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Realization of triplet–triplet annihilation in planar heterojunction exciplex-based organic light-emitting diodes

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ABSTRACT

Triplet–triplet annihilation (TTA) for enhancement of luminous efficiency occurs with difficulty in exciplex-based organic light-emitting devices (OLEDs) because it is an interaction among several neighboring donor and acceptor molecules. However, TTA has been realized in our planar-heterojunction (PHJ) exciplex-based OLEDs by using a thin recombination zone to enhance the interfacial density of the triplet states. The TTA process, which is characterized by a high-field decrease (HFD) in the magneto-electroluminescence from the PHJ OLEDs, appears at approximately 150 K and becomes stronger with decreasing temperature. At a given temperature, the higher the injected current is, the stronger HFD is observed. Additionally, we find that TTA could even happens at room temperature with appropriate selection of the donor molecule, which may be attributed to the favorable electron-donating ability of the methoxy group ($-OCH_3$) in the donor molecule and the matched overlaps of the intermolecular conformation of the donor and the acceptor.

Enhancement of electroluminescence (EL) efficiency, which is dependent on the microscopic dynamics of the electron–hole (e-h) pairs in organic light-emitting devices (OLEDs), is a long-standing focus of research in the OLED field [1–12]. The e-h pairs in OLEDs commonly include excitons and exciplexes [13,14]. An exciton is formed in a single molecule by the recombination of an electron and a hole, while an exciplex is usually generated at an organic/organic interface [15] via electron transfer from the lowest unoccupied molecular orbital (LUMO) of the acceptor to the highest occupied molecular orbital (HOMO) of the donor. While the EL efficiency in previously fabricated exciplex-based OLEDs is relatively low [14,16,17], exciplex emission has still received considerable attention because of its superior properties, including emission color tuning [18–20] and fabrication of white OLEDs [14]. In particular, after Adachi et al. reported very high external quantum efficiency in exciplex-based OLEDs using reverse intersystem crossing (RISC) [6–8], study of the enhancement of exciplex-emission efficiency has become a hot research topic. In addition to RISC, triplet–triplet annihilation (TTA) is another well-known and significant pathway to enhancement of EL efficiency that uses triplet states [1–5]. Although, the energy levels of singlet and triplet exciplex states are very close [8,13,21], that is, the total of twice the triplet energy is higher than the singlet energy, TTA still occurs with difficulty in exciplex-based OLEDs because it is an interaction among several neighboring molecules and the underlying mechanism of TTA remains unclear. Clearly, realization and exploration of TTA in exciplex-based OLEDs is very important for the understanding of this underlying mechanism and improvement of the EL efficiency of this type of device.

In general, two methods are used to detect TTA in the literature: the super-linear behavior of the luminance-current in OLEDs [22] and time-resolved photoluminescence (PL) or EL spectra [1,2]. However, the former cannot probe TTA clearly in our device because the delayed fluorescence contribution from TTA is not very strong. It is also difficult to discern the RISC and TTA merely from time-resolved PL or EL spectra because of their complex but similar delayed fluorescence behavior [23]. However, magneto-EL (MEL), as a non-contact and non-destructive probing tool, is capable of distinguishing the two processes and has been used to study TTA in non-magnetic OLEDs [23–27]. This is because both RISC and TTA are highly spin-related processes [23,28,29] that can generate different characteristic MEL responses (including their line-shapes

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and magnitudes) under application of an external magnetic field [23]. Thus, MEL could be used as a simple and effective method to explore TTA in OLEDs. In this letter, we used MEL to explore the TTA of exciplexes in planar-heterojunction (PHJ) OLEDs by appropriate selection of donor and acceptor materials to obtain large interfacial energy barriers. Clearly, the large interfacial LUMO–LUMO and HOMO–HOMO energy barriers between two materials could effectively confine holes and electrons within the donor and acceptor layers and produce high-density exciplex states in the vicinity of the hetero-interface. Results show that the MEL responses exhibit a rapid low-field increase followed by an obvious high-field decrease (HFD) at relatively low temperatures, which was understood on the basis of the magnetic-field mediated intersystem crossing process [13,23] and TTA [23,25]. Additionally, a HFD has been observed at room temperature in PHJ OLEDs with appropriately selected donors, reflecting the fact that room temperature TTA was realized in this kind of device. Our discoveries enrich the microscopic mechanisms and provide a feasible pathway to enhance EL efficiency by using the triplet states in exciplex-based OLEDs.

Six PHJ OLEDs and two bulk-heterojunction OLEDs (active area: ~2 × 2 mm^2) were fabricated by thermal evaporation under high vacuum (~10^{-6} Pa) conditions. The hole-transport materials used in these devices include 4,4′,4″-Tris(N-3-methylphenyl-Nphenylamino)triphenylamine (*m*-MTDATA) and N1,N4-diphenyl-N1,N4-dim-tolylbenzene-1,4-diamine (TTP). Also, tris(8-hydroxyquinoline) aluminum (Alq_3), 1,3,5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi), and 2,8-bis(diphenylphosphoryl) dibenzo-[b,d]thiophene (PPT) were used as electron-transport materials. The device structures include ITO/*m*-MTDATA (or TTP) (80 nm)/Alq_3 (80 nm)/LiF (1 nm)/Al (120 nm) and another four similar structures of *m*-MTDATA (or TTP) (80 nm)/TPBi (80 nm) and *m*-MTDATA (or TTP) (80 nm)/PPT (80 nm). Four bulk-heterojunction device structures of ITO/*m*-MTDATA (40 nm)/25wt.% *m*-MTDATA:PPT (80 nm)/PPT (40 nm)/LiF (1 nm)/Al (120 nm) and ITO/TTP ((160-x)/2 nm)/25wt.% TTP:PPT (x nm)/PPT ((160-x)/2 nm)/LiF (1 nm)/Al (120 nm) (x = 80, 40, 10)were also fabricated. The evaporation rates and the thicknesses of the deposited layers were detected using a calibrated quartz crystal monitor (XTM/2). Immediately after preparation, the samples were mounted on the cold finger of a close-cycle cryostat (Janis: CCS-350S, temperature range: 10–325 K) located between the pole pieces of an electromagnet (Lakeshore EM647). A magnetic field with a range from −500 to 500 mT was applied parallel to the device surface and measured using a Hall probe gaussmeter when the sample was tested. The EL intensity was measured using a Si photodiode connected to a Keithley 2000 multimeter, and the PL or EL spectra were measured by a grating spectrograph (SpectraPro-2300i).

To achieve pure exciplex emission, we fabricated six PHJ devices that were composed of different materials with various energy levels. The LUMO and HOMO energies of the five organic materials used here were obtained from the literature [8,13,30,31]. Fig. 1 shows normalized EL spectra for six PHJ devices and two bulk heterojunction devices and the PL spectra of neat films of the organic materials used in the devices at 20 K. Also the energy-level diagrams of the six PHJ devices are displayed. As shown on the right of Fig. 1a, the energy barriers between the LUMO levels and the HOMO levels of *m*-MTDATA and Alq_3 are 1.1 and 0.7 eV, respectively. Therefore, holes injected from the anode could overcome the relatively small energy barrier and enter the Alq_3 layer, leading to the formation of excitons with electrons injected from the cathode and the resulting fluorescence emission. This process can be seen in the spectra on the left of Fig. 1a, where the EL spectrum of the *m*-MTDATA/Alq_3 device is basically consistent with the typical radiative emission of Alq_3-based OLEDs [13]. However, the situation changes when Alq_3 is replaced with TPBi. As shown in Fig. 1b, the spectra show that the EL spectrum of the *m*-MTDATA/TPBi device has two peaks (at 420 and 531 nm), which indicates that composite states (excitons and exciplexes) are generated in this device. When combined with the energy-level and spectral diagrams shown in Fig. 1b, the weak peak is approximately in agreement with the PL spectrum peak of *m*-MTDATA (426 nm), thus reflecting that a small proportion of the electrons overcome the small interfacial energy barrier of 0.7 eV and then generate a small quantity of excitons in the *m*-MTDATA layer, leading to weak fluorescence emission. Additionally, the strong peak has a notable red-shift when compared with the PL peaks of *m*-MTDATA (426 nm) or TPBi (442 nm), which indicates that most of the electrons remain in the TPBi layer and form vast exciplex states in the vicinity of the *m*-MTDATA/TPBi hetero-interface by recombination of electrons and holes in the TPBi acceptor and the *m*-MTDATA donor, respectively. While the PPT has a slightly larger electron affinity than TPBi, similar results were also obtained in *m*-MTDATA/PPT devices because the interfacial energy barriers are not high enough, as shown in Fig. 1c.

Because pure exciplex emission could not be obtained in *m*-MTDATA/TPBi or *m*-MTDATA/PPT devices, we replaced *m*-MTDATA with TTP, which has a smaller ionization potential, to realize large interfacial energy barriers. Demonstrating consistency with the situations of *m*-MTDATA/Alq_3 and *m*-MTDATA/TPBi devices, pure excitons and composite states were generated in TTP/Alq_3 and TTP/TPBi devices, respectively, because the interfacial energy barrier is still not large enough, as shown in Fig. 1d and e. However, as shown in Fig. 1f, pure exciplex states were successfully realized in the TTP/PPT device because the comparatively large interfacial energy barriers between TTP and PPT are 1.4 and 1.9 eV, respectively, which effectively confine the holes and the electrons within the donor- and acceptor-layers and produce exciplex states in the vicinity of the hetero-interface. This process can be reflected by the PL and EL spectra shown in Fig. 1f, where the pure exciplex emission from the TTP/PPT device shows an evident red-shift to 501 nm when compared with the respective PL peaks of 392 and 361 nm from the TTP and PPT films. In addition, this is approximately in line with the EL spectrum of the bulk-heterojunction TTP:PPT device. Thus, Fig. 1 demonstrates that the type of excited state is determined by the interfacial energy barriers in the PHJ devices, and pure exciplex emission would be realized when large interfacial energy barriers are obtained between two materials in these devices.

With the aim of investigating TTA in exciplex-based devices, we have measured the MEL of the TTP/PPT device, along with the MELs of four other PHJ devices and the two bulk-heterojunction devices for comparison. These MELs are measured under a constant bias voltage at a current flow of 150 μA over a temperature range from 20 to 300 K. As shown in Fig. 2, each MEL of these devices presents both low-field and high-field components. The former component shows a sharp increase, which can be understood based on the magnetic-field suppressed intersystem crossing process [13,24,25]. The latter component exhibits gradual variation, and its tendency is either positive or negative (HFD), depending on the evolution processes of the excited states at different temperatures in these devices. Previous research showed that the HFD in MEL could be regarded as a fingerprint of TTA [23,25]. As shown in Fig. 2a–d, the HFD in each MEL appears when temperature decreases to around 100 K in the four *m*-MTDATA (or TTP)/Alq_3 and *m*-MTDATA (or TTP)/TPBi devices. This is because a magnetic-field mediated TTA process occurs among the pure excitons [24,26] or the composite states at relatively low temperatures in the devices. It was found that while there are only small numbers of excitons in the composite-state *m*-MTDATA (or TTP)/TPBi devices, we cannot exclude their