the hot plate at 65 °C and at 95 °C, respectively, during 24 h. After that, the solutions were blended at 65 °C during one hour. Concentrations of Alq₃ in MEH-PPV were set by weight at 10%, 15%,

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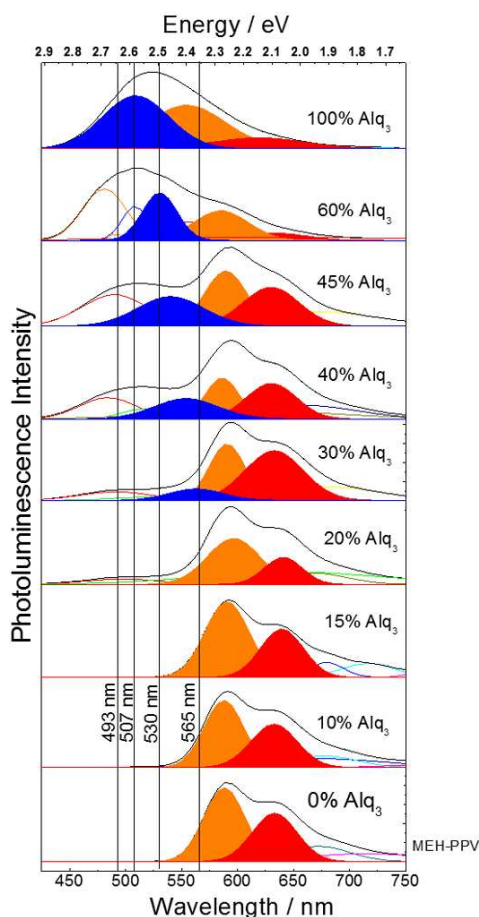


Fig. 4. Photoluminescence measurements at room temperature of MEH-PPV:Alq₃.

a blue shift emission is presented, while for 40% Alq₃ concentration, the maximum emission returns to the observed in 10% and 20% concentration. It is likely that the quenching of trap states occur for Alq₃ concentrations below 40%, while for higher densities of Alq₃ in the MEH-PPV polymer matrix, trap passivation is completed and then PL emission is dominated from Alq₃ molecules. For Alq₃ concentrations higher than 30%, charge injection is favored from the ITO anode to the Alq₃ HOMO, thus charge carriers have to overcome a higher barrier. The same behavior has been reported by Krautz et al. and Kumar et al. [21, 22].

At 20% Alq₃ concentration, bands at 493 nm and 530 nm are registered. Light emission comes from the superposition of MEH-PPV and Alq₃ emissions. The composed PL is assigned to independent emission centers without formation of new molecular complexes, which is in agreement with the UV-vis spectra reported in Fig. 3. One reason for the independent emission is the low homogeneity of the Alq₃ molecule in the solvent.

Bendable OLED devices were developed with the formulated ink. A scheme of the OLED band diagram alignment of ITO/MEH-PPV:Alq₃/Al is depicted in Fig. 5. It was found that inclusion of Alq₃ nanoparticles to the

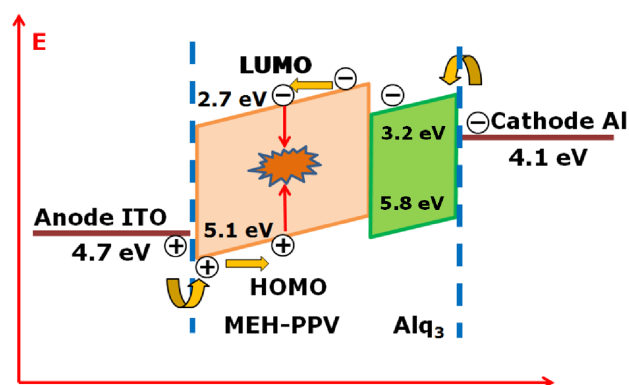


Fig. 5. Energy diagram of the doped OLED.

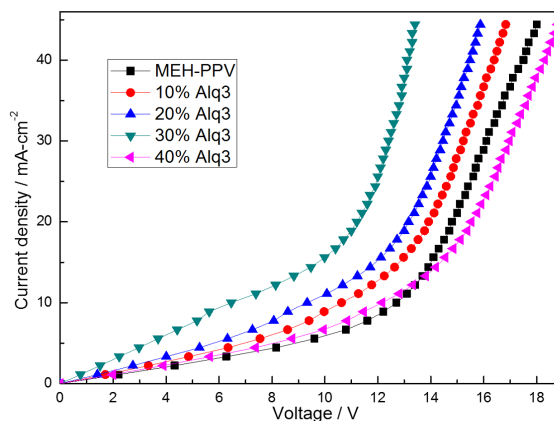


Fig. 6. J - V characteristics with % increments of Alq₃ in MEH-PPV OLED Schottky diodes.

MEH-PPV matrix reduces the energy barrier of injected electrons from the Al cathode [18, 23]. The current density versus voltage characteristic of the devices with MEH-PPV at different concentrations of Alq₃ (10%, 20%, 30%, and 40%) is depicted in Fig. 6 (J - V). For Alq₃ concentrations among 10% and 30%, the switch on voltage of pixels is reduced from approximately 16 V to 8 V, while for devices with 40% Alq₃, the current density increases accompanied with an increment of the switch on voltage; this implies that there is always an injection in the system load, independent of the degree of doping, and as a consequence a passivation of the trap levels of MEH-PPV shown by the Alq₃ occurs. However, for Alq₃ concentrations over 40%, an increase of the diode potential barrier is presented, indicating that traps are found in deeper energy levels and close to the anode work function.

In Fig. 6, it is observed that there is an increase in the current intensity in all samples when the percent of Alq₃ increases. The higher J/V ratio for samples made with 10% Alq₃ shows that these films have a lower ohmic resistance, which is probably due to the high density of pinholes in thinner organic films. Pinholes provide the path of parasitic anode-cathode currents via direct contact, which contributes to the ohmic component of net current. The same behavior has been reported in previous works based on OLEDs [24]. At the same time,

significant electron trap states rather than hole traps are induced. In this case, electron–hole recombination will mostly take place near the electron-transporting layer. Thus, solution processing may lead to a reduction in the electron transport mobility as a result of electron charge traps [21, 25–28].

4. Conclusions

We investigated a doped semiconducting ink consisting of a blended MEH-PPV with Alq₃ and diluted in toluene. The MEH-PPV:Alq₃ revealed dramatic changes on the PL. PL shows that for dopings equal or lower than 15% concentrations the MEH-PPV profile remains unmodified. In contrast, PL spectrum of the MEH-PPV:Alq₃ formulation with a 30% doping is characterized by a band at 565 nm (2.19 eV) and is continuously blueshifted to 530 nm (2.33 eV) for higher Alq₃ concentrations. Photoluminescence emission of MEH-PPV:Alq₃ is composed of independent emission of each molecule. For concentrations above 15% a significant effect of Alq₃ in the MEH-PPV matrix is observed. Therefore, the ink formulation MEH-PPV:Alq₃ prepared at 65 °C lacks of formation of molecular complexes or hybridization between the HOMO of MEH-PPV and the LUMO of Alq₃. An explanation of the individual contribution to the PL of Alq₃ and MEH-PPV is assigned to low homogeneity of Alq₃ in the solvent, which is confirmed through the UV-vis spectra.

Despite at higher concentrations of 30% Alq₃ the PL is dramatically modified, the current–voltage characteristics turn into lower current densities and higher switch-on voltages. UV-vis measurements assessed a weak molecular doping, since only a minor broadening of the spectra of MEH-PPV:Alq₃ was observed. Therefore, appearance of a ground-state charge-transfer complex is formed, in which occupation of the available states results in a weak doping mechanism. The MEH-PPV:Alq₃ blends are a promissory alternative to minimize the interchain interaction during the film processing. In addition, doping increases the effective conjugation length of MEH-PPV and reduces the switch on voltage of OLEDs.

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