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Efficient Organic Light Emitting Diode through Triplet Exciton Reharvesting by Employing Blended Electron Donor and Acceptor as the Emissive Layer

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KEYWORDS: organic light emitting diode (OLED), intermolecular exciplex, weak coupled donor and acceptor, triplet exciton reharvesting, thermally activated delayed fluorescence (TADF)

ABSTRACT: A blended bimolecular exciplex formation was demonstrated between two individual donor and acceptor molecules, which are tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and 2,4,6-tris(3’-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (Tm3PyBPZ). The photoluminescence spectrum of the exciplex in the solid state showed an emission with a peak around 514 nm (~2.49 eV). By applying this exciplex as an emitting layer, a highly efficient all-fluorescent organic lighting emitting diode with maximum efficiencies of 13.1% and 53.4 lm/W can be realized under an extremely low turn-on voltage of only 2.4 V. The thermally activated delayed fluorescence (TADF) process is believed to be responsible for the excellent device performance.
Since Tang and VanSlyke developed the first organic light emitting diode (OLED) in 1987, there have been continuous efforts to overcome the problem of limited internal quantum efficiency (IQE) due to the charge recombination spin statistics.\textsuperscript{1,2} Although Forrest et al. made a breakthrough to realize an OLED device with theoretical 100 % IQE by introducing the phosphorescent emitters employing heavy transition metals in 1998, these emitters containing iridium, platinum, osmium and ruthenium inevitably have the problems of high cost and environment pollution.\textsuperscript{3} In recent years, novel concepts of reharvesting triplet excitons through two up-conversion mechanisms including triplet–triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF) have been successfully demonstrated to yield high efficiency OLEDs with pure organic materials that are free of rare metals.\textsuperscript{4,5} Compared to TTA with theoretically maximum IQE of only 62.5 %, TADF with potential 100 % IQE is more promising for the future application.\textsuperscript{6,7}

TADF is a process existing in certain molecules with small singlet-triplet exchange energy ($\Delta E_{ST}$). In TADF process, the reverse intersystem crossing (RISC) from triplet excited state ($T_1$) to singlet excited state ($S_1$) by the assistance of thermal energy will cause the repopulation of $S_1$, followed by delayed fluorescence (DF). In addition to prompt fluorescence (PF), DF can make an extra contribution to the total fluorescent quantum yield. The rate of RISC is relevant with $\Delta E_{ST}$ which is scaled with the overlap between highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level.\textsuperscript{8} Therefore, suitable candidates fulfilling this requirement should have weak-coupled electron-donating (D) group and electron-accepting (A) group situated on well separated locations either in the same molecule or in different molecules.\textsuperscript{9} In the former case, it is called intramolecular exciplex, and in the latter case, it is called intermolecular exciplex.\textsuperscript{10,11} Although at present the intramolecular exciplex attracts
considerable research interests, it takes a lot of efforts to design an individual molecule with high fluorescent quantum yield as well as small $\Delta E_{ST}$.\textsuperscript{12} Intermolecular exciplex, which is achieved by physically blending individual D and A molecules with appropriate selection from present materials, has excellent performance comparable to the phosphorescent emitter.\textsuperscript{7}

Previous reports showed that building blocks of electron donors such as aromatic amine and carbazole can interact with electron acceptors containing heterocyclic cores like oxadiazole and triazine to form a charge transfer state with small $\Delta E_{ST}$.\textsuperscript{13} To confine the triplet excitons on the exciplex, the D and A molecules should have high enough triplet energy levels to prevent the transition from the exciplex to the D or A molecules.\textsuperscript{14} In this work, tris(4-carbazoyl-9-ylyphenyl)amine (TCTA) with high triplet energy level of ~2.75 eV was selected as the electron donor and 2,4,6-tris(3′-(pyridin-3-yl)biphenyl-3-yl)-1,3,5-triazine (Tm3PyBPZ) with high triplet energy level of ~2.72 eV was selected as the electron acceptor.\textsuperscript{15,16} By employing physically blended TCTA and Tm3PyBPZ as the emissive layer, a green OLED device exhibits high performance with a maximum external quantum efficiency (EQE) of 13.1 %, a maximum current efficiency (CE) of 44.2 cd/A, maximum power efficiency (PE) of 54.5 lm/W and low turn-on voltage of only 2.4 V (at luminance of 10 cd/m\textsuperscript{2}).

The scheme of the exciplex formation between TCTA and Tm3PyBPZ is shown in Figure 1. Since the excited states of the blended exciplex film are present at the heterojunctions of electron donors and acceptors, a well-mixed blend with small-scale phase separation is highly desired.\textsuperscript{17} $C_3$-symmetry feature of TCTA and Tm3PyBPZ can provide better conformational compatibility for the exciplex formation.\textsuperscript{15} The morphology of the exciplex was analyzed using atomic force microscopy (AFM) as shown in Figure S1. AFM topographic image of 30-nm-thick mixed TCTA:Tm3PyBPZ (1 : 1) shows a root mean square surface roughness value of 0.32 nm.
Figure 1. Scheme of exciplex formation between TCTA and Tm3PyBPZ.

Figure 2 shows the optical absorption and photoluminescence (PL) spectra of TCTA:Tm3PyBPZ (1:1), neat TCTA and Tm3PyBPZ thin films in UV-visible range at room temperature. There is no new absorption feature appearing in TCTA:Tm3PyBPZ compared with neat TCTA and Tm3PyBPZ, indicating that it is not ground-state charge transfer complex. The PL peak wavelength of the TCTA:Tm3PyBPZ film is located at ~514 nm, which has a significant redshift compared to the neat TCTA and Tm3PyBPZ (located at ~388 nm and 413 nm). This result confirms the exciplex formation between the TCTA and Tm3PyBPZ molecules.
**Figure 2.** The absorption and PL spectra of neat TCTA, neat Tm3PyBPZ and TCTA:Tm3PyBPZ (1:1) thin films at room temperature.

Figure 3 depicts time-resolved PL characteristics of blended TCTA:Tm3PyBPZ (1:1) film at different temperatures. All time-resolved PL are analyzed by bi-exponential decay using Equation 1. Here, I is the photoluminescence intensity, A₁ and A₂ are the quantities of each emission component, and τ₁ and τ₂ are the lifetimes of the corresponding emission components.¹⁸ The PL lifetime parameters are listed in Table S1. With decreasing temperature from 300 K to 12 K, the composition of the delayed component was reduced from 25.2 % to 9.8 %. At 300 K, the lifetimes of PF and DF are estimated to be 53.7 ns and 2.3 μs, respectively. The observation of delayed component under low temperature is also reported elsewhere.¹⁹ However, its origin in this work is under further investigation. This result verifies the temperature dependence of TADF process.²⁰ Since under optical excitation triplet excitons can only be generated from singlet excitons through intersystem crossing (ISC) process, the contribution of DF to the total fluorescent quantum yield should be much more significant under electrical excitation in an OLED device.
The PL spectra of the exciplex in chlorobenzene and tetrahydrofuran (THF) were measured. The exciplex emission cannot be observed in air-equilibrated solution as a consequence of oxygen quenching. However, the emission can be observed in oxygen-free solution as shown in Figure S2. In the oxygen-free chlorobenzene and THF, the peak wavelengths of the emission are redshifted to 553 nm and 558 nm, respectively. The spectral redshift observed in a polar solvent is due to the change of dipole moment of the molecules in the ground and excited states.

![Figure 3](image)

**Figure 3.** The time-resolved PL of TCTA:Tm3PyBPZ (1:1) thin film at different temperatures.

**Equation**

\[ I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

(1)

Time-delayed PL spectra of TCTA:Tm3PyBPZ (1:1) film from immediately after optical excitation to 5 µs at different temperatures were also recorded. As shown in Figure 4, there is no TCTA and Tm3PyBPZ emissions observed in the TCTA:Tm3PyBPZ film at 300 K, indicating an efficient exciplex formation. As the delayed time increased from 20 ns to 5 µs, a red shift from 492 nm to 525 nm is observed. This phenomenon can be due to that the energy difference between the excited states and ground states changes with the time. The more complete the charge transfer, the smaller the difference is. Thus, a more red-shifted emission generally was
observed in the measurement. This phenomenon was also found in other organic materials such as m-MTDADA: PBD and Alq₃.²³,²⁴ Time-delayed PL spectra under other temperatures are summarized in Figure S3.

**Figure 4.** The time-delayed PL spectra of TCTA:Tm3PyBPZ (1:1) film at 300 K.

Based on the exciplex of blended TCTA and Tm3PyBPZ, a series of OLED devices were fabricated. The structure is ITO / Hat(CN)₆ (5 nm) / TAPC (55 nm) / TCTA:Tm3PyBPZ (30 nm) / Tm3PyBPZ (40 nm) / Liq (2 nm) / Al (100 nm), where ITO is indium tin oxide; Hat(CN)₆ is 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile; TAPC is 1,1-bis(4-(N,N-di(p-tolyl)-amino)phenyl)cyclohexane as a hole transport layer; Tm3PyBPZ is the electron transport layer; Liq (8-hydroxy-quinolinato lithium) is the electron injection layer. Because the efficiency of OLED device strongly depends on the charge carrier balance, the charge carrier injection and transport within the emitting layer is quite important. In order to fine tune the charge carrier balance within the exciplex, three devices with different ratios of TCTA:Tm3PyBPZ (3:7 for Device A, 1:1 for Device B and 7:3 for Device C) were fabricated. The electroluminescence (EL) spectra of all three devices showed a green emission with a peak around 528 nm as shown
in Figure 5a. The current density and luminance versus voltage characteristics were shown in Figure 5b; PE and EQE versus current density were shown in Figure 5c. EQE versus luminance were shown in Figure 5d. Device B, with a ratio of 1:1 for TCTA:Tm3PyBPZ, exhibited high performance of a maximum EQE of 13.1 %, maximum CE of 44.2 cd/A, and maximum PE of 54.5 lm/W. The efficiencies slightly rolled off to 11.8 %, 39.6 cd/A, 44.5 lm/W at 100 cd/m². This performance is comparable with other highly efficient all-fluorescent OLED devices based on intermolecular/intramolecular exciplex. The detailed performances of the three OLED devices are summarized in Table S2.
Figure 5. (a) EL spectra of the OLED devices. (b) current density and luminance versus voltage characteristics. (c) PE and EQE versus current density. (d) EQE versus luminance.

In conclusion, we have demonstrated a highly efficient green OLED device based on intermolecular exciplex using fluorescent materials TCTA and Tm3PyBPZ. By using the exciplex as the emissive layer, the OLED device showed excellent performances, which are comparable with other reported record efficiencies. The time-resolved PL of the exciplex consists of prompt fluorescence in nanosecond region and the delayed fluorescence in microsecond region. The contribution of the delayed fluorescence caused by TADF is temperature dependent and it plays a crucial role in the device performance.
ASSOCIATED CONTENT

Supporting Information

Atomic force microscopy (AFM) image of 30-nm-thick mixed TCTA:Tm3PyBPZ (1:1) film is shown in Figure S1. The PL spectra of TCTA: Tm3PyBPZ in oxygen-free chlorobenzene and THF are shown in Figure S2. The time-delayed spectra in 12 K, 80 K and 150 K are shown in Figure S3. All the fitting parameters of the time-resolved PL under 12 K, 80 K, 150 K and 300 K were summarized in Table S1. The detailed performances of the OLED devices are summarized in Table S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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The working principle of OLED device employing blended TCTA:Tm3PyBPZ as the emissive layer