



# Organic light-emitting diodes exploiting aggregation-induced exciton and exciplex emissions



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## ABSTRACT

The derivatives of carbazole and tetraphenylethylene exhibiting aggregation-induced emission and 4,4',4'-tris[3-methylphenyl(phenyl)amino]triphenylamine were used for the preparation of organic light-emitting diodes the electroluminescence spectra of which include exciton and exciplex emissions. The low-energy exciplex emission of the electroluminescence spectrum was formed at the interface of the emissive layers. The best fabricated device showed turn-on voltage of 2.7 V for electroluminescence (at 10 cd/m<sup>2</sup>); maximum current efficiency of 11.5 cd/A, maximum brightness of 17,700 cd/m<sup>2</sup> (at 11 V), and external quantum efficiency of ca. 3.9% with CIE 1931 chromaticity coordinates (0.20, 0.38).

## 1. Introduction

Organic light-emitting diodes (OLEDs) are established as a modern generation of light solid-state sources for display and illumination technologies [1,2]. Flexibility, large-area, light weight, a wide viewing angle, fast response rate, high brightness are the advantages of OLEDs. Conventional high-efficiency OLEDs are based on phosphorescence of materials containing heavy metal atoms such as iridium, platinum, or osmium [3]. Such molecules exhibit phosphorescence at room temperature which is untypical for fully organic materials. The internal quantum efficiency (IQE) for phosphorescent OLEDs theoretically can reach 100%, while the maximum value for fluorescent OLEDs is 25% [4,5]. However, the application of phosphorescent emitters in OLEDs is limited because of high costs of heavy metal complexes and due to the environmental reasons.

Recently, exciplex-based emitters based on solid-state mixture of heavy-metal-free donor and acceptor molecules were applied for the fabrication of efficient OLEDs [6,7] and vertical organic light-emitting transistors [8]. In terms of the simplified molecular design and OLED structure, operational stability, extremely low turn-on voltages ( $\approx$  2.1 V), possibility to obtain deep blue emission, high power efficiency (over 100 lm/W) exciplex emitters are on par with single-molecule emitters exhibiting thermally activated delayed fluorescence (TADF) [9–13]. Such parameters can be reached partially due to (1) unique properties of exciplex forming materials to form “active” pn-heterojunction, which provides the absence of energy barriers for charges [14]; (2) high triplet-energy levels which prevent energy leakage and enable efficient reverse intersystem crossing (RISC) [15]. However,

100% of IQE for one-color exciplex-based OLEDs was achieved so far only at low temperatures [16]. To get it at room temperatures, non-radiative processes through triplet exciplex levels have to be practically absent. IQE of exciplex-based OLEDs can be improved by the development of new exciplex-forming molecular systems exhibiting low extent of non-radiative processes of triplet exciplexes, TADF, high photoluminescence quantum yields (PLQY), well balanced hole and electron mobilities etc.

Efficiency of OLEDs directly depends on PLQY of emitters in solid state [5]. However, for most of organic compounds PLQY of the solid samples is lower than that of dilute solutions due to the aggregation caused quenching [17,18]. It is possible to overcome this effect using emitters showing aggregation-induced emission enhancement (AIEE) [19]. Such approach was successfully realized in efficient heavy-metal-free OLEDs using stereoregular tetraphenylethylene derivatives for both light-emitting and electron-transporting layers [20]. The strategy of tuning the singlet–triplet energy gap of AIEE materials for OLEDs was shown [21]; however, the information on the exploitation in OLEDs of exciplexes based on AIEE materials is still absent.

In this work, the study of guest-host free OLEDs combining emission from both excitons and exciplexes based on AIEE from carbazole and tetraphenylethylene derivatives **3CzTPE**, **2CzTPE** and **9CzTPE** is presented. The structures of **3CzTPE**, **2CzTPE** and **9CzTPE** are shown in Fig. 1. The singlet excitons recombine in a light-emitting layer based on these materials. The singlet exciplexes recombine at the interface formed between the layer of carbazole and tetraphenylethylene derivative and the layer of hole-transporting compound 4,4',4'-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA). The triplet

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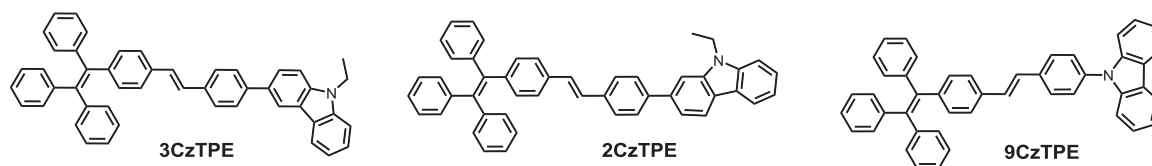


Fig. 1. Chemical structures of 3CzTPE, 2CzTPE and 9CzTPE.

excitons can not only to non-radiatively recombine but also can form lower-energy exciplexes at the interface. Furthermore, the triplet exciplexes can transform into the singlet exciplexes by the reverse intersystem crossing process through the thermally activated up-conversion mechanism at the room temperature due to small  $\Delta E_{ST}$  for the exciplexes [8]. Therefore, the performance of such OLEDs can be improved compared to OLEDs based only on the singlet or exciplex emissions.

## 2. Experimental

Synthesis of the derivatives carbazole and tetraphenylethylene, namely, 3-(4-(4-(1,2,2-triphenylvinyl)phenylethenyl)phenyl)-9-ethylcarbazole (3CzTPE), 2-(4-(4-(1,2,2-triphenylvinyl)phenylethenyl)phenyl)-9-ethylcarbazole (2CzTPE), and 9-(4-(4-(1,2,2-triphenylvinyl)phenylethenyl)phenyl)carbazole (9CzTPE) is reported elsewhere [22]. Their chemical structures are displayed in Fig. 1.

OLEDs with the following structures were fabricated: ITO/MoO<sub>3</sub> (5 nm)/3CzTPE (2CzTPE or 9CzTPE) (45 nm)/TPBi (30 nm)/Ca (17 nm)/Al(80 nm) (devices IA, IB, and IC, respectively); ITO/MoO<sub>3</sub> (5 nm)/m-MTDATA (70 nm)/3CzTPE (2CzTPE or 9CzTPE) (10 nm)/TPBi (30 nm)/Ca (17 nm)/Al (80 nm) (devices IIA, IIB, and IIC, respectively); ITO/MoO<sub>3</sub> (5 nm)/m-MTDATA:3CzTPE (2CzTPE or 9CzTPE) (80 nm)/TPBi (30 nm)/Ca (17 nm)/Al (80 nm) (devices IIIA, IIIB, and IIIC, respectively).

Indium tin oxide (ITO) coated glass with a sheet resistance of 70–100  $\Omega$ /sq was used as a substrate. Molybdenum trioxide (MoO<sub>3</sub>) was used for the hole-injection layers; 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) was used for the preparation of electron-transporting and hole-blocking layers; 4,4',4'-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) was used for hole-transporting and electron-blocking layers; 3CzTPE, 2CzTPE or 9CzTPE were used for the light-emitting layers. Calcium layer covered by aluminum layer was used as cathode. All organic and metal layers were vacuum deposited step by step onto precleaned ITO-coated glass substrates under the vacuum of  $1\text{--}5 \times 10^{-6}$  mBar using vacuum equipment from Kurt J. Lesker in-built in an MB EcoVap4G glove box. The emitting layers of m-MTDATA:3CzTPE (2CzTPE or 9CzTPE) of the devices IIIA, IIIB, and IIIC were deposited from one source boat at the ratio of 50% (m-MTDATA):50% (3CzTPE (2CzTPE or 9CzTPE)).

Current density–voltage characteristics of OLEDs were recorded by a Keithley source meter 2400 and the current density–luminance characteristics were recorded by a calibrated silicon photodiode with the 6517B Keithley electrometer for the photocurrent measurement. The photodiode was placed in front of OLEDs in a dark room, assuming a Lambertian distribution of electroluminescence (EL) of the OLEDs. EL spectra were taken by an Avantes AvaSpec-2048XL spectrometer. External quantum efficiency was calculated from the luminance, current density, and EL spectrum. The chromaticity coordinates (x, y) of the devices were calculated using EL spectra.

Photoluminescence decay curves of the layers at room and low temperatures were recorded with the Edinburgh Instruments FLS980 spectrometer at room temperature using nF920 nanosecond flash lamp or PicoQuant LDH-D-C-375 laser (wavelength 374 nm) as the excitation source. Photoluminescence quantum yields (accuracy  $\pm 2\%$ ) of exciplex-forming layers (m-MTDATA:3CzTPE, m-MTDATA:2CzTPE and m-MTDATA:9CzTPE) were measured using integrated sphere. Variable

temperature liquid nitrogen cryostat (Optistat DN2) was exploited for the characterization of photophysical properties of the exciplexes at different temperatures in inert atmosphere (N<sub>2</sub>).

## 3. Results and discussion

Since 3CzTPE, 2CzTPE, 9CzTPE showed strongly enhanced blue emission in the aggregated state [22], it was of interest to study EL of the materials. PLQY of the solid samples of 3CzTPE, 2CzTPE, 9CzTPE in solid state was found to range from 26.8% to 43.9% [22]. These materials are characterized by high thermal stability. Their 5% weight loss temperatures are in the range of 354–425  $^{\circ}\text{C}$  [22]. 3CzTPE, 2CzTPE and 9CzTPE have appropriate HOMO and LUMO energy levels to inject both holes and electrons from conventional electrodes (ITO, Ca, LiF/Al) in OLEDs [22]. Hole drift mobilities for the layers of these materials were found to be higher than  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at electric field  $< 3.4 \times 10^5 \text{ V cm}^{-1}$  [22].

First, we fabricated blue OLEDs of the following structures: ITO/MoO<sub>3</sub>/3CzTPE (2CzTPE or 9CzTPE)/TPBi/Ca/Al (devices IA, IB, and IC, respectively). EL spectra of the devices IA, IB, and IC are shown in Fig. 2a. They were found to be similar to the photoluminescence (PL) spectra of 3CzTPE, 2CzTPE or 9CzTPE (Fig. 2b). This observation confirms that EL originates from the layers of 3CzTPE, 2CzTPE or 9CzTPE in devices IA, IB, or IC respectively. Devices IA, IB, and IC showed the values of a turn-on voltage ( $V_{on}$ ) in the range of 3.6–4.2 V for electroluminescence (at 10  $\text{cd/m}^2$ ); maximum current efficiency in the range of 0.7–9.8  $\text{cd/A}$ , maximum brightness of 2500–10,020  $\text{cd/m}^2$  (at 11 V), and external quantum efficiency of ca. 0.4–3.2% (Table 1, SI Fig. S1a, b). Commission Internationale de l'Eclairage (CIE 1931) chromaticity coordinates (x, y) of the devices IA, IB, and IC were found to be (0.20, 0.38), (0.21, 0.37) and (0.21, 0.36), respectively, i.e. they belong to the blue color (Fig. 2c). Despite the similarities of the structures of 3CzTPE, 2CzTPE, 9CzTPE, the efficiency of the fabricated blue OLEDs exhibited differences mostly due to HOMO levels which provided different energy barriers for holes ( $0.17 < 0.25 < 0.34 \text{ eV}$  for 3CzTPE, 2CzTPE and 9CzTPE, respectively) (Fig. 3).

To enhance the performance of the devices by improving the charge balance, the additional hole-transporting and electron blocking layers of m-MTDATA were used. Blue-green OLEDs of the following structures ITO/MoO<sub>3</sub>/m-MTDATA/3CzTPE (2CzTPE or 9CzTPE)/TPBi/Ca/Al (devices IIA, IIB, and IIC, respectively) were fabricated. The devices IIA, IIB, and IIC showed lower  $V_{on}$  of 2.7 V for EL (at 10  $\text{cd/m}^2$ ) than devices having no m-MTDATA layer. The later devices also showed enhanced brightness and other parameters (Fig. 4a–b, Table 1).

Enhancement of the performance of the devices after the incorporation of hole-transporting and electron blocking layers can be explained by the changes of the charge barriers between ITO and the layers of 3CzTPE, 2CzTPE or 9CzTPE that leads to the improvement of the charge balance in the devices. The maxima of EL spectra of the devices IIA, IIB, and IIC were red-shifted up to 35 nm relative to the maxima of EL of devices IA, IB, and IC (Fig. 2a). EL spectra of the devices IIA, IIB, and IIC do not resemble to PL spectrum of m-MTDATA (peak of 425 nm (Fig. 2b)). This observation allows us to presume that the red-shift of the emission maxima observed in the EL spectra of the devices IIA, IIB, and IIC (Fig. 2a) can be explained by the formation of exciplexes between m-MTDATA and 3CzTPE (2CzTPE or 9CzTPE) at the interface m-MTDATA/3CzTPE (2CzTPE or 9CzTPE) [23–25]

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