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Analysis of exciton annihilation in high-efficiency sky-blue organic light-emitting diodes with thermally activated delayed fluorescence

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ABSTRACT

We study external quantum efficiency (η_{EQE}) roll-off in organic light-emitting diodes (OLEDs) using thermally-activated delayed fluorescence (TADF) of 4,5-di (9H-carbazol-9-yl) phthalonitrile (2CzPN). Using 2CzPN intramolecular rate constants from optical analyses, we construct an exciton quenching model incorporating intersystem crossing and reverse intersystem crossing. The model indicates that singlet–triplet annihilation and triplet–triplet annihilation dominate η_{EQE} roll-off because of the relatively long 2CzPN triplet lifetime of 273 μs. This work yields a method to relax the exciton quenching process in TADF based OLEDs.

1. Introduction

Phosphorescence technology has paved the way for the practical use of organic light emitting diodes (OLEDs) in displays and lighting applications. Over the past decade, the internal quantum efficiency (η_{int}) of phosphorescence based OLEDs, using iridium or platinum complexes, has improved to nearly 100% in the blue to red emission region [1–5].

As an alternate phosphorescence technology to achieve η_{int} = 100% without rare metals, such as iridium or platinum, we propose the use of thermally-activated delayed fluorescence (TADF). Electrical excitation of organic molecules results in 25% and 75% of singlet and triplet excitons, respectively. Triplet excitons formed by electrical excitation in TADF up-convert to singlet excitons through reverse intersystem crossing (ISC) from the lowest triplet excited state (T_1) to the lowest singlet excited state (S_1) by thermal activation. Therefore, in principle, η_{int} can be 100% when the reverse ISC rate (k_{RISC}) is so high that all triplet excitons up-convert into S_1. From the Boltzmann distribution relation, $k_{RISC} \propto \exp(-\Delta E_{ST}/k_B T)$, where k_B is the Boltzmann constant and T is the temperature, we see that k_{RISC} can be increased by reducing the energy gap ΔE_{ST} between S_1 and T_1 to the thermal energy at room temperature (26 meV): ΔE_{ST} is proportional to the overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

After the first demonstration of OLEDs based on TADF of Sn-porphyrin complexes in 2009 [6], we developed new TADF emitters with a donor–acceptor aromatic structure providing a small ΔE_{ST} together with a comparatively high radiative decay rate associated with the π–π^* transition [7–11]. Recently, we designed phthalonitrile derivatives as TADF emitters with colors ranging from sky-blue to orange, achieving a very high external quantum efficiency (η_{EQE}) of 19.3% with green emission

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(corresponding to $\eta_{int} = 100\%$ with 20% light-outcoupling efficiency) [12]. However, the sky-blue OLEDs with 4,5-di (9H-carbazol-9-yl) phthalonitrile (2CzPN) shown in Fig. 1, resulted in η_{EQE} below 10% and showed a large η_{EQE} roll-off with current increase, thus rendering them difficult to use under high current density regions.

In this letter, we show that η_{EQE} roll-off in OLEDs with 2CzPN emitters is dominated by strong contributions of singlet–triplet annihilation (STA) and triplet–triplet annihilation (TTA). We determined the 2CzPN intramolecular rate constants by optical measurements, and optimized the OLED structure to ensure exciton confinement in a 2CzPN emitter. We analyzed the η_{EQE} roll-off by employing an exciton quenching model with ISC and reverse ISC.

2. Experimental

We used thermal evaporation at a base pressure $<5 \times 10^{-4}$ Pa to deposit organic thin films. A co-deposited 50 nm thick film on a Si substrate was excited with a 337 nm N_2 laser or 266 nm ND:YAG laser in transient photoluminescence (PL) measurements. Detection was done with a streak camera. We measured the total PL quantum efficiency (ϕ_{Total}) using an integration sphere with a co-deposited 50 nm thick film on a quartz substrate at excitation wavelengths of 337 nm or 275 nm. Organic and cathode metal layers were successively deposited on patterned indium–tin–oxide (ITO) substrates with an effective area of 1 mm^2 in OLED fabrication. Evaluations of current density (J)–voltage (V) and η_{EQE} characteristics were performed with a Hamamatsu-Photonics C9920-12 η_{EQE} measurement system.

3. Optical characteristics

To clarify the TADF ability, we measured a transient PL of a co-deposited film consisting of 6 wt.% 2CzPN as a guest and N,N′-dicarbazolyl-3,5-benzene (mCP) as a host. Because mCP has a sufficiently high singlet energy of 3.57 eV and triplet energy of 2.90 eV [13], combined with rapid transfer of photoexcited excitons to $S1_1$of 2CzPN via Förster-type energy transfer, the observed transient PL exhibits 2CzPN intrinsic optical properties.

As shown in Fig. 2(a), a transient PL at 300 K clearly shows a prompt component with a transient decay time ($\tau_p = 1/k_p$) of 16 ns and a delayed component ($\tau_d = 1/k_d$)

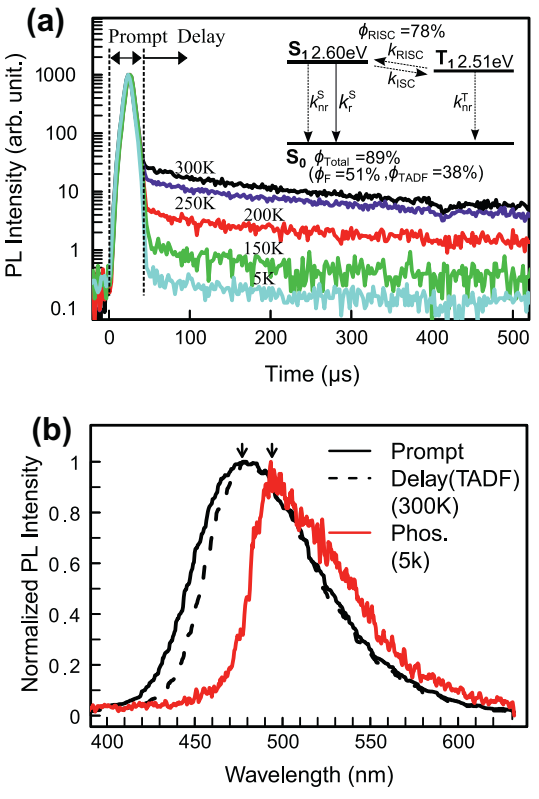

Fig. 2. (a) Transient PL of mCP:6 wt.% 2CzPN co-deposited film at temperatures ranging from 5 K to 300 K. Note that a prompt component in the graph is elongated due to the response of the measurement condition. The inset shows the optical diagram of 2CzPN. (k^S_r: radiative decay rate from S_1 to S_0, k^S_{nr}: non-radiative decay rate from S_1 to S_0, k_{ISC}: ISC rate from S_1 to T_1, and k_{RISC}: reverse ISC rate from T_1 to S_1). (b) PL spectrum of a prompt component at 300 K, a delayed component at 300 K and phosphorescence at 5 K. Prompt and delayed components are collected from 0 μs to 40 μs and from 40 μs to 1 ms after excitation, respectively. A phosphorescent spectrum was collected from 1 ms to 10 ms after excitation under 5 K: at this temperature the TADF intensity is negligibly-small.

of 273 μs. Since the delayed component emission intensity decreases with decreasing temperature, and the spectra of the delayed and prompt components in Fig. 2(b) agree well with each other, we assigned a delayed component as a TADF. We also verified that 2CzPN has a sufficiently small ΔE_{ST} of 0.09 eV, estimated from peak emission fluorescence and phosphorescence wavelengths of

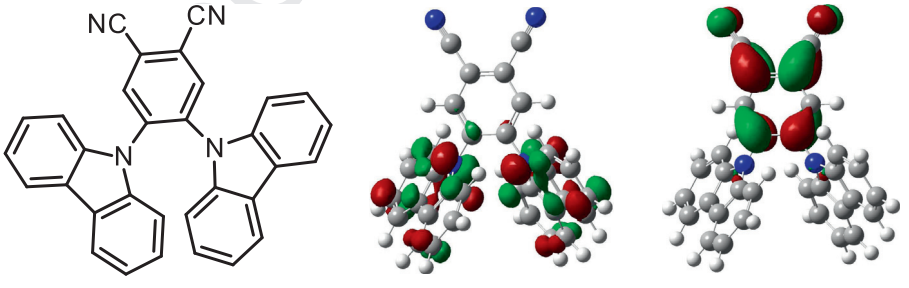

Fig. 1. Molecular structure of 2CzPN (left) and its HOMO (middle), and LUMO (right) calculated using density-functional theory via GAUSSIAN09 (B3LYP/6-311G). The separation of HOMO and LUMO allows 2CzPN to have an extremely small ΔE_{ST}.

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