

# Polymer/Gold Nanoparticle Nanocomposite Light-Emitting Diodes: Enhancement of Electroluminescence Stability and Quantum Efficiency of Blue-Light-Emitting Polymers

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The potential use of polymer light-emitting diodes is ultimately limited by their low quantum efficiency as well as by their poor stability due to oxygen. We report experiments on polymer light-emitting diodes made with poly(9,9'-dioctylfluorene)/gold nanocomposites to solve these drawbacks. Blue polymer light-emitting diodes with enhanced luminescent stability were obtained by incorporating 5–10-nm gold nanoparticles as the quenchers of the triplet states of blue emitting polymer. The nanocomposite light-emitting diodes exhibited an enhanced quantum efficiency due to the roughening of the surface onto which the Al cathode is deposited and to balanced charge injection.

## Introduction

Molecular semiconductors have proven to be fascinating candidates for the emitting materials used in light-emitting diodes (LEDs).<sup>1,2</sup> By varying the band gap energy through alterations to the molecular architecture, a variety of emitting colors can be obtained.<sup>3</sup> Moreover, conjugated polymers are easily processed into thin films, which simplifies the fabrication of polymer-based LEDs. However, a significant stumbling block to the rapid commercialization of luminescent polymer-based LEDs is their high susceptibility to photooxidation under ambient conditions.<sup>4,5</sup>

The main materials employed in device fabrication are fluorescent dyes and polymers, which emit light as a result of the radiative decay of singlet excitons. The operation of LEDs generates spin-symmetric triplets and spin-antisymmetric singlets in the ratio of 3:1,<sup>6</sup> but the energy of the triplet excitons is wasted via nonradiative decay processes. Further, oxidation in many luminescent polymers begins with the formation of singlet oxygens via energy transfer from long-lived triplet excitons, resulting in chain scission and carbonyl defect

formation on polymer chain ends.<sup>7</sup> A general picture of the oxidation process in conducting polymers is presented in Figure 1. To prevent photooxidation and enhance device stability, devices are usually encapsulated with metal or glass caps, but this process is costly and will not be compatible with the promising "role-to-role process" for fabricating flexible LEDs, and oxygen sources such as entrapped gas and the indium tin oxide (ITO) anode are present even after encapsulation. Various techniques for preventing oxygen penetration into the emissive layer have been tried, such as the use of a polyaniline buffer layer on top of the ITO anode,<sup>8</sup> or use of an environmentally stable cathode such as Al, or using novel organic/inorganic composite luminescent materials with two-dimensional geometries.<sup>9</sup> Another method for the protection of luminescent polymer films against oxidation is the addition of a stabilizer that blocks the action of oxygen. Because the oxidation of many luminescent polymers begins with the formation of singlet oxygens via energy transfer from long-lived triplet excitons, triplet exciton energetics and dynamics play an important role in the oxidation process.<sup>7</sup> Recently, some approaches aimed at enhancing the oxidation stability of luminescent polymers by incorporating metal nanoshells into devices have been reported.<sup>10,11</sup> The triplet excitons of luminescent polymers are

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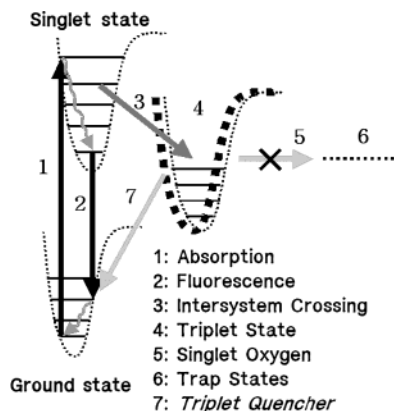
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**Figure 1.** Oxidation mechanism in luminescent conjugated polymers.

quenched as a result of the overlap of their energy levels with the optical absorptions of the added nanoshells. However, the proposed polymer/metal nanoshell nanocomposite systems cannot be used in PLEDs because the nanoshells are larger than the typical emitting-layer thickness of PLEDs (50–100 nm).

In previous work we reported a large enhancement in the PL stability of a blue-emitting polymer produced by doping with gold nanoparticles.<sup>12</sup> Herein, we report the fabrication of a blue PLED with enhanced luminescence stability obtained by incorporating 5–10-nm gold nanoparticles as the quenchers of the triplet states of poly(9,9'-dioctylfluorene) (PDOF) that lead to polymer oxidation. In addition, the PDOF/gold-nanocomposite-based PLED exhibited an enhanced quantum efficiency.

### Experimental Section

**Materials.** The gold nanoparticles were synthesized according to a method reported in the literature.<sup>13</sup> An aqueous gold chloride solution ( $\text{HAuCl}_4$ ,  $3 \times 10^{-2}$  M, 10 mL) was added to 80 mL of  $\times$  tetraoctylammonium bromide solution ( $2.5 \times 10^{-2}$  M) in toluene. The transfer of the metal salt to the toluene phase was clearly observed within a few seconds. An aqueous solution of  $\text{NaBH}_4$  (0.4 M, 25 mL) was added to the mixture while stirring, which immediately caused the reduction reaction. After 30 min the two phases were separated, and the toluene phase was washed with 0.1 M  $\text{H}_2\text{SO}_4$ , 0.1 M NaOH, and  $\text{H}_2\text{O}$  (3 $\times$ ), and then dried over anhydrous  $\text{NaSO}_4$  to obtain the gold nanoparticles. The diameters of the gold nanoparticles were in the range 5–10 nm, as determined using a JEOL JEM-2010 transmission electron microscope operating at 200 kV.<sup>12</sup> PDOF was synthesized according to the synthesis scheme reported elsewhere.<sup>14</sup> Gold nanoparticles were sonicated in monochlorobenzene solvent for 3 h for dispersion before use. PDOF was dissolved in monochlorobenzene by stirring for 12 h. Each solution was mixed and then sonicated for 2 more hours and then stirred for an additional 2 h. The volume fractions of gold nanoparticle were changed from  $1.5 \times 10^{-6}$  to  $3.0 \times 10^{-5}$ .

**Emission and Infrared Spectroscopy.** EL and PL spectra were measured using an ISS PC1 photon-counting spectrofluorometer equipped with a photomultiplier tube (Hamamatsu R928) as a detector. FTIR measurements were performed

using an IBM Instruments model IR-32 spectrometer in reflection mode.

**Fabrication of Devices and Their I–V–L Characteristics.** Polymer light-emitting devices of pure PDOF and the PDOF/gold nanocomposite films were fabricated as follows. Emitting layers of 80–100-nm thickness were spin-cast from solutions in monochlorobenzene onto poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT/PSS)-coated ITO glass substrates. A 150-nm-thick aluminum cathode was vacuum-deposited onto the emitting layers at  $5 \times 10^{-6}$  Torr. The electrical and luminescence characteristics of the device were measured by using a current/voltage source measurement unit (Keithley 236) and an optical power meter (Newport 1830-C) connected to a photodiode (Newport 818-UV). EL and PL spectra were measured using an ISS PC1 photon-counting spectrofluorometer equipped with a photomultiplier tube (Hamamatsu R928) as a detector.

### Results and Discussion

Triplet energy transfer from donor to acceptor molecules generally proceeds via Dexter-type energy transfer or electron–hole capture by the acceptor molecules.<sup>15</sup> The Dexter transfer mechanism involves the tunneling of electrons between the donor and the acceptor, and is therefore a short range process that requires an intermolecular separation of only a few angstroms.<sup>16</sup> Electron–hole capture is favored by overlap between the plasma resonance of the metal nanoparticles and the polymer triplet state.<sup>17</sup> Thus, the triplet excitons that play a primary role in the oxidation of luminescent materials can be quenched as a result of the overlap of their energy levels with the optical absorption bands of metal nanoparticles.<sup>10</sup> The excitation lifetimes of the metal nanoparticles and the host polymer are also important factors affecting energy transfer from the polymer to the metal nanoparticles.

Gold nanoparticles of 5–10-nm size were selected because their excitation states interact with the triplet exciton energy band of PDOF centered at  $\sim 530$  nm.<sup>12,18</sup> As particle size decreases and approaches the nanometer scale, the specific surface area of particles increases dramatically. Thus, as the gold particle size decreases, the contact area between the polymer and the nanoparticles also increases and the nanoparticles become effective scavengers of the polymer triplet state. To investigate the dispersal of the gold nanoparticles within the nanocomposite film, morphological characterization of the PDOF/gold nanocomposite film with a volume fraction of  $\sim 1 \times 10^{-3}$  was investigated by TEM as shown in Figure 2. TEM revealed a uniform distribution of spherical particles, 5–10-nm in size, throughout the bulk of the film.

The normalized electroluminescence (EL) spectra of the PLEDs prepared using a pristine PDOF film and the PDOF/gold nanocomposite films are shown in Figure 3. The EL spectral features of the PDOF PLED are virtually unaffected by the addition of gold nanoparticles to the luminescent polymer matrix.<sup>12</sup> The stability of the devices was investigated under air atmosphere by

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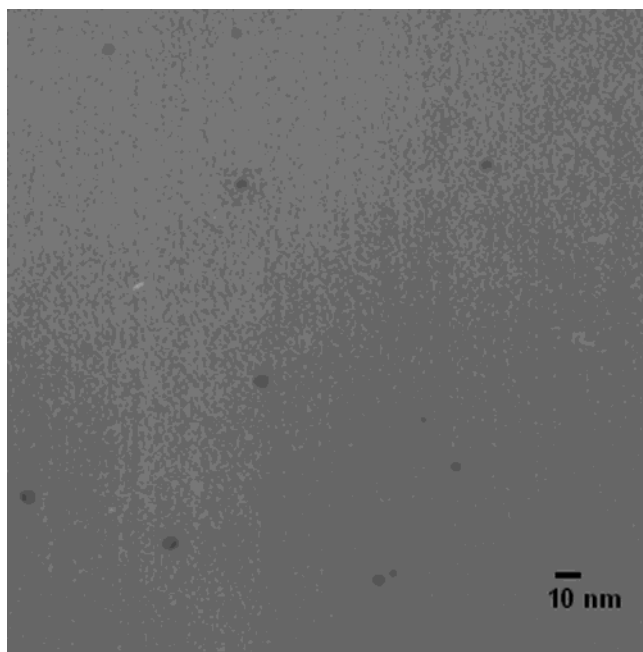
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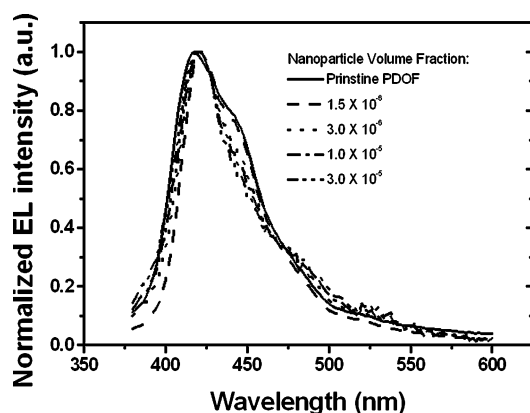
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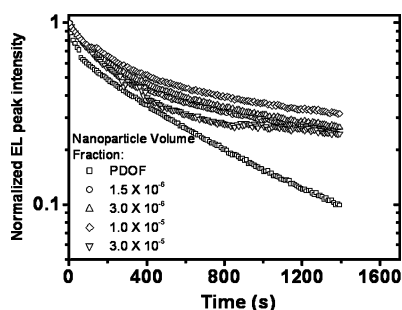
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**Figure 2.** TEM image of the PDOF/gold nanoparticle nanocomposite film ( $\approx 1 \times 10^{-3}$  volume fraction).

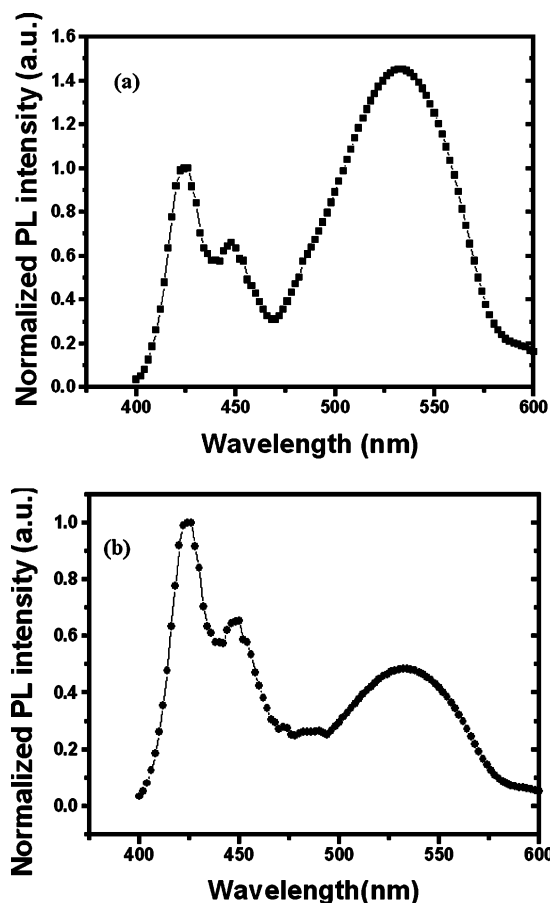


**Figure 3.** Normalized electroluminescence (EL) spectra of the PDOF/gold nanoparticle nanocomposite devices with different nanoparticle volume fractions.



**Figure 4.** Electroluminescence (EL) intensity decay profiles of the PDOF/gold nanoparticle nanocomposite devices with different nanoparticle volume fractions.

recording their EL peak intensity as a function of time while applying a driving voltage of 10 V. The EL decay profiles of the nanocomposite devices with different gold nanoparticle concentrations are shown in Figure 4. The addition of gold nanoparticles to the PDOF PLED at a low volume fraction of  $1.5 \times 10^{-6}$  retards the EL intensity decay rate of the device. Because the metal nanoparticles' resonance has an excitation lifetime of



**Figure 5.** Photoluminescence (PL) spectra of the PDOF layer before and after electrical degradation of a working device: (a) pristine PDOF film; (b) PDOF/gold nanoparticle composite film.

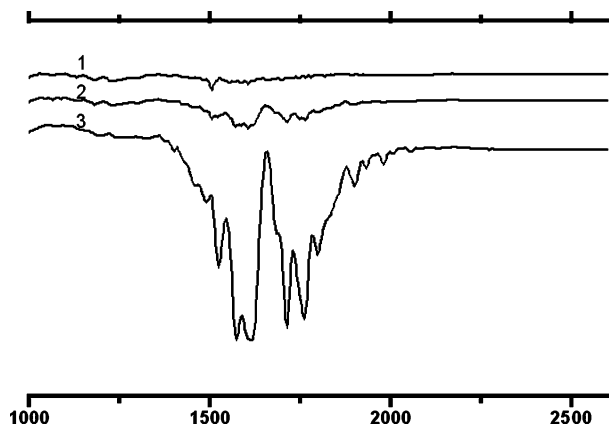
only a few picoseconds, their donor–acceptor interaction with the relatively long-lived triplet excitons of PDOF effectively quenches the triplet state of PDOF. Accordingly, the performance of our devices has been improved significantly. We believe the device longevity can be improved more significantly if it is run in argon.

Recently, Bliznyuk et al. reported the degradation mechanisms of PLEDs based on blue-emitting polyfluorene polymers.<sup>19</sup> In the presence of oxygen, they showed that the changes in fluorescence are accompanied by evidence for photooxidation. Chemical oxidation formed via energy transfer from the polymer triplet state attacks the polymer main chain, resulting in decreased conjugated length and formation of carbonyl species. The carbonyl groups formed on the ends of polymer chains have been identified as efficient exciton quenchers in emitting polymers.<sup>19,20</sup> The strong electron affinity of the carbonyl groups leads to charge transfer between pristine polymer conjugation units and defect units, causing exciton dissociation. The effects of electrical degradation on emission have been studied after dissection of failed polymer devices. After devices electrically degraded in air were peeled apart, PL spectra were obtained. The data of Figure 5 clearly show the effects of electrical degradation on PL emission char-

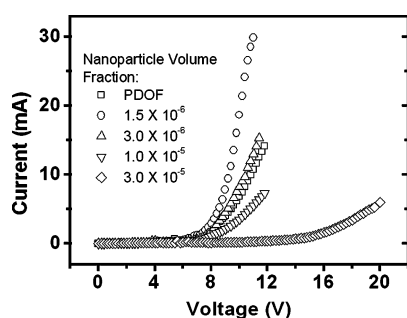
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**Figure 6.** FTIR spectra of (1) a fresh PDOF film, (2) a PDOF/gold nanoparticle nanocomposite film after electrical degradation in air after 10 min at 10 V, and (3) a PDOF film after electrical degradation in air after 10 min at 10 V.

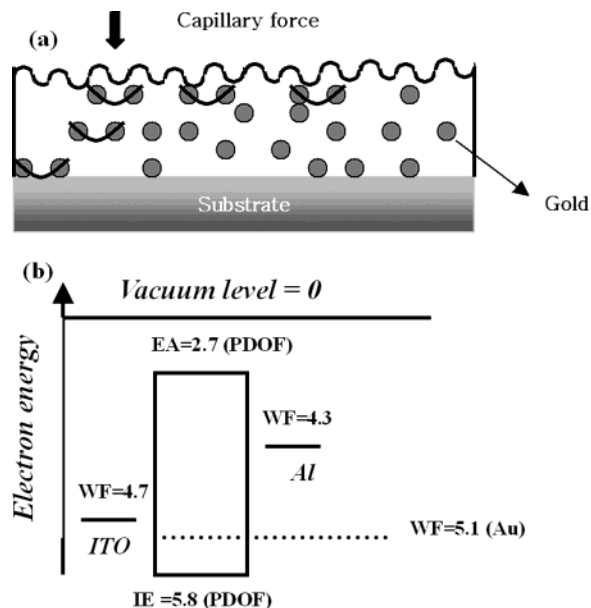


**Figure 7.** (a) Current vs voltage characteristics of the PDOF/gold nanoparticle nanocomposite devices with different nanoparticle volume fractions.

acteristics. The primary characteristic of the pristine PLED is a decreased exciton-to-excimer ratio compared to that of the PLED with  $1.0 \times 10^{-5}$  gold volume fraction.

Chemical changes that occur during and after degradation were also monitored using FTIR spectroscopy. Figure 6 shows the IR transmission spectra of (1) a fresh PDOF film, (2) a film with  $1.0 \times 10^{-5}$  gold volume fraction after electric degradation in air, and (3) the PDOF film after electric degradation in air. The most obvious changes in the IR spectra of degraded samples are observed between  $1500$  and  $1800\text{ cm}^{-1}$  region, but only in the case of pristine PLEDs are the spectroscopic changes well pronounced. In electrically degraded pristine PDOF film and nanocomposite film, two new bands appear around  $1717$  and  $1606\text{ cm}^{-1}$ . The former is consistent with carbonyl stretch of an aromatic ketone or ester and the latter may be interpreted as a stretching mode of an asymmetrically substituted benzene ring.<sup>19</sup> The intensities of these two peaks may be the results of photooxidation. In the case of the pristine PDOF sample, the intensities of these two peaks are more obvious and clear compared with those of the nanocomposite film.

Figure 7 shows the current versus voltage characteristics of the PDOF and PDOF/gold nanocomposite LED. One of the interesting phenomena observed here is the drastically increased current when a volume fraction of the gold nanoparticles of  $1.5 \times 10^{-6}$  was incorporated into the luminescent polymer, suggesting that the nanoparticles enhance the carrier injection or mobility.

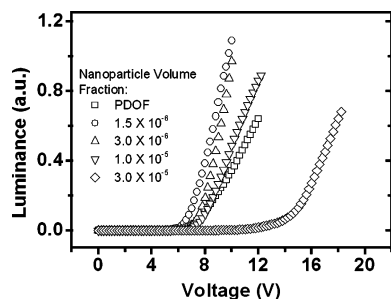


**Figure 8.** (a) Schematically illustrated mechanism of the formation of roughened surface. (b) Proposed energy level diagram of device.

During the spin-casting of the PDOF/gold nanoparticle nanocomposite film, the nanoparticles may become attached to the anode and to each other due to strong electrostatic forces; capillary forces then draw the polymer solution around the nanoparticles. This would create a roughening of the surface onto which the Al electrode is deposited and thus result in a larger interface between the Al cathode and the luminescent nanocomposite layer. The mechanism is illustrated schematically in Figure 8(a). The increased current for the nanocomposite device with a volume fraction of gold nanoparticles of  $1.5 \times 10^{-6}$  possibly demonstrates that electron injection at the cathode is facilitated by a nanomorphologically roughened interface. Recently, Carter et al. have also reported improved electron current in a MEH-PPV/SiO<sub>2</sub> composite device, which they explained by suggesting that changes in interface morphology due to the incorporation of the nanoparticles may have played a key role.<sup>17</sup>

The current density of the nanocomposite devices decreases with further increases in the doping level of the gold nanoparticles. This can be explained by the hole trapping effect, which is another important role of the gold nanoparticles. It has been reported that gold nanoparticles act as efficient hole trap sites in PVK/metal nanoparticle nanocomposite films because of the work function level of metal nanoparticles.<sup>21</sup> In devices, holes are injected from the PEDOT:PSS contact into the PDOF emitting layer and transported toward the cathode. Some of injected holes may be trapped at the gold nanoparticles owing to the relative energy alignment of the highest occupied molecular orbital (HOMO) level of PDOF and work function of gold nanoparticles (see the energy diagram in Figure 8(b)). For these charged gold nanoparticles the barrier to hole injection from the cathode and hole transport rate can be reduced. For PLEDs doped with a very small amount of gold nano-

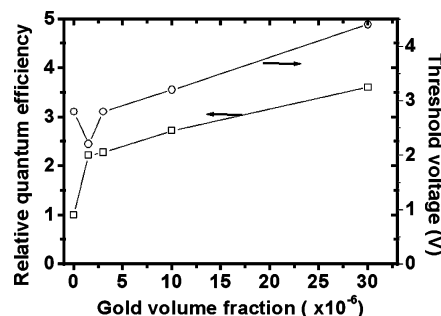
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**Figure 9.** Luminescence vs voltage characteristics of the PDOF/gold nanoparticle nanocomposite devices with different nanoparticle volume fractions.

particles, the enhanced electron injection produced by the gold nanoparticles is dominant over their hole blocking effect, resulting in an increased current density in the device. However, when the doping concentration of the gold nanoparticles in the emitting layer is further increased the hole blocking effect of the nanoparticles starts to dominate their electron injection effect and the total current density decreases. Figure 9 shows the luminance versus voltage characteristics of the devices. The EL intensity at a particular electric field increases as the gold volume fraction increases up to  $1.0 \times 10^{-5}$ . However, when the gold volume fraction is further increased, the EL intensity starts to decrease and the operating voltage suddenly shifts from 11 to 20 V for the highest gold-particle concentration. This is caused by the dramatic increased hole blocking effect of gold nanoparticles located in the PEDOT:PSS-emitting layer interface. If we assume that the luminance is proportional to the electron current in hole-only light-emitting devices,<sup>22</sup> the higher luminance of the device may indicate that more electrons are injected into the device. The turn-on threshold voltage for the EL device with a volume fraction of gold nanoparticles of  $1.5 \times 10^{-6}$  was slightly lower than that of the pristine PDOF device. Further increases in the nanoparticle volume fraction required higher electric fields before any EL was observed (Figure 10).

Figure 10 also demonstrates an improvement in the quantum efficiency of the nanocomposite devices, as measured by a previously reported procedure.<sup>23</sup> Generally, unbalanced carrier transport is known to lower the efficiency of PLEDs, but PDOF is a unipolar conductor that exhibits much more hole injection than electron injection.<sup>24</sup> Because of the enhanced electron injection



**Figure 10.** Relative quantum efficiency and turn-on threshold voltage of the PDOF/gold nanoparticle nanocomposite devices with different nanoparticle volume fractions.

and hole blocking effect of the gold nanoparticles, the external quantum efficiency of the nanocomposite device is enhanced compared to that of the pristine PDOF device. However, the device with a gold volume fraction of  $3.0 \times 10^{-5}$  exhibits decreased light output, although the material does exhibit an enhanced external quantum efficiency, probably because the hole injection and mobility are seriously decreased.

## Conclusions

In summary, we have fabricated PLEDs with enhanced environmental stability by employing PDOF/gold nanoparticle nanocomposite emitting layers. The gold nanoparticle-doped PLEDs are protected against oxidation by the quenching of the triplet state of the emissive polymer. In addition, the gold nanoparticles appear to modify the device interfacial morphology, which not only facilitates electron injection but also blocks hole migration. To improve both the luminescent lifetime and the quantum efficiency of a PLED simultaneously, an optimized amount of gold nanoparticles should be incorporated into the emitting polymer. The PDOF/gold nanoparticle nanocomposite devices have external quantum efficiencies higher than that of the pristine PDOF device.

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