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# Thermally Activated Delayed Fluorescence from Azasiline Based Intramolecular Charge-Transfer Emitter (DTPDDA) and a Highly Efficient Blue Light Emitting Diode

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**ABSTRACT:** For electroluminescence with delayed fluorescence, the azasiline unit has been introduced for the first time as a donor in a thermally activated delayed fluorescence (TADF) material. The TADF material (DTPDDA) shows strong intramolecular charge transfer (CT) character with large spatial separation with the acceptor of triazine leading to narrow splitting of singlet and triplet excited states for the efficient reverse intersystem crossing (RISC). A blue organic light emitting diode (OLED) based on DTPDDA not only displays deep blue in the Commission Internationale de L'Eclairage (CIE) coordinates of (0.149, 0.197) but also exhibits a high external quantum efficiency (EQE) of 22.3% which is the highest value ever reported for a blue fluorescent OLED. Theoretical prediction based on transient photoluminescence (PL) and optical simulation result agrees well with the achieved EQE indicating the successful conversion of triplet excitons to singlet in the blue fluorescent OLED by using DTPDDA.

#### ■ INTRODUCTION

Enhancing electroluminescence (EL) efficiency might be never ending pursuit from displays to lightings where organic light emitting diodes (OLEDs) are being used. For past years, phosphorescent OLEDs (PhOLEDs) based on heavy metal complexes have been considered as an only solution to realize high efficiencies by harvesting both singlet and triplet excitons as light.<sup>1-7</sup> However, recently reported OLEDs utilizing delayed fluorescence challenged the conventional idea of achieving high EL efficiencies and has demonstrated an equal performance to PhOLEDs by achieving 30% external quantum efficiency (EQE).<sup>8-n</sup> There are two different mechanisms that drive fluorescence, which are delayed triplet-triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF).<sup>12-13</sup> Fluorescent materials showing TADF enables additional harvest of triplet excitons as well as singlet excitons to light via thermally activated reverse intersystem crossing (RISC) from triplet (T<sub>1</sub>) to singlet (S<sub>1</sub>) state due to small charge transfer singlet-triplet state splitting ( $\Delta E_{ST}$ ).

Replacing phosphorescent materials by efficient TADF materials will eventually lower cost with the potential of

clearing stability issues. Especially, blue dyes among the three primary colors have been considered as the most crucial ones due to their important role in generating white light with good color purity. So far, blue fluorescent materials are being used for commercial OLEDs in spite of their low efficiency due to short device lifetime of phosphorescent blue OLEDs. Even with such importance, there are only a few reports on efficient blue TADF materials which meet both the high EL efficiency and color purity up to now. TADF materials are charge transfer (CT) type emitters which are composed of electron donating and accepting units to have small but a certain degree of overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) to minimize the singlet-triplet energy gap, yet still to have large enough radiative transition rate. Carbazole and dimethyl dihydroacridine have been mainly used as the donor moieties and sulfone oxide and triazine as the acceptor unit in the blue TADF molecules. However, it seems quite challenging to search for an appropriate combination of donor and acceptor moieties to achieve good color purity and high EL efficiency for blue fluorescent OLEDs at the same time. Even a highly efficient blue fluorescent OLED of 20.6%

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was reported recently yet the OLED displayed sky-blue light with the CIE coordinates of (0.19, 0.35).



**Figure 1.** (a) Chemical structure of DTPDDA. DFT calculation data: (b) Molecular structure of DTPDDA. (c) HOMO level at the phenyl-dibenzo azasiline unit. (d) LUMO level at the triphenyl triazine unit.

The highest EQE ever reported in deep blue fluorescent OLEDs, in terms of CIE Y value below o.2, was ~19.5%, which is still lower than the achieved EQE in this work.<sup>14-</sup><sup>19</sup> In this article, we have utilized a new donor unit of azasiline group to synthesize a deep blue TADF dye, 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azasiline (DTPDDA). An efficient blue fluorescent OLED with an unprecedented high EQE of 22.3% was fabricated by doping the TADF material in a mixed co-host system. The device emitted deep blue with the CIE coordinates of (0.149, 0.197). The comparison with the theoretical prediction of the EQE

indicated that the RISC is efficient in the molecule to convert almost all the triplet excitons to the singlet excitons and the device has little electrical loss.

#### RESULTS AND DISCUSSION

The azasiline has 6-membered heterocyclic structure which is composed of a nitrogen atom, two aromatic carbon-carbon  $\pi$ -bonds and a silicon atom. The azasiline unit was introduced for the first time in this article as a donor in the donor-acceptor type molecule to lower HOMO energy level by using silicon connection instead of carbon connection, thereby to enlarge the energy gap between the HOMO and LUMO states for blue emission.<sup>20</sup> Also, the azasiline unit is spatially separated from the triazine unit, leading to the low  $\Delta E_{ST}$ .

The introduction of silicon atom in a bridge between adjacent aromatic groups has several beneficial effects. Unlike carbazole unit, the azasiline unit has more rigidity and bulkiness resulting in large dihedral angle due to its sp<sub>3</sub> bridge. Rigid tetravalent silicon bridge structure offers morphological stability and reduces the conformation disorder, which can increase efficiency due to decrease in vibronic transitions.<sup>21</sup> Moreover, since silicon-carbon bond is slightly longer than a carbon-carbon bond, the

anti-bonding lobes located on the butadiene fragments adjacent to the silicon bridge are separated further from each other, which ultimately should lead to a reduction of the HOMO energy level.<sup>22</sup> The reduction of HOMO energy level can increase band gap, leading to deep blue emission.

Prior to synthesis of the blue fluorescent material with the chemical structure described in Figure 1a, the quantum chemical properties of the molecule have been investigated through the density functional theory (DFT) calculation. Firstly, the geometry optimization (Figure 1b) and the energy levels of the compound and Kohn-Sham orbitals of the HOMO (Figure 1c) and the LUMO states (Figure 1d) were calculated through the DFT calculation. Then, Singlet and triplet energies of DTPDDA were calculated with optimized geometry using the timedependent(TD)-DFT. The details of calculation method were explained in experimetal section. The result showed that the HOMO and LUMO of DTPDDA are separated distinctively on two different units: the phenyl-dibenzo azasiline and the triphenyl triazine, respectively, by distorting 92~93° of dihedral angle. The TD-DFT calculation predicted the  $\Delta E_{ST}$  of 0.01 eV, indicating that the separation of Kohn-Sham orbitals of HOMO and LUMO lowered the exchange energy to enhance the RISC. However, the HOMO and LUMO levels were weakly overlapped in the phenyl unit, which is known to increase radiative transition rate.<sup>8</sup> As the HOMO of DTPDDA is distributed over the azasiline unit while the LUMO resides at the triphenyl triazine unit at the other side of DTPDDA molecule, the replacement of a carbon bridge with silicon in the phenyl-dibenzo azasiline resulted in deepening the HOMO level of DTPDDA consequently enlarging the bandgap of DTPDDA, which is desired for blue emission. To further demonstrate the benefit of having azasiline unit, HOMO and LUMO levels of DTPDDA and 2-phenoxazine-4,6-diphenyl-1,3,5-triazine (PXZ-TRZ) were compared through DFT calculation.<sup>23</sup> DTPDDA and PXZ-TRZ have same acceptor unit as diphenyl-triazine, but different donor units. DTPDDA with an azasiline unit has 0.5 eV lower HOMO level than PXZ-TRZ with phenoxazine unit owing to a silicon bridge in the moiety. (Table S1)

Overall, from the DFT calculation, DTPDDA was expected to be an efficient CT type emitter for blue fluorescent OLEDs.

The synthetic scheme of the new blue emitting material is shown in Scheme 1. The Buchwald-Hartwig amination was carried out to obtain bis(2-bromophenylamine).<sup>24-26</sup> The proton of amine group was blocked by 4-methoxybenzyl group, and the cyclization for azasiline was carried out by nucleophilic substitution of dilithiated compound.

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Scheme 1. Synthetic Scheme of DTPDDA.

After deblocking reaction, the new emitting material, 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azasiline (DTPDDA), was obtained by the Buchwald-Hartwig amination between 2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine and 10,10diphenyl-5,10-dihydrodibenzo[b,e][1,4]azasiline.

The basic synthetic scheme of azasiline unit as well as the material itself has never been introduced nor considered application for an for OLED materials or electroluminescence up to now to our best knowledge. The phenomenon of cyclization forming diphenylsilynene through desulfurization was reported back in 1960s yet none of them demonstrated the same unit or the same synthetic scheme of the blocking and deblocking reaction.<sup>27</sup> Furthermore, the spatial separation of the two different moieties of the triazine and the azasiline units is firstly reported in this study. DTPDDA displays good thermal stability with the decomposition temperature (Td: temperature at 5% weight loss to initial weight) close to 404°C and the high glass transition (Tg) of 325°C determined from the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurement under nitrogen atmosphere (Figure S5-6). HOMO and LUMO levels were calculated to be -5.57 eV and -2.80 eV  $(HOMO = -[E^{ox}_{onset}+4.43 \text{ eV}], LUMO = -[E^{red}_{onset}+4.43 \text{ eV}])$ by considering oxidation onset potential (E<sup>ox</sup><sub>onset</sub>, +1.14 V) and reduction onset potential (E<sup>red</sup><sub>onset</sub>, -1.63 V) (Figure S<sub>7</sub>, Table S2). The PL spectra of DTPDDA exhibited solvatochromic shifts as shown in Figure 2a assuring CT nature of the material.

The mixed co-host of N,N'-dicarbazolyl-3,5-benzene (mCP) and Diphenyl-4-triphenylsilylphenyl-phosphine oxide (TSPO1) with molar ratio of 1:1 was selected as an emitting layer (EML) for DTPDDA. Figure 2b shows the photoluminescence (PL) spectra of the materials used in this work. The resemblance of spectrum of mCP:TSPO1 film to mCP film can be understood from the mixed CT and locally excited (LE) states of exciplexes between mCP and TSPO1.<sup>28</sup> The PL spectra of the DTPDDA doped films **(a)** 



**Figure 2.** (a) The absorption spectrum of DTPDDA measured in toluene and PL spectra of DTPDDA in various solvents. Numbers in the brackets are the dielectric constants of the solvents. (b) The PL spectra of DTPDDA and TSPO1 measured in toluene and methylene chloride, espectively. The rest of the PL spectra of mCP, mCP:TSPO1, mCP:DTPDDA, TSPO1:DTPDDA and mCP:TSPO1:16 wt% DTPDDA were measured with 50 nm

thick films on 1 mm thick fused silicas. Inset: the chemical structures of two hosts used for EML, mCP and TSPO1  $\,$ 

of mCP:DTPDDA, TSPO1:DTPDDA and mCP:TSPO1:16 wt% DTPDDA showed the emission solely from DTPDDA without the emission from the hosts, indicating that energy transfer from the host molecules to the dopant is efficient in this system. The photoluminescent quantum yield (PLQY) of the mCP:TSPO1:16 wt% DTPDDA film was  $74 \pm 2\%$ .



**Figure 3.** (a) Prompt and delayed PL spectra of mCP:TSPO1: 16 wt% DTPDDA at 35 K. Prompt and delayed components were collected at 20 ns and 300 µs, respectively. (b) Transient PL decays of mCP:TSPO1:16 wt% DTPDDA film measured at 450 nm at temperature of 300 K and 35 K. Inset: Transient PL within the range of 0 to 50 ns after excitation. Red dotted line is the single exponential fitting with decay time of 11.8 ns for the prompt fluorescence.

Experimentally achieved  $\Delta E_{ST}$  of DTPDDA was 0.14 eV with S1 and T1 levels of 2.79 and 2.65 eV measured from the prompt and delayed PL spectra (Figure 3a) at 35 K, respectively. However, from the TD-DFT calculation, S1 and T1 levels were estimated to be 2.65 and 2.64, respectively, resulting in  $\Delta E_{ST}$  of 0.01 eV. The gap between the achieved and calculated  $\Delta E_{ST}$  can be caused by the selection of DFT calculation scheme.<sup>29</sup> The transient PL decays of the film measured at the wavelength of 450 nm showed larger delayed emission and faster decay rate at room temperature (RT) than 35 K (Figure 3b), indicating that the delayed emission is coming from a thermally activiated process consistent with the nature of TADF material.

The transient PL decays showed multiexponential decays fitted with the prompt lifetime of 11.8 ns and three delayed lifetimes of 100 ns, 2.3 µs and 25.4 µs at. The ratio of the prompt to delayed emission intensity in PL calculated from the decay pattern at RT is 0.13:0.87. Emission dipoles of DTPDDA in the mCP:TSPO1:16 wt% DTPDDA film are randomly oriented with the horizontal transition dipole ratio ( $\Theta$ ) of 0.66 characterized by theoretical fitting of the angle dependent p-polarized PL spectrum shown in Figure S1.<sup>2:30-33</sup>



**Figure 4.** (a) Schematic diagram of the device structure and energy levels (eV) of the device. (b) Contour plot of the predicted maximum EQEs as function of the thickness of HIL and EIL for blue fluorescent OLEDs. A star indicates the achieved EQE in this work.

TADF OLEDs were fabricated using mCP:TSPO1:16 wt% DPTDDA as the emitting layer. The device structure was ITO (70 nm) / 4 wt% ReO3:mCP (y nm) / mCP (15 nm) / mCP:TSPO1:16 wt% DPTDDA (15 nm) (0.42:0.42:0.16 in wt%) / TSPO1 (15 nm) / 4 wt% Rb2CO3:TSPO1 (x nm) / Al (100 nm) shown in Figure 4a. The hole injection layer (p-doped mCP, HIL) and electron injection layer (n-doped TSPO1, EIL) were inserted in the device structure to enhance charge injection, but assumed to have the same refractive indices as the un-doped layers.<sup>34-39</sup> Optical simulation was performed using the classical dipole

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58 59 60 model with the measured  $\Theta$  = 0.66 and PLQY = 0.74 of DTPDDA to predict the maximum achievable EQE of the blue fluorescent OLEDs as functions of the thickness of the HIL and EIL under the assumption of no electrical loss and all the triplet excitons are converted to the singlet excitons at RT in the device. Details of the simulation procedure was described before.<sup>2</sup>



**Figure 5**. (a) EL spectrum of the blue fluorescent OLED Inset : (top) the image of blue emission from the OLED. (bottom) A star denotes the CIE coordinate of the EL spectrum at (0.149, 0.197). (b) Current density–voltage– luminance characteristics of the OLED. Inset: Angular distribution of the EL intensity of the OLED. The solid line represents the Lambertian distribution. (c) EQE and power efficiency of the blue fluorescent OLED to current densities.

The simulation results displayed in Figure 4b indicates that maximum EQE of 22% is achievable in the blue

fluorescent OLEDs when the thicknesses of the hole and electron injection layers are 45 nm and 50 nm, respectively.

The fabricated OLED with the optimized structure emitted blue fluorescence which is 13 nm red shifted from the PL spectrum due to the cavity effect as shown in Figure 5a. The CIE coordinates of the blue fluorescence from the device is (0.149, 0.197) (inset of Figure 5a). Figure 5b and 5c show the current density@voltage@luminance (JIVIL) characteristics and the power efficiency of optimized OLED, respectively. The factor of 1.07 was used for the calibration of efficincy obtained from the broader angular distribution of the EL intensity of the OLED than the Lambertian as shown in the inset of Figure 5b. The turn-on voltage of the OLED was 3.0 V and the driving voltage was 5.7 V and 6.5 V at 1,000 cd/m2 and 2,000 cd/m2, respectively. Maximum power efficiency of the OLED was 30.4 lm/W. In comparison with the previously reported efficient blue fluorescent OLED with 20.6% EQE, the device using DTPDDA demonstrated not only higher EL efficiency but also deeper blue emission with lower turn-on voltage.17

The device exhibited the maximum EQE of 22.3%, which is by far the highest efficiency reported in blue fluorescent OLEDs with high color purity. The experimentally obtained EQE matches very well with the theoretically predicted maximum EQE indicating that the device was well optimized with little electrical loss and all the triplet excitons are converted to singlet excitons via RISC. The efficiency roll off was not so large compared to other blue TADF devices.<sup>14-19</sup> The voltages, current efficiencies, EQEs and power efficiencies of the OLED at different luminances are summarized in Table 1.

#### CONCLUSION

In this article, azasiline unit was introduced for the first time as the donor moiety to synthesize a new deep blue TADF dye, 5-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10,10-diphenyl-5,10-dihydrodibenzo[b,e][1,4]azasiline

(DTPDDA). The azasiline unit was separated spatially from the acceptor of triazine owing to large dihedral angle formed at nitrogen-carbon bridge. Replacing carbon connection by silicon connection widens the bandgap suitable for blue emission. An efficient blue fluorescent OLED with the CIE coordinates of (0.149, 0.197) was fabricated with an unprecedented high EQE of 22.3% and low efficiency roll-off by doping DTPDDA in a mixed cohost system of mCP:TSPO1. Theoretical prediction assuming the fraction of radiative exciton as unity agrees well with EQE indicating efficient harvest of triplets occuring in DTPDDA through RISC.

Voltage [V]			Current Efficiency [cd/A]			EQE [%]			Power Efficiency [lm/W]		
Turn on	1,000 cd/m²	2,000 cd/m <sup>2</sup>	Max.	1,000 cd/m²	2,000 cd/m²	Max.	1,000 cd/m²	2,000 cd/m <sup>2</sup>	Max.	1,000 cd/m²	2,000 cd/m²
3.0	5.7	6.5	35.6	17.9	13	22.3	10.6	8	30.4	9.8	5.7

Table 1. The voltage, current efficiency, EQE, and power efficiency of the OLED.

#### ■ EXPERIMENTAL SECTION

Geometry optimization and energy level of HOMO and LUMO were calculated through DFT calculations with B3LYP level of theory, the 6-31G(d) basis set for all the atoms without solvent model and singlet and triplet energies which were performed with TD-DFT calculations with Gaussiano9.<sup>40</sup>

Detailed information of the optimized molecular geometry was addressed in Table S<sub>3</sub>.

UV-vis absorption spectra and photoluminescence (PL) spectra were measured with a Shimadzu UV-1650PC spectrophotometer and LS-50B luminescence spectrophotometer, respectively. Cyclic voltammetry (CV) was performed using an EG&G Parc model 273 potentiostat/galvanostat system with a three-electrode cell in a solution containing Bu4NClO4 (0.1 M) in chloroform at a scan rate of 100 mV/s. A Pt wire was used as the counter electrode, and an Ag/AgNO3 (0.1 M) electrode as the reference electrode.

Organic films for the measurement of the PLQY and PL spectra were fabricated by thermal evaporation on precleaned quartz substrates at a base pressure of  $< 5 \times 10-7$  Torr. The PLQY was measured by using an integrating sphere. A continuous-wave He/Cd laser (325 nm) was used as an excitation light source and a monochromator-attached photomultiplier tube (PMT) was used as an optical detection system.<sup>41</sup> The PL spectra was also measured by PMT with a xenon lamp (260 nm) as an excitation light source.

Orientation of transition dipole moments was measured using a continuous wave diode laser (405 nm, Edmund optics Inc.). The incident angle of the excitation light was fixed at 45° from the plane normal direction of substrate and the p-polarized emitted light was detected at 465 nm that is close to the peak wavelength of the PL spectrum of the fluorescent dye.

The OLEDs were fabricated on clean glass substrates prepatterned with 70-nm-thick ITO under a pressure of 5210-7 Torr by thermal evaporation without breaking

thevacuum. Before the deposition of organic layers the ITO substrates were pre-cleaned with isopropyl alcohol and acetone, and then exposed to ultraviolet (UV)-ozone for 10 min. Organic layers were deposited at a rate of 1 Å/s and the deposition rate of the co-deposited layers was 1 Å/s in total. Current density, luminance, and EL spectra were measured using a programmable source meter

(Keithley 2400) and a spectrophotometer (Spectrascan PR650, Photo Research). The angular distribution of the EL was measured with a programmable source meter (Keithley 2400), goniometer, and fiber optic spectrometer (Ocean Optics S2000). The EQE and the power efficiency of the OLEDs were calculated from J-V-L characteristics, EL spectra, and the angular distribution of the EL intensity.

#### ■ ASSOCIATED CONTENT

Supporting Information Supplemental tables and figures; experimental details; synthesis and computational geometries of the investigated compounds.

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The authors declare no competing financial interest.

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