Effect of reverse intersystem crossing rate to suppress efficiency roll-off in organic light-emitting diodes with thermally activated delayed fluorescence emitters

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Abstract

Electroluminescence efficiency roll-off in organic light-emitting diodes with thermally activated delayed fluorescence emitters 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene (2CzPN) and 3-(9,9-dimethylacridin-10(9H)-yl)-9H-xanthen-9-one (ACRXTN) is investigated by considering intramolecular exciton relaxation processes. Electroluminescence efficiency roll-off at high current density is dramatically suppressed using ACRXTN as an emitter instead of 2CzPN because of suppressed bimolecular exciton annihilation processes such as singlet–triplet and triplet–triplet annihilation. The rate constant of reverse intersystem crossing from triplet to singlet excited states of ACRXTN is about 300 times higher than that of 2CzPN, decreasing triplet exciton density and suppressing exciton annihilation processes under optical and electrical excitation.

1. Introduction

Because organic light-emitting diodes (OLEDs) can exhibit nearly 100% internal electroluminescence (EL) quantum efficiency (η_{int}), they are attractive for next-generation lighting sources as well as display applications. Although nearly 100% η_{int} has been achieved, the decrease of EL efficiency, known as roll-off, at high brightness [1] is a serious problem limiting the development of high-brightness OLEDs. Over the past two decades, two types of organic luminescent compounds have mainly been developed as emitters for OLEDs. OLEDs using fluorescent materials as emitters exhibit rather weak roll-off characteristics, although their η_{int} is intrinsically limited to 25% because only 25% of excitons, corresponding to singlet excitons, could be harvested under electrical excitation [1,2]. In contrast, although efficient room-temperature phosphorescent materials such as tris(2-phenylpyridinato)iridium(III) (Ir(ppy)_3) can provide nearly 100% η_{int} , the large accumulation of triplet excitons in an emitter layer causes considerable bimolecular deactivation, *i.e.*, triplet–triplet annihilation (TTA), because of the rather long lifetimes of triplet excitons (a few μs) compared with those of typical singlet excitons (a few ns) [1–5]. In fact, according to reported simulations [1,4,6], the efficiency roll-off of OLEDs using (E)-2-(2-(4-(dimethylamino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile as a fluorescent emitter and Ir(ppy)_3 as a phosphorescent emitter has been ascribed to mainly singlet–triplet annihilation (STA) [1,6] and TTA [1,4], respectively.

Recently, we proposed a unique triplet harvesting process in OLEDs, namely thermally activated delayed fluorescence (TADF) [7–9]. In OLEDs using TADF molecules as an emitter (TADF-OLEDs), although a maximum η_{int} of nearly 100% has been achieved, they also exhibit substantial roll-off behavior similar to that of phosphorescence-based OLEDs [8–10]. To understand the origin of the roll-off of TADF-OLEDs, here we investigate the exciton annihilation processes in OLEDs containing the sky-blue TADF molecules 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene (2CzPN) and 3-(9,9-dimethylacridin-10(9H)-yl)-9H-xanthen-9-one (ACRXTN), and reveal that both STA and TTA contribute to the roll-off of TADF-

OLEDs. We demonstrate that the rate constant of reverse intersystem crossing (RISC) from triplet to singlet excited states (k_{RISC}) of ACRXTN ($k_{\text{RISC}} = \sim 10^5 \text{ s}^{-1}$) is about 300 times higher than that of 2CzPN ($k_{\text{RISC}} = \sim 10^3 \text{ s}^{-1}$), and this larger k_{RISC} of ACRXTN decreases the triplet exciton density, suppressing STA and TTA under electrical excitation.

2. Experimental

The molecular structures of TADF emitters 2CzPN and ACRXTN are shown in Figure 1(a). OLEDs containing 2CzPN and ACRXTN as emitters were fabricated by conventional vacuum deposition on glass substrates coated with a 100-nm-thick indium tin oxide (ITO) layer under a base pressure of around 7×10^{-4} Pa. The OLEDs possessed the structure glass substrate / ITO (100 nm) / α -NPD (30 nm) / mCP (10 nm) / 5 mol% 2CzPN- or ACRXTN-doped mCP (15 nm) / PPT (10 nm) / TPBi (40 nm) / LiF (0.8 nm) / Al (100 nm), where α -NPD, mCP, PPT and TPBi are 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl, *N,N'*-dicarbazolyl-3,5-benzene, 2,8-bis(diphenylphosphoryl)dibenzo-[b,d]thiophene, and 2,2',2''-(1,3,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole], respectively. Current density (J)–voltage (V)–external quantum efficiency (η_{EQE}) characteristics and EL spectra of the OLEDs were measured using an integrating sphere connected to a source meter (2400, Keithley Instruments) and a photonic multichannel analyzer (PMA-12, Hamamatsu Photonics). For optical measurements, 100-nm-thick mCP films doped with 5 mol% 2CzPN or ACRXTN were fabricated on quartz substrates by vacuum deposition. Photoluminescence (PL) spectra and PL quantum yields (PLQYs) of these films were measured by a spectrofluorometer (FluoroMax-4, Horiba Jobin Yvon) and PLQY measurement system (C9920-02, Hamamatsu Photonics), respectively. PL lifetimes of the films were measured under vacuum using a streak camera (C4334, Hamamatsu Photonics), and a nitrogen gas laser (MNL200, Lasertechnik) with an excitation wavelength of 337 nm and pulse width of 500 ps as an excitation source. The rate constants

shown in Figure 1(b) were calculated from the values of PLQY and PL lifetime as previously reported [10]. The transient EL response of the OLEDs during long pulse voltage excitation was also measured using a photomultiplier tube (C9525-02, Hamamatsu Photonics) and pulse generator (WF 1974, NF corporation). The pulse width was 500 μ s and the repetition frequency was 0.5 Hz for this measurement.

3. Results and discussion

PL and EL spectra, and J - V and η_{EQE} - J characteristics of the OLEDs with 2CzPN and ACRXTN are presented in Figure 2. The maximum η_{EQE} ($\eta_{\text{EQE, max}}$), current density when η_{EQE} decreases to half of the initial η_{EQE} (J_0), η_{EQE} at 1,000 cd m^{-2} , rate constant of STA (k_{STA}), and rate constant of TTA (k_{TTA}) are summarized in Table 1. These OLEDs showed almost the same sky-blue EL spectra [Figure 2(a)]. The slight red shift of EL spectra compared with the PL spectra of the composite films was ascribed to an optical microcavity effect. Before the onset of the η_{EQE} roll-off, the $\eta_{\text{EQE, max}}$ values of the OLEDs with 2CzPN and ACRXTN were similar values of 10.3% and 12.1%, respectively. The small difference in $\eta_{\text{EQE, max}}$ originates from the different PLQYs of 2CzPN (81%) and ACRXTN (92%). Because both OLEDs showed similar J - V characteristics [Figure 2(b)], it is expected that the carrier balance factor would have a small influence on $\eta_{\text{EQE, max}}$. However, J_0 of the OLEDs with ACRXTN and 2CzPN differed markedly. At $L = 1,000 \text{ cd m}^{-2}$, η_{EQE} of the OLED with ACRXTN ($\eta_{\text{EQE}} = 11.0\%$) was about five times larger than that of the OLED with 2CzPN ($\eta_{\text{EQE}} = 2.2\%$), indicating that the roll-off at high current density was strongly suppressed using ACRXTN. Here, k_{STA} and k_{TTA} were estimated using rate equations based on STA and TTA models, [10]

$$\frac{dN_{\text{S}}}{dt} = -(k_{\text{r}}^{\text{S}} + k_{\text{ISC}})N_{\text{S}} + k_{\text{RISC}}N_{\text{T}} - k_{\text{STA}}N_{\text{S}}N_{\text{T}} + \alpha k_{\text{TTA}}N_{\text{T}}^2 + \frac{J}{4de} \quad (1)$$

$$\text{and } \frac{dN_{\text{T}}}{dt} = k_{\text{ISC}}N_{\text{S}} - (k_{\text{RISC}} + k_{\text{nr}}^{\text{T}})N_{\text{T}} - (1 + \alpha)k_{\text{TTA}}N_{\text{T}}^2 + \frac{3J}{4de}, \quad (2)$$

where N_S and N_T are the singlet and triplet exciton densities, respectively, k_r^S is the rate constant of radiative emission from the lowest singlet excited state (S_1), k_{ISC} is the rate constant of intersystem crossing (ISC) from S_1 to the lowest triplet excited state (T_1), k_{nr}^T is the rate constant of non-radiative decay from T_1 to the ground state, and α is the singlet exciton production ratio *via* TTA, which is 0.25 according to spin statistics [10]. Fitting the experimental η_{EQE} - J data with eqs. (1) and (2) [Figure 2(c)] yields $k_{STA} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_{TTA} = 5.0 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for 2CzPN, and $k_{STA} = 1.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_{TTA} = 5.1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for ACRXTN (Table 1). Although k_{STA} and k_{TTA} of the OLEDs with ACRXTN and 2CzPN are quite similar, a large difference in their roll-off characteristics was observed. Actually, N_T in the OLEDs with ACRXTN, calculated using eqs. (1) and (2), is much smaller than that in the OLEDs with 2CzPN at all current densities [Figure 2(c)]. The experimental J , η_{EQE} , and $\eta_{EQE}/\eta_{EQE, \max}$ for the OLEDs containing ACRXTN and 2CzPN at different N_T are summarized in Table 2. It is interesting that the $\eta_{EQE}/\eta_{EQE, \max}$ values for 2CzPN are the same as those for ACRXTN at the same N_T while there is no clear relationship between other parameters, indicating that the roll-off characteristics are essentially controlled by N_T .

To investigate the origin of the suppressed roll-off behavior and lower N_T for ACRXTN than 2CzPN, the intramolecular exciton relaxation processes of ACRXTN and 2CzPN were examined. The rate constants of the intramolecular relaxation processes were calculated from the PLQYs and PL lifetimes of the composite films according to ref. 10. Table 3 summarizes the calculated $\lambda_{\max}$, ΔE_{ST} , Φ_{total} , Φ_{prompt} , Φ_{delayed} , τ_{prompt} , τ_{delayed} , k_r^S , k_{ISC} , k_{RISC} , and k_{nr}^T , for ACRXTN and 2CzPN, where $\lambda_{\max}$ is the PL peak wavelength; ΔE_{ST} is the energy gap between S_1 and T_1 ; Φ_{total} , Φ_{prompt} , and Φ_{delayed} are the PLQYs of the total, prompt, and delayed components, respectively; and τ_{prompt} and τ_{delayed} are the PL lifetimes of the prompt and delayed components, respectively. Although there is no large difference in k_r^S and k_{ISC} between 2CzPN and ACRXTN, it is noteworthy that k_{RISC} of ACRXTN is about 300 times higher than that of

2CzPN because of its smaller ΔE_{ST} of 33 meV. The larger k_{RISC} makes it possible to decrease the N_T under electrical excitation, resulting in the suppression of STA and TTA.

To further investigate how k_{RISC} affects the STA and TTA characteristics of emitters at high current densities, the roll-off characteristics when the OLEDs were driven under pulse voltage excitation were measured (Figure 3). We assume that the OLED breakdown observed at high current densities and voltages is caused by melting of organic layers due to Joule heating. The Joule heating-induced breakdown is suppressed by a reduction of device active areas and use of high-thermal-conductivity substrates and short pulse voltages because of suppressed Joule heating [11,12]. Therefore, a very high voltage of up to 48 V could be applied to our OLEDs under the pulse voltage excitation, enabling very high current injection of up to 4.5 A cm^{-2} without irreversible device breakdown. The J - V characteristics of both the OLEDs measured under the pulse voltage excitation agree well each other (see Figure S1 in the Supplementary Information). The η_{EQE} - J curves measured under pulse voltage excitation exhibited roll-off characteristics similar to those measured under DC conditions below 100 mA cm^{-2} [Figure 3(a) and (b)]. At high current density (over 100 mA cm^{-2}), the roll-off was still greater for the 2CzPN-based OLEDs than the ACRXTN-based ones. Here, we calculated N_{RISC} ($= k_{RISC} \times N_T$), N_{STA} ($= k_{STA} \times N_S \times N_T$), and N_{TTA} [$= (1+\alpha) \times k_{TTA} \times N_T^2$] using eqs. (1) and (2), which are plotted as a function of current density in Figure 3(a) and (b). N_{RISC} is the number per unit time of the decrease of triplet excitons or increase of singlet excitons by RISC. N_{STA} is the number per unit time of the decrease of singlet excitons by STA, while N_{TTA} is the number per unit time of the decrease of triplet excitons by TTA. N_{STA} and N_{TTA} were higher than N_{RISC} at most current densities for the OLEDs with 2CzPN, resulting in the observed marked efficiency roll-off. Conversely, at most current densities, N_{RISC} was higher than N_{STA} and N_{TTA} in the OLEDs with ACRXTN and N_{STA} and N_{TTA} in the OLEDs with ACRXTN were lower than those of the OLEDs with 2CzPN, effectively suppressing the efficiency roll-off in ACRXTN based OLEDs. These

results suggest that RISC, STA, and TTA compete during operation of the OLEDs, and that the faster RISC overcomes STA and TTA in the OLEDs with ACRXTN.

Additionally, an initial change in EL intensity during pulse voltage excitation at a high current density of 4.5 A cm^{-2} was observed between the OLEDs with 2CzPN and ACRXTN [Figure 3(c)]. The EL intensity suddenly decreased after an initial increase in EL intensity for the 2CzPN-based OLEDs while the ACRXTN-based OLEDs showed no such EL decrease. Similar decreases in EL and PL intensities have been observed for fluorescent OLEDs and composite films of TADF materials and attributed to STA [6,13,14]. We found that the PL intensities of 2CzPN composite films decreased under optical excitation at high light intensities of over 40 W cm^{-2} , although decreases of PL intensities were not observed at lower excitation intensities for the 2CzPN composite films or at all for the ACRXTN composite films (see Figure S2 in the Supplementary Information). Therefore, we conclude that the initial decrease of the EL and PL intensities observed for 2CzPN is further proof of the occurrence of strong STA. There is a possibility that triplet–polaron annihilation (TPA) also causes the efficiency roll-off. However, the contribution of TPA is quite small because of the small TPA rate constant k_{TPA} of $< 1.0 \times 10^{-12} \text{ cm}^{-3} \text{ s}^{-1}$ [6,10,15].

4. Conclusions

We investigated the roll-off characteristics of TADF-OLEDs with 2CzPN and ACRXTN as emitters. We revealed that efficient RISC is important to suppress roll-off in TADF-OLEDs. In fact, the large k_{RISC} of $3.2 \times 10^5 \text{ s}^{-1}$ of ACRXTN dramatically suppressed both STA and TTA processes. We conclude that molecular design of TADF materials with small ΔE_{ST} is requisite for not only obtaining high η_{EQE} but also suppressing efficiency roll-off.

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Table 1. Summary of $\eta_{\text{EQE, max}}$, J_0 , η_{EQE} at 1,000 cd m⁻², k_{STA} , and k_{TTA} of OLEDs containing 2CzPN and ACRXTN as emitters.

TADF materials	$\eta_{\text{EQE, max}}$ [%]	J_0 [mA cm ⁻²]	η_{EQE} at 1,000 cdm ⁻² [%]	k_{STA} [10 ⁻¹¹ cm ³ s ⁻¹]	k_{TTA} [10 ⁻¹⁵ cm ³ s ⁻¹]
2CzPN	10.3	1.6	2.2	2.1	5.0
ACRXTN	12.1	104	11.0	1.9	5.1

Table 2. Summary of J , η_{EQE} , and $\eta_{\text{EQE}} / \eta_{\text{EQE, max}}$ of OLEDs containing 2CzPN and ACRXTN at different N_{T} .

TADF materials	N_{T} [10 ¹⁷ cm ⁻³]	J [mA cm ⁻²]	η_{EQE} [%]	$\eta_{\text{EQE}} / \eta_{\text{EQE, max}}$
2CzPN	1.0	0.1	8.7	0.84
	5.0	0.6	6.6	0.64
	10.0	1.8	4.8	0.47
ACRXTN	1.0	7.8	10.3	0.85
	5.0	51.0	7.7	0.64
	10.0	100	6.0	0.49

Table 3. Summary of $\lambda_{\max}$, ΔE_{ST} , Φ_{total} , Φ_{prompt} , Φ_{delayed} , τ_{prompt} , τ_{delayed} , k_{r}^{S} , k_{ISC} , k_{RISC} , and k_{nr}^{T} of 2CzPN and ACRXTN molecules.

TADF materials	$\lambda_{\max}$ [nm]	ΔE_{ST} [meV]	Φ_{total} [%]	Φ_{prompt} [%]	Φ_{delayed} [%]	τ_{p} [ns]	τ_{d} [ms]	k_{r}^{S} [10^7 s^{-1}]	k_{ISC} [10^7 s^{-1}]	k_{RISC} [10^5 s^{-1}]	k_{nr}^{T} [10^5 s^{-1}]
2CzPN	471	90	81	66	15	19	164	3.5	1.8	0.011	0.0097
ACRXTN	478	33	92	74	18	26	2.4	2.2	0.79	3.2	1.0

Figure 1. (a) Molecular structures of 2CzPN and ACRXTN and (b) illustration of intramolecular relaxation processes of TADF materials. The rate constants of each intramolecular relaxation process are summarized in Table 3.

Figure 2. (a) EL spectra of OLEDs containing 2CzPN and ACRXTN as emitters measured at 50 mA cm⁻² and PL spectra of composite films, and (b) J - V and (c) η_{EQE} - J characteristics of the same OLEDs. The inset of (b) is an energy-level diagram of the OLEDs containing 2CzPN and ACRXTN as emitters. The solid and dashed lines in (c) are the fitting results and calculated N_{T} using the rate equations (1) and (2) based on STA and TTA models [ref. 10]. It was confirmed that shapes of EL spectra are independent of applied current densities.

Figure 3. $\eta_{\text{EQE}}-J$ characteristics of OLEDs containing (a) 2CzPN and (b) ACRXTN driven by pulsed voltages with a pulse width of 500 μs and repetition frequency of 0.5 Hz. (c) Change of EL intensity of OLEDs containing 2CzPN and ACRXTN under pulse voltage excitation at a high current density of 4.5 A cm^{-2} . The solid, dashed, and dot-dashed lines in (a) and (b) are $N_{\text{RISC}} (= k_{\text{RISC}} \times N_{\text{T}})$, $N_{\text{STA}} (= k_{\text{STA}} \times N_{\text{S}} \times N_{\text{T}})$, and $N_{\text{TTA}} [= (1 + \alpha) \times k_{\text{TTA}} \times N_{\text{T}}^2]$, respectively, calculated using rate equations (1) and (2).

Graphical abstract