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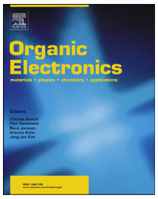

# Highly efficient orange fluorescent OLEDs based on the energy transfer from bilayer interface exciplex

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## ABSTRACT

We demonstrated highly efficient traditional orange emission fluorescent OLEDs with simple device structure by utilizing energy transfer from bilayer interface TADF exciplex to dopant. With rubrene as the dopant, under the optimized concentration of 1.5%, the device achieved maximum current efficiency, power efficiency and EQE of 25.3 cd/A, 22.6 lm/W and 8.1%, respectively. Even at the luminance of 1000 cd/m$^2$, the EQE also remained 6.9%. The obtainment of so high efficiency could be attributed to highly efficient RISC efficiency of triplet excitons and energy transfer efficiency from TADF exciplex to dopant. The more detailed working mechanism was also argued.

## 1. Introduction

Recent years, the appearance of thermally activated delayed fluorescence (TADF) opens up a new research direction of organic light-emitting diodes (OLEDs). The TADF mechanism is consistent, no matter the intramolecular TADF or intermolecular TADF (also called exciplex TADF), that is the up-conversion of triplet excitons and then achieve the emission of delayed fluorescence from excited singlet state due to the small singlet-triplet energy level gap ($\Delta E_{S-T}$). Many excellent intramolecular TADF materials were reported in the last few years [1–4]. At the same time, highly efficient delayed fluorescence exciplex with various emitting color also developed rapidly [5–9].

Except for as the emitter, the other application of exciplex is as the host, which also received much attention because of the advantage of carrier transport bipolar, barrier free and broad recombination zone et al. Kim et al. reported a series of low voltage, high efficiency phosphorescent OLEDs with exciplex-forming as the co-host [10–13]. Further more, the delayed fluorescence exciplex provide us another new idea, which is as the host to break 5% external quantum efficiency (EQE) upper limit with traditional fluorescent materials as the emitters. Lee et al. achieved the best C545T-doped OLEDs employing delayed fluorescence exciplex of TAPC: DPTPCz as the host, which showed the maximum EQE of 14.5% [14]. My previous work, utilizing delayed fluorescence exciplex of TCTA: 3P-T2T as the host and conventional material of DCJTB as the dopant to fabricate red fluorescent OLEDs, which harvested the maximum EQE as high as 10.15% [15]. The realization of high efficiency stems from the efficient reverse intersystem crossing (RISC) of triplet excitons and efficient Förster energy transfer from the exciplex host to dopant. Finally, almost all the excitons

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produced on exciplex host could contribute to fluorescent emission through the radiative transition from excited singlet state of dopant. But up to now, all the fluorescent OLEDs based on delayed fluorescence exciplex as the host are formed by the mixing of donor and acceptor, superadding the dopant, the fabrication of emitting layer (EML) need tri-source co-evaporation, which add the complexity and weaken the repeatability.

In this manuscript, we designed the bilayer interface delayed fluorescence exciplex of TCTA/3P-T2T to sensitize traditional orange material of (5,6,11,12)-tetraphenyl-naphthacene (Rubrene). This simple device structure harvest high efficiency emission of rubrene and under the optimized concentration of 1.5%, the maximum current efficiency, power efficiency and EQE reach up to 25.3 cd/A, 22.6 lm/W and 8.1%, respectively. By the device performance and energy transfer process analysis, we consider the high efficiency derives from the efficient RISC and energy transfer of delayed fluorescence exciplex that formed between TCTA and 3P-T2T. Here, TCTA is 4,4′,4″-tri(N-carbazolyl)triphenylamine and 3P-T2T is 2,4,6-tris(3-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine.

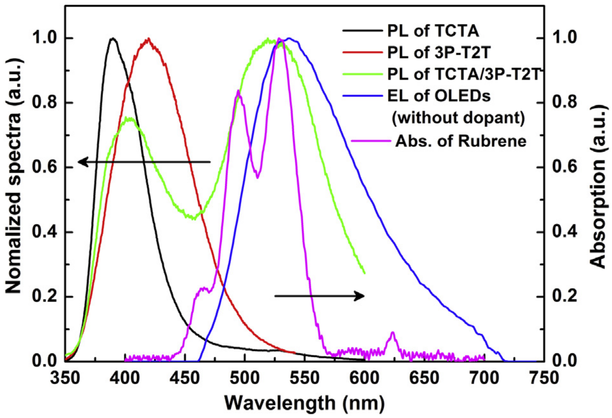

**Fig. 1.** The PL spectra of TCTA, 3P-T2T, TCTA/3P-T2T, the EL spectrum of OLEDs without dopant and absorption spectrum of rubrene (Sample of TCTA/3P-T2T for PL measurement was fabricated with the structure of glass substrate/3P-T2T (22 nm)/TCTA (8 nm); Sample for absorption measurement was fabricated by depositing neat Rubrene with the thickness of 20 nm on quartz substrate.).

## 2. Experiments methods

All the OLEDs were fabricated on Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 10 Ω/sq. The ITO substrates were cleaned first with acetone, deionized water, acetone and then treated by ultraviolet-ozone for 15 min, after that the ITO substrates were loaded into high vacuum chamber (approximately $3 \times 10^{-4}$ Pa) for subsequent deposition. Finished the deposition of organic layers, Al cathode was deposited in the end with a shadow mask, which defined the device area of $3 \times 3$ mm$^2$. The photoluminescence (PL) spectra were measured with FluoroMax-4 fluorescence spectrometer (HORIBA Jobin Yvon). The UV–Vis absorption spectrum was recorded with Hitachi U-3900 scanning spectrophotometer. Electroluminescence (EL) spectra were measured through PR-655 spectra scan spectrometer with computer controlled. The current-voltage-luminance curves were measured with Keithley 2400 power supply combined with a ST-900M spot photometer. EQE was calculated from the current density-voltage-luminance curve and spectra data. All the organic materials were procured commercially without further purification. All the measurements were carried out at room temperature and under ambient conditions without any protective coatings.

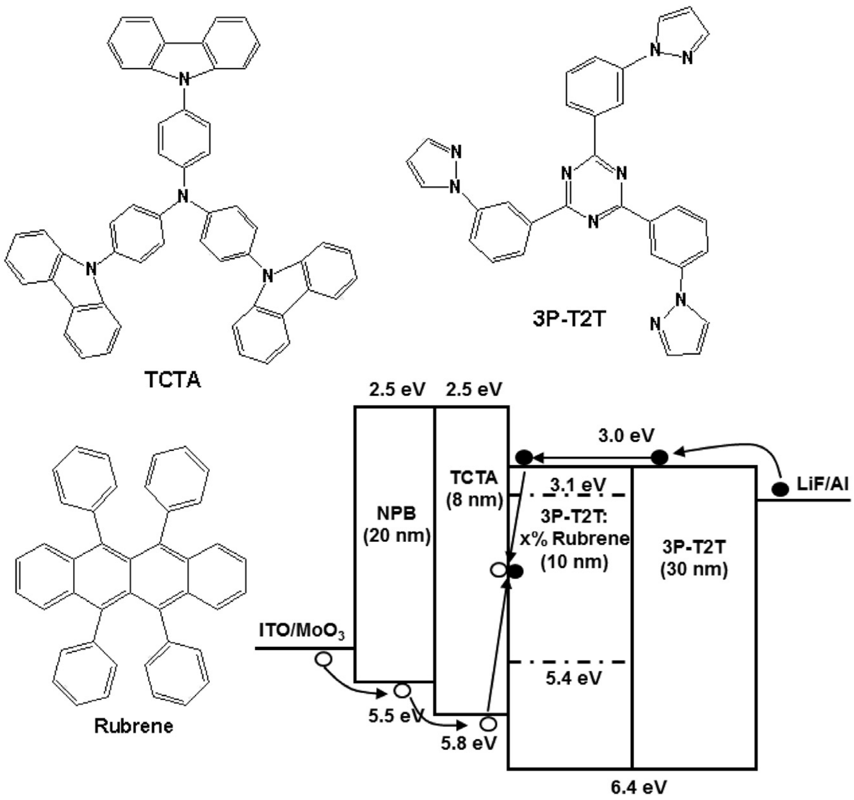

**Fig. 2.** The energy level diagram and molecular structures of TCTA, 3P-T2T and Rubrene.

## 3. Results and discussion

Fig. 1 shows the PL spectra of pure TCTA, 3P-T2T and bilayer film of TCTA/3P-T2T, the EL spectrum of OLEDs without dopant and absorption spectrum of rubrene are also exhibited in Fig. 1. We can see that the PL spectra of TCTA/3P-T2T appear two emission peaks with 402 nm and 520 nm. The peak at 402 nm is the overlap between pure emission of TCTA and 3P-T2T because the exciplex only form at the donor/acceptor interface, the pure TCTA and 3P-T2T would also be excited and emitting far away from the interface. The long wave emission peak at 520 nm is the exciplex emission, which is comparable to the previous report [16]. But the EL spectrum of OLEDs with bilayer interface exciplex (without dopant) exhibits pure exciplex emission at 537 nm and shows red-shift compared to PL spectrum of TCTA/3P-T2T. This could be explained by the different excited mechanism between the PL and EL processes, which have been expounded in my previous paper [17]. Under electrical excitation, the exciplex forms from the recombination between electron on lowest unoccupied molecular orbital energy level of acceptor ($\mathrm{LUMO}_{\mathrm{acceptor}}$) and hole on highest occupied molecular orbital energy level of donor ($\mathrm{HOMO}_{\mathrm{donor}}$). While under light excitation, the electron on $\mathrm{HOMO}_{\mathrm{donor}}$ is excited first into its LUMO and then transferred into $\mathrm{LUMO}_{\mathrm{acceptor}}$. The electron on $\mathrm{LUMO}_{\mathrm{acceptor}}$ and hole leaving at $\mathrm{HOMO}_{\mathrm{donor}}$ are coupled by coulomb interactions and then the coupled electron and hole are relaxed to ground state to form exciplex. In addition to this, we are so pleasantly surprised that the overlap between PL spectrum of exciplex and absorption spectrum of rubrene is rather large, which indicate the highly efficient energy transfer would occur from exciplex to rubrene [18,19].

Based on the PL spectra showed in Fig. 1, we designed the simple device structure as follows: ITO/$MoO_3$ (3 nm)/NPB (20 nm)/TCTA (8 nm)/3P-T2T: x% rubrene (10 nm)/3P-T2T (30 nm)/LiF (1 nm)/Al, where x = 0, 1.0, 1.5, 2.0, 2.5 and 3.0. Fig. 2 shows the energy level diagram and molecular structures of TCTA, 3P-T2T and Rubrene. In the simple OLEDs, $MoO_3$ as the hole injection layer (HIL); NPB is N,N’-bis-(1-naphthl)-diphenyl-1,1'-biphenyl-4,4'-diamine and as the hole transport layer (HTL); 3P-T2T as the electron transport layer (ETL); TCTA/3P-T2T: x% rubrene plays the role of exciplex-forming layer and EML. When the OLEDs are excited by electric field, electrons and holes inject from the electrode. From the energy level diagram in Fig. 2, we can know that the holes need cross 0.3 eV barrier to the interface of TCTA/3P-T2T, but electrons could transport barrier free to the interface. Furthermore, the electrons and holes would be accumulated at the interface due to large energy barrier (0.6 eV for holes and 0.5 eV for electrons). Exciplex between TCTA and 3P-T2T would form first and then the emission of rubrene could be earned through the energy transfer from exciplex to dopant.

Generally speaking, the energy transfer efficiency from excited singlet state of exciplex to dopant molecule is related to the guest concentrations [20]. Therefore, we check the OLEDs performance by changing the doped concentrations to get a better understanding of the energy transfer mechanism.

Fig. 3 depicts the performance of all the OLEDs under various concentrations. Fig. 3a shows the current density-voltage-

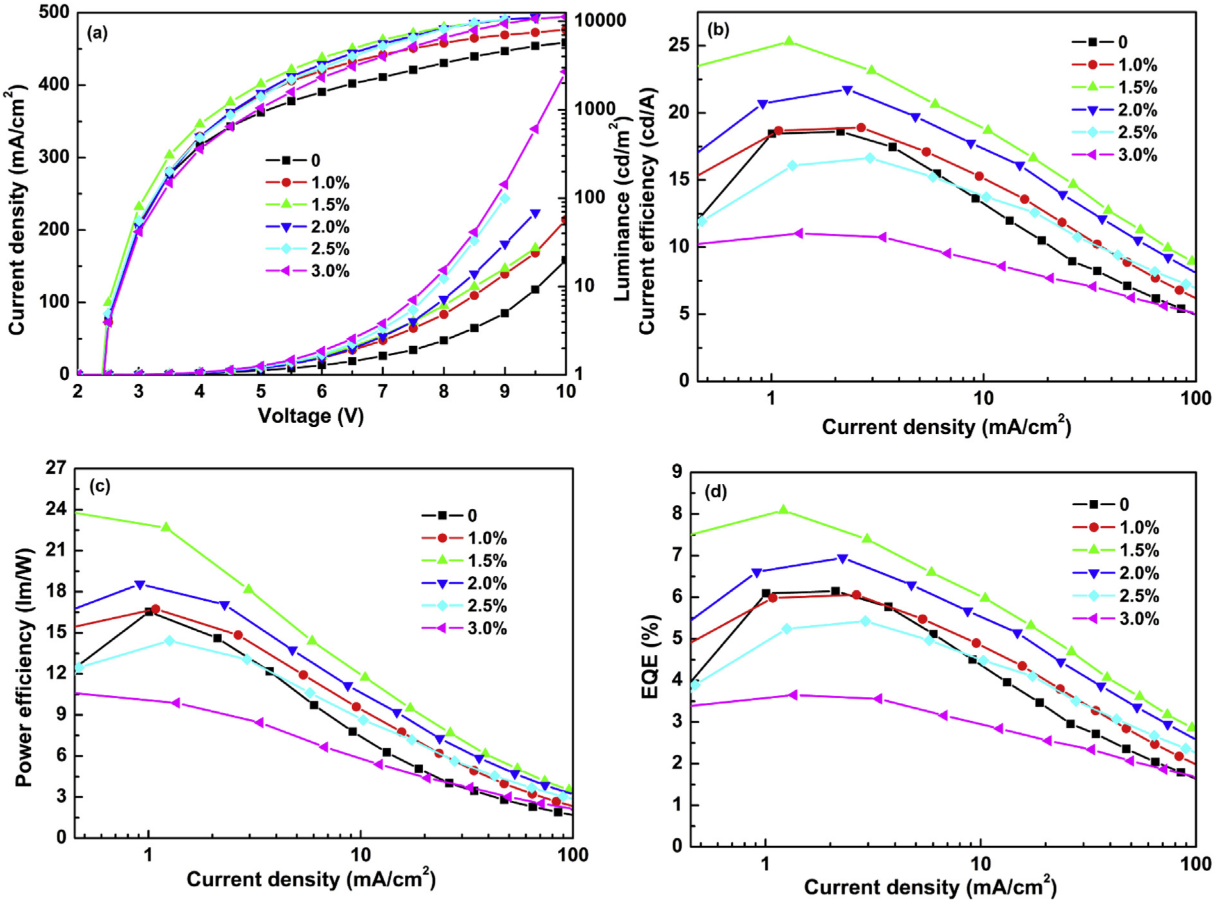

**Fig. 3.** The EL performance of all the OLEDs in this paper. (a) Current density-Voltage-Luminance (b) Current efficiency-Current density (c) Power efficiency-Current density (d) EQE-Current density.

**Table 1**
The summary EL data of OLEDs with different concentration in this paper.

| | $V_{on}$[a] [V] | $\eta_{c,Max.}/\eta_{p,Max.}/EQE_{Max.}$[b] [cd/A/lm/W/%] | $\eta_{c,1000}/\eta_{p,1000}/EQE_{1000}$[c] [cd/A/lm/W/%] | $\eta_{c,5000}/\eta_{p,5000}/EQE_{5000}$[d] [cd/A/lm/W/%] |
|---|---|---|---|---|
| 0 | 2.39 | 18.6/16.5/6.1 | 15.1/9.3/4.9 | 4.9/1.6/1.6 |
| 1.0% | 2.38 | 18.9/16.7/6.0 | 16.8/11.6/5.4 | 7.7/3.2/2.5 |
| 1.5% | 2.37 | 25.3/22.6/8.1 | 21.6/15.9/6.9 | 12.6/6.1/4.1 |
| 2.0% | 2.38 | 21.7/18.6/6.9 | 19.5/13.5/6.2 | 11.3/5.3/3.6 |
| 2.5% | 2.38 | 16.6/14.4/5.4 | 14.9/10.2/4.9 | 8.4/3.8/2.7 |
| 3.0% | 2.38 | 11.0/10.6/3.6 | 8.7/5.6/2.9 | 5.2/2.2/1.7 |

[a] Turn-on voltage (The voltage at 1 cd/m$^2$).
[b] Current efficiency ($\eta_c$), power efficiency ($\eta_p$) and EQE at maximum.
[c] $\eta_c$, $\eta_p$ and EQE at 1000 cd/m$^2$.
[d] $\eta_c$, $\eta_p$ and EQE at 5000 cd/m$^2$.

luminance curves. It is a surprise to us that all the devices achieve a very low turn-on voltage less than 2.4 V, which could be ascribed to the barrier free transport and recombination of carriers, efficient formation and energy transfer of delayed fluorescent exciplex. Besides, almost the same turn-on voltage of ~2.4 V, independent with the doped concentrations, also confirms the carrier recombination pathway is delayed fluorescent exciplex formation and energy transfer in all the devices. Fig. 3b–d plots the current efficiency, power efficiency and EQE curves. The un-doped device exhibits pure emission of interface exciplex with TCTA/3P-T2T and the maximum current efficiency, power efficiency and EQE are 18.6 cd/A, 16.5 l m/W and 6.1%, respectively. The high efficiency of the exciplex is result from TADF characteristics, which have been confirmed by previous report [16]. However, when rubrene doped into 3P-T2T, the main emission peak changed from exciplex into rubrene, which showed in Fig. 5. Meantime, the efficiency increases with the enhancement of doped concentration and the device harvest the best performance under the concentration of 1.5%. The maximum current efficiency, power efficiency and EQE reach up to 25.3 cd/A, 22.6 l m/W and 8.1%, respectively. So high EQE of 8.1% is also much higher than the report before with rubrene as the emitter [21]. Even at the luminance of 1000 cd/m$^2$, the current efficiency, power efficiency and EQE also remain 21.6 cd/A, 15.9 l m/W and 6.9%, respectively. When the doped concentration exceeds 1.5%, the efficiency decreases gradually with the enhancement of concentration, which also exhibited in Fig. 3b–d. The detailed data of all the OLEDs in this paper are summarized in Table 1.

The OLEDs with doped rubrene realize the maximum EQE at the concentration of 1.5%, lower or higher concentration is disadvantageous for high efficiency emission of rubrene. To explore the reason, we depict the schematic diagram of energy transfer and EL emission process, which showed in Fig. 4. The $S_0$, $S_1$ and $T_1$ represent the ground state, excited singlet state and excited triplet state, respectively. In this system, the highly efficient emission of doped rubrene derives from the Förster energy transfer of singlet excitons and up-converted triplet excitons [14]. That is, the electrons and holes that injected from the electrode recombine at the interface of TCTA/3P-T2T to form exciplex. As mentioned above, the exciplex has the TADF feature, so the singlet excitons transfer directly to $S_1$ of rubrene and triplet excitons up-convert to $S_1$ of exciplex, and then also transfer to $S_1$ of rubrene. At last, all the excitons produced on exciplex could be utilized and achieve the high efficiency emission of rubrene by efficient radiative transition from $S_1$ to $S_0$. At a low concentration, the Förster energy transfer from exciplex to rubrene is incomplete and result in the weak emission of exciplex, which could be observed from the EL spectra showed in Fig. 5. At a high concentration, the emission of exciplex disappears, but Dexter energy transfer between exciplex and rubrene would happen, which lead to the waste of triplet excitons due to the non-radiative transition from $T_1$ of rubrene. Therefore, the radiative transition from $S_1$ of exciplex host and Dexter energy transfer, which exhibited with dash line in Fig. 4, should be avoided as far as possible in this system. The high RISC efficiency and Förster energy transfer efficiency are the key to achieve highly efficient emission of fluorescent dopant with TADF exciplex as the host.

Next, we discuss the energy transfer efficiency by an equation. The interface exciplex of TCTA/3P-T2T could be regarded as energy transfer host, so the energy transfer efficiency ($\phi_{ET}$) of singlet and triplet could be expressed as follows [22]:

$$\phi_{ET} = \frac{k_{et}}{k_r + k_{nr} + k_{et}} = \frac{k_{et}}{{}^{1}/_{\tau} + k_{et}}$$

In the equation, $k_{et}$ is the energy transfer rate from exciplex host

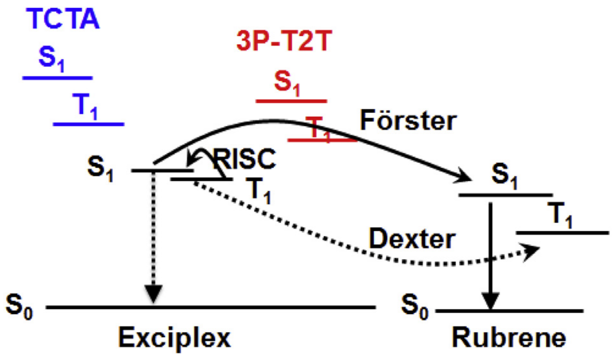

**Fig. 4.** The schematic diagram of energy transfer and EL emission process.

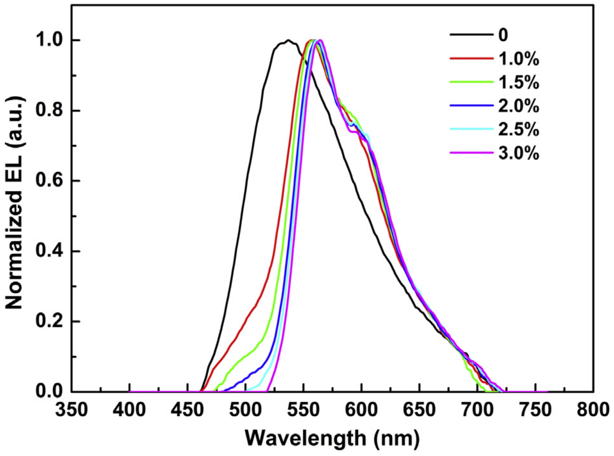

**Fig. 5.** The EL spectra of all the OLEDs under various concentrations.

to dopant; $k_r$ is the radiative transition rate of exciplex; $k_{nr}$ is the non-radiative transition rate of exciplex; $\tau$ is the emission lifetime of exciplex host. From the equation, as we can see that in order to achieve a high $\varphi_{ET}$, a higher $k_{et}$ and longer $\tau$ should be required. From Fig. 1, we know that there is a rather large overlap between the PL spectrum of exciplex host and absorption spectrum of rubrene, which suggests the highly efficient energy transfer rate from exciplex host to rubrene (that is high $k_{et}$). On the other hand, exciplex host of TCTA/3P-T2T has a long delayed fluorescent lifetime ($\tau$) about 2.0 μs at 300 K by transition PL decay measurement [15,16], which also illustrates the high RISC efficiency. Therefore, a high energy transfer efficiency ($\varphi_{ET}$) could be realized in this system.

Fig. 5 exhibits the EL spectra of all the OLEDs under various concentrations. As referred before, the main EL peak changed into dopant when rubrene doped into 3P-T2T. But under a low concentration, the emission of exciplex appears though it is weak, which implies incomplete energy transfer from exciplex to dopant. And with the enhancement of doped concentration, the intensity of exciplex reduces gradually and disappears finally. The weakness and disappearance of exciplex emission with increased concentration further demonstrates the emission of rubrene stems from the energy transfer of exciplex. It is regretful that the weak emission of exciplex under the concentration of 1.5%, which is the best one among the OLEDs, could also be observed. We believe that the highly efficient pure emission of rubrene would be achieved by more elaborate optimization.

## 4. Conclusions

In conclusion, we fabricated orange fluorescent OLEDs with simple bilayer structure and achieved high efficiency emission of rubrene by efficient energy transfer from TADF exciplex to dopant under the optimized concentration of 1.5%. The maximum current efficiency, power efficiency and EQE reach up to 25.3 cd/A, 22.6 l m/W and 8.1%, respectively. The achievement of high efficiency is attributed to the high RISC efficiency and energy transfer efficiency, which could be reflected from the schematic diagram of energy transfer, equation analysis and EL spectra; meanwhile, the optimized concentration of 1.5% also suppress efficiently the Dexter energy transfer between excited triplet state of TADF exciplex and dopant. Believing that further investigation help to realize higher efficiency with traditional fluorescent material as the emitter by utilizing the simple system.

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