

**Nearly 100% horizontal dipole orientation and up-conversion efficiency in blue thermally activated delayed fluorescent emitters**

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**Abstract**

The relationship between anisotropic orientation and molecular structure of thermally activated delayed fluorescent (TADF)-based organic light emitting devices (OLEDs) was studied using TADF emitters with carbazole, biscarbazole, and triscarbazole donor units. The bicarbazole and triscarbazole donors were more effective than the carbazole donor in driving the anisotropic orientation of the TADF molecules. A near-perfect in-plane orientation of the TADF dipole moment was demonstrated using the triscarbazole donor. In addition, the triscarbazole donor based OLED

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showed high photoluminescence quantum yield and an up-conversion efficiency close to 100%. As a consequence, an external quantum efficiency > 30% was obtained.

Keywords: blue device·delayed fluorescence·triscarbazole·efficiency·donor

## Introduction

Recently there has been significant progress in improving the external quantum efficiency (*EQE*) of thermally activated delayed fluorescent (TADF) devices since the demonstration of *EQE*  $\approx$  20% in organic light-emitting diodes (OLEDs).<sup>[1-5]</sup> Today, the highest *EQE* of red, green and blue TADF OLEDs currently stand at 17.5, 31.2, and 36.7%, respectively.<sup>[2,6-7]</sup> In the development of high efficiency TADF OLEDs, advances in device performance were mainly achieved by engineering the donor and acceptor groups of the emitting molecules.<sup>[8-10]</sup> The combination of strong donors and acceptors has resulted in the complete harvesting of all excitons generated in both singlet and triplet excited states.<sup>[11]</sup> Representative donor moieties such as dimethylacridine, dicarbazolylcarbazole, di(diphenylaminocarbazole) efficiently harvest the excited states. Carbazole-based donor moieties have a strong donor character by combining multiple donor units, and the dimethylacridine moiety is an intrinsically strong donor.<sup>[12-15]</sup> These groups narrow the singlet-triplet energy gap ( $\Delta E_{ST}$ ) and thus lead to enhanced efficiency in green and blue TADF emitters. The donors have also shown a tendency for their molecular transition dipole moments to preferentially align in the in-plane (horizontal) direction relative to the substrate.<sup>[16-18]</sup> For example, 2,4-bis{3-(9*H*-carbazol-9-yl)-9*H*-carbazol-9-yl}-6-phenyl-1,3,5-triazine (CC2TA) which features the carbazolylcarbazole donor shows a preferred horizontal dipole orientation in vacuum-deposited CC2TA:DPEPO films.<sup>[16,19]</sup> Also, dimethylacridine-derived 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (DMAC-TRZ) has also shown horizontal alignment.<sup>[20]</sup> However, correlations between

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the molecular structure and the dipole orientation was not established.<sup>[21-23]</sup> Furthermore, the CC2TA emitter showed low *EQE* despite its horizontal dipole orientation<sup>[16]</sup>.

Carbazole, biscarbazole, and triscarbazole were adopted as donor units in TADF emitters to study effects of the donor on dipole orientation. We demonstrate that carbazole cannot induce dipole orientation of the TADF emitters, whereas biscarbazole and triscarbazole can. The *EQE* of OLEDs employing rod-like triscarbazole donor-derived emitters achieve *EQE* > 30% due to their near-perfect in-plane orientation. The strong donor character of the triscarbazole results in a uniform distribution of the electron density in the highest occupied molecular orbital, and hence a high photoluminescence (PL) quantum yield. Furthermore, the donor structure leads to a relatively short delayed fluorescence lifetime leading to efficient conversion of triplet to singlet excitons. To our knowledge, this work presents the first demonstration of the simultaneous achievement of nearly 100% horizontal dipole orientation and 100% exciton conversion efficiency in TADF-based OLEDs.

## Results and discussion

Three carbazole-based compounds studied were: 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9*H*-carbazole (CzTrz), 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9'-phenyl-9*H*,9'*H*-3,3'-biscarbazole (BCzTrz), and 9'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9,9''-diphenyl-9*H*,9'*H*,9''*H*-3,3':6',3'''-tercarbazole (TCzTrz). Selected material properties are listed in **Table 1**, and a detailed analysis is found in Supporting Information (**Figure S1 and S2**). TCzTrz was synthesized following procedures in Experimental, while the other compounds were prepared as previously reported.<sup>[30]</sup>

The geometric structures and transition dipole moments of the emitters are critical to their ability to orient in the thin film<sup>[24-25]</sup>. A rod-like extended molecular structure or planar molecular

backbone induces orientation of the dipole moment in the substrate plane.<sup>[26-27]</sup> The three emitting molecules contain different donor moieties that are compared in **Figure 1**. The dihedral angles between the donor and the phenyl link between the donor and acceptor moieties were 51.8, 50.7, and 50.1° for CzTrz, BCzTrz and TCzTrz, respectively, indicating similar distortion of the donor unit in all three molecules. In the case of the BCzTrz and TCzTrz, the dihedral angles between the carbazole units were 39.4°, and 38.6°, indicating the presence of a small distortion between the carbazole units. Therefore, BCzTrz and TCzTrz have an extended donor structure that may induce anisotropic horizontal orientation, as found in other fluorescent molecules.<sup>[17]</sup>

The transition dipole moments of the optimized geometries of the three compounds were calculated using time dependent density functional theory based on the B3LYP 6-31 basis set. CzTrz, BCzTrz and TCzTrz showed dipole moments preferentially oriented along the molecular axis of the donor-acceptor structure perpendicular to the carbazole unit (see **Figure 2**). Thus, the transition dipoles lie in the same plane as the donor units.

**Figure 3** shows the dipole alignment measurements of the three compounds analyzed using angle-dependent photoluminescence (PL)<sup>[16]</sup>. The emitters were doped in bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) at a concentration of 10 wt%. The horizontal-to-vertical dipole alignment ratios relative to the substrate of TCzTrz, BCzTrz and CzTrz were  $\theta_{hor} = 0.95 \pm 0.02$ ,  $0.89 \pm 0.02$ , and  $0.66 \pm 0.01$ , respectively<sup>[13]</sup>. The order of the horizontal dipole ratio was, therefore: TCzTrz > BCzTrz > CzTrz, indicating that the triscarbazole and bicarbazole donor moieties lead to preferential in-plane alignment compared to carbazole due to the rod-like extended molecular structures of the former donor units. As the transition dipole moment of the emitter lies in the acceptor plane and the donor is in the same plane, the rod-like donors induce the anisotropic orientation of the emitters.<sup>[16]</sup>

**Figure 4** shows the *EQE* of the CzTrz, BCzTrz and TCzTrz-based OLEDs with the emitters doped at 10 wt% in DPEPO. The rather high 10 wt% doping concentration was used since carriers are balanced by hole hopping through the emitters. Current density, voltage and luminance data are presented in SI (**Figure S3**). The maximum *EQE* of the CzTrz-, BCzTrz-, and TCzTrz-based devices were  $4.2 \pm 0.04$ ,  $23.6 \pm 0.24$ , and  $31.8 \pm 0.31\%$ , respectively. As expected, a relatively high *EQE* was obtained in the TCzTrz-based OLED compared with the CzTrz device. In general, the *EQE* of the TADF devices is a function of the PL quantum yield, horizontal dipole ratio, and triplet up-conversion efficiency. The PL quantum yields of CzTrz, BCzTrz, and TCzTrz under a N<sub>2</sub> atmosphere were  $0.71 \pm 0.01$ ,  $0.96 \pm 0.02$ , and  $0.99 \pm 0.02$ , respectively, which follows the order of *EQE* of the OLEDs. From the PL quantum yield under an oxygen/nitrogen ratio of CzTrz (0.68/0.71), BCzTrz (0.70/0.96), and TCzTrz (0.76/0.99) in **Table 1**, the up-conversion efficiencies of triplet excitons in the three emitters were calculated to be  $9.5 \pm 1.9$ ,  $88 \pm 5.3$ , and  $96 \pm 4.6\%$ , respectively<sup>[13]</sup>. The high up-conversion efficiency of the TCzTrz is due the short delayed fluorescence lifetime as presented in **Table 1**. For CzTrz material, very little delayed fluorescence was observed since the carbazole donor does not lead to a significant reduction in  $\Delta E_{ST}$ .

Combining the PL quantum yield, the up-conversion efficiency, and out-coupling factor related to the horizontal dipole orientation (**Figure 5**), the *EQE* for the three OLEDs was calculated based on the dyadic Green's function analysis<sup>[28-29]</sup>. The maximum calculated *EQEs* of the CzTrz, BCzTrz, and TCzTrz devices were  $9.0 \pm 0.6$ ,  $27.3 \pm 1.3$ , and  $35.4 \pm 1.3\%$ , respectively. Although there is some discrepancy between the calculated and measured *EQEs* possibly due to electrical losses not accounted for in the simulations, the *EQEs* were nevertheless similar to within experimental and theoretical accuracies.

Electroluminescence spectra of the devices are shown in **Figure 6**. Blue emission spectra were observed and the order of peak wavelengths was TCzTrz (496 nm) > BCzTrz (485 nm) > CzTrz (449 nm). Color coordinates of the CzTrz, BCzTrz and TCzTrz devices were (0.17,0.11), (0.23,0.42) and (0.20,0.44), respectively. Performances of the CzTrz, BCzTrz, and TCzTrz OLEDs are summarized in **Table 2**.

## Conclusions

We have demonstrated a direct correlation between the molecular structure of the donor moiety of vacuum deposited TADF emitting molecules with their anisotropic dipole orientation in OLEDs in which they were employed. Triscarbazole donor units were shown to be effective in inducing a nearly perfectly aligned horizontal dipole relative to the substrate plane. Moreover, the triscarbazole donor unit results in nearly complete up-conversion of triplet excitons to singlet excitons. As a result of these factors, the triscarbazole donor-based TCzTrz TADF emitter showed  $EQE = 31.8 \pm 0.31\%$  when employed in OLEDs. These results point to the advantages of designing molecules with extended molecular donor moieties to achieve high efficiency through dipole alignment and high luminance efficiencies for emission across the visible spectrum.

## Experimental

### General information

2-Chloro-4,6-diphenyl-1,3,5-triazine, 3-bromo-9H-carbazole and 3,6-dibromo-9H-carbazole were purchased from Sun Fine Global Co. Ltd., tetrakis(triphenylphosphine)palladium(0) and (9-

phenyl-9H-carbazol-3-yl)boronic acid from P&H tech Co., sodium hydride and (4-fluorophenyl)boronic acid from Alfa Aesar Co., 9H-carbazole and dimethylsulfoxide-d<sub>6</sub> from Sigma-Aldrich Co. LLC., N,N-dimethylformamide (DMF, from Duksan Sci. Co.), and tetrahydrofuran (THF, from Samchun pure chemical Co. Ltd). Information regarding analytic methods was provided previously.<sup>[30]</sup>

### Synthesis

#### 9'-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9''-diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (TCzTrz)

Sodium hydride (0.09 g, 0.23 mmol) was poured into a round-bottomed flask and stirred after vacuum drying for 2 h. 9''-Diphenyl-9H,9'H,9''H-3,3':6',3''-tercarbazole (1.00 g, 0.15 mmol) was dissolved in DMF (6 ml), and slowly injected into the reaction vessel. 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (0.40 g, 0.23 mmol) dissolved in DMF (10 ml) was slowly added to the reaction and stirred for 1 h. The reaction was quenched using distilled water, and the yellow-colored precipitate was filtered. The precipitate was further purified by column chromatography using an eluent of MC and HEX 1:1 (0.8 g, yield 55%).

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 8.22 (d, 2H, J=7.0 Hz), 7.71 (t, 4H, J=8.25 Hz), 7.43-7.32 (m, 14H), 7.27 (t, 4H, J=7.5 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 158.3, 140.8, 139.5, 131.3, 126.3, 123.7, 122.4, 120.5, 120.4, 118.0, 117.8, 109.9. MS (APCI) *m/z* 958.0 [(M + H)<sup>+</sup>].

### **Device fabrication and measurements**

The OLED structure is indium tin oxide (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/emitting layer (25 nm)/TSPO1 (5 nm)/TPBi (20 nm)/LiF (1.5 nm)/Al (200 nm), where PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), TAPC was 1,1-bis [(di-4-tolylamino) phenyl] cyclohexane, mCP is 1,3-di(9*H*-carbazol-9-yl)benzene, TSPO1 is diphenylphosphine oxide-4-(triphenylsilyl), and TPBi is 1,3,5-tris-(2-*N*-phenylbenzimidazolyl)benzene. The emitting layer comprises a DPEPO film doped with 10 wt% TADF molecules. All devices were fabricated under high vacuum ( $<1.0 \times 10^{-7}$  torr). Current density-voltage-luminance (*J-V-L*) characteristics were carried out using an electrical and photometric measurement system equipped with a Keithley 2400 sourcemeter (Keithley Instruments, Inc) for *J-V* measurement and a CS 2000 (Konica Minolta Inc.) spectro-radiometer.

### **Optical measurements.**

Alignments of the transition dipole moments are inferred from angle dependent p-polarized emission<sup>[31-32]</sup>. The substrate was placed perpendicular to the plane of detection and the emission is outcoupled from the substrate using a 2 cm radius, half-cylindrical lens. The emission along the plane of detection was decomposed into transverse electric (*TE*) and magnetic (*TM*) modes using a polarization analyzer. A motorized stage was used to position the detector. Simulations of the angular intensity profiles are based on the dyadic Green's function in a birefringent medium<sup>[28]</sup>. A least-squares algorithm was used to fit the experimental data to the simulation. The refractive indices and extinction coefficients of materials were measured using variable-angle spectroscopic ellipsometry.



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**Table 1.** Selected properties of CzTrz, BCzTrz and TCzTrz

	$\lambda_{\text{abs}}$ (nm)	$E_g$ (eV)	$E_S^{\text{a}}$ (eV)	$E_T^{\text{b}}$ (eV)	$\Delta E_{\text{ST}}$ (eV)	HOMO/ LUMO <sup>c</sup> (eV)	$\Phi^{\text{d}}$ (%)	$\tau^{\text{e}}$ ( $\mu\text{s}$ )	$k_{\text{ISC}}^{\text{f}}$	$k_{\text{RISC}}^{\text{f}}$	$\Theta_{//}^{\text{g}}$ (%)
<b>CzTrz</b>	265/360	3.14	3.18	2.82	0.36	-6.04/-3.39	71 (68)	N/A	N/A	N/A	66
<b>BCzTrz</b>	265/372	2.94	2.83	2.79	0.04	-5.80/-3.24	96 (70)	31.2	$2.46 \times 10^7$	$5.49 \times 10^4$	89
<b>TCzTrz</b>	273/385	2.84	2.73	2.72	0.01	-5.75/-3.41	99 (76)	23.6	$2.22 \times 10^7$	$5.34 \times 10^4$	95

<sup>a)</sup> Singlet energy derived from onset of the fluorescence spectra of 10 wt% TADF emitter-doped DPEPO films. <sup>b)</sup> Triplet energy derived from onset of the phosphorescence spectra of 10 wt% TADF emitter-doped DPEPO films at 77 K. <sup>c)</sup> HOMO and LUMO energies using cyclic voltammetry, with internal standard of ferrocene. <sup>d)</sup> Absolute PL quantum yield measured under nitrogen and oxygen atmosphere. <sup>e)</sup> Excited state lifetime for 10 wt% TADF emitter-doped DPEPO films at room temperature. <sup>f)</sup> Calculated rate constant derived from 10 wt% emitter doped DPEPO films. <sup>g)</sup> Horizontal orientation ratio for 10 wt% TADF emitter-doped DPEPO films.

**Table 2.** Summary of performances of CzTrz-, BCzTrz- and TCzTrz-based OLEDs.

	External quantum efficiency (%)		Power efficiency (lm/W)		Current efficiency (cd/A)		Color coordinates	
	[1000 cd/m <sup>2</sup> ]	[Max]	[1000 cd/m <sup>2</sup> ]	[Max]	[1000 cd/m <sup>2</sup> ]	[Max]	x	y
<b>CzTrz</b>	0.6	4.2	0.1	2.7	0.53	3.8	0.17	0.11
<b>BCzTrz</b>	5.2	23.6	3.5	46.6	11.8	53.3	0.23	0.42
<b>TCzTrz</b>	11.3	31.8	10.0	61.5	39.4	86.4	0.20	0.44

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**Scheme 1.** Synthetic scheme of CzTrz, BCzTrz and TCzTrz.

**Figure 1.** Molecular and geometrical structures of the CzTrz, BCzTrz and TCzTrz optimized by density functional theory simulations. Dihedral angles of the chemical bonds are noted in the geometrical structures.

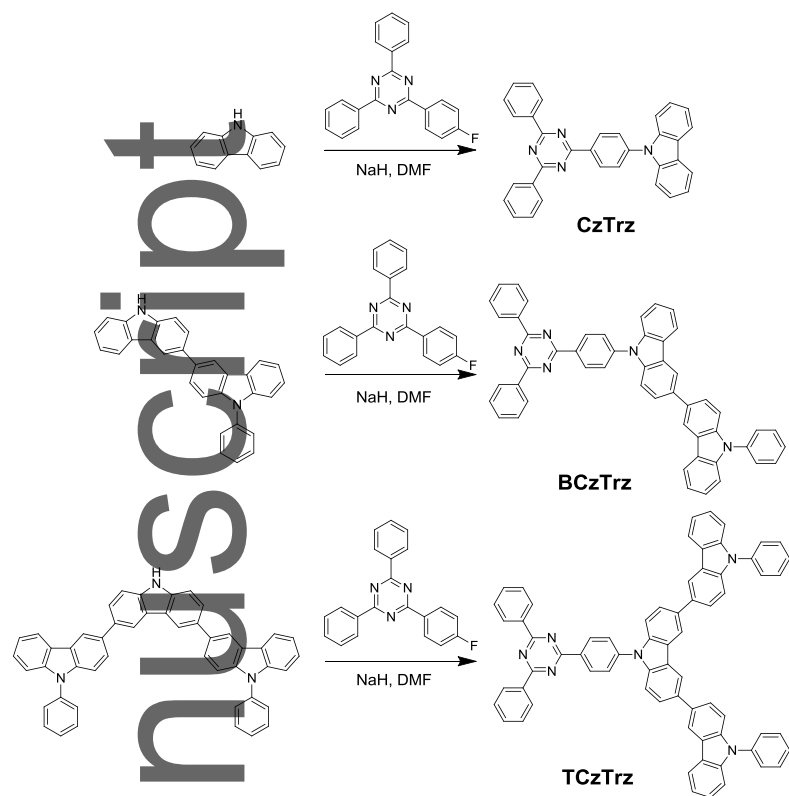
**Figure 2.** Direction and relative strengths (from arrow lengths, **Table 1**) of the transition dipole moments of CzTrz, BCzTrz and TCzTrz calculated by density functional theory.

**Figure 3.** Measured horizontal transition dipole moment ratio of (a) CzTrz, (b) BCzTrz, and (c) TCzTrz (data points) obtained using angle-dependent PL data and calculated by optical simulation (lines). Simulated angle-dependent photoluminescence intensity of isotropic and horizontally oriented emitters dipoles are also shown.

**Figure 4.** External quantum efficiency vs. luminance of (a) CzTrz, (b) BCzTrz and (c) TCzTrz OLEDs at a TADF doping concentration of 10 wt% in DPEPO.

**Figure 5.** Simulations of the external quantum efficiencies of (a) CzTrz, (b) BCzTrz and (c) TCzTrz, vs. hole (HTL) and electron transport layer (ETL) thicknesses of the OLEDs. The experimental OLEDs are indicated by 'X'.

**Figure 6.** Electroluminescence spectra of CzTrz, BCzTrz and TCzTrz-based OLEDs at a luminance of 1000 cd/m<sup>2</sup>. Doping concentration of the TADF emitters is 10 wt% in DPEPO.



Scheme 1

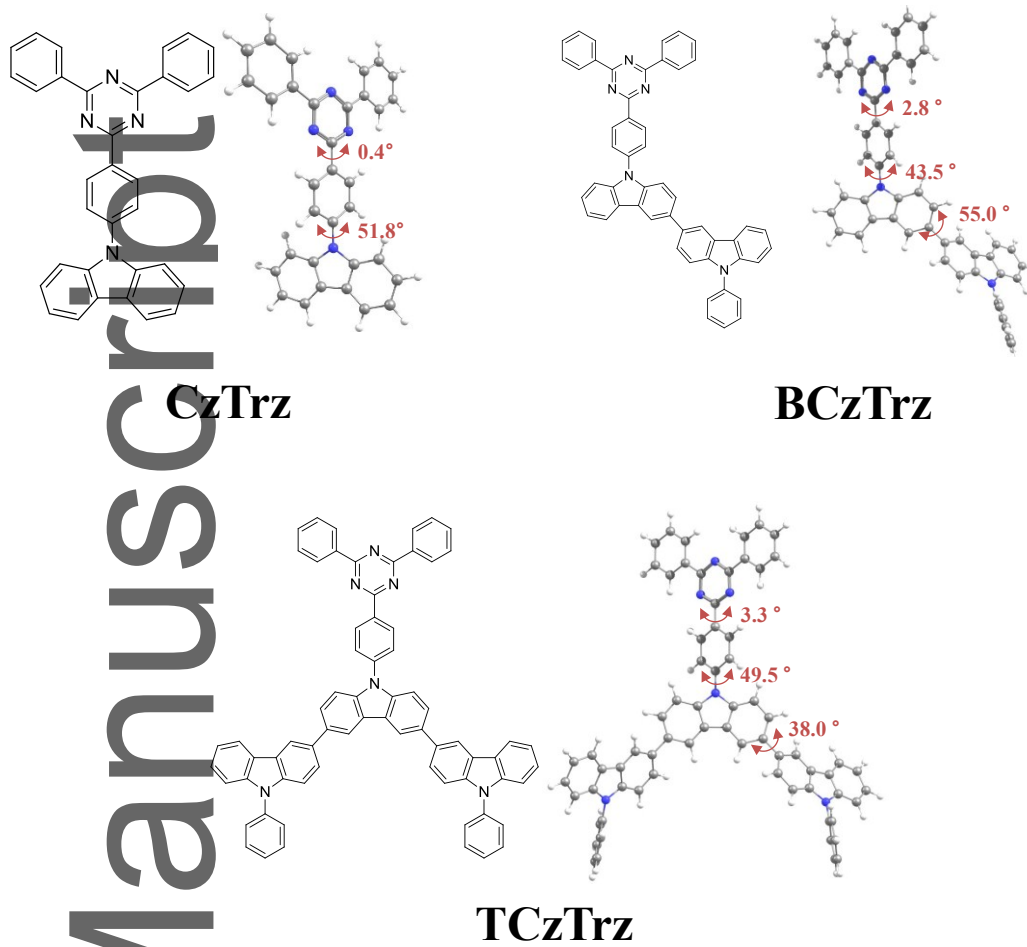


Figure 1

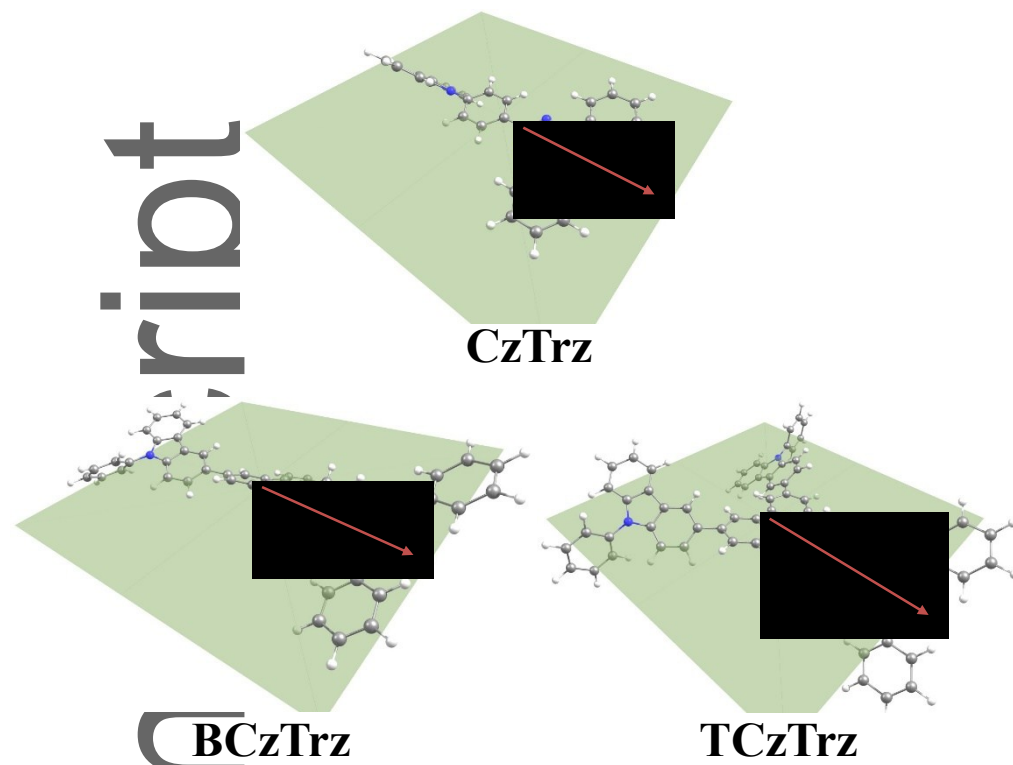


Figure 2



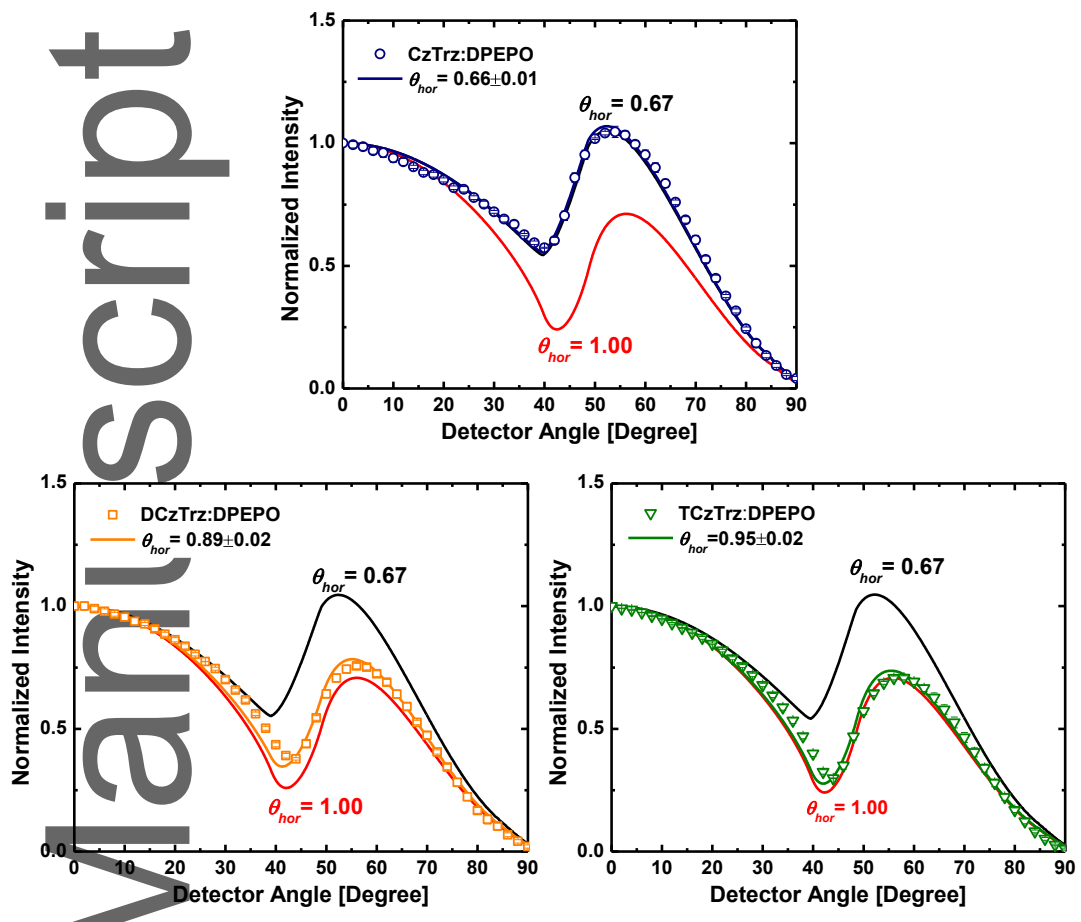


Figure 3

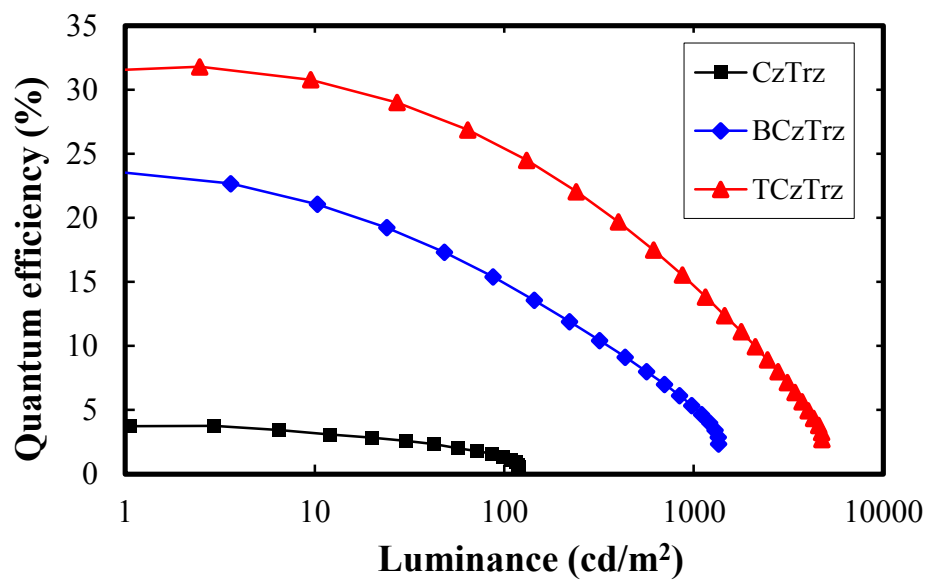


Figure 4

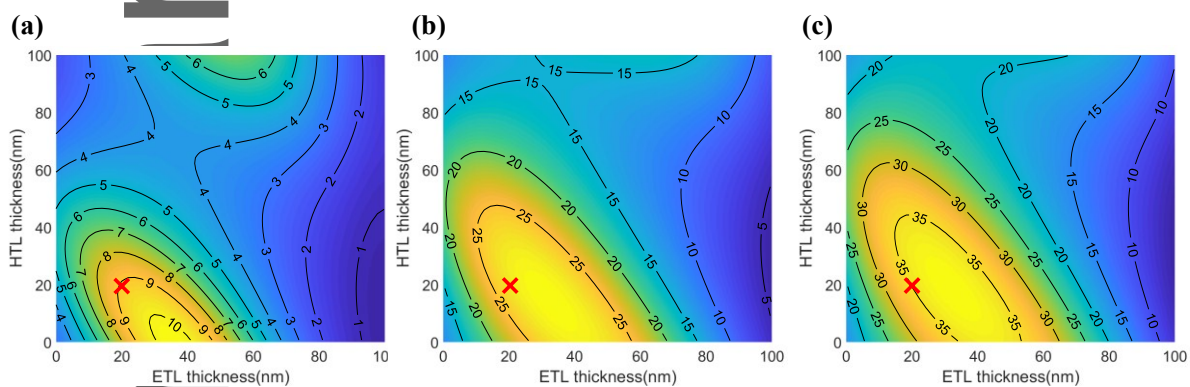


Figure 5

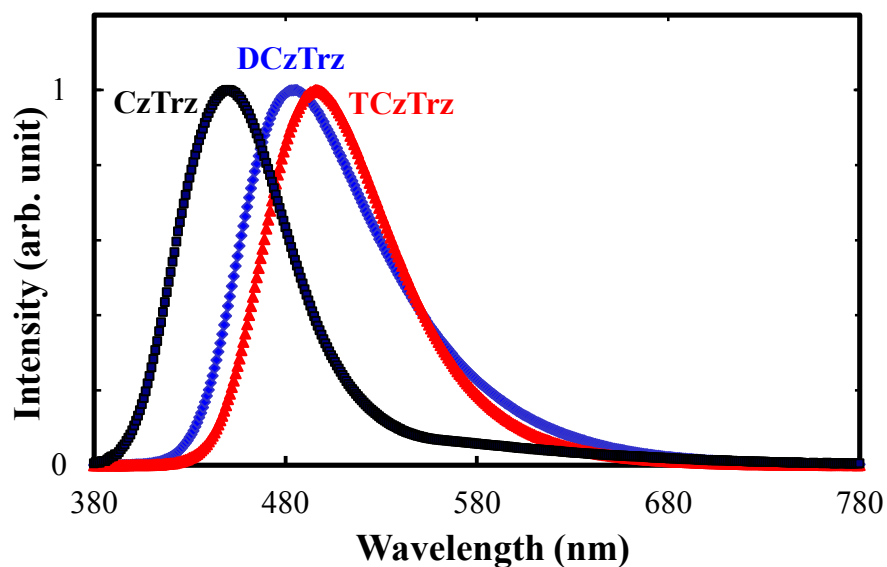
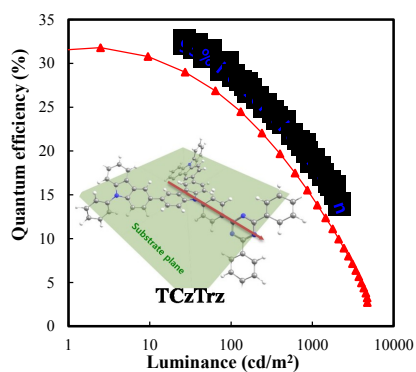


Figure 6



A systematic study correlating donor structure with horizontal dipole orientation of blue triscarbazole thermally activated delayed fluorescent emitters show an exceptionally high horizontal dipole orientation of 95%. The dipole orientation and high photoluminescence quantum yield result in an external quantum efficiency > 30%.