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Citation: *Appl. Phys. Lett.* **90**, 013504 (2007); doi: 10.1063/1.2424667

View online: <http://dx.doi.org/10.1063/1.2424667>

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Large enhancement of intersystem crossing in polyfluorenes by iridium-complex doping

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(Received 14 July 2006; accepted 24 November 2006; published online 3 January 2007)

Photoinduced absorption is used to study the intersystem crossing (ISC) rate of two polyfluorenes doped with iridium (III) tris[2-(4-totyl)pyridinato-*N*, *C2*]. It is found that the triplet exciton lifetime of polyfluorene is reduced by the dopants. But instead of decreasing, the population density of polyfluorene triplet exciton increases by almost one order of magnitude. The finding shows that the ISC rate can increase over 100 times due to the spin-orbital interaction with the Ir ion even though it is covered by the ligands. Specifically, the ISC lifetime changes from the intrinsic value of 62 ns to as short as 0.28 ns upon 10% doping. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2424667]

Organic electrophosphorescent devices have generated great interests in the past decade. After the realization of 100% internal quantum efficiency for small molecule phosphorescent organic light-emitting diodes (PhOLED),¹ nearly 100% internal quantum efficiency has also been demonstrated recently for phosphorescent polymer light-emitting diodes (PhPLED),² which proves the importance of the doping of transition metal complex in organic devices. Many works have been devoted in studying this doping material system, but most of them are focused on the energy transfer from the host to the phosphorescent dopant³⁻⁹ or the decay of the phosphorescent dopant itself.¹⁰⁻¹² The host singlet to triplet exciton intersystem crossing (ISC) rate is usually assumed as a constant even when the metal complexes are doped into the organic semiconductor host. Such assumption appears reasonable because the host excitons are separated from the metal ion by the ligands and the spin-orbital interaction of the ion is short ranged. Therefore, the transition metal induced spin-orbital coupling effect would be confined within the complex rather than influence the transitions among the host excitons due to the long distance. In particular, the host singlet to triplet ISC rate would be independent of the metal complex doping and remain an intrinsic property of the host small molecule or polymer semiconductors. However, there is no direct experimental evidence so far that testifies such assumption. In this work we use photoinduced absorption (PA) spectroscopy to monitor the host triplet excitons of polyfluorene doped by Ir complex and found surprisingly that despite the reduced lifetime of the host triplet exciton by the doping, the population density of host triplet exciton is significantly increased. This indicates that the ISC rate from host singlet to host triplet excitons is enhanced by

Ir complex over 100 times, far from being a constant.

Poly(9,9-dioctylfluorenyl-2,7-diy) end capped with dimethylphenyl (PFO) and poly[9,9-di-(2-ethylhexyl)fluorenyl-2,7-diy] end capped with *N,N*-bis(4-methylphenyl)-4-aniline (PF) are chosen as the host polymers. Iridium (III) tris[2-(4-totyl)pyridinato-*N*, *C2*] [Ir(mppy)₃] is doped into polyfluorene as the phosphorescent dopant. All the organic materials are purchased from American Dye Source. The PA experimental details are described elsewhere.¹³ All the film thicknesses are 750±50 Å.

PA is used to detect the nonemissive triplet excitons of the polyfluorene host by the induced infrared absorption to higher triplet levels. The magnitude of PA is proportional to the population density of the triplet excitons.¹³ The peak of the induced absorption is at 1.45 eV for PFO and 1.5 eV for PF. A 405 nm diode laser is used as the excitation source. The PA spectrum is shown in Fig. 1(a) at 100 Hz modulation. 100 Hz is always used for steady state results below. Figure 1(b) shows the PA frequency modulation of host triplet exciton at its absorption peak in three different material combinations at 100 K. The triplet exciton lifetime can be fitted from the modulation rate equations:¹⁴ the total amplitude signal $PA^{\text{total}} \propto 1/\sqrt{k_T^2 + \omega^2}$, the in-phase signal $PA^{\text{in}} \propto k_T/(k_T^2 + \omega^2)$, and the out-of-phase signal $PA^{\text{out}} \propto \omega/(k_T^2 + \omega^2)$. k_T is the host triplet exciton decay rate and $\omega = 2\pi f$. The total amplitude curve is first fitted by the rate equation in two limiting conditions, $\omega\tau \ll 1$ and $\omega\tau \gg 1$, to determine the lifetime τ_T . After that, the same τ_T is used for in-phase and out-of-phase fittings. There are some deviations in the cross-over region of the out-of-phase fitting and in the high frequency region for the in-phase region. The deviation may result from the bimolecular recombination which is not included in the formula. However, a valid mean lifetime can always be obtained by the fitting even with bimolecular recombination.¹⁵ As PFO is doped with Ir(mppy)₃, the

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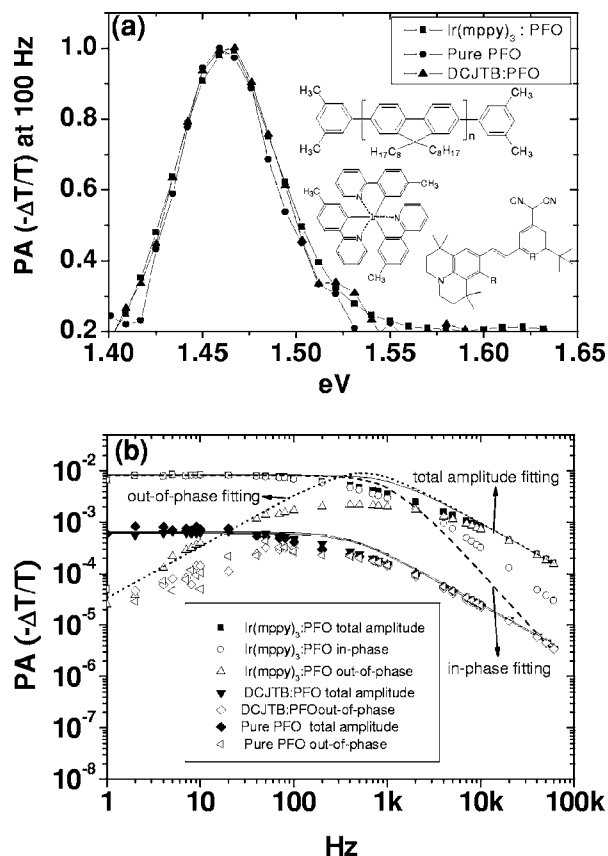


FIG. 1. (a) PA spectrum is shown and PA peak is at 1.45 eV. A 405 nm diode laser is used to be the pumping source. The absorption of PFO at 405 nm is very high, but the absorption of Ir(mppy)₃ at this wavelength is very weak. The temperature is at 100 K. (b) The PA frequency modulation of PFO triplet exciton in three different doping conditions. The modulation of 10% DCJTBPFO is identical with pure PFO. The fitted lifetime is 0.4 ms. The lifetime of 10% Ir(mppy)₃ doped PFO triplet exciton is decreased to 0.14 ms. The solid lines are the theoretical fitting curves. Note that the PA intensity of Ir(mppy)₃ doped PFO is higher than that of pure PFO. The inset in (a) are the chemical structures of PFO, Ir(mppy)₃, and DCJTBPFO in the top and from left to right, respectively.

lifetime of its triplet exciton is reduced from 0.4 ms for the pure polymer to 0.14 ms, but its PA intensity increases by about one order of magnitude. In comparison, PFO is also doped by an organic fluorescent dye molecule 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTBPFO) which does not have strong spin-orbital coupling. As shown in Fig. 1, contrary to Ir(mppy)₃, the PA lifetime and the intensity are not affected by the doping of DCJTBPFO. This implies that the large effects seen in Ir(mppy)₃ are due to the heavy-metal spin-orbital coupling. The PFO triplet exciton lifetime decreases because its spin forbidden decay is enhanced by the Ir complex or transfer to triplet states of Ir(mppy)₃. Through Dexter energy transfer, trap recombination can be neglected because no effect is observed from DCJTBPFO. Despite of the enhanced decay of the PFO triplet exciton, its population density is increased, implying that the generation of PFO triplet exciton increases much more than decays. In other words, even though the Ir ion is covered by the ligands, it has a dramatic effect on the internal intersystem transition of the host polymer. The role played by the transition metal complexes in the doped polymer system is therefore not simply a carrier trap or a phosphorescent emitter as commonly assumed. Because the host triplet exciton is a significant in-

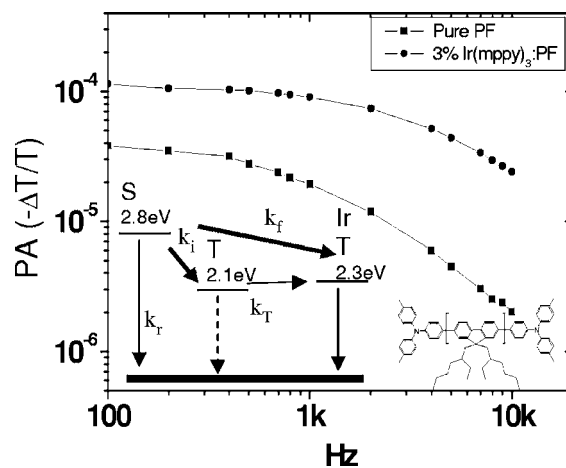


FIG. 2. The PA frequency-modulation curve of PF triplet exciton. 0.02 and 0.06 ms are the PF triplet exciton lifetimes in 3% Ir(mppy)₃ doped PF and pure PF, respectively. The lower inset shows the exciton energy levels of polyfluorene and the transitions. The upper inset is the chemical structure of PF. The temperature is at 100 K, and PA peak is at 1.5 eV.

intermediate state for the light emission process, their enhanced generation by the dopant must be taken into account in the physics of phosphorescent OLED. In order to show that this behavior is not specific to only one kind of polyfluorene, PF is also used as the host and doped with Ir(mppy)₃. The singlet exciton level of PF is higher than that of PFO and so is its triplet exciton PA absorption peak. Figure 2 shows the PA frequency modulation of PF triplet exciton. Even with a slight 3% Ir(mppy)₃ doping, the lifetime of PF triplet exciton decreases while its population density increases. This is similar to the case of PFO.

The inset of Fig. 2 shows the relative energy levels of host singlet and triplet excitons and the transition rates. In a steady state, the generation of triplet excitons must be equal to the decay of triplet excitons, i.e., $N_S k_i = N_T k_T$, and $k_i = N_T k_T / N_S$. N_S , k_i , N_T , and k_T are singlet exciton density, polymer singlet to triplet intersystem crossing (ISC) rate, triplet exciton density, and triplet exciton decay rate, respectively. k_T includes the decay routes from PFO triplet state to the ground state and from host triplet state to Ir triplet state through Dexter energy transfer. If we make $k_i^d = \alpha k_i^0$, where k_i^d is ISC rate in Ir doped PFO and k_i^0 is ISC rate in pure PFO, then α can be expressed as

$$\alpha = \frac{k_i^d}{k_i^0} = \frac{N_T^d k_T^d N_S^0}{N_T^0 k_T^0 N_S^d} \quad (1)$$

The superscripts *d* and 0 represent the doped and pure cases, respectively. N_T^d and N_T^0 are proportional to the PA intensity. k_T^d and k_T^0 are the reciprocals of triplet exciton lifetime τ_T^d and τ_T^0 which are determined by fitting PA frequency modulation curves. N_S^0 and N_S^d can be determined by the photoluminescence (PL) intensity. Consider 10% Ir(mppy)₃ doped PFO. From Fig. 2 and Eq. (1), N_T^d / N_T^0 is proportional to the steady state PA intensity ratio of $8.5 \times 10^{-3} / 7.2 \times 10^{-4}$. $k_T^d / k_T^0 = \tau_T^0 / \tau_T^d = 3.4 \text{ ms} / 0.38 \text{ ms}$. The ratio of PL intensity of pure PFO and 10% Ir(mppy)₃ doped PFO is 1826/279 (Fig. 4). Therefore, the value of α for 10% Ir(mppy)₃ doped PFO is 220, which means that the ISC rate is enhanced by 220 times by the Ir doping. The α values calculated by Eq. (1) for different Ir(mppy)₃ concentrations are shown in Fig. 3.

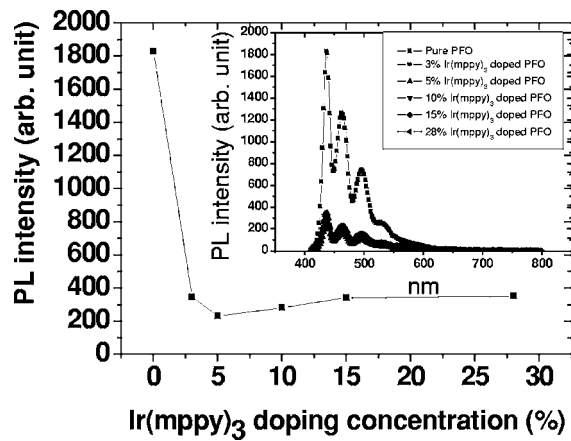


FIG. 4. PL intensity of the blue emission from PFO host at different Ir(mppy)₃ doping concentrations. The inset is the PL spectrum.

Another interesting consequence of the large α is that it requires the ISC transition only constitutes a small portion of the total singlet exciton decay without doping. The steady state rate equation of singlet exciton is $\dot{N}_S = P - N_S(k_S + k_i + k_f) = 0$, where P is singlet exciton generation by laser pumping and k_S , k_i , and k_f are singlet exciton decay rate, ISC rate, and Förster energy transfer rate to Ir complex, respectively. Assuming $k_i = xk_S$ and $k_f = yk_S$, then the population density of singlet exciton with doping can be expressed as $N_S^d = P/k_S(1+x+y)$. Without doping we have $N_S^0 = P/(k_S + k_i^0) \approx P/k_S$ because it is widely known that $k_i^0 \ll k_S$.¹⁶ Letting N_S^d divided by N_S^0 , we get $x = N_S^0/N_S^d - 1 - y$. From $k_i^d = \alpha k_i^0$ and $k_i^d = xk_S$, we have $\alpha k_i^0 = xk_S$ and $k_i^0 = (x/\alpha)k_S$, which lead to

$$k_i^0 = \frac{k_S}{\alpha} \left(\frac{N_S^0}{N_S^d} - 1 - y \right) < \frac{k_S}{\alpha} \left(\frac{N_S^0}{N_S^d} - 1 \right). \quad (2)$$

$y > 0$ because Förster transfer process happens. For 10% Ir(mppy)₃ doped PFO, $k_S \approx 1/0.4$ ns,¹⁷ $\alpha = 220$, and $N_S^0/N_S^d \approx 6.5$, and then $k_i^0 < \frac{1}{0.4 \cdot 220} (6.5 - 1)(1/\text{ns}) \approx 1/50$ ns. This result indicates that k_i^0 is smaller than k_S by two orders of magnitude. Such difference is somewhat larger than that previously expected.¹⁶ In terms of lifetime, $\tau_i^0 = 50$ ns for pure PFO. After 10% Ir(mppy)₃ doping, $\tau_i^d \approx 0.07$ ns which is faster than τ_S .

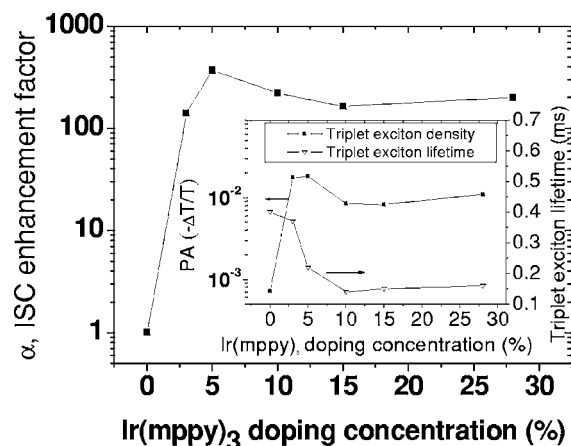


FIG. 3. Intersystem enhancement factor α is plotted as a function of Ir(mppy)₃ doping concentration. The inset is the PA intensity and fitted triplet exciton lifetime. α is proportional to the former divided by the latter.

It is somewhat surprising that the transitions on the polymer backbone can be strongly affected by the heavy-metal ion which is surrounded by the ligands and has no wave function overlap with the backbone. We believe that transition occurs through an intermediate state caused by second order perturbation, which occurs even without direct contact with Ir ion or the polymer backbone. The intermediate state here is probably the ligand singlet exciton. A matrix element of the Förster dipole-dipole coupling operator exists between the initial polymer singlet exciton state and the ligand singlet exciton state. The ligand singlet exciton has a triplet component because of the strong spin-orbital interaction in the complex. In addition, the ligand can easily come in direct contact with the polymer backbone. Therefore, a second matrix element of the Dexter exchange operator exists between the ligand singlet exciton and the final polymer triplet exciton. Such second order process is efficient because Förster transfer is wide ranged (over 100 Å). Another possible choice for the intermediate state is the metal-to-ligand charge-transfer triplet states,^{3,18} which has a singlet component extending to the ligands.

In summary, we study the ISC rate of polyfluorene doped with Ir complex and find that the ISC rate from host singlet to triplet exciton is made very efficient by the spin-orbital interaction of the dopant. In addition to its significant contribution to phosphorescent PLED, this result can be applied to solar cell where transferring the singlet excitons to triplet exciton with long diffusion length may improve the charge transfer efficiency.

This work is supported by the National Science Council and the Ministry of Education of Taiwan, the Republic of China.

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