Analysis Method for Dynamics of Exciton in Organic Light-Emitting Diodes Based on Thermally Activated Delayed Fluorescence Emitters: Magnetic Field Effect as Footprint of Exciton

Masaki Tanaka[1], Ryo Nagata[1], Hajime Nakanotani[1,2] and Chihaya Adachi[1,2]

[1]Center for Organic Photonics and Electronics Research (OPERA), Kyushu University,
744 Motooka, Nishi, Fukuoka 819-0395, Japan
[2]International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University,
744 Motooka, Nishi, Fukuoka 819-0395, Japan
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ABSTRACT

We investigated magnetic field effects (MFEs) of thermally activated delayed fluorescence based organic light-emitting diodes (TADF-OLEDs) to understand exciton dynamics under device operation. Our analysis showed a clear evidence of triplet annihilation such as triplet exciton-polaron interaction.

1 INTRODUCTION

Recently, internal electroluminescence (EL) quantum efficiency (IQE) of nearly 100% can be achieved in organic light-emitting diodes (OLEDs) by harvesting electrically-generated triplet excitons for EL. However, in order to make OLEDs as an ultimate device in display and lighting applications, further improvement of the stability is one of the crucial issues to be urgently solved, especially, in blue OLEDs. To improve the device lifetime, several degradation mechanisms have been proposed [1,2]. In particular, some unwanted reactions leading to chemical decomposition have presumed to occur from upper triplet excited-states and polaron states, followed by triplet-triplet annihilation (TTA) and triplet-polaron interactions (TPI), respectively. Our group also reported that the generation of carrier traps during continuous device operation significantly affected OLED lifetime [2]. Based on these reports, it is strongly suspected that the dynamics of triplet excitons are highly responsible for OLED device degradation. However, the direct evidence is still unclear, and the detailed analysis of exciton dynamics via nondestructive analysis seems mandatory.

To understand the dynamics of triplet excitons, the utilization of a magnetic field as a prober is useful method because the degeneracy of triplet states is dissolved by the application of an external magnetic field. Magnetic field effects (MFEs) on the EL properties of OLEDs are firstly reported in 2003 [3], indicating that the externally applied magnetic field can modulate the ratio of singlet/triplet exciton formation yield because singlet and triplet polaron pairs (^{1}PP and ^{3}PP), which are the intermediate states for singlet and triplet excitons, can be modulated by the magnetic field. Based on the previous research of MFEs, three mechanisms are mainly proposed to explain the origin of MFEs; i.e., PP, TPI and TTA mechanisms [4]. However, the interpretation of MFEs on the EL properties is still unclear.

Here, we demonstrate that the analysis of magnetic-field-modulated EL (MEL) is one of the powerful tools to track the dynamics of triplet excitons in OLEDs under operation.

2 EXPERIMENT

2.1 TADF emitters

In this study, we adopted various TADF molecules as emitters in OLEDs. Figure 1 shows the chemical structures and the delayed lifetime of photoluminescence (PL) of TADF molecules. 4CzIPN, PXZ-TRZ and ACRXTN have relatively shorter exciton lifetimes (τ_d) than the lifetimes of 2CzPN, PIC-TRZ and 3CzTRZ. 4CzIPN, PXZ-TRZ, ACRXTN, 2CzPN, PIC-TRZ and 3CzTRZ are 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 10-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-10H-phenoxazine, 3-(9,9-dimethylacridin-10(9H)-yl)-9H-xanthen-9-one, 1,2-bis(carbazol-9-yl)-4,5-dicyanobenzene, 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazol-11-yl)-1,3,5-triazine and 9-(3-(9H-

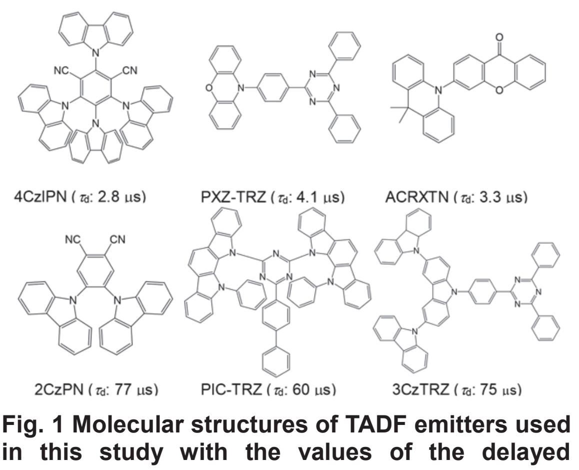

Fig. 1 Molecular structures of TADF emitters used in this study with the values of the delayed emission lifetimes.

carbazol-9-yl)-9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9H-carbazol-6-yl)-9H-carbazole, respectively.

2.2 Device fabrication

OLEDs were fabricated by vacuum vapor deposition processes without exposure to ambient air. The device structure (Fig. 2) is ITO (100 nm) / HAT-CN (10 nm) / Tris-Pcz (30 nm) / mCBP or mCP (5 nm) / EML (30 nm) / SF3-TRZ (10 nm)/30 wt.% Liq:SF3-TRZ (50 nm) / Liq (2 nm) / Al (100 nm). The EMLs were formed using a co-deposition technique with doping concentration of 20 wt% emitter:Host. In case of 3CzTRZ, mCP was adopted as a host matrix and an electron-blocking layer (EBL) to confine triplet excitons of 3CzTRZ. In other cases, mCBP was used as a host and an EBL. ITO, HAT-CN, Tris-PCz, mCBP, mCP, SF3-TRZ, and Liq are indium tin oxide, 1,4,5,8,9,11-hexaazatriohenyleane hexacarbonitrile, 9,9'-diphenyl-6-(9-phenyl-9H-carbazol-3-yl)-9H,9'H-3,3'-bicarbazole, 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl, 1,3-bis(N-carbazolyl)benzene, 2-(9,9'-spirobi[fluoren]-3-yl)-4,6-diphenyl-1,3,5-triazine and 8-hydroxyquinolinolato-lithium, respectively.

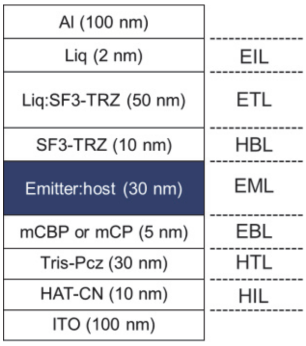

Fig. 2 Device structure of TADF-OLEDs

2.3 Characterization of magnetic field effects

In MFE measurements, external magnetic field was applied to devices with the direction along to the substrate, and that magnitude (*B*) was varied from 0 T to 0.57 T by an electromagnet. Under constant current conditions, EL spectra and driving voltage (*V*) of each magnetic field magnitude were collected by a fiber spectrometer and a source-measure unit. MELs were calculated by the formula below:

$$MEL_J = \frac{I_{EL}(B) - I_{EL}(0)}{I_{EL}(0)}$$

where $I_{EL}(B)$ and $I_{EL}(0)$ are the EL intensity under *B* and without *B*, respectively.

3 RESULTS and DISCUSSION

3.1 MEL profiles of TADF-OLEDs

In this study, we compared the MEL profiles of TADF-OLEDs with the emitters having short and long τ_d. Figure 3 shows the MEL profiles of the devices based on various emitters under the constant current condition of 3 mA cm^{-2}. Evidently, we found that the devices based on the emitters with long τ_d showed larger modulation of MEL that those with short τ_d. Further, because the shapes of the profiles slightly differed with the doped emitters, several different mechanisms are expected in these devices.

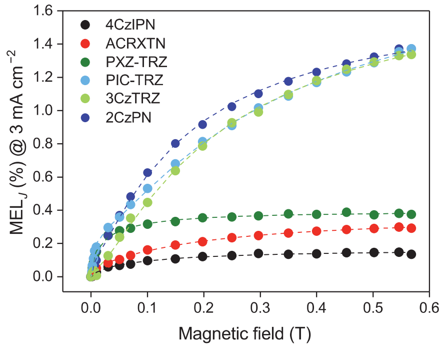

Fig. 3 MEL profiles of various TADF-OLEDs

3.2 Assessment of MEL profiles of TADF-OLEDs

To assess the origins of the MEL modulations of the devices, we performed an analysis of the MEL profiles with a fitting analysis. Here, we adopted Lorentzian and non-Lorentzian equations that are generally used for low-field effect (LFE) and high-field effect (HFE) for the fitting of MFE profiles in organic devices.

$$\mathrm{MFE} = \mathrm{LFE} + \mathrm{HFE} = \frac{A_L B^2}{B^2 + B_L^2} + \frac{A_H B^2}{(B + B_H)^2}$$

where A_L, B_L, A_H and B_H are the fitting parameters for the amplitudes and characteristic magnetic fields of LFE and HFE, respectively. The fitting results are summarized in Fig. 4 and Table 1. Since the B_Ls are well comparable value for the PP mechanism, we can assign that the LFE results from the PP mechanism. The generation yield of singlet excitons originates from an increase of the generation probability of ^{1}PP by the magnetic field.

In contrast, the large values (~100 mT) are found for B_H. We compared the B_H with a zero-field splitting (ZFS) values, i.e., |*D*|s and |*E*|s, of the triplet excited states of TADF emitters reported previously (5,6) and obtained a good agreement between them, indicating that the HFE results from the reaction process of triplet excitons such as TTA and TPI during electrical excitation. To assign an origin of HFE of the MEL$_J$ modulation in more detail, a magneto-photoluminescence (MPL) measurement was performed, and we confirmed that the MPL of 20 wt.% 4CzIPN:mCBP and 2CzPN:mCBP films showed almost no change of PL even at the high magnetic field region. Therefore, we concluded that the TPI mainly contributes to the MEL modulations of HFE. TPI process is composed of several reaction procedures that depend on the spin state of the trion that is formed from the fusion of a triplet exciton and a polaron species having a doublet or a quartet spin state. While the doublet trion shows the triplet exciton-polaron annihilation (TPA), resulted in the formation of a hot-polaron state with enough high energy to decompose organic molecules, the quartet trion shows a dissociation and a scattering processes because of the spin-forbidden reaction of energy transfer to a polaron from a triplet exciton. Applied external magnetic field suppresses the interaction probability between a triplet exciton and a polaron, leading to the reduction of the reaction rates of TPA, dissociation and scattering. In TADF-OLEDs, because triplet excitons have a chance to upconvert to an emissive singlet state by reverse intersystem crossing (RISC), suppressed magnetic response based on TPI model contributes to increase the EL intensity by applied magnetic field.

Regarding A_Hs in Table 1, the devices based on the emitters having long τ_d showed larger values than those with short τ_d. These results clearly indicate that the excited state of the emitters with long τ_d suffers from more significant exciton annihilation induced by TPI than those with short τ_d. Although our previous research mentioned the effect of TPI on device degradation from the investigation of hole-only and electron-only devices, the analysis based on MFE reported here nondestructively revealed the effect of TPI under device operation [2].

Table 1 Fitting parameters of MEL of TADF-OLEDs by LFE and HFE. |*D*| and |*E*| are the absolute values of ZFS parameters. (Ref:5,6)

	A_L (-)	B_L (mT)	A_H (-)	B_H (mT)	|*D*| (mT)	|*E*| (mT)
4CzIPN	0.058	5.3	0.11	58.5	46	11
PXZ-TRZ	0.239	6.6	0.18	58.5	49	5.4
ACRXTN	0.091	4.1	0.29	101.0	No data	
2CzPN	0.117	4.8	1.62	81.0	68	15
PIC-TRZ	0.264	5.7	1.83	192.7	98	9.6
3CzTRZ	0.038	4.3	1.87	112.5	No data	

4 CONCLUSION

In this study, we investigated the exciton dynamics in TADF-OLEDs and revealed the presence of TPI acting as the origin of device degradation probably due to the formation of charge carrier traps and quenchers. The MFE analysis and our proposed interpretations can nondestructively clarify the dynamics of triplet excitons in OLEDs.

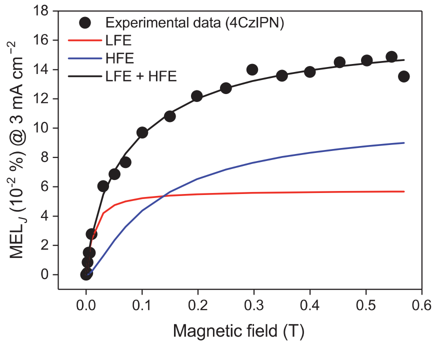

Fig. 4 Fitting result of MEL profile of 4CzIPN-based OLED

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