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# Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes

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A material possessing a very small energy gap between its singlet and triplet excited states,  $\Delta E_{1-3}$ , which allows efficient up-conversion of triplet excitons into a singlet state and leads to efficient thermally activated delayed fluorescence (TADF), is reported. The compound, 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a] carbazole-11-yl)-1,3,5-triazine, breaks the restriction of a large energy gap, with a  $\Delta E_{1-3}$  of just 0.11 eV, while maintaining a high fluorescent radiative decay rate ( $k_r \sim 10^7$ ). The intense TADF provides a pathway for highly efficient electroluminescence.

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Because exciton formation under electrical excitation results in 25% singlet excitons and 75% triplet excitons, phosphorescent materials have been requisite for obtaining high electroluminescence (EL) efficiency in organic light emitting diodes (OLEDs).<sup>1</sup> In particular, devices containing metal complexes such as tris(2-phenylpyridinato)iridium(III) [ $\text{Ir(ppy)}_3$ ] and their derivatives have resulted in nearly 100% internal EL efficiency by harvesting both singlet and triplet excitons.<sup>2</sup> Until now, phosphorescence has been considered the sole solution for high efficiency OLEDs. Herein, we demonstrate a pathway for obtaining high efficiency EL using up-conversion of triplet into singlet excited states. We have designed and synthesized an emitter molecule with a relatively small energy gap between its singlet and triplet excited states ( $\Delta E_{1-3}$ ). This molecule allows the realization of efficient up-conversion by maintaining a high radiative decay rate [ $k_r(\text{s}^{-1})$ ] of fluorescence.

There are two possible pathways for up-conversion from a triplet excited state into a singlet one. One possible mechanism is up-conversion via triplet-triplet annihilation (TTA).<sup>3</sup> Although the TTA process is usually detrimental in phosphorescence-based devices, the production of singlet excitons by TTA can enhance EL efficiency in fluorescence-based devices. This additional singlet exciton production can increase the efficiency between 15% and 37.5% depending on the up-conversion mechanism.<sup>4,5</sup> Thus, the maximum internal EL efficiency can be enhanced by up to  $\Phi_{\text{EL(int)}} = 40\%$  or 62.5%, though it cannot lead to complete EL efficiency. Another possible up-conversion process is thermally activated delayed fluorescence (TADF) (i.e., E-type delayed fluorescence),<sup>6</sup> which converts triplet excitons into singlet excited states. By preparing molecules with a small  $\Delta E_{1-3}$ , reverse intersystem crossing can be realized by harvesting environmental thermal energy. This eventuates in delayed fluorescence, which could lead to total EL efficiency if the conversion efficiency is 100%. Eosin,<sup>7</sup> fullerene,<sup>8</sup> and

porphyrin<sup>9</sup> derivatives are well known to demonstrate TADF. We demonstrated a first example of TADF under electrical excitation using tin(IV) fluoride-octaethylporphine ( $\text{SnF}_2\text{-OEP}$ ),<sup>10</sup> although the TADF efficiency was very small, with values of  $\Phi_{\text{TADF}} = 0.55\%$  at 300 K and  $\Phi_{\text{TADF}} = 2.43\%$  at 400 K. Furthermore, a copper complex was recently shown to exhibit efficient TADF and high EL efficiency.<sup>11</sup> However, purely aromatic compounds that exhibit highly efficient TADF have not yet been developed.

Aromatic ketones such as benzophenone derivatives are well known to have fairly small  $\Delta E_{1-3}$  of 0.1–0.2 eV.<sup>12</sup> However, these molecules exhibit intense phosphorescence at low temperature but not fluorescence and TADF. On the other hand, although aromatic compounds such as anthracenes and fluorenes have high fluorescent efficiency,  $\Delta E_{1-3}$  is rather large at around 1 eV, removing the expectation of up-conversion.<sup>13</sup> To overcome this problem, we designed a material possessing a small  $\Delta E_{1-3}$  with intense fluorescence from a quantum mechanical viewpoint.<sup>14</sup> The energy gap between singlet excited state ( $S_1$ ) and triplet excited state ( $T_1$ ) is given by  $\Delta E_{1-3} = E_S - E_T = 2J_{\text{LU}}$ , indicating that  $\Delta E_{1-3}$  is proportional to the exchange integral ( $J_{\text{LU}}$ ) between the spatial wave functions of a ground level (highest occupied molecular level) (U-level) and an excited level (lowest unoccupied molecular level) (L-level) levels. Thus, non-bonding (lone pair) n orbital- $\pi^*$  orbital transitions, present in molecules such as benzophenone, possess small  $\Delta E_{1-3}$  due to the orthogonal overlap between n and  $\pi^*$  orbitals. In contrast,  $\pi$ - $\pi^*$  transitions usually possess large  $\Delta E_{1-3}$  because of the large overlap between  $\pi$  and  $\pi^*$  orbitals. In other words, a small overlap between the two levels provides a small radiative decay constant so molecules that exhibit n- $\pi^*$  transitions always show very weak emission. Thus, another molecular design was required that combined a small  $\Delta E_{1-3}$  with a fairly large  $k_r$ .

Because molecules that demonstrate n- $\pi^*$  transitions are unsuitable due to their very small radiative decay rate, we focused on aromatic molecules exhibiting  $\pi$ - $\pi^*$  transitions.

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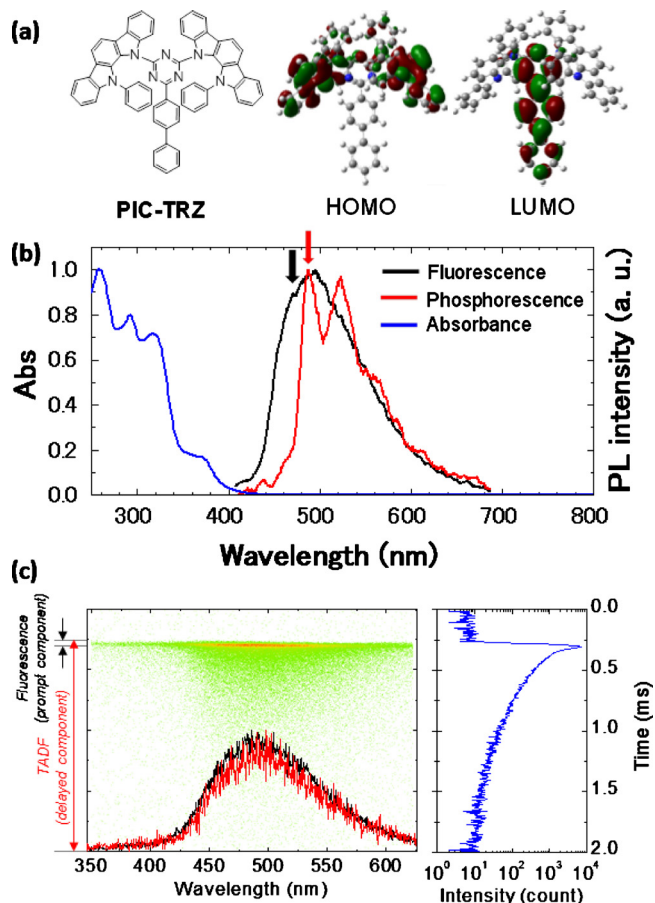


FIG. 1. (Color online) Molecular structure of PIC-TRZ and its PL characteristics. (a) Molecular structure of PIC-TRZ and its HOMO and LUMO calculated by Gaussian 03. (b) Absorption (at RT), fluorescence, and phosphorescence spectra (at  $T=5$  K) of a 6 wt % PIC-TRZ:m-CP codeposited film. (c) Two-dimensional transient decay (streak) image of transient PL of a 6 wt % PIC-TRZ:m-CP codeposited film showing the prompt component (fluorescence) (red, light color) and the delayed component (TADF) (black, dark color). In the streak image, the spots correspond to the intensity of PL: red, yellow, and green signal strong, intermediate and weak emission, respectively.

Our strategy for material design was based on the introduction of electron donor and acceptor units in which the  $\pi$ -conjugation is significantly distorted by steric hindrance introduced through bulky substituents. In this design, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals can be located around donor and acceptor moieties, respectively, leading to a small  $\Delta E_{1-3}$  while maintaining a reasonably high  $k_r$ . We also used a guest-host system to suppress nonradiative decay from the triplet excited states, because neat films usually resulted in intense concentration quenching, leading to complete disappearance of fluorescence, phosphorescence and TADF. Based on these concepts, we designed a TADF material possessing both a small  $\Delta E_{1-3}$  and a high  $k_r$ .

Figure 1(a) shows the molecular structure of 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ) containing an indolocarbazole donor unit and a triazine acceptor unit. Details of the synthetic procedure are provided in Ref. 17. The HOMO and LUMO orbitals for PIC-TRZ were calculated using Gaussian 03 (B3LYP/cc-pVDZ). Because the indolocarbazole unit is a bulky substituent, it induced significant steric hindrance around the biphenyl triazole unit, leading to localized HOMO and

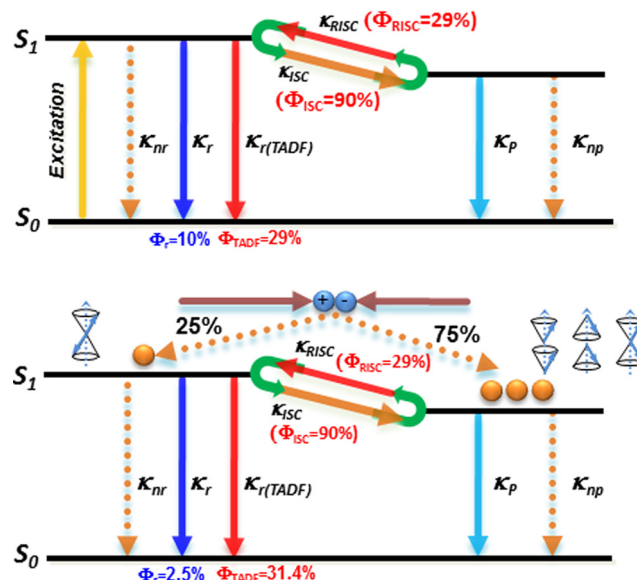


FIG. 2. (Color online) Photoluminescence process and electrophotoluminescence process.  $k_r$ ,  $k_{nr}$ ,  $k_{ISC}$ ,  $k_{RISC}$ ,  $k_p$ ,  $k_{np}$ ,  $k_{r(TADF)}$ ,  $\Phi_r$ ,  $\Phi_{TADF}$ ,  $\Phi_{ISC}$ , and  $\Phi_{RISC}$  represent the fluorescence decay rate, non-radiative decay rate from  $S_1$ , intersystem crossing rate from  $S_1$  to  $T_1$ , reverse intersystem crossing rate, phosphorescence decay rate, non-radiative decay rate from  $T_1$  to  $S_0$ , TADF decay rate, fluorescence efficiency, TADF efficiency, intersystem crossing efficiency and reverse intersystem crossing efficiency, respectively. Here  $k_r$  and  $k_{r(TADF)}$  are exactly the same because TADF takes the same route of radiative decay as fluorescence.

LUMO levels on the indolocarbazole and biphenyl triazole units, respectively. This design means PIC-TRZ shows limited overlap between its HOMO and LUMO levels.

The photoluminescence (PL) characteristics of a 6 wt % PIC-TRZ: 1,3-bis(9-carbazolyl)benzene (m-CP) codeposited film were measured as shown in Fig. 1(b). Because m-CP has a high triplet energy level of  $E_T=2.91$  eV,<sup>15</sup> the triplet excitons ( $E_T=2.55$  eV) of PIC-TRZ were perfectly confined by the m-CP host. Significant overlap was observed between the fluorescence and phosphorescence spectra ( $T=5$  K) with peaks appearing at 466 nm ( $S_1=2.66$  eV) and 483 nm ( $T_1=2.55$  eV), respectively, indicating that a very small  $\Delta E_{13}$  of 0.11 eV had been achieved (see Ref. 17). Figure 1(b) also shows the presence of a large Stokes shift, which indicates that the origin of the emission is based on intramolecular charge transfer between the donor and acceptor units (an exciplex). Figure 1(c) presents the transient PL characteristics of a 6 wt % PIC-TRZ:m-CP film, showing prompt and delayed PL spectra obtained at 300 K. A prompt component with a transient decay time of  $\tau \sim 10$  ns and a delayed component with  $\tau \sim 230$   $\mu$ s (not single exponential decays) were clearly observed. We note that the phosphorescent lifetime of PIC-TRZ at 5 K was confirmed to be longer than 100 ms. Both components are composed of multiple exponential decays and the total PL efficiency was  $\Phi_{PL}=39 \pm 3\%$ . Because both spectra are nearly coincident, the delayed component is attributed to TADF. Very similar spectral behavior was also observed in a toluene solution with a PIC-TRZ concentration of  $10^{-4}$  mol L<sup>-1</sup> and bubbling nitrogen through the solution, i.e., elimination of dissolved oxygen, influenced  $\Phi_{PL}$  significantly. Here, both transient decay curves are almost single exponential with a delayed component of  $\tau \sim 120$   $\mu$ s and a prompt component of  $\tau \sim 12$  ns. Although the nitrogen degassed solution showed  $\Phi_{PL}=35 \pm 3\%$  with an intense de-



layed emission component, the solution that was not degassed gave only  $\Phi_{\text{PL}} = 10 \pm 3\%$  and the delayed component completely disappeared (see Ref. 17). The sensitivity of the emission to degassing with nitrogen provides further evidence that the delayed component is caused by TADF that occurs via triplet excited states. Since the triplet level of oxygen is lower than that of PIC-TRZ, the triplet energy transfer from PTC-TRZ to oxygen occurs efficiently, leading to the complete quenching of triplet excitons.

In Fig. 2, we estimated the theoretical enhancement of EL efficiency when the unique TADF process is considered in the deactivation process of an OLED device. In optical excitation, part of the singlet excitons promptly decay to ground level ( $S_0$ ), the majority of the singlet excitons decay nonradiatively to the triplet level ( $T_1$ ) via intersystem crossing and some are up-converted within the singlet level ( $S_1$ ). These remaining singlet excitons repeat the same decay process until they are finally deactivated radiatively or nonradiatively. The observed efficiency of each process is, therefore, 10% for the prompt component via direct radiative singlet exciton decay and 29% for the delayed component through the multiple recycling process between the  $S_1$  and  $T_1$  levels. From this, we can see that the prompt fluorescence efficiency is  $\Phi_r = 10\%$ , and 90% of singlet excitons decay to the  $T_1$  level. 29% of triplet excitons are up-converted into the  $S_1$  level and decay radiatively, and the other 61% of triplet excitons decay nonradiatively from the  $T_1$  level. Here, we assumed that nonradiative decay from  $S_1$  to  $S_0$  is negligible. This assumption is valid because the fluorescence intensity (prompt component) is independent of temperature and PIC-TRZ has a rather large singlet exciton energy in the blue-green region, which leads to intrinsic suppression of nonradiative decay based on the energy gap rule.<sup>16</sup>

Under electrical excitation, the triplet excitons directly formed by carrier recombination are up-converted into the  $S_1$  level, leading to a total internal EL efficiency of

$$\Phi_{\text{EL(int)}} = \eta_r(S_1)\eta_r + [\eta_r(S_1)\Phi_{\text{ISC}}\Phi_{\text{RISC}} + \eta_r(T_1)\Phi_{\text{RISC}}],$$

where  $\eta_r(S_1)$  is the branching ratio of singlet exciton formation,  $\eta_r(T_1)$  is the branching ratio of triplet exciton formation,  $\Phi_{\text{ISC}}$  is the efficiency of intersystem crossing, and  $\Phi_{\text{RISC}}$  is the efficiency of reverse intersystem crossing. Thus,  $\Phi_{\text{EL(int)}} = 0.25 \times 0.10 + (0.25 \times 0.90 \times 0.32 + 0.75 \times 0.32) = 34\%$  and we can expect that the maximum external EL efficiency can be  $\Phi_{\text{EL(ext)}} = 6.8\%$  assuming a light out-coupling efficiency of 20%. We fabricated an OLED with the structure indium tin oxide/N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,10-biphenyl-4,4'-diamine ( $\alpha$ -NPD)/m-CP/6 wt %-PIC-TRZ:m-CP/BP4mPy/LiF/Al containing an electron blocking layer of m-CP and a hole blocking layer of BP4mPy to confine charge carriers and triplet excitons efficiently. It demonstrated a high  $\Phi_{\text{EL(ext)}}$  of 5.3% at low current density, approaching the theoretical limitation. Although a roll-off of  $\Phi_{\text{EL(ext)}}$  was observed at higher current density, the maximum luminance reached nearly 10 000 cd/m<sup>2</sup>. When a conventional fluorescent material with  $\Phi_{\text{PL}} = 39\%$  is used as an emitter, the theoretical  $\Phi_{\text{EL(ext)}}$  is only  $\Phi_{\text{EL(ext)}} = 2\%$ . Thus, we have confirmed that TADF is

a fascinating mechanism that can be used to enhance EL efficiency. The transient EL decay profiles of the OLED showing the prompt and delayed EL spectra support the presence of TADF under electrical excitation (see Ref. 17). We believe that optimization of device parameters such as the thickness of the organic layers and electrode materials designed for carrier balance could increase the efficiency close to the limitation. Furthermore, the roll-off characteristics of the EL efficiency should be improved by broadening the exciton formation width and the further decrease in  $\Delta E_{1-3}$ , which accelerates reverse intersystem crossing and reduces the probability of triplet-polaron annihilation. Further analysis of exciton annihilation will be discussed in a separate paper.

In summary, we designed and synthesized the molecule PIC-TRZ, which exhibits a very small  $\Delta E_{1-3}$  along with a radiative decay rate of  $k_r \sim 10^7$ , providing both efficient up-conversion from  $T_1$  to  $S_1$  levels and intense fluorescence that leads high EL efficiency. Our study opened up another means to harvest triplet excitons for light emission using a simple idea for molecular design with conventional aromatic structures. Also, we expect that compounds possessing a small or nonexistent  $\Delta E_{1-3}$  will produce not only unique scientific aspects in photochemistry but also unexpected device applications. Thus, our goal is the preparation of zero-gap molecules with a high efficiency singlet decay channel.

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