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Sensitized Fluorescence Organic Light-Emitting Diodes with Reduced Efficiency Roll-off

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Abstract:
Thermally activated delayed fluorescence (TADF) sensitized fluorescence is a promising strategy to maintain the advantage of TADF materials and fluorescent materials. Nevertheless, the delayed lifetime of TADF sensitizer is still relatively long, which cause heavy efficiency roll-off. Here we reported a valid tactic to construct fluorescent devices with low efficiency roll-off by utilizing the TADF sensitizer with reduced delayed lifetime. By construct the sensitization system, the energy transfer efficiency can up to 90%. The high energy transfer efficiency and the TADF’s short delayed lifetime result in the high sensitization over 95%, maximum external quantum efficiency of 16.2%. Meanwhile the TADF sensitized-fluorescent devices exhibit reduced efficiency roll-off with a “onset” current density of 23 mA cm-2. Our results provide an effective strategy to reduce the efficiency roll-off of TADF sensitization system.

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Sensitized Fluorescence Organic Light-Emitting Diodes with Reduced Efficiency Roll-off

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Abstract Thermally activated delayed fluorescence (TADF) sensitized fluorescence is a promising strategy to maintain the advantage of TADF materials and fluorescent materials. Nevertheless, the delayed lifetime of TADF sensitizer is still relatively long, which cause heavy efficiency roll-off. Here we reported a valid tactic to construct fluorescent devices with low efficiency roll-off by utilizing the TADF sensitizer with reduced delayed lifetime. By construct the sensitization system, the energy transfer efficiency can up to 90%. The high energy transfer efficiency and the TADF’s short delayed lifetime result in the high sensitization over 95%, maximum external quantum efficiency of 16.2%. Meanwhile the TADF sensitized fluorescent devices exhibit reduced efficiency roll-off with a “onset” current density of 23 mA cm\textsuperscript{-2}. Our results provide an effective strategy to reduce the efficiency roll-off of TADF sensitization system.

Key words OLED, fluorescence, TADF

Introduction

Recently, pure organic thermally activated delayed fluorescence (TADF) materials, also known as E-type delayed fluorescence, has drawn great attention in organic electroluminescence device (OLED),\textsuperscript{1} organic photovoltage,\textsuperscript{2} bioimaging\textsuperscript{3} and photocatalysis.\textsuperscript{4} Through rational molecular design strategy, TADF materials can achieve a small singlet-triplet energy gap ($\Delta E_{ST}$).\textsuperscript{5} For TADF materials, the lowest excited triplet state can up-convert to lowest excited singlet state by fast reverse intersystem crossing (RISC).\textsuperscript{6} The up-conversion need to overcome the small $\Delta E_{ST}$ barrier. Meanwhile, the up-conversion need electron spin-flip.\textsuperscript{7} The TADF materials usually exhibit relatively long delayed fluorescence lifetime.\textsuperscript{8} The relatively long delayed fluorescence lifetime would enhance triplet-related exciton annihilation process.\textsuperscript{9} The triplet-related exciton annihilation process, like triplet-triplet annihilation and triplet-polaron annihilation, will cause heavy efficiency roll-off at high current density.\textsuperscript{10} At same time, the triplet-related exciton annihilation process will also create high-energy excitons.\textsuperscript{11} The high-energy excitons will lead to the cleavage of chemical bonds of TADF emitters.\textsuperscript{12} This will cause the device degradation. Thus, reducing the delayed lifetime of TADF materials is meaningful for the commercial application.

It is reported that the delayed lifetime of TADF materials can be reduced in TADF sensitized fluorescence system.\textsuperscript{13} In the system, it combined advantages of the TADF molecules and advantages of the fluorescence materials with Förster resonance energy transfer (FRET) process.\textsuperscript{14} In 2014, Adachi’s group reported first TADF sensitized fluorescent OLED.\textsuperscript{15} In the devices, through heavy doped TADF sensitizers, the excitons mainly formed on TADF materials.\textsuperscript{16} Formed triplet excitons can upconvert to singlet excitons by RISC process, thus realizing a theoretically exciton utilization efficiency of 100%.\textsuperscript{17} Then, the Förster resonance energy transfer (FRET) process from the singlet state of TADF molecules to the singlet state of fluorescent materials can occur in the system.\textsuperscript{18} Recent years, TADF sensitized fluorescent OLED realize remarkable progress, and the device efficiency has reached up to 20%.\textsuperscript{19} Our group reported an efficient TADF sensitized red fluorescence device with excellent color purity. We propose a new factor, sensitization efficiency (SE), to quantitatively evaluate the emission contribution of TADF sensitizer.\textsuperscript{20} Subsequently, we reported a TADF sensitized fluorescent device with low efficiency roll-off.\textsuperscript{21} However, the efficiency roll-off can be
Further reduced by further reduced the delayed lifetime of TADF materials.

Recently, we reported two highly efficient TADF emitters SAT-DAC and SATX-DAC.22 Because of its two-channel RISC process, the emitters exhibit reduced delayed lifetime. In this work, we construct a sensitization system with SAT-DAC as TADF sensitizer and TBRb as orange fluorescence emitter. From SAT-DAC to TBRb, the energy transfer efficiency can up to 90%. Based on the sensitization system, we construct the sensitization devices. Benefitting high energy transfer efficiency, the devices exhibit a maximum EQE of 16.2%, a current efficiency of 52.4 cd/A, a power efficiency of 45.7 lm/W, a sensitization efficiency of near 100% and reduced efficiency roll-off.

Results and Discussion

Figure 1 (a) the molecular structure of SAT-DAC and TBRb; (b) UV-vis absorption spectra and PL spectra of TBRb in solution, and PL spectra of the SAT-DAC-doped host film.

To investigate the interaction between TADF sensitizer and fluorescent materials, we measured the UV-vis absorption spectrum and photoluminescence (PL) spectrum of TBRb in solution and the PL spectrum of SAT-DAC in doped film. As shown in Figure 1, TBRb exhibit several characteristic absorption peaks in 370-570 nm and a characteristic fluorescent spectrum centered at 569 nm. The SAT-DAC exhibit an emission spectrum located at 521 nm with a full width at half maximum of 95 nm, which indicates its intramolecular charge transfer character. What’s more, there is a wide overlap between the emission spectrum of TADF sensitizer and the absorption spectrum of fluorescent emitter at 450-550 nm. According to the expression for the rate constant of energy transfer (KET, see Supporting Information E1), KET is proportion to the spectral integral.23 The broad overlap integral is beneficial to large transfer rate constant and will facilitate the energy transfer process from TADF material to fluorescent material. And the Förster radius (R0) is estimated to be 6.1 nm, which indicates the high energy transfer efficiency.

As reported early, highly efficient energy transfer process can reduce the efficiency roll-off and increase the sensitization efficiency. To study the energy transfer process, the PL spectrum of the doped film was measured, as shown in Figure 2. For comparison, we also measured the emission spectra of the TADF sensitizer and fluorescence molecule. In the doped film, the doping concentration of SAT-DAC was kept at 40 wt% to ensure the excitation mainly formed on the TADF sensitizer. When the film only doped with SAT-DAC it exhibits the inherent emission of SAT-DAC. When the doping concentration of TBRb was 0.3 wt%, it exhibits two major emission peaks. One of the peaks that located at around 500 nm can be ascribed to the emission of SAT-DAC, which accounts for 18.2% of the emission spectrum. Another emission peak that dominates the emission spectrum centered at 560 nm, almost completely coincides with the emission spectrum of TBRb. Therefore, the emission peak can be assigned to TBRb, and its emission contribution is 81.8%. With the doping concentration of TBRb raises from 0.3 wt% to 1.0 wt%, the emission contribution of TADF sensitizer rapidly decrease from 18.2% to 3.8%, meanwhile, the emission contribution of fluorescent molecule increases from 81.8% to 96.2%. With the adding of TBRb in the doped film, the molecular distance (R) between SAT-DAC and TBRb diminish. According to the relation of KET and R (as expression E2 in Supporting Information), the sixth order dependence of KET on R explain the giant influence of doping concentration on emission contribution.24 Besides, the energy transfer efficiency (ΦET) can be written as ΦET=1-ΦD/ΦD0,25 Where ΦD is photoluminescence quantum yield (PLQY) of SAT-DAC in existence of TBRb; ΦD0 is the PLQY of SAT-DAC in the absence of fluorescent material. According to the varying of the emission contribution of SAT-DAC, ΦET was estimated to increases as the doping concentration of TBRb adding. The maximum ΦET can reach up to 90%. These results illustrate highly effective energy transfer process from TADF sensitizers to fluorescent molecules.

To further demonstrate TRET process, transient PL decay curves of SAT-DAC and TBRb co-doped film was investigated, as shown in Figure 3. All the film was excited by 390 nm. To eliminate the emission of TBRb, 490 nm was chosen as detection wavelength of TADF sensitizer’s delayed lifetime; 620 nm was...
Transient PL decay curves of the doped films at (a) 490 nm and (b) 620 nm. (c) Delayed lifetimes of TBRb and SAT-DAC and average dynamic cycles of SAT-DAC at different doping concentrations of TBRb.

selected as detection wavelength to study the transient PL decay of TBRb. All the doped films display obvious prompt and delayed component. For the only SAT-DAC doped film, it exhibits a distinct prompt fluorescence lifetime of 100 ns and delayed fluorescence decay lifetime of 2.47 μs and 7.14 μs, both delayed lifetimes can be attributed to TADF emission. As described above, the delayed lifetime of TADF sensitizer can be reduced by adding fluorescence materials. With the doping concentration of TBRb increase from 0.3 wt% to 1.0 wt%, the delayed lifetime decreased from 1.72 μs and 5.35 μs to 0.62 μs and 2.39 μs. The average number of excited-state cycles (N) before the photon emission or nonradiative decay can be written as N = φpΦf. The N decrease from 469 to 25 as the doping concentration of TBRb increases from 0 to 1.0 wt%. According to the expression of delayed lifetime τDF (see Supporting Information E3), both τDF and N decrease with increase of doping concentration indicates that the decrease in τDF can be vested to the suppression of triplet formation of SAT-DAC after excitation. In addition, the PL decay at 620 nm, which corresponding to the emission of TBRb, also exhibits two components. With the increase of TBRb’s doping ratio, the delayed lifetime also decreases from 1.06 μs and 4.37 μs to 0.35 μs and 1.60 μs. The trend is consistent with that of SAT-DAC. These results can demonstrate that the delayed component of TBRb originated from the energy transfer from TADF sensitizer.

The highly efficient FRET process motivates us to evaluate the device performance of the sensitization system. Based on the sensitization system, we fabricated the TADF-sensitized OLED devices with the device structure as following: ITO/TAPC (30 nm)/mCP (10 nm)/DPEPO: 40wt% SAT-DAC: x wt% TBRb (20 nm)/DPEPO (30 nm)/TmPyPB (30 nm)/LiF (1.1 nm)/Al (100 nm), when x=0.5, 1.0 and 2.0, the device donated as F1, F2 and F3. For comparison, we also fabricated the fluorescent device (F4) as control device, which has the emission layer structure of DPEPO:5 wt% TBRb (20 nm). As expected, the fluorescent device displays a turn-on voltage of 3.1 V and a maximum external quantum efficiency (EQE) of 4.7%. Due to the exciton formed on TBRb, the fluorescent device shows a low turn-on voltage and device performance. As shown in Figure 4, all the sensitization devices exhibit TBRb-dominant EL characteristics. Compared with the EL spectrum of F4, only very weak emission of TADF sensitzers can be observed in the EL spectra of F1~F3. Significantly, all the sensitization devices exhibit a maximum EQE over 10%, which exceeding the limitation of traditional fluorescent device of 5% without light out-coupling technique.28

Notably, the EL spectra of device F1 overlap well with the pure EL spectrum of TBRb. According to our reported work, the sensitization efficiency (SE) was estimated to be as high as 96% at turn-on voltage and 94% at high driving voltage. And the SE can reach nearly 100% for device F3. Notably, from F1 to F3, the maximum EQE decrease with doping concentration of TBRb increases; while, the turn-on voltage and SE increases at higher doping concentration. At higher doping concentration of TBRb, energy transfer reaches higher efficiency and SE, as described former. However, more excitons formed on fluorescent molecules caused lower EQE and higher turn-on voltage. Among of all the devices, device F1 shows highest efficiency with a maximum EQE, current efficiency, power efficiency and turn-on voltage of 16.2%, 52.4 cd/A, 45.7 lm/W and 3.1 V, respectively. Meanwhile, the device still maintain an EQE of 11.4% at lumiance of 1000 cd/m². The EQE of F1 as a function of current density was fitted according to triplet-triplet annihilation (TTA) mechanism (Supporting Information E4).29 The value of J0 can be used as an indicator of efficiency roll-off. Benefiting from the high energy transfer process and the reduced delayed lifetime of TADF sensitizer in the sensitization system, the J0 can reach up to 23.7 mA/cm², which reveals the low efficiency roll-off of the device. These results demonstrate that the key role of shorten the delayed lifetime in reducing the efficiency roll-off.

Conclusions
In conclusion, we demonstrate an effective strategy to reduce the efficiency roll-off of TADF-sensitized fluorescent devices. We construct a sensitization system by utilizing SAT-DAC, which has short delayed lifetime, as TADF sensitizer and TBB as fluorescence emitters. The energy transfer process was proved by steady and transient PL spectra. The sensitization system shows a high energy transfer efficiency up to 90% and a photoluminescence quantum yield over 75%. Based on the sensitization system, the optimized devices exhibit a maximum EQE, current efficiency, power efficiency and turn-on voltage of 16.2%, 52.4 cd/A, 45.7 Im/W and 3.1 V, respectively. Meanwhile, the devices reveal a sensitization efficiency over 95% and reduced efficiency roll-off. Our results illustrate that the efficiency roll-off of sensitization devices can be reduced the delayed lifetime of TADF sensitizers. These results provide new perspectives to reduce the device efficiency roll-off of both TADF and fluorescent materials.

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Acknowledgment
We thank Dr. H. Lu for the help in transient PL measurements.

Supporting Information
YES (this text will be updated with links prior to publication)

Primary Data
NO.

Conflict of Interest
The authors declare no conflict of interest.

References and Notes
(22) OLEDs were fabricated on glass substrates precoated with 150 nm ITO. The substrates should be cleaned with detergent, ultrasonicated in water, acetone and ethyl alcohol, and subsequently dried at 75 °C (10 min) in an oven. Afterward, the substrates were exposed to oxygen plasma (10 min) in order to remove organic residues and improve the work function of ITO. Then the substrates were transferred to a thermal evaporation chamber with a pressure lower than 5 × 10−4 Pa for organic semiconductor layers and metal cathode deposition. The devices were fabricated by evaporating organic materials onto the substrate at a rate of 1-2 Å s−1 while LiF at a rate of 0.05 Å s−1 and Al metal through a rate of 5 Å s−1. The pixel sizes of each OLED are 0.09 cm2. The electroluminescence (EL) spectra were measured by a Spectra scan PR655 photometer. The current-voltage-brightness characteristics were measured by using a computer-controlled Keithley source measurement unit (Keithley 2400) with a Konica Minolta CS-200 luminance-meter under dark and ambient atmosphere. External quantum efficiencies (EQE, %), current efficiencies (cd A−1) and power efficiencies (lm W−1) were calculated from the electrical and optical properties. For this calculation, we assumed Lambertian light distribution.
Supporting Information

Sensitized Fluorescence Organic Light-Emitting Diodes with Reduced Efficiency Roll-off

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Expression E1

\[ K_{ET} = \frac{9000 \ln(10) \kappa^2 \Phi_D^0}{128 \pi^2 N_A n^4 \tau_D R^6} \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \]  

Expression E2

\[ K_{ET} = \frac{1}{\tau_D} \left( \frac{R_0}{R} \right)^6 \]  

Expression E3

\[ \frac{1}{\tau_{DF}} = \frac{1}{\tau_P^0} + B \exp \left( -\frac{\Delta E_{ST}}{k_B T} \right) \]  

where \( B = (1 - \Phi_{ISC}) A \), \( A \) is a constant, \( \Phi_{ISC} \) is the quantum yield of triplet formation, \( \tau_P^0 \) is formally identical to the low temperature phosphorescence lifetime, \( \Delta E_{ST} \) is the singlet-triplet energy gap, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature.

Expression E4

\[ \eta = \frac{J}{J_0} \sqrt{1 + \frac{8J}{J_0} - 1} \]

where \( \eta \) represents the EQE of the device, \( \eta_0 \) is the device EQE in the absence of TTA, \( J \) is the current density of the device, and \( J_0 \) is the “onset” current density at \( \eta = \eta_0/2 \).

Table S1. Summary of photophysical properties.

<table>
<thead>
<tr>
<th></th>
<th>PLQY (%)</th>
<th>( \tau_D^a ) (( \mu s ))</th>
<th>( \tau_D^b ) (( \mu s ))</th>
<th>N</th>
<th>( \Phi_{ET} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPEPO: 40wt% SAT-DAC</td>
<td>53.0</td>
<td>2.47/7.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPEPO: 40wt% SAT-DAC: 0.3 wt% TBRb</td>
<td>60.3</td>
<td>1.72/5.35</td>
<td>1.06/4.37</td>
<td>152</td>
<td>79.3</td>
</tr>
<tr>
<td>DPEPO: 40wt% SAT-DAC: 0.6 wt% TBRb</td>
<td>78.5</td>
<td>0.99/3.55</td>
<td>0.55/2.42</td>
<td>46</td>
<td>92.8</td>
</tr>
<tr>
<td>DPEPO: 40wt% SAT-DAC: 1.0 wt% TBRb</td>
<td>78.5</td>
<td>0.62/2.39</td>
<td>0.35/1.60</td>
<td>26</td>
<td>94.4</td>
</tr>
</tbody>
</table>

"\( a \) Measured at 490 nm; \( b \) measured at 620 nm.

Table S2. Summary of device performance.
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Short Communication

<table>
<thead>
<tr>
<th>V_{on} [V]</th>
<th>CEmax [cd A^{-1}]</th>
<th>PEmax [lm W^{-1}]</th>
<th>EQEmax [%]</th>
<th>SEmax [%]</th>
<th>CIE</th>
<th>At 1000 cd m^{-2}</th>
<th>CE [cd A^{-1}]</th>
<th>PE [lm W^{-1}]</th>
<th>EQE [%]</th>
</tr>
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<tbody>
<tr>
<td>F1</td>
<td>3.2</td>
<td>52.4</td>
<td>45.7</td>
<td>16.2</td>
<td>96.1</td>
<td>(0.43,0.52)</td>
<td>36.9</td>
<td>20.7</td>
<td>11.4</td>
</tr>
<tr>
<td>F2</td>
<td>3.2</td>
<td>45.9</td>
<td>45.0</td>
<td>14.5</td>
<td>99.2</td>
<td>(0.48,0.50)</td>
<td>24.6</td>
<td>12.4</td>
<td>7.74</td>
</tr>
<tr>
<td>F3</td>
<td>3.2</td>
<td>34.0</td>
<td>33.3</td>
<td>11.3</td>
<td>99.8</td>
<td>(0.51,0.48)</td>
<td>17.1</td>
<td>8.67</td>
<td>5.69</td>
</tr>
</tbody>
</table>

**Figure S1.** Current efficiency-luminance-power efficiency curves of device F1, F2, F3 and F4.

**Figure S2.** The EL spectra of F1-F3 at different drive voltages.
**Figure S3.** UV–vis absorption spectra and PL spectra of TBRb in film and PL spectra of the SAT-DAC-doped host film.