



# Efficient exciplex organic light-emitting diodes with a bipolar acceptor



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## ARTICLE INFO

### Article history:

Received 10 May 2015

Received in revised form 2 June 2015

Accepted 11 June 2015

Available online 13 June 2015

### Keywords:

Organic light-emitting devices

Exciplex/electroplex

Charge transfer

Excited state

Triplet exciton

## ABSTRACT

Efficient exciplex organic light-emitting diodes (OLEDs) have been fabricated with an intermixed light-emitting layer comprising electron-rich m-MTDATA or TAPC as a donor and bipolar material 26DCzPPy as an acceptor. Intermolecular charge–transfer interaction between various donor materials with different highest occupied molecular orbital (HOMO) levels and 26DCzPPy are systematically investigated to explore the formation principle of the exciplex. Various techniques like steady state absorption and photoluminescence (PL) spectra, temperature dependent transient PL decay and time-resolved emission spectra (TRES) using time-correlated single-photon counting (TCSPC) principle were adopted to probe the electronic and optical properties of these exciplex systems. Strong exciplex emission was found from the m-MTDATA:26DCzPPy and TAPC:26DCzPPy mixed systems. The devices comprising these two exciplex systems as the emission layer exhibited a promising external quantum efficiency and a high exciton utilization efficiency due to the triplet exciton up-conversion from triplet to singlet states inspired by their small singlet–triplet exchange energy. Our current work contributes to know more about the unique intermolecular charge–transfer property between electron-rich donors and bipolar acceptors, and provides valuable exploration on developing novel high-performance exciplex OLEDs.

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## 1. Introduction

Since their discovery [1], how to efficiently utilize the electro-generated triplet excitons to give the radiation decay is always one of the most challenging issues in the research field of organic light-emitting diodes (OLEDs). According to the selection rule deduced from the quantum spin statistics, in organic semiconducting devices, only 1/4 fraction of the electro-generated excitons in the singlet state can be utilized to give radiation decay, while the other 3/4 fraction of excitons in the triplet state are waste of giving nonradiation decay due to the quantum spin forbidden principle. This results in a theoretically maximal radiative exciton ratio ( $\eta_r$ ) of 25% for conventional fluorescent emitters. The strategy of incorporating organometallic phosphors as the emitters has been widely demonstrated to break the spin forbidden rule to gain a theoretical unit  $\eta_r$  due to the spin–orbital coupling effect induced by the heavy metal atoms [2,3]. However, high cost of the rare metals in the organometallics is still a big hindrance for the commercial application of the OLEDs with organometallic emitters.

Continuous research effort has been devoted to develop metal-free cheap organic emitters capable of using both the singlet and triplet excitons to give radiation decay. Recently, much attention has been paid on the up-conversion mechanisms via triplet–triplet annihilation (TTA) or thermally activated reverse intersystem crossing (RISC) approaches to obtain this target. Given that all the electrically generated triplet excitons can be up-converted to the singlet state, a theoretical maximal  $\eta_r$  of 100% is possible for the OLEDs including the thermally activated delayed fluorescence (TADF) emitter via RISC process, while the theoretically maximal  $\eta_r$  for the OLEDs containing TTA emitters is limited to be 62.5% (25% + 75%/2). This indicates that TADF compounds have a greatly promising potential to develop highly efficient OLEDs. Indeed, the TADF emitters have been rapidly developed; various highly efficient RGB and white OLEDs comprising TADF emitters with a  $\eta_r$  much higher than 25% have been reported [4–7].

In a TADF process, the energy difference ( $\Delta E_{ST}$ ) between the lowest singlet excited state ( $S_1$ ) and triplet excited state ( $T_1$ ) of the emitters should be minimized to be equal to or smaller than the thermal energy at room temperature ( $\sim 25$  meV); once the triplet excitons are generated on the TADF molecules under the electric field, they can be easily up-converted to the radiative  $S_1$  state assisted by the environmental thermal energy. A unit internal

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quantum efficiency of the OLEDs comprising TADF emitters is thus theoretically possible. A small  $\Delta E_{ST}$  can be achieved by decreasing the exchange interaction integral which is proportional to the wave-function overlap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Hence, donor–acceptor (D–A) type molecules with the intramolecular charge–transfer (ICT) interaction between the separated electron-rich donor groups and electron-withdrawing acceptor groups are usually applicable to develop TADF materials.

Alternatively, a small  $\Delta E_{ST}$  can also be achieved by spatially separating the LUMO and HOMO on two dissimilar donor and acceptor molecules. In such a heterojunction D–A system, intermolecular excited charge–transfer (CT) states, namely exciplex, are easily formed. Due to the complete separation of the wave-function of LUMO and HOMO, the  $\Delta E_{ST}$  between the singlet CT state ( $CT_1$ ) and the triplet CT state ( $CT_3$ ) is quite small [9], which can inspire the electrically generated triplet exciton reverse intersystem conversion from  $CT_3$  to  $CT_1$ . This approach provides a potential effective method to change the triplet excitons to give radiation decay. Actually, the exciplex-based OLEDs have been developed for many years [14,15], and the featured broad emission band of exciplex can be used to develop white OLEDs with high color rendering index (CRI) [16–19]. The current further recognition of exciplex complexes with a TADF character implies that highly efficient exciplex-based OLEDs with the capability to obtain a unit  $\eta_r$  could be theoretically achieved. To construct an effective exciplex system, an electron-rich hole-transport material (HTM) and an electron-deficient electron-transport material (ETM) should be combined via intermixing within one layer or by separated layer-to-layer contact [20]. Various combinations of the commercial HTMs and ETMs to construct exciplex emitters have been investigated, and some of them have yielded highly efficient OLEDs with a high  $\eta_r$  and thus high external quantum efficiency (EQE) [9,20–23]. The device architecture of the exciplex-based OLEDs can also benefit in simplification of the device structure, thereby, lower the fabrication cost of the devices.

In this study, we provide a novel approach to fabricate highly efficient exciplex-based OLEDs based on the strategy of combining a bipolar transport material (26DCzPPy) as an acceptor [13,24]. The electronic and optical properties between various HTMs with different electron-donating abilities and 26DCzPPy have been investigated (Fig. 1). Strong exciplex emissions were observed from the m-MTDATA:26DCzPPy and TAPC:26DCzPPy mixed systems. A small  $\Delta E_{ST}$  was observed for m-MTDATA:26DCzPPy, which suggests that the electro-generated triplet excitons can be utilized through up-conversion process from  $CT_3$  to  $CT_1$ . Efficient green OLEDs comprising an emissive layer of m-MTDATA:26DCzPPy were demonstrated with a maximal EQE of 5.03% and a maximal

current efficiency (CE) of  $15.9 \text{ cd A}^{-1}$ , corresponding to a maximal  $\eta_r$  value of 82.6%. Mixed exciplex and electroplex emissions were observed for the TAPC:26DCzPPy based OLEDs, resulting in a white light emission with an exciplex peak at 450 nm and an electroplex peak at 585 nm. A maximal EQE and CE of 1.13% and  $2.19 \text{ cd A}^{-1}$  were obtained for the device comprising TAPC:26DCzPPy. It is corresponding to a high  $\eta_r$  value of 36.9% even if only considering the excitons decaying from the high-energy intermolecular CT state, regardless of a relatively larger  $\Delta E_{ST}$  of 0.39 eV for the TAPC:26DCzPPy system. The current findings indicate that the exciplexes with an intermolecular CT character between the electron-rich donors and the bipolar acceptors can be utilized as the emitters to fabricate efficient OLEDs.

## 2. Experiments

The OLED devices were fabricated on the patterned 95-nm-thin indium tin oxide (ITO)-coated glass substrates with a sheet resistance of  $20 \Omega/\text{square}$ . Prior to the device fabrication, the ITO substrates were cleaned in sequence by ultrasonic bath of acetone, detergent, deionized water, isopropyl alcohol and then dried at  $80^\circ\text{C}$  for more than 3 h. The devices were fabricated by step-by-step deposition of various functional layers under unbroken vacuum of  $<5 \times 10^{-4} \text{ Pa}$ . All binary-mixed films investigated in this work are obtained by vacuum co-deposition with a molar ratio of 1:1. The light emissive area of the devices was masked to be  $0.09 \text{ cm}^2$ . Current density–voltage–luminance (J–V–L) characteristics of the OLEDs were measured by Keithley source-measure unit 2400 and Konica Minolta chromameter CS-200. Electroluminescent (EL) spectra of the devices were measured by a spectrophotometer (Photo Research, Model: SpectraScan PR-705). EQEs are calculated from the current densities, current efficiencies, and their corresponding EL spectra, provided that the emission of the OLEDs follows a Lambertian model. Steady state and transient photoluminescent (PL) spectra of the samples were measured with the Edinburgh Instruments FLS920 spectrometer equipped with an Oxford Instruments nitrogen cryostat (Optistat DN) to control the sample temperature. Absorption spectra were measured using a spectrophotometer (Shimadzu, UV-3600). Photoluminescent quantum yields (PLQYs) were measured by using an integrating sphere on an absolute PL quantum yield spectrometer (HAMAMATSU C11347).

## 3. Results and discussion

PL spectra of pure 26DCzPPy and m-MTDATA, TAPC, NPB, TCTA films as well as their binary-mixed films with 26DCzPPy are shown

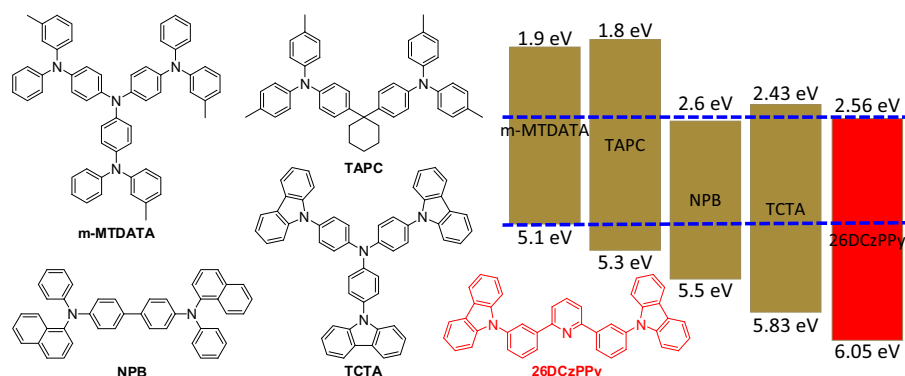


Fig. 1. Molecular structures of the investigated electron-rich donor materials m-MTDATA, TAPC, NPB, and TCTA, and the bipolar acceptor material 26DCzPPy, as well as their corresponding energy levels from the references [8–13].

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