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Blue exciplex emission and its role as a host of phosphorescent emitter

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ABSTRACT

Electroluminescence (EL) and photoluminescence (PL) characters of a series of blue exciplexes from combinations between three electron acceptors (A) and one electron donor (D) were studied. The emissions of three exciplexes, ranging from sky blue to purple blue, though with quiet different acceptor triplet levels, possess the same thermally activated delayed fluorescence character. Temperature dependence of the PL decay measurement suggests that the long-lived exciplex would be quenched heavily by phonon, while the monomer triplet quenching effect was not the origin of low efficiency. Detailed analysis indicates that the RISC rate could be more affected by the spatial structure of D/A materials and substituent group in the D or A molecules. Trap effect and energy transfer from exciplex to the yellow dopant were also studied.

1. Introduction

Blue exciplex type organic light emitting diodes (OLEDs) have been studied since 2002 [1–4]. However, most of the device efficiencies were quite low. Recently, in order to improve the external quantum efficiency (EQE) of OLEDs, Adachi and coworkers have proposed a new strategy, i.e., the enhancement of EQE from thermally activated delayed fluorescence (TADF) via reverse intersystem crossing (RISC) process from triplet states to the singlet state [5,6]. In the process of TADF, a small singlet–triplet energy difference ($\triangle E_{(S-T)}$) are needed to thermally activated the triplet states to the singlet state. Based on the TADF mechanism, several highly efficient electroluminescence (EL) emissions resulted from exciplexes formed at the interface between donors (D) and acceptors (A) have been demonstrated [4–8]. Although the blue exciplex also behaves small $\triangle E_{(S-T)}$, efficient blue exciplex based OLEDs rarely reported. The highly efficient exciplex OLEDs only achieved in several donor and acceptor combinations, indicating that some other critical limiting factors exist beyond the TADF mechanism. Most of the reported blue exciplex OLEDs were being remained at a phenomenal stage, suggesting that the development of the blue exciplex EL is still a big challenge. On the other hand, because the emitting layer (EML) with wider band gap must be required, the achievement of blue emission has been little reported to date [1–4].

In this work, we address blue exciplex emission of a series of acceptor components with one donor component. To achieve blue exciplex emission, the donor material with deep highest occupied molecular orbital (HOMO) level and acceptor material with a high lowest unoccupied molecular orbital (LUMO) level are required. In terms of such a consideration, mCP was used as the donor component because its HOMO and LUMO levels are located at 6.1 eV and 2.4 eV, respectively. Three electron-transporting materials, including 4,7-diphenyl-1, 10-phenanthroline (Bphen), 1,3,5-tri(phenyl-2-benzimidazoly)-benzene (TPBi) and 2,4,6-tris (3-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine (3PT2T), were selected as the acceptor components in the D:A exciplex system. The PL decay characters of these three exciplexes under different temperatures with the monomer triplet quenching effect are systematically studied. The role of our exciplex as phosphor host was also detailed investigated. Based on these studies, we outlined the limiting factors of low efficiency exciplex and gave a comprehensive description of the exciplex-host system.

2. Experimental section

OLED devices were fabricated using pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω/cm^2 and ITO thickness of 150 nm. They were patterned so that the OLED devices had

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a pixel size of about 9 mm^2. The small molecule and cathode layers were thermally evaporated using the multiple-source organic molecule deposition method. PL spectra of all the films were measured using Hitachi F7000 spectrometer and EL spectra were determined by OPT-2000 spectrophotometer. PL decay times of all the films were measured by FL920. All the EL measurements were carried out at room temperature under ambient condition.

3. Results and discussion

3.1. Formation of blue exciplex and its PL characters

Molecular structures of materials used in forming exciplexes are shown in Fig. 1a. The architecture of our blue exciplex based OLED and the schematic exciplex energy level diagram are indicated in Fig. 1b. All the exciplex based OLEDs comprise a 20 nm co-deposited films of mCP:50 wt.% A, where A denotes Bphen, TPBi and 3PT2T. The EL spectra and device performances of the three exciplex based OLEDs are shown in Fig. 2c,d and listed in Table 1. The PL spectra of the exciplexes are depicted in Fig. 2a. The PL spectrum of mCP:Bphen was red-shifted with respect to that of mCP:TPBi (Fig. 2a and c) though Bphen have a higher HOMO level (2.5 eV) than that of TPBi (2.7 eV). However, the higher LUMO level does not conflict with the experimental result, because the exciplex emitting energy is not only related with the HOMO–LUMO energy gap value but also related with the coulombic binding energy which can be different in different systems. In the previous study, we also found that the m-MTDATA:TPBi and m-MTDATA:Bphen exhibited the reverse energy relation [7]. The PL spectra of the co-deposited films are obviously red-shifted as compared to the PL spectra of either the donor or the acceptor components. In Fig. 2a, the well resolved PL spectra of mCP, Bphen and TPBi exhibited non gaussian distributions, indicating a $\pi\pi$ transitions [9]. On the other hand, the mixed films all exhibited gaussian distributions, suggesting the formation of exciplexes [10]. The PL decay characters of these exciplexes are depicted in Fig. 2b. All the exciplex PL decay curves are composed of two components i.e., a shorter component of ca. 4 ns and a longer component of ca. 20 ns. The PL lifetime of the neat mCP film was determined as ca. 3 ns, as shown in Fig. 2b. And the lifetime of the neat TPBi film is only ca. 1.2 ns [11]. Because the lifetime of D(A) monomer was quenched by A(D) and exciplex to ps level, the two components PL decay character should not result from the overlap of emission of the D/A and exciplex [12,13]. The character of long component in decay times are quite different from the PL decay character of both the D- and A-components, further demonstrated that the exciplex formed in the D:A mixed film. Therewith, we can confirm that the PL decay of two components should be assigned to the delayed fluorescence based on a TADF mechanism. This conclusion was supported by further study of PL intensities and decays of exciplex under different temperatures, as discussed in the next section.

3.2. Temperature dependence of PL characters and triplet quenching effect in the PL process

To further ascertain whether the aforementioned delayed components in the PL decays of three mixed files were from a thermally activated process, temperature dependence of the PL decay characters for the three exciplexes were explored, as shown in Fig. 3a–c, respectively. The relative PL intensities (defined as PL intensity of three exciplexes divided by the same arbitrary number) of all three exciplexes increased with temperature increasing to about 50 K in Fig. 3d, suggesting not only a thermally activated process but also a small $\triangle E_{S\text{-}T}$ between the singlet and triplet states [7,12,13]. It is interesting that the PL intensities of all three exciplexes decreased dramatically with the temperature increasing to above 200 K, indicating that the exciplexes were quenched by phonon at high temperature. Similar result can be found in previous report [5]. One of the main obstacles of the efficient blue exciplex is the monomer triplet quenching effect due to the low acceptor or donor triplet level. In this work, Bphen, TPBi and 3PT2T cover a wide range of triplet levels from 2.5 eV to 2.8 eV [12,14,15]. The triplet energy levels of the three exciplexes of mCP:Bphen, mCP:TPBi and mCP:3PT2T are 3.04 eV, 3.12 eV and 2.78 eV respectively. The triplet levels of exciplexes in mCP:Bphen is higher than the triplet levels of Bphen and mCP, therefore, would be quenched by the monomer triplet states. However, the PL lifetime of the mCP:Bphen was of the same order as mCP:3PT2T for which no quenching effect exist because the triplet level of mCP:3PT2T exciplex is well confined in the combination (a T_1 level of 2.9 eV for mCP) [15,16]. In Fig. 3b and c, the long component decreases with the rising of temperature, especially for mCP:Bphen film, indicating a competition exist between the thermally activated RISC process and the phonon quenching effect. The PL decay profile of mCP:TPBi film was independent of temperature in Fig. 3a, indicating that both the singlet and triplet exciplexes were quenched by the phonon. Nonetheless, all three exciplexes perform universal

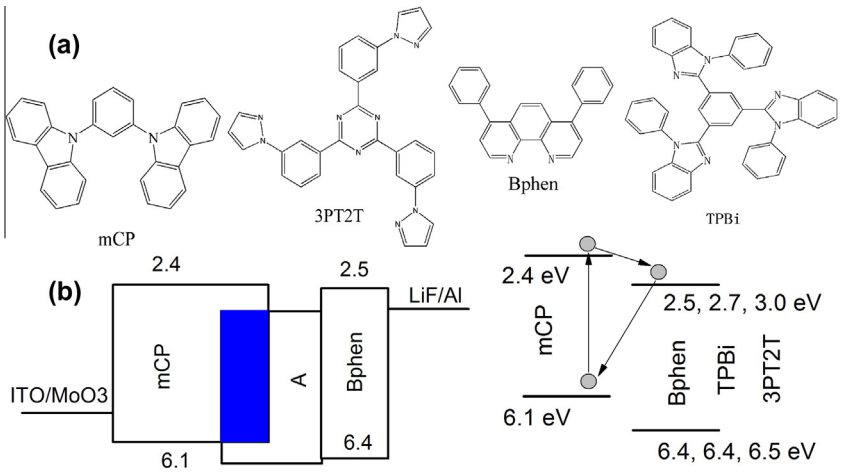

Fig. 1. (a) The molecular structures of 3PT2T, mCP, Bphen and TPBi. (b) Left: device structure of our blue exciplex OLED and right: the schematic exciplex energy level diagram. The device structure is: ITO/mCP (20 nm)/mCP:50 wt.% acceptors (20 nm)/acceptors (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)