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Spectroscopic observation of triplet exciton dynamics during operation in polymer light emitting diodes

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ABSTRACT

In typical fluorescent organic light emitting diodes (LEDs), the observation of triplet excitons is difficult because of their non-radiative features of decay. The generation process of triplet excitons was successfully monitored by employing spectroscopic techniques combined with LED operation. The generation dynamics of singlet excitons are then simultaneously examined by time-resolved electroluminescence measurements, enabling relative comparison of the generation processes of singlet and triplet excitons. As a result, the generation ratio of singlet excitons is shown to be enhanced by applied voltage. The enhancement is concluded to result from the increase of the generation rate in signlet excitons induced by electric field.

KEYWORDS

organic light emitting diode; exciton generation process; spectroscopy

Introduction

Organic light emitting diodes (OLEDs) operate through the injection of carriers (polarons), the conversion into polaron-pairs and the generation of emissive excitons from polaron-pairs. In the generation process of exciton, it is generally believed that the ratio of singlet exciton to triplet exciton is 1:3 based on simple spin statistics and the OLED efficiency is limited by the statistics [1]. However, experimental results confirming the exciton ratio have not been shown, presumably because triplet excitons in fluorescent OLEDs are typically non-radiative and difficult to observe. In particular, it was previously suggested that the exciton ratio would depend on the magnitude of applied voltage [2,3].

In this article, we attempt to visualize the generation and decay processes of such non-radiative triplet excitons by spectroscopic techniques combined with the OLED operation, device modulation (DM) techniques [4,5]. By combining the DM techniques with electroluminescence (EL) measurements, we succeeded in simultaneous monitoring of singlet and triplet exciton during the LED operation. Moreover, we show that the ratio of singlet exciton is enhanced with increasing the applied voltage. The enhancement is concluded to result from the effect of electric field on the exciton generation processes.

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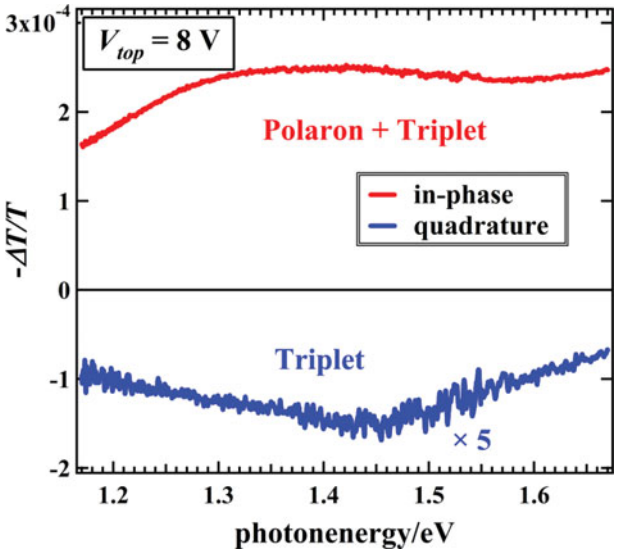

Figure 1. Device Modulation (DM) spectra measured by lock-in techniques when applying $V_{top} = 8$ V (100 Hz) to the MEH-PPV LED.

Experimental methods

The polymer LED used in this study consisted of following five-layers; ITO/PEDOT-PSS/MEH-PPV/Ca/Al. The DM measurements were performed by applying a square-wave AC voltage (100 Hz) to the polymer LEDs and detecting the modulation signals of the transmitted probe light synchronized with the voltage. The probe light was produced using a tungsten/halogen lamp or LEDs. The DM spectra were measured by using a phase-sensitive lock-in technique for the modulated probe light detected by a Si and an InGaAs photo-detectors for the visible and near-infrared regions, respectively. Time resolved (TR) -DM and -EL were measured simultaneously under the applied squared AC voltage (80 Hz) with the various top voltage and recorded using a digital oscilloscope. All measurements were performed at room temperature under vacuum conditions.

Result and discussion

DM spectra measured under the voltage of $V_{top} = 8$ V are shown in FIG. 1. The DM spectra consist of both the in-phase and quadrature components with peaks observed at 1.40 eV and 1.45 eV, respectively. The quadrature spectrum is similar to the spectrum of triplet exciton identified from photo-induced absorption (PA) detected-magnetic resonance measurements for MEH-PPV films [6], and the peak is assigned to the T_1-T_n transition (T_i is the i-th energy level of the triplet exciton) at triplet excitons generated by operating the LED. The absorption peak of in-phase components is close to that of the polarons determined previously from PA measurements [6]. The in-phase signals are thus given by overlapped two components; triplet excitons and the injected polarons that serve as trapped or mobile carriers.

Figure. 2 shows the results of the simultaneous measurements of TR-DM at 1.45 eV and TR-EL under the V_{top} voltages of 3 V, 6 V and 8 V, which monitor the generation and decay processes of triplet and singlet excitons. As shown in the top of FIG. 2, the DM signals at 1.45 eV consist of two components: rapid and slow components that rise and decay within 10 μs and millisecond timescales, respectively. The slow component is observed under the V_{top}

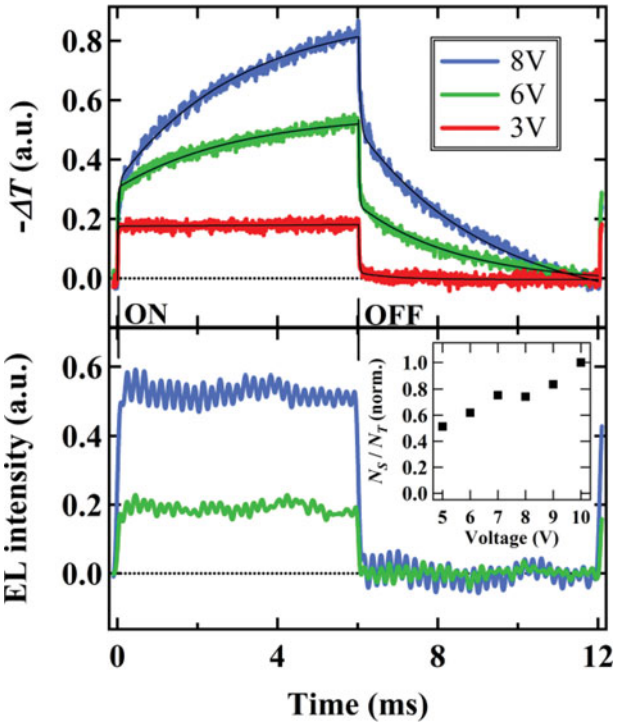

Figure 2. Time-resolved -DM (1.45 eV) (top) and -EL signals (bottom) measured for the MEH-PPV LED under the top voltage of 3 V, 6V and 8 V. Inset: relative ratio of singlet exciton density to that of triplet exciton vs. applied voltages.

voltage beyond 3 V, which coincides with the voltage at which EL occurs. In contrast to the TR-DM signals, the TR-EL signals (the bottom of FIG. 2) consist only a rapid component and do not show delayed EL which usually results from triplet-triplet annihilation (TTA) [7,8]. The absence of such delayed EL signals demonstrates that the effect of TTA is negligible in the MEH-PPV LED.

In the case of neglecting the TTA effects, the triplet exciton-generation dynamics is described by the following simple rate equation for the triplet exciton density (n_T):

$$\left[\frac{dn_T}{dt} = G_T - \frac{n_T}{\tau_T}\right] \tag{1}$$

where G_T and τ_T are the generation rate and the lifetime of the triplet exciton, respectively. By fitting the exponential function obtained from the solution of Eq. (1) to TR-DM data, τ_T, relative G_T and the relative density of triplet exciton in the equilibrium state ($N_{T,e}$), corresponding to $G_T\,\tau_T$, are obtained. The time evolution of the carrier signals might be difficult to accurately derive from the obtained TR-DM signals because of insufficient time resolution of the experimental system. Here, by simply approximating the rising process of carriers with a single exponential function, the overall rising process of the TR-DM signals was fitted by the sum of the two exponential functions. The decay process was also similarly fitted by the sum of exponential decay functions. The fit results are shown in the top of FIG. 2 and found to reproduce well the TR-DM data. The normalized density ratio of the singlet-exciton to that of triplet exciton ($N_{S,e}/N_{T,e}$) was then calculated from the steady-state EL intensity divided by that of DM signals and is plotted in the inset of FIG. 2. It indicates that the singlet exciton ratio increases with the applied voltage.

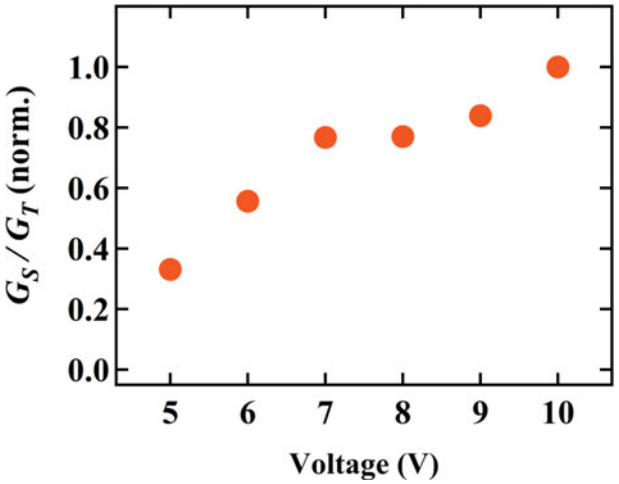

Figure 3. Normalized ratio of the generation rate of singlet excitons (G_S) to that of triplet excitons (G_T) vs. applied voltage.

The origin of the voltage-induced increase of the singlet exciton ratio is herein discussed by the relative intensity of G_S/G_T (where G_S is the generation rate of singlet excitons). The relative G_S/G_T was calculated using the determined τ_T by assuming that the lifetime of singlet exciton does not depend on applied voltage because of its rapid decay. The result is plotted in FIG. 3, and indicates that the ratio of G_S is enhanced by increasing the voltage. The obtained finding demonstrates G_S/G_T to be enhanced by applied voltage despite the usual assumption that G_S/G_T follows simple spin statistics independently of voltage. One of the principal factors determining the rate of exciton generation from polaron-pairs is the energy separation between polaron-pairs and excitons expressed as ΔE_S and ΔE_T for singlet and triplet excitons, respectively [9,10](FIG. 4). To discuss the observed voltage-dependent G_S/G_T, we focus on

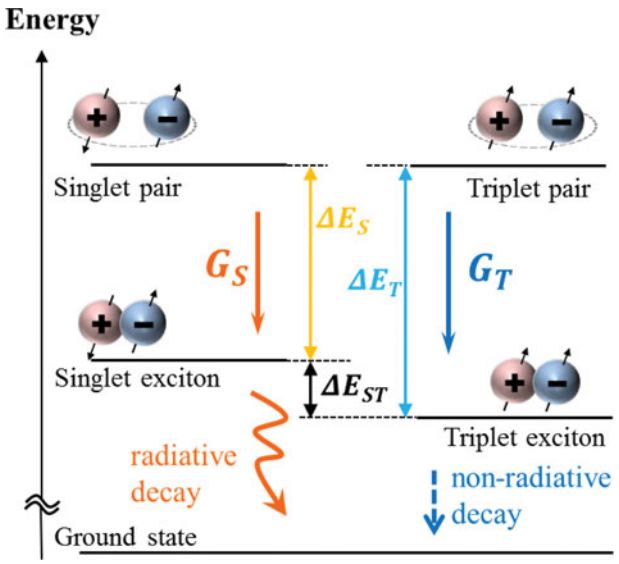

Figure 4. Schematic representation of the energy diagram of excited states during operating OLEDs. $\Delta E_{S\,(T)}$ is the energy separation between singlet (triplet) exciton and polaron pair. ΔE_{ST} is the energy splitting between singlet and triplet exciton.

the dipole moment formed between the electron and hole of the polaron-pair. The moment should be much larger than that of the exciton because of the larger distance between the electron and hole in polaron-pair. The larger dipole moment of the polaron-pair can exhibit a stronger interaction with an electric field, resulting in much larger energy reductions depending on the voltage compared to that of excitons. We note that ΔE_S is typically much smaller than ΔE_T. It is expected that the smaller separation of ΔE_S leads to a larger generation rate of singlet excitons and causes the enhancement of G_S/G_T upon increasing the voltage.

Related to the mechanism, the influence of the electric field on the cross section of exciton formation was previously examined through a quantum-chemical calculation [11]. This calculation performed on long-chain conjugated molecules showed that when the energy levels of polaron-pair decrease with an increase of electric field strength via the interaction between the field and the polaron-pair-dipole moment, the ratio of the formation cross section of singlet to triplet exciton increases with the magnitude of the electric field. Our finding of voltage-dependent G_S/G_T agrees with the result of the calculation, suggesting that voltage-dependent enhancement of G_S/G_T should result from the electric field effect on the smaller energy separation of ΔE_S.

In summary, the dynamics of non-radiative triplet excitons during the polymer LED operation were studied using TR-DM techniques. Simultaneous TR-DM and -EL measurements enabled to monitor the voltage-dependent generation and decay processes of both triplet and singlet excitons. The generation ratio of singlet excitons was found to be enhanced by increasing the applied voltage, which is concluded to result from the voltage-dependent increase of G_S/G_T. This result indicates that the electric field directly affects the generation rates of singlet and triplet excitons. The increased G_S/G_T is concluded to result from the condition of $\Delta E_S < \Delta E_T$. Our findings show that the consideration of voltage-dependent generation ratio of singlet excitons must be important for designing efficient OLEDs.

Acknowledgments

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