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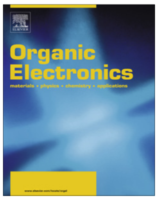

# Highly efficient Organic Light-Emitting Diodes from thermally activated delayed fluorescence using a sulfone–carbazole host material

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ABSTRACT

Organic Light-Emitting Diodes (OLEDs) using the thermally activated delayed fluorescence (TADF) emitter (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) are demonstrated using a novel ambipolar host 3,5-di(carbazol-9-yl)-1-phenylsulfonylbenzene (mCPSOB). When doped in a 5 wt.% concentration, OLEDs with EL efficiency values of more than 81 cd/A for current efficacy and 26.5% for external quantum efficiency are reported. These devices exhibit a low turn-on voltage of 3.2 V at 10 cd/m$^2$, as well as reduced efficiency roll-off at high current densities. To the best of our knowledge, these are among the highest ever reported efficiencies for TADF OLEDs, and are even comparable to the highest reported efficiencies for phosphorescent OLEDs.

## 1. Introduction

Organic Light-Emitting Diodes (OLEDs) have been attracting increasing attention for their use in flat panel displays and solid-state lighting technology due to their high electroluminescence efficiency and ability to be manufactured on various substrates at moderate temperature. Typically, high-efficiency OLEDs are fabricated with phosphorescent emitters, such as iridium- or platinum-containing complexes [1–3]. Unlike common fluorescent emitters, which emit light from a singlet excited state, these heavy-metal containing phosphorescent emitting materials harvest excitons from both the singlet and triplet excited states for electroluminescence via enhanced intersystem crossing (ISC) [3]. This results in an internal quantum efficiency (IQE) close to 100% in phosphorescent based OLEDs (PHOLEDs). However, the precious metals (such as iridium) found in these present their own set of challenges, which have made it difficult for OLEDs to become competitive in the solid-state lighting markets.

Recently, Adachi and co-workers were able to show highly efficient OLEDs from thermally activated delayed fluorescence (TADF) [4–8]. This novel approach utilizes emitter molecules wherein the small energy difference between the singlet and triplet states in select organic molecules to achieve TADF [6]. Like typical fluorescent emitters, the light emission in these emitters arises from the singlet excited state; however, efficient TADF allows for excitons from the triplet state to be harnessed from the singlet state by reverse intersystem crossing through thermal activation – producing IQE's near 100% from singlet state emission compared to the 25% in conventional fluorescent emitters [4–8]. This mechanism has allowed for a new class of efficient heavy-metal-free fluorescent emitters to be developed that have yielded efficiencies comparable to those of the most efficient heavy-metal phosphorescent-emitter–based OLEDs [4,8–10].

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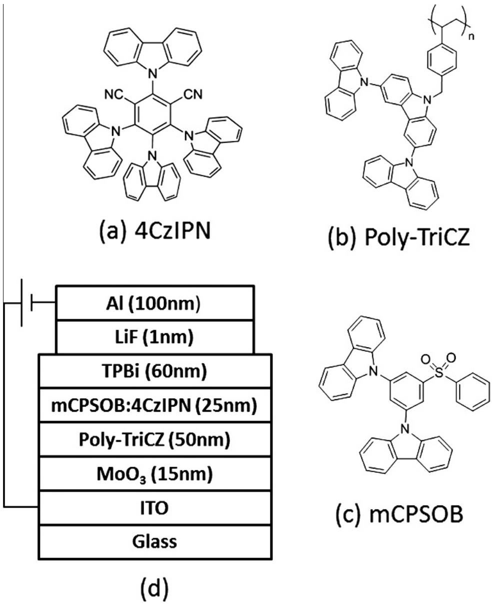
In general, (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN) has been used as the benchmark green TADF emitter, producing a maximum external quantum efficiency (EQE) of 19.3% when doped in a CBP host-matrix at a 1 wt.%. concentration [4]. However, recent work has shown that this efficiency can be further improved with the use of ambipolar host materials, and TADF devices with EQEs over 25% have been reported utilizing materials with similar hole and electron mobility values [10]. These host materials with ambipolar charge transport properties have been shown to be critical to the development of highly efficient phosphorescent OLEDs because they facilitate charge injection and charge balance within the emissive layer of these devices [11,12].

In this work, we report on an emissive layer comprising the ambipolar host material 3,5-di(carbazol-9-yl)-1-phenylsulfonylbenzene (mCPSOB, Fig. 1), we have recently developed [13], and the TADF emitter 4CzIPN. The ambipolar host material shows high singlet and triplet energies of 2.93 eV and 3.02 eV, respectively, measured from the phosphorescence spectra in 2-methyltetrahydrofuran at 77 K. The ionization energy (IE) (for simplicity, also identified here to be the highest occupied molecular orbital (HOMO) energy) and the electron affinity (EA) (also identified here to be the lowest unoccupied molecular orbital (LUMO) energy) were determined to have values of 5.8 eV and 2.5 eV, respectively. When doped in this host matrix, 4CzIPN based OLEDs were produced that yielded EQEs of 26.5% and 21.5% at luminance values of 10 cd/m$^2$ and 1000 cd/m$^2$, respectively and very low roll-off at high current densities. These are among the highest efficiencies reported for TADF based OLEDs.


(a) 4CzIPN

(b) Poly-TriCZ

(c) mCPSOB

(d)

**Fig. 1.** (a) Chemical structure of TADF dopant 4CzIPN. (b) Chemical structure of hole-transporting material Poly-TriCZ. (c) Chemical Structure of ambipolar host material mCPSOB. (d) Device structure of the TADF OLED using mCPSOB as the host material. CBP host device used the same structure.

## 2. Experimental

OLED substrates consisting of indium tin-oxide coated glass sheets (Colorado Concepts Coatings LLC) with a sheet resistance of 15 Ω/sq were cut into 1 × 1 inch squares and patterned using 1/2 in. strips of Kapton tape and exposing the remaining ITO to an acid bath of HCl:HNO$_3$ (3:1) for 5 min. The substrates were then cleaned by ultrasonication (5510, Branson Ultrasonics) for 25 min in each of the following: water with detergent, distilled water, acetone, and isopropanol. They were then blown dry with nitrogen before exposed to oxygen plasma (Plasma-Preen II, Plasmatic Systems, Inc) for 5 min. Immediately after, the samples were transferred to a glove box with a nitrogen atmosphere and loaded into a ultra-high vacuum thermal evaporation system (EvoVac, Armstrong Engineering Inc) and a 15 nm-thick hole injection layer of molybdenum trioxide (MoO$_3$) was deposited at a rate of 0.2 Å/s.

The samples were then transferred to a wet glove-box via a nitrogen sealed transport tube and a solution of the tris-carbazole polymer (Poly-TriCZ) [14] (Fig. 1) was prepared by dissolving 1 mg of Poly-TriCz in 1 mL of anhydrous chlorobenzene (Aldrich). The solution was dispensed through a 0.20 μm polyvinylidine fluoride filter and 50 nm-thick films were deposited by spin-coating the solution at 750 rpm for 60 s. The films were then annealed on a hot-plate at 110 °C for 2 min and transferred back to the deposition system glove box via a nitrogen sealed transfer tube.

The 25 nm emissive layer (EML) was then deposited via a co-evaporation of mCPSOB:4CzIPN with a 0.95:0.05 dopant concentration, followed by a 60 nm-thick electron transport layer (ETL) of 1,3,5-tris(2-N-phenylbenzimidazolyl) benzene (TPBi). A 1.0 nm-thick layer of lithium fluoride (LiF) was deposited at a rate of 0.1 Å/s to improve the electron injection between a 50 nm-thick aluminum cathode and organic layers. A 100 nm-thick layer of silver was deposited atop the aluminum to assist with the contact between the devices and the test set-up. The typical OLED active area was 3.5 × 3.0 mm$^2$. All depositions were performed at pressures below $1.0 \times 10^{-7}$ Torr. 4CzIPN and TPBi were both purchased from Luminescence Technology Corporation (Lumtec), and all others were purchased from Sigma–Aldrich. All organic materials were purified by gradient-zone sublimation prior to thermal evaporation.

After fabrication, the electrical and optical properties of the devices were characterized with a Keithley 2400 source meter and a calibrated photodiode (FDS 100 from Thorlabs, Inc.) fixed at the surface normal of the OLED under measurement. The electroluminescence spectra were captured with a radiometrically calibrated Ocean Optics USB4000 spectrometer.

## 3. Results and discussion

The mCPSOB host used in this report was designed to exhibit ambipolar charge transport properties, and combines carbazole hole transporting materials with a phenylsulfone electron transporting moiety [13]. Additionally, it