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Citation: *Appl. Phys. Lett.* **77**, 1393 (2000); doi: 10.1063/1.1290275

View online: <http://dx.doi.org/10.1063/1.1290275>

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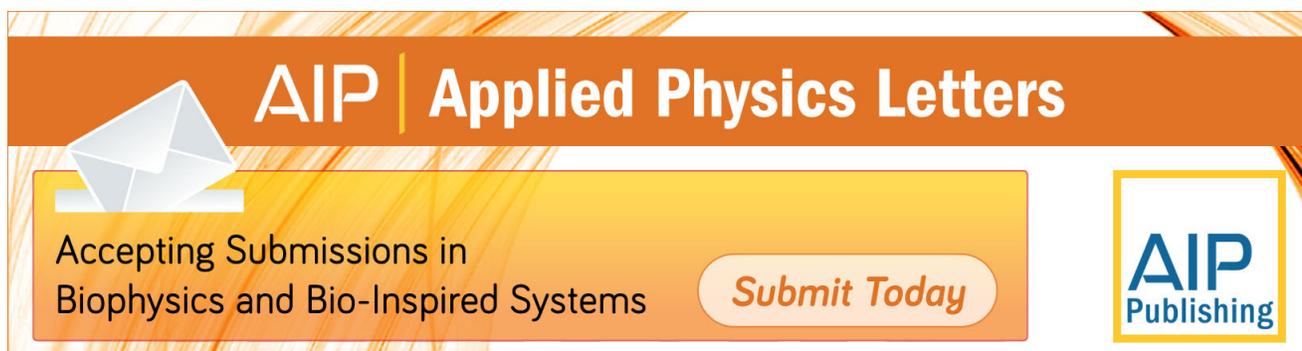
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# Hole blocking in carbon nanotube–polymer composite organic light-emitting diodes based on poly (*m*-phenylene vinylene-co-2,5-dioctoxy-*p*-phenylene vinylene)

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(Received 4 January 2000; accepted for publication 11 July 2000)

In order to investigate the role of carbon nanotubes in a polymer matrix, organic light-emitting diodes were fabricated from a polymer composite composed of poly (*m*-phenylene vinylene-co-2,5-dioctoxy-*p*-phenylene) (PmPV) and dispersed single-wall carbon nanotubes (SWNTs). Tris-(8-hydroxyquinolinolato) aluminum (Alq<sub>3</sub>) doped by Nile Red was used as an emissive material between the polymer composite and cathode. The device fabricated without SWNTs dispersed in the PmPV shows a dominant emission near red at 600 nm, which is in the range of the characteristic emission of Nile Red-doped Alq<sub>3</sub>, with a small amount of green emission from the PmPV. However, the devices fabricated with the polymer composite show an increase in the oscillator strength of the green emission with a dominant emission peak near 500 nm, the characteristic emission of PmPV. This was observed for SWNT concentrations up to 0.1 wt %. The shift in the emission indicates that the SWNTs in the PmPV matrix act as a hole-blocking material that results in a shifting of the recombination region from the Nile Red-doped Alq<sub>3</sub> layer to the PmPV composite layer. © 2000 American Institute of Physics. [S0003-6951(00)05135-4]

Organic and polymeric materials have generated interest in recent years for their potential applications in electronic devices. Among the polymer devices, organic light-emitting diodes (OLEDs) are promising candidates for use in flat-panel displays. The fluorescent emission in OLEDs is due to the radiative recombination of singlet excitons. A more balanced charge injection leads to an increase in the external quantum efficiency in the OLED. This can be achieved by consideration of the charge mobilities, the ionization potentials and electron affinities of organic materials, and the work functions of metal electrodes.<sup>1,2</sup> The use of a buffer layer and doping of the emissive material can also increase the device performance. This performance increase is a result of a reduction of the hole-injection potential barrier, a more even charge distribution with a larger contact area at the anode and the organic interfaces, and an excitation migration from host to guest molecules, respectively.<sup>3–6</sup>

Dispersion of nanostructures within emissive polymers has been suggested as a way of increasing the efficiency of the recombination process without modification of the polymer backbone which can lead to a degradation of the polymer. While a number of initial results have proven promising, thus far there has been very little quantitative analysis of the effects of nanodispersants in OLEDs. Recent work shows that the blending of the single-walled carbon nanotubes (SWNTs) in a host-emissive polymer matrix increases the OLEDs performance in terms of the turn-on voltage and the efficiency.<sup>7</sup> This polymer composite of SWNTs is expected

to create a polymer–nanostructure matrix with cooperative behavior between the host and additive, thus modifying the electronic properties of the polymer composite. Polymer composites of carbon nanotubes are attractive materials for the investigation of transport properties in carbon nanotubes and also for the many potential applications in optoelectronic devices such as OLEDs and photovoltaic devices.<sup>8</sup> In spite of this importance, the optoelectronic properties of carbon nanotube–polymer composites have not been reported as much as those of the pure carbon nanotubes.

Recent transport experiments suggest that SWNTs act as *p*-type semiconductors with holes as charge carriers.<sup>9,10</sup> Such *p*-type conductivity can arise from the tube-to-metal contact where charge transfer might induce holes into the system. Such charge-transfer mechanisms have recently enjoyed tremendous theoretical interest. In this letter, we propose that interactions within the hole-transport copolymer matrix, poly (*m*-phenylene vinylene-co-2,5-dioctoxy-*p*-phenylene) (PmPV), leads to the hole-blocking nature of SWNTs. By investigating the characteristic emissions from double-emitting OLEDs (DE-OLEDs) based on this PmPV–SWNT composite (referred to as the PmPV composite) and Nile Red-doped tris-(8-hydroxyquinolinolato) aluminum (Alq<sub>3</sub>), we show that hole traps are induced into the matrix by SWNTs. Without changing the thickness or the ordering of the layers in the devices, we measured the electroluminescence (EL) spectra as a function of the SWNT concentration in the PmPV composite and Nile Red-doped Alq<sub>3</sub> and compared it to the spectra of pure PmPV and Nile Red-doped Alq<sub>3</sub> devices.

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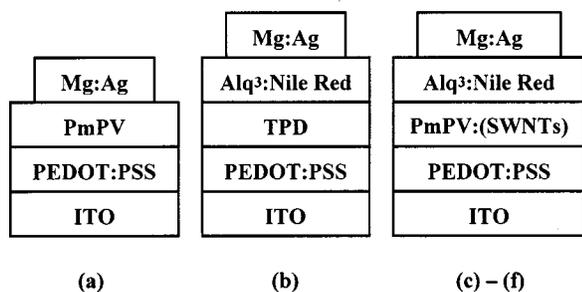


FIG. 1. Schematic diagram of the typical device structure of the OLEDs. Note that device letter (c) is pure PmPV without SWNTs.

In this study, the probe-emissive material, PmPV, was synthesized as described elsewhere.<sup>11</sup> The SWNTs were grown by the arc-discharge method and characterized by electron microscopy as described elsewhere.<sup>12</sup> Polyethylene dioxythiophene-polystyrenesulfonate (PEDOT:PSS) from Bayer was used for all devices as a buffer between the indium-tin-oxide (ITO) anode and the hole-transport layer (HTL) or the emissive layer (EML). Single-emitting OLEDs of pure PmPV and Nile Red-doped Alq<sub>3</sub> were also prepared as a comparison to the EL spectra of the DE-OLEDs. In the Nile Red-doped Alq<sub>3</sub> device without PmPV, vacuum-evaporated *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1-1'-biphenyl-1-4,4'-diamine (TPD) with a thickness of 20 nm was used for the HTL between the buffer and emitting layers. The PmPV composites with SWNT concentrations of 0.02, 0.05, and 0.1 wt % were prepared through the ultrasonic dispersion of SWNTs in chloroform, and then the dispersed nanotubes were blended with a PmPV solution (7.5 mg of PmPV in 1 cc chloroform). PEDOT:PSS and PmPV composites were spun with speeds of 5000 and 1500 rpm in ambient conditions, respectively. This resulted in a film thickness of about 80 nm for both materials. The Alq<sub>3</sub> and Nile Red were vacuum coevaporated to produce a film thickness of 20 nm with a Nile Red concentration of 1 wt %. For all devices, a 10:1 wt ratio of Mg and Ag alloy was used as a cathode with a thickness of 200 nm. Evaporation rates of 0.1 and 0.5 nm/s, at an evaporation pressure of about  $5 \times 10^{-6}$  Torr, were maintained during the depositions of the

TABLE I. Summary of device structures. Devices (a) and (b) are single emitting, and devices (c)–(f) are double emitting. The doping concentrations of Nile Red in Alq<sub>3</sub> for devices (b)–(f) are all the same (1 wt %).

Device	Anode	HTL or EML	EML	Cathode
(a)	ITO/PEDOT:PSS	PmPV		Mg:Ag
(b)	ITO/PEDOT:PSS	TPD	Alq <sub>3</sub> : Nile Red	Mg:Ag
(c)	ITO/PEDOT:PSS	PmPV	Alq <sub>3</sub> : Nile Red	Mg:Ag
(d)	ITO/PEDOT:PSS	PmPV:SWNT (0.02 wt. %)	Alq <sub>3</sub> : Nile Red	Mg:Ag
(e)	ITO/PEDOT:PSS	PmPV:SWNT (0.05 wt. %)	Alq <sub>3</sub> : Nile Red	Mg:Ag
(f)	ITO/PEDOT:PSS	PmPV:SWNT (0.1 wt. %)	Alq <sub>3</sub> : Nile Red	Mg:Ag

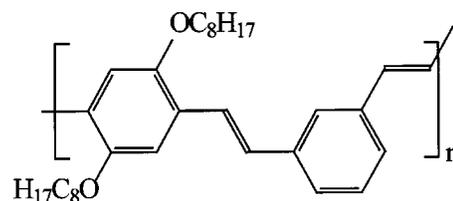


FIG. 2. Repeat unit structure of PmPV.

organics and the cathode metals, respectively. The device structures used in this study are summarized in Table I.

A schematic diagram of the typical device structure is shown in Fig. 1, and Fig. 2 depicts the repeat unit structure of PmPV. Figure 3 shows the EL spectra of the devices labeled (a)–(f). The EL spectra were measured with a Perkin-Elmer LS-50B luminescence spectrometer. A forward bias of 7V was applied to all of the devices. For devices (c)–(f), the EL spectra were normalized with the red emission peaks. In Fig. 3, the EL from the Nile Red-doped Alq<sub>3</sub> has a peak near 618 nm while the pure PmPV emits green with a main peak near 500 nm. Small vibronic features can be seen near 470 and 540 nm.

It is clear that the DE-OLED device without SWNTs [device (c)] emits near red at 600 nm, which is in the range of the characteristic emission of Nile Red in Alq<sub>3</sub>, with a small contribution from the 470 nm feature in PmPV. This indicates that the PmPV in device (c) acts as a hole-transport material so that most of the radiative recombination takes place in the Alq<sub>3</sub>: Nile Red layer. However, the devices fabricated with the PmPV composites show that the oscillator strength of the green emission increases as the SWNT concentration increases, and the EL near 600 nm shifts to the blue. As the SWNT concentration increases up to 0.1 wt % [device (f)], a noticeable enhancement of green emission, with a shifting of the emission peak nearer to 500 nm, was observed. We also noted that a large blueshift of the 600 nm feature occurs in device (f) with its peak near 560 nm. This implies that the SWNTs in PmPV composites act as a hole-trapping material blocking the holes in the PmPV composite, and thus shift the recombination regions from the doped Alq<sub>3</sub> layer to the PmPV composite layer. This is in contrast to recent data for poly(p-phenylene vinylene)–multiple-walled carbon nanotube films, where hole or electron transfer was not observed, but primarily energy transfer occurred in the composite region.<sup>13</sup> The EL of the PmPV composite with a

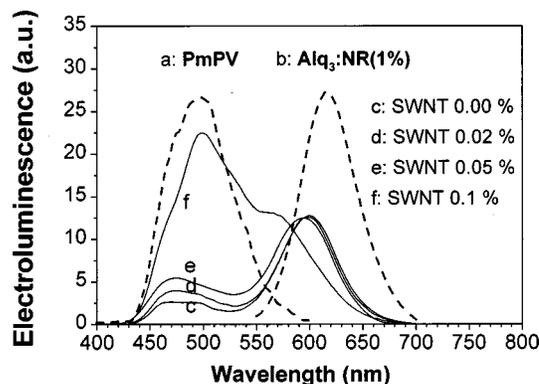


FIG. 3. Normalized double-emitting EL spectra of devices (c)–(f) as compared with the EL spectra of single-emitting devices (a) and (b).

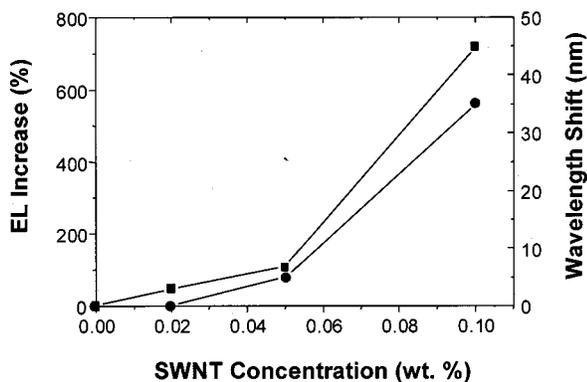


FIG. 4. Percent increase in integrated oscillator strength of the green emission and the blueshift of the red peaks relative to those of the 0 wt % concentration of SWNTs.

SWNT concentration of 0.1 wt % has the same emission peak (500 nm) as that of pure PmPV, indicating that the SWNTs do not act as an exciton migration center in PmPV as is usual for organic dopants. As a function of the SWNT concentration, the percent increase in integrated oscillator strength of the green emission and the blueshift of the red peaks relative to those of the 0 wt % concentration of SWNTs are shown in Fig. 4. For device (f) (0.1 wt % SWNTs), the oscillator strength in green increases by about 700% with a 35 nm blueshift of the 600 nm peak as compared to device (c) (0 wt % SWNTs). The trends in increasing green emission and the blueshifting of the red peaks, as the SWNT concentration increases, are very similar to each other. This is also an indication of a shifting of the recombination region from the doped Alq<sub>3</sub> layer to the PmPV composite layer.

In conclusion, we have demonstrated that the SWNTs in the PmPV composite shift the radiative recombination region in DE-OLEDs, from the Nile Red-doped Alq<sub>3</sub> layer to the PmPV composite layer, without changing the PmPV emission energy. This implies that the SWNTs in PmPV are responsible for blocking hole transport in the PmPV composite by forming hole traps in the polymer matrix without changing the singlet exciton binding energy or acting as an exci-

tation migration center. It has been proposed that in the PmPV composites a polymer–nanostructure matrix is created by the wrapping of the carbon nanotubes with PmPV chains.<sup>14</sup> However, recent transport studies with PEDOT composites have shown that nanotube-induced hole traps are not necessarily related to the morphology of the tube–polymer interaction.<sup>15</sup> It is, therefore, likely that these traps are induced through long-range interactions within the matrix. This would be the case if the hole traps were formed through image charge effects between the tubes and the charge carriers. Further optical and transport studies are necessary to understand the role of carbon nanotubes in various polymer composites.

The authors gratefully acknowledge funding from AFOSR, DURIP, and the state of South Carolina. The authors also acknowledge the support of J. T. Morrison of Bayer for supplying the PEDOT:PSS and P. M. Ajayan for the use of his arc-discharge equipment.

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