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# ARTICLE

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Abstract text goes here. While great advances have been achieved in organic electroluminescence fields, highly efficient true blue organic electroluminescence with small CIE coordinates and satisfactory color purity are still limited. Here, we practise a simple and effective molecular avenue for true blue organic electroluminescence, and the strategy is to use the biphenyl-bridging hybrids of 1,2,4-triazoles (acceptors) and various donors (D) as the emitters. The as-prepared  $D-\pi-A$ hybrid (TPATZ) containing 2,3,4-triphenyl-1,2,4-triazole and triphenylamine emits bright blue light in both solution and solid states, and the non-doped device with TPATZ as emitter exhibits true blue electroluminescence (EL) with the emission peak at 430 nm and the Commission Internationale de L'Eclairage coordinate of (0.155, 0.047). Moreover, the satisfactory EL color purity with the full width at half maximum (FWHM) of only 50 nm and the maximum external quantum efficiency of 5.92% are obtained, which is among the best true blue OLEDs reported to date. This impressive EL properties are experimentally and theoretically analyzed and emphasize that this simple D- $\pi$ -A hybrid mode is an effective molecular strategy for highly efficient true blue FL emitters.

# Introduction

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Organic luminophores have persistently attracted research attention due to their promising applications in light-emitting diodes (LEDs), fluorescent sensors and switches, and nonlinear optics.<sup>[1-6]</sup> Considering that the highly efficient phosphorescent materials are mostly expensive Ir and Pt complexes and the satisfactory deep-blue phosphorescent LEDs are not obtained, organic fluorescent emitters are recently refocused because of their unique advantages of low cost, structure diversity, fantastic flexibility, appreciable stability, and good processability.<sup>[7-10]</sup> Up to now, a large number of green, red, and light blue organic emitters with excellent electroluminescence (EL) performances have been developed by designing new principle and concept materials with thermally activated delayed fluorescence (TADF),<sup>[11]</sup> triplet-triplet annihilation (TTA),<sup>[12]</sup> hybridized local and charge transfer (HLCT) excited state,<sup>[13]</sup> triplet-polaron interaction (TPI) induced upconversion,<sup>[14]</sup> and aggregation-induced emission natures.<sup>[15]</sup> The most impressive blue OLEDs are the doped devices reported by Adachi et al. based on carbazole-cyaphenine hybrid with the maximum of (0.148, 0.098)<sup>[11b]</sup> and by Chou et al. based on a 2-(styryl)triphenylene derivative with the maximum EQE of 10.2% and CIE coordinate of (0.14, 0.14).<sup>[12b]</sup> Recently, a new method of the combinational molecular design is promising for highly efficient deep-blue emitters by Bian.<sup>[12c]</sup> However, highly efficient non-doped true blue OLEDs with small CIE coordinates (such as  $x \le 0.16$ ,  $y \le 0.06$ ), short peak emission wavelength (such as  $\lambda \leq 430$  nm), and narrow full width at half maximum (FWHM) are still limited and challenging. Such true blue EL is not only the important member of the three primary colors but also serves as the excitation light source and the host matrix to generate other emissions.[16-20] However, the true blue emission signifies the narrower band gap and smaller molecular conjugation size of organic EL emitters, which generally causes inferior charge transporting and also restrains molecular design space.<sup>[20b]</sup> As well known, integrating electron donor (D) and acceptor (A) units into a single molecule is a common way for obtaining highly efficient EL emitters, but the selection of D and A units and the linking spacer ( $\pi$ -conjugation bridge) and position can play a crucial role in determining the EL color and properties. For example, some strongly twisted D– $\pi$ –A motifs with short spacers (such as phenyl) might form TADF emitters, but the strong intramolecular charge transfer (ICT) effect has red-shifted EL to greatly deviate from true blue emissions, [21-24] whereas the incorporation of long and/or planar conjugation spacers usually extends  $\pi$ -conjugation to move the EL out of the true blue region.<sup>[25]</sup> Therefore, not any D and A combinations can certainly optimize the highly efficient true blue EL emitters,

external quantum efficiency (EQE) of 19.2% and CIE coordinate

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and these design conflicts have made the highly efficient true blue EL still scarce and challenging.

Encouragingly, preliminary progresses have been achieved recently. Tong et al. link the donors at the 6,9-positions of phenanthroimidazole to form a V-type D– $\pi$ –A hybrid and fabricate a non-doped OLED with the maximum EQE of 7.20% and CIE coordinate of (0.150, 0.063),<sup>[13e]</sup> and Li et al. synthesize the branched triazole-based  $D-\pi-A$  hybrids and obtain nondoped OLEDs with the maximum EQE of 6.3-6.8% and the CIE coordinates of (0.158, 0.038–0.043).<sup>[14c]</sup> Very recently, we have demonstrated that the simple 3,4,5-triphenyl-1,2,4-triazole-9phenylcarbazole hybrid (PCZTZ) can fabricate the non-doped OLED emitting near-ultraviolet EL (408 nm) with the maximum EQE of 6.6% and CIE coordinate of (0.17, 0.07).<sup>[26]</sup> Moreover, PCZTZ is found to exhibit high and balanced hole and electron mobilities up to 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This signifies that triaryltriazoles are weak electron-withdrawing and good electrontransporting units, and the distorted structure is favor of solidstate fluorescence. In the current work, we further design and facilely synthesize a new 1,2,4-triazole-based D- $\pi$ -A hybrid (TPATZ) with triphenylamine (TPA) as the donor. It is found that the non-doped OLEDs still display true blue emission with the CIE coordinate of (0.155, 0.047) and a narrow FWHM of 50 nm although TPA is a strong donor unit and can red shift the emission. Moreover, the maximum EQE is up to 5.92% and among the best true blue OLEDs reported to date. These results further signify that constructing quasi-linear 1,2,4triazole-based D– $\pi$ –A hybrids with biphenyl as the conjugation bridge is an universal and effective avenue for highly efficient true blue EL emitters.

# **Experiment section**

#### **General information**

#### Materials

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All raw materials were commercially purchased from Aldrich Chemical Co. or Energy Chemical Co., China. Tetrahydrofuran (THF) was distilled over metallic sodium over calcium hydride before use. The other organic solvents and reagents were all commercially available analytical-grade products and used as received without further purification.

#### Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC500 spectrometer at 500 and 125 MHz, respectively, when the compounds were dissolved in deuterated hloroform (CDCl<sub>3</sub>). The chemical shift for each signal was reported in ppm units with tetramethylsilane (TMS) as an internal reference, where  $\delta$  (TMS) = 0. The MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. Elemental analysis was characterized by a Flash EA 1112 instrument. UV-vis absorption and fluorescence spectra of solution and films were measured using a Hitachi U-4100 spectrophotometer and a Hitachi F-4600 spectrophotometer, respectively. Fluorescence quantum yield, low temperature fluorescence and phosphorescence spectra were measured on an Edinburgh FLS-

980 spectrometer with an EPL-375 optical laser, The natural transition orbitals (NTOs) of  $S_0 \rightarrow S_1$  we recall that do by 3776the TD-M062X/6-31G(d, p) method based on the optimized lowest singlet excited state configuration. Single-crystal X-ray diffraction data were collected using a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo K $\alpha$  radiation. The structure was solved with direct methods using the SHELXTL programs and refined with ful-matrix least squares on  $F^2$ . Anisotropic thermal parameters were refined for all the nonhydrogen atoms. All the hydrogen atoms of ligands were generated geometrically. CCDC 1587403 containing the crystallographic data can be obtained free from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data\_request/cif.

#### Synthesis of N'-benzoyl-4-bromobenzohydrazide (M<sub>1</sub>)

4-Bromobenzoic chloride (3.63 g, 16.5 mmol) was dissolved in dichloromethane (25 mL) and added dropwise into a solution of benzoyl hydrazine (2.25 g, 16.5 mmol) and triethylamine (3 mL) in dichloromethane (25 mL). The resulting mixture was stirred for 4 h at room temperature and then washed with water. The organic phase was evaporated to remove the solvent, and the residue was dried under reduced pressure and purified by recrystallization using absolute ethyl alcohol to afford a white powder. (4.8 g, yield 91 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.62 (s, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 4H), 7.40–7.52 (t, *J* = 7.2 Hz, 1H).

Synthesis of 3-(4-bromophenyl)-4, 5-diphenyl-1,2,4-triazole (M<sub>2</sub>) Aniline (5.59 g, 60.0 mmol) and o-dichlorobenzene (60 mL) were added into a 500 mL of two necked round-bottom flask equipped with a reflux condenser. PCl<sub>3</sub> (2.06 g, 15.0 mmol) was slowly added dropwise to the flask through syringe under nitrogen atmosphere. Subsequently, M1 (3.19 g, 10.0 mmol) in o-dichlorobenzene (60 mL) was added by dropping funnel, The resulting mixture was stirred under N2 at 150°C for 12 h and then cooled to room temperature. Diethyl ether (200 mL) was poured into mixture, and an orange precipitate was formed, filtered, and washed with Et<sub>2</sub>O. The solid was dried under reduced pressure and further purified by a silica gel column chromatography using ethyl acetate/dichloromethane mixture as the eluent. A white powder was obtain (2.7 g, yield 72 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53–7.39 (m, 7H), 7.36 (t, J = 7.4 Hz, 1H), 7.33–7.27 (m, 4H), 7.15 (d, J = 7.2 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.97, 153.82, 134.92, 131.72, 131.67, 130.28, 130.12, 130.08, 129.79, 129.70, 129.21, 128.73, 128.40, 127.67, 126.65, 125.82, 124.22. MALDI-TOF MS (mass m/z): 375.04 [M<sup>+</sup>]. Anal. calcd. for C<sub>20</sub>H<sub>14</sub>BrN<sub>3</sub>: C, 63.84; H, 3.75; Br, 21.24; N, 11.17. Found: C, 63.79; H, 3.72; N, 11.16.

#### Synthesis of 4'-(4,5-diphenyl-4H-1,2,4-triazol-3-yl)-*N, N*-diphenyl-[1,1'-biphenyl]-4-amine (TPATZ)

A mixture of (4-(diphenylamino)phenyl)boronic acid (1.84 g, 6.4 mmol), M<sub>2</sub> (2 g, 5.3 mmol), potassium carbonate (1.1 g, 8.0 mmol), THF (100 mL), deionized water (20 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.18 g, 0.2 mmol) was refluxed at 70°C for 24 h under nitrogen. After cooling to the room temperature, deionized water (100 mL) was added and extracted with dichloromethane for three times. After the organic phase was dried over anhydrous

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magnesium sulphate, the solvent was evaporated from the filtrate. The residue was purified through silica gel column chromatography using ethyl acetate/dichloromethane as the eluent to give a white solid (2.47 g, 86%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.53–7.39 (m, 11H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.29 (dd, *J* = 14.9, 7.9 Hz, 5H), 7.25 (s, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.11 (dd, *J* = 7.9, 5.1 Hz, 6H), 7.04 (t, *J* = 7.3 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  154.77, 154.60, 147.71, 147.48, 141.62, 135.31, 133.49, 129.98, 129.60, 129.29, 129.08, 128.80, 128.38, 127.87, 127.62, 126.94, 126.36, 125.13, 124.56, 123.55, 123.13. MALDI-TOF MS (mass m/z): 540.145 [M<sup>+</sup>]. Anal. calcd. for C<sub>38H28N4</sub>: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.44; H, 5.26; N, 10.32.

# **Results and Discussion**

#### Synthesis and Characterization

Starting from commercially available low-cost 4-bromobenzoyl chloride and benzohydrazide, *N*'-benzoyl-4-bromobenzohydrazide ( $M_1$ ) was formed and then cyclized with aniline to afford  $M_2$  in an overall yield of 64%. The target compound TPATZ was readily synthesized by the Suzuki coupling reaction of  $M_2$  with the inexpensive (4-(diphenylamino)phenyl)boronic acid in a high yield of 86% (Scheme 1). NMR, mass spectroscopy, and elemental analysis were employed to confirm the compound's structure and composition (Fig. S1-S3).



Scheme 1 Molecular structure and synthetic route of TPATZ.

TPATZ was soluble in common organic solvents and exhibited a distinct solvatochromic effect. Upon changing the solvents from the non-polar hexane, low-polar dialkylethers, to middle-polar THF and ethyl acetate, to high-polar acetone and acetonitrile, the photo-luminescence spectra were gradually red-shifted by a total spectral shift of 65 nm (from 393 to 458 nm) (Fig. 1a). The ground-state dipole moment ( $\mu_e$ ) was estimated to be 5.975 D through the DFT (density function theory) calculation at the level of B3LYP/6-31G-(d,p). To understand the intramolecular charge transfer (CT) nature of TPATZ under the excited states, we employed the Lippert-Mataga relationship to estimate the excited state dipole moment  $(\mu_e)$ .<sup>[27]</sup> The plot of the Stokes shift  $(v_a - v_f)$  versus the solvent polarity function f revealed a two-section linear relation with the increase of solvent polarities (Fig. 1b). The calculated dipole moments were 12.78 and 18.47 D in the lowand high-polarity regions, respectively, which suggested the coexistence of a weak CT (locally excited, LE) state and a strong CT state. Such excited state characters have been named the

hybridized LE and CT (HLCT) state and were commonly favoring fluorescence emission. DOI: 10.1039/C8TC03777A



Fig. 1 (a) Solvatochromic PL spectra of TPATZ with the increased solvent polarity; (b) Linear fitting of Lippert–Mataga model (the semisolid squares represent the Stokes shifts in different solvents, and the lines are fitted for solvatochromic model).

To theoretically examine excited state natures of TPATZ molecule, the quantum chemical calculations were carried out (Fig. 2). The optimized molecular geometry showed that both the conjugation backbone and the peripheral phenyl units were seriously distorted to some extent. The frontier molecular orbital (FMO) calculation indicated that the HOMO electrons were mainly located on donor unit and biphenyl bridge, whereas the LUMO electrons dominantly concentrated on the 5-phenyltriazole-biphenyl moiety. That is, the middle biphenyl unit acted as an integral part of both orbitals and contributed much to the HLCT state nature. The calculated natural transition orbital (NTO) revealed that the hole was primarily distributed on the donor and biphenyl moieties with a little residual on the triazole ring. In contrast, the particle was mostly localized on the biphenyl bridge. The good overlap between hole and particle indicated the existence of the HLCT state, which was qualitatively consistent with above

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Fig. 3 UV and PL spectra of TPATZ in both THF solution and evaporated film. View Article Online

HOMO/LUMO analysis and solvatochromic effect. Organic luminophores with distinct HLCT state nature and high oscillator strength (f = 1.2774 for TPATZ) might be promising light-emitting materials.

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Fig. 2 NTO for  $S_1/S_0$  transition in TPATZ. Herein, *f* represents for the oscillator strength, and the percentage weights of hole–particle are given for the  $S_1/S_0$  emission.

#### Photophysical, thermal, and electrochemical properties

Generally, the linear D– $\pi$ –A molecules with distinct solvatochromic effect should show the gradually or sharply decreased fluorescence efficiency with the increase of solvent polarity. However, TPATZ solutions in n-hexane, diisopropyl ether, diethyl ether, THF, and acetonitrile could qualitatively show an increasing fluorescence efficiency of 60%, 77%, 86%, 92%, and 86%, respectively, measured by a fluorescence integrating sphere, which was possibly related to its strong LE state nature. The vacuum-deposited film of TPATZ showed the absorption and emission peaks at 358 nm and 444 nm, respectively, which were slightly red-shifted relative to those in THF solution (350 and 437 nm) (Fig. 3). Importantly, the film still maintained a commendable fluorescence efficiency of 49%. The optical band gap was estimated to be 2.92 eV based on the onset of absorption.





Fig. 4 Lifetime measurement of TPATZ in n-hexane, isopropyl ether, diethyl ether, teterahydrofuran and acetonitrile.

To further elucidate the excited-state properties, the transient PL spectra of TPATZ in different solvents were measured at room temperature. As shown in Fig. 4, the molecule exhibited the mono-exponential decay in different solvents of n-hexane (1.08 ns), n-butyl ether (1.49 ns), THF (1.97 ns), and acetonitrile (2.77 ns). These slightly increased life-times within nanosecond scales with increase of solvent polarity signified the HLCT state character of the molecule. Meanwhile, we also measured the fluorescence and phosphorescence spectra of TPATZ in THF solution at 77 K (Fig. 5). The fluorescence emission (no delay) was in true blue region with the dual emission peak of 412 and 424 nm, and the delay emission spectrum showed the peak wavelength at 512 nm. Based on the low temperature fluorescence and phosphorescence spectra, the energy levels of  $S_1$  and  $T_1$  were calculated to be 3.01 and 2.42 eV, respectively. Thus, the energy gap between  $S_1$  and  $T_1$  ( $\Delta E_{ST}$ ) was estimated to be 0.59 eV, which is not favorable for the effective reverse intersystem crossing (RISC) from low-lying  $T_1$  to  $S_1$  states. On the other hand, the large band gap between S<sub>1</sub> and T<sub>1</sub> was also revealed by quantum chemical calculation (0.75 eV). Detailed photophysical parameters are listed in Table 1.



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Fig. 5 Fluorescence and phosphorescence of TPATZ in THF at 77 K.

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Table 1. Photophysical, thermal, and electrochemical data of TPATZ.

	$\lambda_{abs}{}^{a)}$	$\lambda_{em}^{b}$	T <sub>q</sub> c)	T <sub>d</sub> <sup>d)</sup>	HOMO <sup>e)</sup>	LUMO <sup>e)</sup>	E <sub>q</sub> <sup>f)</sup>
Compound	[nm]	[nm]	[°Č]	[°C]	[eV]	[eV]	[eᢆV]
TPATZ	350/358	430/454	103	422	-5.24	-2.25	2.99

a)UV-Vis absorption spectra measured in THF solution/film state at room temperature; b)Fluorescence spectra were measured in THF solution/film state at room temperature;  $c_{1}T_{e}$  = glass transition temperature; <sup>d</sup>)T<sub>d</sub> = decomposition; <sup>e</sup>)Measured by cyclic voltammetry; <sup>f)</sup>Optical gap calculated from the absorption onset in THF.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed in a nitrogen atmosphere to evaluate the thermal properties of TPATZ solid. TGA measurement found no weight loss before 400 °C (Fig. S4). Owing to its twist structure resulted from the carbazole group, its crystallization was suppressed and DSC analysis indicated the appearance of a relatively high glass transition temperature at 103 °C (Fig. S5).[28] Thus, TPATZ had the excellent thermal stability and good morphological stability, which is essential for solid state applications such as light-emitting devices. Cyclic voltammetry measurements afforded the onset oxidation and reduction potentials of 0.66 and -2.46 V, respectively (Fig. S6), which corresponded to the HOMO and LUMO energy levels of and -2.25 eV, respectively. The calculated -5.24 electrochemical band gap was 2.99 eV and was well consistent with the optical band gap 2.92 eV (vide supra).

X-ray crystal structure analysis and crystal function





Fig. 6 (a) The single molecule structure of TPATZ determined by single crystal; (b) Existed short range interactions of compound TPATZ with the neighboring molecule.

The single crystal of TPATZ was obtained by sublimation and analyzed by X-ray crystallography. The corresponding crystallographic data were listed in Table S1. The results revealed that TPATZ adopted a twisted molecular conformation, and the torsion angles between triazol and 5-phenyl, 4-phenyl, and 3phenyl were 32.68°, 74.24°, 32.84°, respectively (Fig. 6). The biphenyl bridge was also twisted by 34.04°, and the triphenylamine donor was propeller-like. These twisted molecules are packed together and formed the triclinic system containing 16 molecules with a Fdd2 space group and the centrosymmetric

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alignment without strong  $\pi$ - $\pi$  interactions. The twisted conformation and packing structure were stabilized by both intramolecular and intermolecular C-H··· $\pi$  interactions (Fig. 6b). The optimized geometry and crystal analysis signified that TPATZ molecules should also tend to aggregate in a twisted conformation in the amorphous state, which could explain the commendable film fluorescence efficiency.

# **Electroluminescence properties**

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To evaluate the potential of TPATZ as a light-emitting material for blue OLEDs, a non-doped device was fabricated with the structure of ITO/HATCN (5 nm)/TAPC (50 nm)/(TPATZ) (20 nm) /TPBi (55 nm)/LiF (1 nm)/Al (100 nm), where ITO and LiF/Al were used as the anode and cathode, respectively, and HATCN (dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexa-carbo-TAPC nitrile. (1,1-Bis[4-N,N'-di(ptolyl)amino]phenyl)cyclohexane, and TPBi (1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene served as the hole injection layer, hole transporting layer, and the electron transporting and hole blocking layer, respectively. As shown in Fig. 7a, the device showed a true blue EL emission with the peak wavelength of 430 nm and the saturated and much deeper CIE coordinates of (0.155, 0.047). The y value is much smaller than

the EBU standard of 0.06. The EL spectra hardly changed with the increase of applied voltage from 4 to 100 VO (Pig. 859).377Re desirable CIE coordinates were ascribed to the short EL emission wavelength and narrow full width at half maximum (FWHM). The FWHM is measured to be 50 nm and is one of the narrowest true blue EL emissions reports to date. More encouragingly, the device showed the excellent EL performance. The turn-on voltage and maximum luminance were 3.1 V and 4970 cd  $m^{-2}$ , respectively (Fig. 7b). The calculated maximum current efficiency, maximum power efficiency, and maximum external quantum efficiency (EQE) were 2.41 cd A<sup>-1</sup>, 2.20 Im W<sup>-1</sup>, and 5.92%, respectively, and the efficiency roll-off of the device is also small (Fig. 7c, d). The corresponding data are listed in Table 2. This commendable EL performance was among the best ones reported previously for the saturated true blue emission with with  $CIE_y$  < 0.06, and such typical reports have been summarized in Table S2. This comparison, combined with our previous results, underlined that constructing quasi-linear 1,2,4-triazole-based D-π-A hybrids with biphenyl conjugation bridge should be an universal and effective avenue for highly efficient true blue EL emitters.

Device	V <sub>Turn-on</sub> a) [V]	CE <sup>b)</sup> [cd A <sup>-1</sup> ]	PE <sup>c)</sup> [Im W <sup>-1</sup> ]	L <sup>d)</sup> [cd m <sup>-2</sup> ]	EQE <sup>e)</sup> [%]	Radiative exciton ratio	λ <sub>EL<sup>f)</sup> [nm]</sub>	FWHM <sub>EL<sup>g)</sup> [nm]</sub>	CIE <sup>h)</sup> [x, y]
TPAT7	31	2.41	2.20	4970	5.92%	60%-40%	430	50	(0.155, 0.047

<sup>a)</sup>Turn on voltage at a luminance of 1 cd m<sup>-2</sup>; <sup>b)</sup>Maximal current efficiency; <sup>c)</sup>Maximal power efficiency; <sup>d)</sup>Maximum luminance; <sup>e)</sup>Maximal external quantum efficiency; <sup>f)</sup>Maximal EL peak value; <sup>g)</sup>Full width half maximum of EL spectrum; <sup>h)</sup>Observer: 2°; obtained at 5 V. Device structure of ITO/HATCN (5 nm)/TAPC (50)/TPATZ (20 nm)/TPBi (55 nm)/LiF (1 nm)/AI (100nm).

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Fig. 7 (a) EL spectrum of the device I, the inset shows the CIE coordinates of the EL (at 5 V); (b) The current density-voltage-luminance characteristics of the device; (c) The current efficiency-luminance-power efficiency characteristics of the device; (d) The external quantum efficiency-luminance curve, the inset shows the device structure (ITO/HATCN (5 nm)/TAPC (50 nm)/TPATZ (20 nm)/TPBi (55 nm)/LiF (1 nm)/Al (100 nm)).

The maximum EQE was up to 5.92% and among the highest value of the nonoped OLEDs with  $CIE_y < 0.06$  (the EBU blue standard). Generally, the EQE for fluorescent OLEDs could be expressed as EQE =  $X_s \times \Phi_{PL} \times \eta_r \times \eta_{out}$  , where  $X_s$  was the ratio of singlets to the total excitions,  $\Phi_{\text{PL}}$  was the fluorescence quantum efficiency of the amorphous emitter,  $\eta_r$  was the fraction of excition formation of the injected charge carriers, and  $\eta_{out}$  was the light out-coupling efficiency. Based on the experimental EQE (5.92%) and film fluorescence efficiency (49%), we used the maximal  $\eta_r$  (100%) and the common  $\eta_{out}$ (20%–30%) to calculate the  $X_s$ . The obtained  $X_s$  was in the range of 60%-40%, which greatly exceeded the theoretical limitation of 25% from the spin statistics for fluorescent OLED (singlet/triplet ratio  $\approx$  1/3). This signified that some triplet excitons may have been converted to singlet states (reverse intersystem crossing, RISC) to generate light emission in the device. At present, RISC could occur through the thermallyactivated delayed fluorescence (TADF), the triplet-triplet annihilation (TTA), and the higher-level triplet to singlet excited states for the D-A molecules with HLCT state nature, etc. Among them, TADF was a highly efficient tactics for harvesting triplets but required the small  $\Delta E_{ST}$  (commonly,  $\leq$ 0.3 eV). To our case, the  $\Delta E_{ST}$  was up to 0.59 eV (experimentally, Fig. 5) and 0.75 eV (theoretically, Fig. S8), and the fluorescence lifetimes of both film and solution were much shorter than the known TADF materials (vide supra), which

was not favor of TADF process. TTA was another way for harvesting the triplet and the induced delayed fluorescence was proportional to the square of the triplet population density. However, a linear correlation between the luminance and current density was observed (Fig. S9), together with no delayed fluorescence in the transient PL decay measured at 77 K, revealing the lack of the TTA process. D–A-type molecules with singlet formation ratio higher than 25% could also occur at the higher-level excited states, e.g., the RISC from T<sub>2</sub> to the singlet manifold. However, this type required the large energy gap between T<sub>2</sub> and T<sub>1</sub> (such as > 1 eV) to lead to inefficient inter-conversion from T<sub>2</sub> to T<sub>1</sub> and thus T<sub>2</sub> was converted to singlet. Time-dependent DFT calculation indicated that the energy gap between T<sub>2</sub> and T<sub>1</sub> of TPATZ was small (0.44 eV), which did not benefit for this process.

While TTA, TADF, and higher level RISC can not explain why the singlet formation ratio is higher than 25% in the TPATZ device, we have alternatively considered that the extra singlets were attributed to the triplet—polaron interaction (TPI) induced up-conversion from triplet to singlet. It has been theoretically and experimentally investigated that the singlet formation cross section could be larger than that of triplets in some polymers and oligomers, and triplet excitons could be converted to singlet gound state or singlet excitons through TPI process.<sup>[14]</sup> Moreover, a recent publication has verified the existence of TPI process in the device with a similar branched

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D-A molecule as the emitting layer, based on the magnetocurrent (MC) of the working device increased with both the applied voltage and the magnetic field. It was also conjectured that some deep-blue OLEDs with much higher singlet ratios than 25% and without observable delayed fluorescence should exist the TPI-induced conversion from triplet to singlet. We thought that the MC effect of the EL devices using linear D-A molecules as the emitters (such as the present TPATZ and the previous PCZTZ) should be more remarkable, although the measurement was not conducted because of the apparatus limitation. The existence of strong couplings between the donor and acceptor moieties of neighbor molecules was a little like "intermolecular heterojunction" in organic photovoltaic devices. It was considered to be possible that the triplet excitons in the OLEDs were dissociated at the "intermolecular heterojunction," then the separated charge recombinated with the opposite charge at the neighbor molecules, which could offer the possibility of converting triplet excitons to singlet excitons through TPI.

### Conclusions

In summary, we have demonstrated that using the 1,2,4triazole derivatives as the acceptors to link electron-donating units by a biphenyl conjugation bridge is an effective strategy for realizing new true blue luminophores. The incorporation of strong donor triphenylamine still retains the true blue emission and high fluorescence efficiency in D- $\pi$ -A molecule (TPATZ). A non-doped OLED using TPATZ as emitter exhibits highly efficient EL with the maximal EQE of 5.92%, and the device emits true blue light with EL peak of 430 nm and CIE coordinates of (0.155, 0.047), which is beyond the European Broadcasting Union standard of (0.15, 0.06). The calculated singlet utilization ratio is in the range of 60%-40% and greatly exceeds the theoretical limitation of 25%. However, the experimental and theoretical analysis do not support the RISC from TTA, TADF, and HLCT mechanisms, and it seems to be the triplet-polaron interaction induced up-conversion from triplet to singlet in view of the molecular structure and EL feature. Nevertheless, the EL performances are among the best ones reported to date and further evidences the universality and effectiveness of this construction mode for highly efficient true blue EL emitters. We believe that further molecular design and device characterization would help to revel the cause of highly efficient EL.

# **Conflicts of interest**

There are no conflicts to declare.

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# Notes and references

- 1 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
- 2 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.
- E. Thompson, S. R. Forrest, *Nature*, 1998, **395**, 151.
  Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, S. R. Forrest, *Nature*, 2006, **440**, 808.
- 4 A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897.
- Q. Wang, D. Ma, *Chem. Soc. Rev.*, 2010, **39**, 2387.
   H.-H. Chou, Y.-H. Chen, H.-P. Hsu, W.-H. Chang, Y.-H. Chen,
- C.-H. Cheng, *Adv. Mater.*, 2012, **24**, 5867.
  Y. Z. Zhao, Q. X. Guo, P. Li, Q. Wang, D. G. Ma, *J Lumin.*, 2017,
- **188**, 612. 8 S. R. Forrest, M. F. Thompson, *Chem. Rev.* 2007, **107**, 923
- S. R. Forrest, M. E. Thompson, *Chem. Rev.*, 2007, **107**, 923.
   Y. Ma, H. Zhang, J. Shen, *Synthetic Metals*, 1998, **94**, 245.
- 10 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, *Nature*, 1990, 347, 539.
- (a) Q. S. Zhang, B. Li, S. P. Huang, H. Nomura, H. Tanaka, C. Adachi, *Nat. Photonics*, **2014**, *8*, 326; (b) L. S. Cui, H. Nomura, Y. Geng, H. Nakanotani, C. Adachi, *Angew. Chem. Int. Ed.*, 2017, **129**, 1593; (c) X. D. Cao, D. Zhang, S. M. Zhang, Y. T. Tao and W. Huang, *J. Mater. Chem. C*, 2017, **5**, 7699; (d) Y.D. Zhao, W. G. Wang, C. Gui, L. Fang, X. L. Zhang, S. J. Wang, S. M. Chen, H. P. Shi and B. Z. Tang, *J. Mater. Chem. C*, 2018, **6**, 2873.
- 12 (a) V. Jankus, C.-J. Chiang, F. Dias and A. P. Monkman, *Adv. Mater.*, 2013, **25**, 1455; (b) P.-Y. Chou, H.-H. Chou, Y.-H. Chen, T.-H. Su, C.-Y. Liao, H.-W. Lin, W.-C. Lin, H.-Y. Yen, I.-C. Chen, C.-H. Cheng, *Chem. Commun.*, 2014, **50**, 6869; (c) M. Y. Bian, Z. F. Zhao, Y. Li, Q. Li, Z. J. Chen, D. D. Zhang, S. F. Wang, Z. Q. Bian, Z. W. Liu, L. Duan, L. X. Xiao, *J.Mater. Chem. C*, 2018, **6**, 745.
- (a) W. J. Li, D. D. Liu, F. Z. Shen, D. G. Ma, Z. M. Wang, T. Feng, Y. X. Xu, B. Yang, Y. G. Ma, *Adv. Funct. Mater.*, 2012, 22, 2797; (b) X. Y. Tang, Q. Bai, Q. M. Peng, Y. Gao, J. Y. Li, Y. L. Liu, L. Yao, P. Lu, B. Yang, and Y. G. Ma, *Chem. Mater.*, 2015, 27, 7050; (c) S. T. Zhang, W. J. Li, L. Yao, Y. Y. Pan, F. Z. Shen, R. Xiao, B. Yang, Y. G. Ma, *Chem. Commun.*, 2013, 49, 11302; (d) S. T. Zhang, L. Yao, Q. M. Peng, W. J. Li, Y. Y. Pan, R. Xiao, Y. Gao, C. Gu, Z. M. Wang, P. Lu, F. Li, S. J. Su, B. Yang, Y. G. Ma, *Adv. Funct. Mater.*, 2015, 25, 1755; (e) B, Liu, Z.-W. Yu, D. He, Z.-L. Zhu, J. Zheng, Y.-D. Yu, W.-F. Xie, Q.-X. Tong and C.-S. Lee, *J. Mater. Chem. C*, 2017, 5, 5402.
- 14 (a) Q. Peng, A. Obolda, M. Zhang, F. Li, *Angew. Chem. Int. Ed.*, 2015, 54, 7091; (b) A. Obolda, Q. M. Peng, C. Y. He, T. Zhang, J. J. Ren, H. W. Ma, Z. G. Shuai, F. Li, *Adv. Mater.* 2016, 28, 4740; (c) A. Abdurahman, A. Obolda, Q. M. Peng, F. Li, *Dyes and Pigments*, 2018, 153, 10.
- (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) J. Mei, Y. N. Hong, Jacky W. Y. Lam, A. J. Qin, Y. H. Tang, B. Z. Tang, *Adv. Mater.* 2014, **26**, 5429; (c) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu, B. Z. Tang, *Chem. Mater.*, 2003, **15**, 1535; (d) Y. J. Cai, C. S. Shi, H. Zhang, B. Chen, K. Samedov, M. Chen, Z. M. Wang, Z. J. Zhao, X. G. Gu, D. G. Ma, A. J. Qin and B. Z.

Journal of Materials Chemistry C Accepted Manuscript

View Article Online DOI: 10.1039/C8TC03777A

Tang, J. Mater. Chem. C, 2018, **6**, 6534; (e) H. J. Liu, J. J. Zeng, J. J. Guo, H. Nie, Z. J. Zhao, B. Z. Tang, *Angew. Chem., Int. Ed.*, 2018, **57**, 9290.

- 16 Q. S. Zhang, J. Li, K. Shizu, S. P. Huang, S. Hirata, H. Miyazaki, C. Adachi, J. Am. Chem. Soc., 2012, **134**, 14706.
- 17 B. Wei, J.-Z. Liu, Y. Zhang, J. H. Zhang, H.-N. Peng, H.-L. Fan, Y.-B. He, X.-C. Gao. Adv. Funct. Mater., 2010, 20, 2448.
- P. Rajamalli, N. Senthilkumar, P. Gandeepan, C. C. Ren-Wu, H. W. Lin, C. H. Cheng, C.H. Cheng, ACS Appl. Mater. Interfaces, 2016, 8, 27026.
- 19 M. R. Zhu, T. L. Ye, C.-G. Li, X. S. Cao, C. Zhong, D. G. Ma, J. G. Qin, C. L. Yang. J. Phys. Chem. C, 2011, 115, 17965.
- 20 (a) X. Qiu, J. J. Shi, X. Xu, Y. S. Lu, Q. K. Sun, S. S. Xue, W. J. Yang, *Dyes and Pigment*, 2017, **147**, 6; (b) X. Xing, L. P. Zhang, R. Liu, S. Y. Li, B. Qu, Z. J. Chen, W. F. Sun, L. X. Xiao, and Q. H. Gong, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2877.
- T. Qin, W. Zajaczkowski, W. Pisula, M. Baumgarten, M. Chen, M. Gao, G. Wilson, C. D. Easton, K. Mullen, S. E. Watkins, J. Am. Chem. Soc., 2014, 136, 6049.
- 22 M. Shimizu, R. Kaki, Y. Takeda, T. Hiyama, N. Nagai, H. Yamagishi, H. Furutani, *Angew. Chem., Int. Ed.,* 2012, **51**, 4095.
- 23 X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun, B. Z. Tang, *J. Phys. Chem. C*, 2012, 116, 10541.
- 24 M. Zhu, C. Yang, Chem. Soc. Rev., 2013, 42, 4963.
- 25 A. L. Korich, L. A. Mcbee, J. C. Bennion, J. I. Gifford, T. S. Hughes, *J. Org. Chem.*, 2017, **79**, 1594.
- 26 S. F. Xue, X. Qiu, S. A. Ying, Y. S. Lu, Y. Y. Pan, Q. K. Sun, C. Gu, W. J. Yang, *Adv. Opt. Mater.*, 2017, 5, 1700747.
- 27 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3899.
- 28 Y-H. Chung, L. Sheng, X. Xing, L. L. Zheng, M. Y. Bian, Z. J. Chen, L. X. Xiao and Q. H. Gong, *J. Mater. Chem. C*, 2015, **3**, 1794.

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A new true blue fluorescent emitter (TPATZ) with simple structure is designed and facilely synthesized. The non-doped device exhibits true blue electroluminescence with CIE coordinates of (0.155, 0.047) and the narrow FWHM of 50 nm, and the y value is fairly small and beyond the European Broadcasting Union standard of 0.06. The device shows an impressive maximum external quantum efficiency up to 5.92%.