Studying singlet fission and triplet fusion by magneto-electroluminescence method in singlet–triplet energy-resonant organic light-emitting diodes

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A B S T R A C T

Organic light emitting diodes (OLEDs) utilizing a singlet–triplet energy-resonant ($E_S \approx 2E_T$) layer (rubrene) were fabricated to investigate the singlet fission and triplet fusion by the magneto-electroluminescence (MEL) of device from R.T. to 20 K. A large positive MEL (23.5%) was obtained at R.T. due to magnetic-field-suppressed singlet fission. With decreasing temperatures, the MELs changed their signs both at low-field and high-field components because of a gradual decrease in singlet fission simultaneously followed by an increasing triplet fusion, leading to a negative MEL around −7.5% at 20 K. Moreover, transient electroluminescence and MELs from the control devices were used to further confirm the exciton fission and fusion processes in rubrene-based OLEDs. Our findings of MEL may provide a useful pathway to study the microscopic dynamics of excited states in organic optoelectronic devices.

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1. Introduction

Organic optoelectronic devices such as light-emitting diodes (OLEDs) have great potential in flat-panel display and lighting applications [1,2]. Further understanding of microscopic mechanisms for excitonic states in organic semiconductor will accelerate their commercialization. In recent years, two types of excitonic interactions, i.e., singlet exciton fission ($S_1 \rightarrow T_1 + T_1$, named as STT) [3–9] and triplet exciton fusion ($T_1 + T_1 \rightarrow S_1$, also called TTA) [8,10–15], have been intensively investigated. The STT process has the potential of doubling the internal quantum efficiency in organic photovoltaic cells [3–7,9], while TTA process [10–15] can significantly improve the efficiency (additional 37.5% [10]) of fluorescent OLEDs and leads to the OLED's quantum efficiencies exceeding the classical theoretical limit of 25% [11,16,17]. Therefore, research on the dynamics of STT and TTA possess both fundamental significance and potential applications. It is noticed that the magnetic field effects (MFEs) [6,13–15,18–22] can be as a unique tool for revealing the interaction mechanisms of excitonic states in OLEDs, for example, electron–hole pair model [23–25] and triplet-charge annihilation [18,24,26]. Moreover, Davis [27], Li [28], and our group [15,29,30] have shown that TTA process also have important impacts on MFEs in OLEDs. However, the effects of STT on the MEL observed in OLEDs have not been investigated so far, although the STT effect on the magneto-photoluminescence (MPL) in organic bulk crystals [31] and thin-film solar cells [3,6] and on the transient decay of MPL from highly disordered rubrene film [9] have been demonstrated. Therefore, the investigation about how the STT influences the MEL in OLEDs under external magnetic fields is an important issue.

Considering the energy match play a predominant role in the excitonic interaction, STT requires $E_S \geqslant 2E_T$ [5],

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while TTA requires $E_S \leqslant 2E_T$ [10], where E_S and E_T represent the singlet and triplet energy levels, respectively. A special material 5, 6, 11, 12-tetraphenylnaphthacene (rubrene) was used as emission layer of OLED in this work, because the singlet and triplet energies are almost in resonance in rubrene ($E_S \approx 2E_T \approx 2.2$ eV) [10]. i.e., STT and TTA processes can coexist in rubrene. Therefore, both STT and TTA processes could be investigated in this OLED through its MELs at different temperature. Our experimental results have proved the feasibility of this method.

In this letter, we investigated the evolution processes of STT and TTA coexisted in rubrene-based OLEDs via MEL method. Strong temperature dependences in the magnitude and curve shape of MELs were observed due to the changes in relative contribution of STT and TTA in rubrene/BCP device range from room temperature to 20 K. Two kinds of control devices (rubrene/Alq$_3$ and Alq$_3$/BCP) were also fabricated to further understand the STT and TTA processes in rubrene. The competition between these two processes was elucidated by analyzing the temperature-dependent MEL, EL efficiency curves, and transient EL properties in these devices at room temperature. Considering only several percent of MEL are typically obtained from conventional OLEDs consisting of a variety of different materials [32–34], it is noted that the value of MEL (∼23.5%) in this work is one of the largest values reported recently in the literatures [23,31,35,36].

2. Experimental

The device was fabricated with structure of ITO (120 nm)/copper phthalocyanine (CuPc) (15 nm)/N,N′-bis (naphthalene-1-y)-N,N′-bis (pheny1) benzidine (NPB) (60 nm)/rubrene (30 nm)/BCP (50 nm)/lithium fluoride (LiF) (0.8 nm)/Al (120 nm), and in the following labeled as rubrene/BCP device. All organic layers were grown using organic molecular beam deposition method under ultrahigh vacuum (base pressure ∼10^{-7} Pa). Control devices of Alq3/BCP and rubrene/Alq3 were also grown in the same conditions for comparison. All devices were prepared with active area of 2×2 mm^2. The device energy level diagram is shown in Fig. 1(a). After preparation, the samples were mounted on the cold finger of the close-cycle cryostat (Janis CCS-350s) that was located between the pole pieces of an electromagnet (Lakeshore EM647) for the measurement of current–brightness–voltage characteristics and MEL of the devices at different temperatures. Transient EL was measured with a Hamamatsu photomultiplier (H6780-P) and a digital oscilloscope (Tektronix DPO7104). All the above measurements for the optical–electrical–magnetic properties of the devices have been described previously in detail [37].

3. Results and discussion

A simplified kinetic scheme for the conversion of an excited singlet state to two triplet states located in adjacent rubrene molecules is shown in Fig. 1(b). The deactivation of a singlet exciton (S_1) in rubrene proceeds not only through prompt fluorescence to ground state (orange dot-
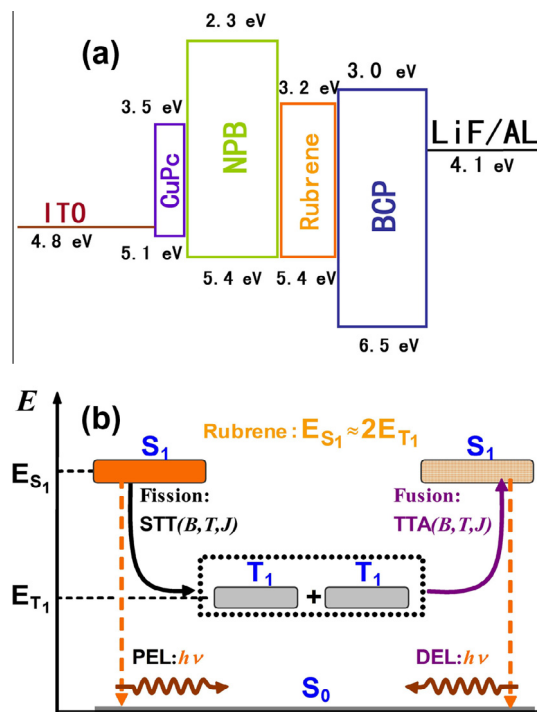

Fig. 1. (a) A schematic representation of singlet fission and triplet fusion processes in rubrene-based OLEDs. Singlet excitons are formed in rubrene, and either decays through fluorescence (orange dotted arrow) to ground state (S_0) or undergoes singlet exciton fission (black solid line arrows) resulting in two triplets. (b) Energy-level diagrams for rubrene/BCP device and rubrene/Alq$_3$ device. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ted arrow) but also via non-radiative spin-dependent fission into two triplet excitons (black solid line arrows) [31], i.e., STT process. At the same time, two spin-dependent triplet excitons can produce an extra singlet exciton by TTA process. Singlet excitons formed from TTA could also contribute to the light-emission (usually named as delayed fluorescence). A general kinetic scheme for the above bimolecular interconversion can be written as [9]:

$$S_1 + S_0 \leftrightharpoons [T_1 \cdots T_1] \leftrightharpoons T_1 + T_1, \tag{1}$$
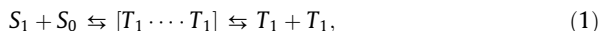
The bracket $[T \cdots T]$ indicates the intermediate complex of two spin tangled triplet exciton. In addition, the processes of fission and fusion were spin selective [31,38].

Fig. 2(a) shows normalized EL spectra of rubrene/BCP device (red line) and Alq$_3$/BCP reference device (green line) at room temperature. The EL Spectra of the two devices have prominent emission bands near 580 nm and 530 nm, showing light emissions from rubrene [6] and Alq$_3$ [39], respectively. Fig. 2(b) shows the time evolutions of EL spectra from these two devices applied with a pulse voltage of 7.77 V at room temperature. The repetitive frequency and the width of the driving pulse are 1 kHz and 100 μs, respectively. It can be seen from the curves that the EL decay signals after turning off the voltage pulse consist of fast and slow components in the two devices. The fast decay components correspond to the radiation decay