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Large contribution of triplet excitons to electro-fluorescence in small molecular organic light-emitting diodes

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ABSTRACT

Singlet exciton formation in working fluorescent devices was investigated by analyzing the magnetic field effects on electroluminescence intensity based on a rate model. Two magnetic field sensitive processes including charge recombination and triplet–triplet annihilation (TTA) are suggested to be involved in the generation of singlet excitons. It reveals that TTA process produces considerable extra singlets which account for as high as 19% of total singlets at 20 K in non-doped device, 34% at 20 K and 17% at room temperature in doped device, causing the total singlet generation yields exceeding the classical 0.25 spin statistics limit.

1. Introduction

Organic light-emitting diodes (OLEDs) have received widespread interest since the discovery of the first efficient fluorescent material of tris(8-hydroxyquinoline) aluminum (Alq_3) [1]. Although the device performances including the efficiency and the operational lifetime have been significantly improved, some fundamental issues are still unclear, such as the processes of light generation. Radiative decay of singlet excitons is generally believed to be the source of electro-fluorescence, but the processes of singlet formation in the fluorescent device are hotly debated [2–8]. Charge recombination (CR), which is the primary channel for the generation of singlet excitons, is not yet confirmed to be spin dependent or independent [4–8]. The interactions between the electronic excitations are thought to be another important channel for singlet generation, such as triplet–triplet annihilation (TTA) in which one extra singlet exciton and one ground state are generated by fusing two triplet excitons. The TTA bimolecular process has been demonstrated intensively in organic materials [9–13]. In our previous work [14,15], we also suggested that TTA process would happen even at room temperature in the fluorescent dye doped devices and it heavily depends on the energy level offset between the host and guest. However, as yet, the contribution of TTA to the electroluminescence (EL) is still an open question. In particular, it has never been clarified how much the quantitative rate of the extra singlet excitons is generated by TTA process in the small molecular fluorescent devices.

In this work, we attempt to elucidate the processes of singlet exciton generation in molecular fluorescent devices by applying a new and simple approach based on magneto-electroluminescence (MEL). The MEL as a powerful experimental tool [16] can be directly applied to a working OLED to reveal the real situation of exciton formation in the device under standard operating conditions. We make measurements of MEL in the fluorescent OLEDs based on Alq_3 doped with 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) at various concentrations

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(by weight ratio, r) ranging from $r = 0\%$ (non-doped) to 6 wt.%. By separating the CR and TTA processes with quantitative analysis of MEL based on a theoretical rate model, we obtain simple analytical expressions allowing the estimation of the singlet yields from CR and TTA processes in the molecular fluorescent devices, respectively.

2. Experimental

The samples used for MEL measurements were fabricated in an organic molecular beam deposition system with bass pressure of $\sim 10^{-6}$ Pa. All organic layers of the 1×2 mm^2 devices were sandwiched between indium tin oxide (ITO) anode and lithium fluoride (LiF)/Al cathode. N,N′-Di(naphthalene-1-yl)-N,N′-diphenyl-benzidine (NPB) and pure Alq_3 layers are utilized as hole transport layer and electron transport layer, respectively. The emissive layer of DCM: Alq_3 with different DCM concentrations were co-evaporated by controlling the relative deposition rate of DCM and Alq_3. The device configurations then consisted of stacked thin films of ITO/NPB (50 nm)/Alq_3: DCM (0, 2, 3, 6 wt.%, 40 nm)/Alq_3 (30 nm)/LiF (0.7 nm)/Al (100 nm).

For the transient EL measurements, we used an Agilent pulse generator (8114A) to apply rectangular pulse voltage to our devices. The pulse repetition rate was 1 kHz with the width of 60 μs. Transient EL of the devices was measured with a Hamamatsu photomultiplier (H6780-P) and a digital oscilloscope (Tektronix DPO7104). The EL spectra were measured by SpectraPro-2300i spectrum units.

The MEL measurements were performed in a close-cycle cryostat system (Janis CCS-350s) which was located between the pole pieces of an electromagnet (Lakeshore EM647). During the measurement process, the samples were mounted on the cold finger of a close-cycle cryostat and operated at temperatures from 20 to 300 K. To exclude the effects of B-field enhanced current on the MEL, the devices were driven under constant current model. Current sourcing was performed using a Keithley 2400 source-measurement unit. The silicon photodetector for EL measurement was tested to make sure there was no field dependence on its output.

3. Results and discussion

Fig. 1(a) and (b) show the room temperature (300 K) MEL at different measuring current levels for the $r = 2$ wt.% and $r = 0\%$ devices, respectively. The MEL was defined as the relative change in EL intensity as a function of B-field, i.e. $\mathrm{MEL} = [I_{EL}(B) - I_{EL}(0)]/I_{EL}(0)$, where $I_{EL}(B)$ and $I_{EL}(0)$ are the EL intensity in the presence and absence of a B-field, respectively. The MEL always increases sharply at low B-field. After reaching the maximum value at around 45 mT, the MEL in the $r = 2$ wt.% device turns to decrease or level off with increasing B-field, depending on the current levels, while the MELs in the non-doped device for $r = 0\%$ turn to saturate over the current measurement range. In our previous work [15,17], the high-field decrease in MEL were qualitatively explained by B-field mediated TTA process. In fact, the room temperature TTA process in the DCM-doped device can be further confirmed by

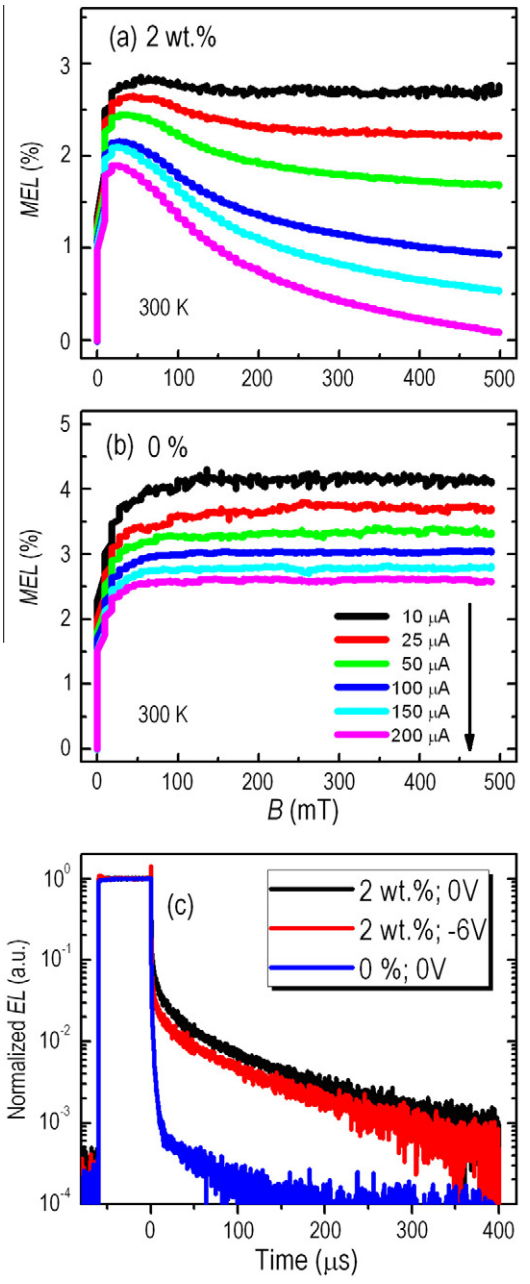

Fig. 1. MEL versus B-field in the 2 wt.% device (a) and non-doped device (b) under different driving current at 300 K. (c) Time-resolved EL intensity response of the $r = 0\%$ and $r = 2$ wt.% DCM-doped devices to 60 μs, 8 V excitation pulse, followed by 0 V or −6 V revise bias.

the transient EL measurements. Fig. 1(c) shows the time evolution of EL after a 60 μs excitation pulse was applied. It can be seen from the figure that the delayed fluorescence (DF) signal from the 2 wt.% device decays much slower than that from the non-doped device, which is consistent with the recent observation by Luo et al. [13]. In addition, nearly identical magnitudes and shapes of decay profiles in the 2 wt.% device after applying −6 V bias suggest the DF is caused by the TTA process [12,13]. Although these results