



# Controlling singlet–triplet splitting in carbazole–oxadiazole based bipolar phosphorescent host materials

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## ABSTRACT

A rational molecular design strategy for carbazole–oxadiazole based bipolar host materials was developed to improve the device efficiency of blue phosphorescent organic light-emitting diodes (PHOLED). Steric effects of strategically placed methyl groups led to an increase of triplet energies (**o**-2MPCzPOXD: 2.66 eV and **o**-3MPCzPOXD: 2.73 eV versus the initial host material **o**-PCzPOXD: 2.62 eV) while less pronouncedly affecting singlet energies and, therefore, retaining low driving voltages, high power efficiencies and remarkably low efficiency roll-offs in PHOLEDs. The maximum quantum efficiencies (EQE) for blue devices (Irpic) were significantly raised for **o**-2MPCzPOXD (13.6%) and **o**-3MPCzPOXD (11.5%) versus **o**-PCzPOXD (9.0%) although yielding comparable values for green devices (Ir(ppy)<sub>3</sub>; 12.9% and 15.4% versus 13.2%). Supported by theoretical calculations a structure–property relationship was established from photo-physical properties, PHOLED performance measurements and structural characterization from single crystal data.

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## 1. Introduction

Organic Light Emitting Diodes (OLEDs) received great attention during the last two decades due to potential applications in flat panel displays and solid state lighting [1–10]. The introduction of phosphorescent emitters by Forrest et al. in 1998 [11,12] significantly enhanced the efficiency of OLEDs due to the fact that phosphorescent transition metal emitters harvest singlet and triplet excitons simultaneously. Thus, phosphorescent OLEDs (PHOLEDs) can theoretically achieve 100% internal quantum efficiency [13,14].

In fact, triplet emitters have to be dispersed in an organic host matrix to avoid concentration quenching [15,16]. Bipolar host materials proved to be especially useful due to balanced charge transport properties resulting in simplified device structure and broader recombination zones [7,17,18]. To efficiently confine triplet excitons on the dopant higher triplet energies ( $E_T$ ) of the host materials compared to the phosphorescent dopant are required [19–21]. However, the combination of p- and n-type moieties in a molecule significantly decreases the triplet energy of host materials [7,17].

Therefore, the molecular design of bipolar host materials focuses on the interruption of the conjugated  $\pi$ -system to reduce the donor–acceptor interaction [7,10,17]. While aiming for increased triplet energies of host materials, the enhancement of singlet energies should be limited in order to achieve the desired device performances. Thus,

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methodologies to independently tune singlet and triplet energies are highly desirable.

Recently, we reported on the concept of planarizing tri-arylamine (TAA) donor structures in TAA–oxadiazole–TAA based materials significantly enhancing the *ortho*-linkage effect [22]. Utilizing phenylcarbazole (PCz) resulted in **o-PCzPOXD** as an efficient bipolar host material for green [Ir(ppy)<sub>3</sub>] PHOLEDs with a remarkably low efficiency roll off. However, lower efficiencies were observed in blue (Flrpic) devices as a consequence of a slightly lower  $E_T$  value (**o-PCzPOXD** = 2.62 eV) compared to Flrpic (=2.65 eV [7]).

The objective of this work is to increase the  $E_T$  values of **o-PCzPOXD** while retaining low driving voltages and high power efficiencies in the device by elevating the singlet energy ( $E_S$ ) less pronounced. This task is being tackled by sterically induced torsion introducing methyl groups at specific sites of the PCz core (Scheme 1) in order to reduce the overall electronic conjugation. Hence, due to the widespread applications of TAA donor structures in many fields of material science the strategy is of general interest for the design of novel donor–acceptor scaffolds. In addition, a distinct correlation between the molecular structures and the observed material properties is revealed.

## 2. Materials and methods

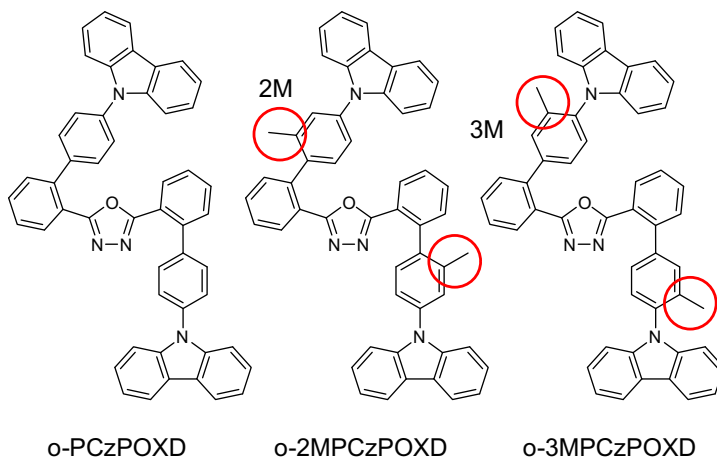
### 2.1. General information

All reagents and solvents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were prepared by filtration through drying columns. Column chromatography was performed on silica 60 (Merck, 40–63  $\mu\text{m}$ ). NMR spectra were recorded on a Bruker Avance DRX-400 Spectrometer or a Bruker Avance 200 Spectrometer. High resolution mass spectra (HRMS) were obtained from a Thermo Scientific LTQ Orbitrap XL hybrid FTMS (Fourier Transform Mass Spectrometer) and Thermo Scientific MALDI LTQ Orbitrap interface;  $\alpha$ -cyano-4-hydroxycinnamic acid was used as matrix. Thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out with a heating rate of 5 K/

min in a flowing argon atmosphere (25 ml/min). For the TG measurements, a Netzsch TG 209 F9 Tarsus system with open aluminum oxide crucibles was used. For the DSC measurements, a Netzsch DSC 200 F3 Maia, working with aluminum pans with pierced lids, was employed. UV/VIS absorption and fluorescence emission spectra were recorded in DCM solutions (5  $\mu\text{M}$ ) with a Perkin Elmer Lambda 750 spectrometer and an Edinburgh FLS920, respectively. Time resolved experiments were obtained using a Quantel Brilliant tripled Nd-YAG laser (355 nm, 20 Hz repetition rate, pulse width  $\sim$ 5 ns). Spectra were measured using a SPEX 270 monochromator equipped with both photomultiplier and CCD. This set-up is controlled using a home-built Labview-based program which allows using different instruments such as photon counting, oscilloscope, and additional mechanical shutters. For the measurement of the triplet emission, a mechanical shutter was triggered by the pulsed laser. A pretrigger period of 0.5 ms was followed by a 1 ms aperture and a rest time of 300–500 ms allowed obtaining the measurements shown in the [Supplementary Material](#). The slit of the monochromator was also opened further (up to 0.5 mm) to measure the triplet emission. Cyclic voltammetry was performed using a three electrode configuration consisting of a Pt working electrode, a Pt counter electrode and an Ag/AgCl reference electrode and a PGSTAT128 N, ADC164, DAC164, External, DI048 potentiostat provided by Metrohm Autolab B.V. Measurements were carried out in a 0.5 mM solution in anhydrous DCM with  $\text{Bu}_4\text{NBF}_4$  (0.1 M) as supporting electrolyte. The solutions were purged with nitrogen for 15 min prior to measurement. HOMO energy levels were calculated from the onset of the oxidation peaks. The onset potential was determined by the intersection of two tangents drawn at the background and the rising of the oxidation peaks.

### 2.2. Synthetic details

9-(4-Bromo-3-methyl-phenyl)-9H-carbazole (**1**) [23] and 2,5-bis(2-bromophenyl)-1,3,4-oxadiazole (**8**) [24] were synthesized according to previously published procedures whereas 1-fluoro-2-methyl-4-nitrobenzene (**3**) was



**Scheme 1.** Molecular structure of **o-PCzPOXD**, **o-2MPCzPOXD** and **o-3MPCzPOXD**.

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