

## Triplet exciton confinement in phosphorescent polymer light-emitting diodes

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A series of iridium complexes, with triplet energy levels above or below the triplet level of host polymer, were used to study the flow of excitons between the host and the dopants. The performance of phosphorescent polymer light-emitting diodes has been shown to be sensitive to the triplet energy of the dopant. When the dopant exciton level was higher than that of the host polymer, a “backward excitation energy transfer” occurred; hence, the photoluminescence is quenched and the device performance is poor. When the triplet energy level of the dopant was lower than that of the host polymer, the exciton is confined to the dopant site, and the device shows better performance due to this confinement. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544658]

Recently, the quantum efficiency of organic light-emitting diodes (OLEDs) has been significantly improved due to the harvest of both singlet and triplet excitons.<sup>1–3</sup> An internal quantum efficiency of nearly 100% has been demonstrated.<sup>4</sup> Iridium(III) complexes have been shown to be the most efficient dopants due to their short excitation lifetime.<sup>2–4</sup> OLEDs doped with Ir-complexes with emission from blue to red have demonstrated efficiency.<sup>5,6</sup> Although many phosphorescent polymer light-emitting diodes (PLEDs) have been reported,<sup>7–12</sup> quantum efficiency comparable to that of OLEDs has not yet been demonstrated, even though the same dopant molecules have been used. In this letter, backward excitation energy transfer from the phosphorescent dopants to the semiconducting polymer was investigated. In this study, a series of Ir-complexes with different triplet energy levels were used as the dopants for phosphorescent PLEDs. The triplet energies of these metal complexes were finely tuned by modifying the chemical structure of the ligands.<sup>5</sup> Except for triplet energies, these dopant molecules have similar photophysical properties, such as metal-to-ligand charge transfer (MLCT) absorption energies and triplet excitation lifetime.<sup>5,6</sup> They provide a suitable system for investigating the influence of dopant excitation energy on the performance of phosphorescent PLEDs. Our results suggest that confinement of triplet excitons is important to achieve high efficiency.

Poly[9,9-bis(octyl)-fluorene-2,7-diyl] (PF) was chosen as the host polymer because of its high photoluminescent (PL) efficiency and high conductivity.<sup>13</sup> Energy diagrams of these compounds are illustrated in Fig. 1. Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of polymers and dopants were deduced from cyclic voltammograms (CVs) or from the literature.<sup>5,13,14</sup> Triplet state energies were estimated from their highest peak of phosphorescence.<sup>15,16</sup>

To achieve charge balance, a 20-nm-thick hole-transporting layer, poly(vinylcarbazole) (PVK), was first spin-coated onto the anode to facilitate charge injection. A second layer of iridium-complexes-doped PF films (~100

nm) was then spin-coated to serve as the emissive active layer.<sup>10</sup> A bilayer electrode, consisting of indium-tin-oxide (ITO)/glass substrate coated with a thin layer of the conducting polymer, 3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT), for the anode. Calcium (500 Å)/aluminum (1000 Å) bilayer cathodes were used in all of our devices. All devices were tested under nitrogen environment.

To investigate the photophysical properties of conjugated polymer/phosphorescent dopant systems, the PL spectra of various phosphorescent-dye-doped PF films were measured. Curve-a in Fig. 2 shows the PL spectra of a neat PF thin film. When the PF film was doped with BtpIr, the emission from PF was quenched; meanwhile, a new, red emission with a peak at 616 nm was observed (curve-b, Fig. 2). This clearly indicates that excitation energy transferred from PF to BtpIr; however, the energy transfer was not completed, even when the BtpIr concentration was as high as 11 wt %. For the PF/BtpIr blend system, although the emission of PF was quenched, only weak dopant PL emission was observed for highly BtpIr-doped films (curve-c, Fig. 2), implying little excitation energy transfer to the dopants. This situation is worse in the PPIr-doped PF films: The PL of PF decreased monotonically with doping of PPIr; no apparent emission from PPIr could be observed (Fig. 2, curve-d). For all of these three samples, the emission from PF was still observed, even at high dopant concentrations. This phenomenon is probably due to some aggregation of dopants.

The absorption spectra of BtpIr and BtpIr have similar

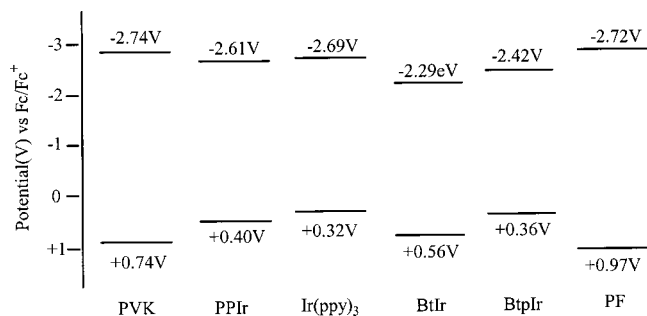


FIG. 1. Energy diagram of materials employed.

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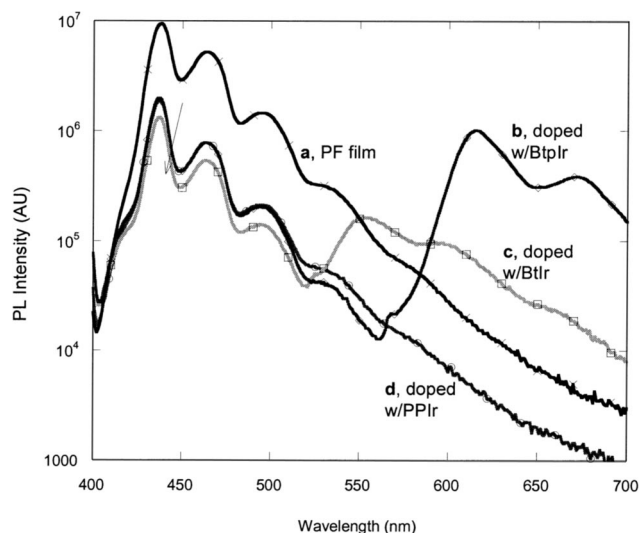


FIG. 2. PL spectra of (a) undoped PF film, PF films doped with (b) 11 wt % BtIr, (c) 10 wt % BtIr, and (d) 10 wt % PPIr. All spectra were obtained by pumping at 382 nm.

overlapping with the PL spectra of PF. The different photo-physical behaviors of the dopants cannot be well understood, considering the different energy transfer efficiencies from PF to dopants.

The different phosphorescent efficiencies of Ir-complexes in the PF films can be qualitatively explained by the relative position of the triplet energy levels of the dopants and to that of the host polymer. For the convenience of discussion, we divide polymer blends into three different categories, based on the position of their dopant triplet energy levels.

**Case 1:** The triplet energy of the dopant is higher than that of the host polymer. This is the case of the PF/PPIr blend system. The excitation energy transfers from the singlet of PF to the triplet of PPIr upon photoexcitation. Because the triplet energy ( $^3\text{MLCT}$ ) of PPIr (2.41 eV) is higher than that of  $^3\text{PF}$  (2.15 eV),<sup>16</sup> thermodynamically, the excitation energy tends to flow to PF triplet energy states. Subsequently, the  $^3\text{PF}$  decays via nonradiative transition to the ground state. Unless the population of PF triplet states is extremely high, which is almost impossible under photoexcitation because of the low efficiency of intersystem crossing (ISC),<sup>17</sup> the PPIr emission can hardly be observed.

**Case 2:** The triplet energy of the dopant is lower than that of the host polymer. This is the case of PF/BtIr system, the lowest triplet energy of BtIr (2.0 eV) is lower than that of  $^3\text{PF}$ . The excitation energy transfers from the singlet of PF to the triplet of BtIr, and it would tend to stay in the BtIr. Backflow of energy is unlikely to happen, since it is thermodynamically unfavorable. In other words, the triplet excitons are confined at BtIr. Thus, the emission of BtIr can be observed (Fig. 2, curve-b).

**Case 3:** The triplet energy level of the dopant is similar to that of the host polymer. In this case, it is a competition between the energy transfer from the dopant to the host polymer and the internal triplet exciton relaxation within the dopant, which is supported by the weak BtIr emission observed in curve-c of Fig. 2.

The dynamic equilibrium between triplet states of

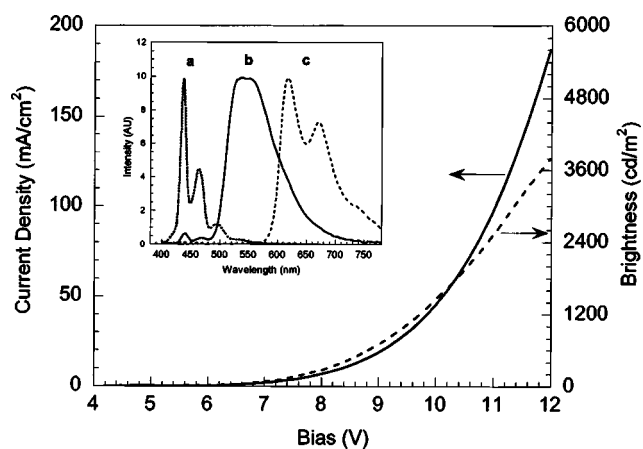


FIG. 3. The curves of the PPIr doped device. Inset shows (a) the device PL, (b) the device EL spectra under  $10 \text{ mA/cm}^2$  biased, and (c) the EL spectrum of the BtIr-doped device biased at the same current density for comparison.

hosts and dopants in phosphorescent OLEDs was first suggested by Baldo *et al.*<sup>15</sup> The free-energy change ( $\Delta G$ ) on triplet transfer determines the resident time of triplet excitons on either host or dopant triplet states. From the discussion just presented, it is expected that a similar equilibrium also existed in semiconducting polymer/phosphorescent dopant systems. For example, in PF/BtIr system ( $\Delta G = 0.08 \text{ eV}$ ), residue dopant emission could be observed in highly doped-PF films (curve-c, Fig. 2). According to this argument, once the triplet energy of phosphorescent dye further decreases, a better exciton confinement is expected. This in fact has been demonstrated by using the blend of PF/PtOEP, in which high efficiency has been demonstrated.<sup>10-12</sup>

There are other possible reasons for the quenching of the host PL, such as the formation of exciplexes or charge transfer ion pairs.<sup>17,18</sup> However, no exciplex emission was observed in the doped films was observed. From the energy levels shown in Fig. 1, the HOMO and LUMO levels of the dopants are within the range of PF; hence, it is unlikely that the blend of PF with Ir-dopants in this study can cause the exciton dissociation, which has been known to be one of the possible processes for the PL quenching.

Figure 3 shows current-light-voltage ( $I-L-V$ ) curves of devices consisting of PPIr (green emission dopant) doped PF as the emitting media. The maximum quantum efficiency was 0.9%. Although the PL intensity of the blend has been significantly quenched due to the reason explained earlier; the remaining PL mainly came from PF. However, the electroluminescence (EL) is mostly from PPIr (curve-b of inset in Fig. 3), which is mainly due to carrier trapping.<sup>19</sup>

However, there was still residual PF host emission in the EL spectra even at low current densities (inset of Fig. 3), indicating incomplete energy/charge transfer between the host and the dopant. In contrast to the low quantum efficiency of PPIr-doped devices, higher efficiency (2.0%) was obtained when BtIr was utilized as the dopant. Moreover, the device EL (inset of Fig. 3) exhibited very little host emission at the same current density, implying better energy transfer and exciton confinement, which is consistent with previous predictions from PL measurements. The performances of devices having different dopants are summarized in Table I.

TABLE I. Comparison of device performance with different dopants.

Dopant (wt % in host)	Turn-on voltage (V)	Maximum quantum efficiency	Maximum luminance efficiency (cd/A)	Triplet energy <sup>a</sup> (eV)
Ir(ppy) <sub>3</sub> (3%)	4.5	0.90%	3.9	2.41
PPIr (3%)	4.5	0.95%	4.1	2.41
BtIr (5%)	5.2	1.0%	3.0	2.23
BtpIr (5%)	5.0	2.0%	1.9	2.02

<sup>a</sup>Deduced from the highest peak of phosphorescent.

The quantum efficiency of the phosphorescent PLED based on BtpIr is still low compared with reported phosphorescent OLEDs.<sup>3–5</sup> It has been suggested that the aggregation of dopants often causes self-quenching and, consequently, decrease of PL efficiency.<sup>17</sup> Because of the large polarity difference between PF and Ir-complexes, it is suspected that dye aggregation occurs in dye-doped films, which results in low device efficiency. This was confirmed by examining the thin film morphology by atomic force microscopy (AFM). The surface root-mean-square (rms) roughness of pure PF film is 0.76 nm. However, for BtpIr-doped PF films, for example, the surface rms roughness increased to 11.3 nm, indicating the formation of dopant aggregation. In addition, from the PL spectra (Fig. 2), the large fraction of excitons formed on the PF also reflects the possibility of inhomogeneous distribution of dyes. To improve the device performance, host/dopant systems have been redesigned.

For semiconducting polymer materials, because of the large singlet-triplet gap, which implies strong electron–electron interaction,<sup>20</sup> the triplet energies are usually low. For fluorescent dopant systems, singlet excitons can be more easily confined. However, in order to confine triplet excitons in phosphorescent dopants, a host material with high triplet energy levels is required, which indicates a host material with a larger band gap is favorable. In kinetics, reducing the nonradiative decay rate of the host provides an alternative; host materials with longer triplet lifetime meet this requirement.<sup>22</sup>

In conclusion, different triplet exciton energies of Ir-complexes lead to various photophysical behaviors in the PF matrix. The phosphorescent efficiencies of Ir-complexes in PF are a function of their triplet energy. The performance of phosphorescent PLED has also been shown to be sensitive to the triplet energies of dopants. Due to its low triplet energy level, PF is not suitable as the host for green dopants. Nevertheless, higher efficiency could be obtained for red phosphorescent PLEDs. From this study, it is apparent that triplet exciton confinement is a crucial factor when dealing with phosphorescent OLEDs. In light of our results, it is clear that in order to achieve high device efficiency for phosphorescent polymer LEDs, the host polymer must have sufficiently high triplet energy level to achieve the exciton confinement. A blue (or even UV) emission polymer is needed for future efficient phosphorescent polymer LEDs. This blue polymer

should have a broad energy gap, high triplet energy level, and bipolar charge transport capability.

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