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Materials for optical, magnetic and electronic devices

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High-Performance non-doped blue OLEDs based on 1,2,4-triazolephenanthroimidazole derivatives with negligible efficiency roll-off

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Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

Received 00th January 20xx.

Triazole and phenanthroimidazole moieties are commonly used to construct efficient blue-emitting materials as acceptors and donors, respectively. Profiting from the D-A coupling of the two moieties, two novel bipolar blue emitters, TAZ-PPI and 4NTAZ-PPI were synthesized. They showed excellent thermal stability and high photoluminescence quantum yield (PLQY). Non-doped blue organic light-emitting diodes (OLEDs) based on 4NTAZ-PPI and TAZ-PPI present maximum external quantum efficiencies of 7.3% and 5.9%, respectively, and exhibit negligible efficiency roll-offs. The CIE coordinates are (0.149, 0.131) and (0.149, 0.130) at the luminance of 1000 cd m⁻², respectively. Because the combination of electron donors and acceptors is a favorable method to balance the carrier injection and transport, 4NTAZ-PPI and TAZ-PPI exhibit excellent holes and electrons transporting capabilities.

1. Introduction

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Organic light-emitting diodes (OLEDs) have great potential for display and lighting application due to their light-weight, flexibility and fast respons.¹⁻⁶ In recent years, a lot of effort has been put into developing highly efficient blue luminescent material, because efficient blue emitters not only act as energy donor to transfer energy to red and green dopants in full-color display but also significantly reduce device power consumption.^{7,8} Up to now, a large amount of efficient blue organic materials based on phosphorescence and thermally activated delayed fluorescence (TADF) have been designed and synthesized.9-14 Generally, both phosphorescent and TADF materials are doped into host materials, which would complicate the structure of devices and increase the manufacturing costs.¹⁵⁻¹⁸ In addition, the performance of most devices is highly dependent on doping concentrations and matrix materials, and the efficiency roll-off at high brightness is mainly ascribed to the accumulation of triplet excitons.¹⁹⁻²¹ Triplet-triplet annihilation (TTA) materials can make use of triplet excitons and boosts the theoretical limit of the internal quantum efficiency (IQE) from 25% to 62.5% through fusing two triplets to a singlet.^{22,23} In rare cases, TTA materials are accessible to non-doped OLEDs with negligible efficiency rolloff. Therefore, it is still a significant challenge to develop highperformance blue emitters suitable for the non-doped devices.

Blue emission implies a wider band gap and limited molecular conjugate size for emitters, and these properties generally

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result in inferior carrier injection and transport, low fluorescent efficiency.^{6,24} To address these issues, molecules based on donor (D)-acceptor (A) types are usually applied to improve charge balance.^{25,26} However, considerable numbers of them would produce an intramolecular charge transfer (ICT) effect, resulting in a red shift of emission. The selection of appropriate electron-donating and -withdrawing moieties can play a vital role in determining the color.^{27,28}

Phenanthroimidazole (PI) derivatives are commonly used to construct efficient blue-emitting materials. Typically, the PI unit has bipolar character, good thermal stability, and high photoluminescence quantum yield.²⁹⁻³⁴ Triazole (TAZ) derivatives have been employed as building blocks for efficient electron-transporting and hole-blocking materials due to the electron-deficient properties.³⁵⁻³⁷ For the past few years, it has been reported that 1,2,4-triazole derivatives were used as the acceptors to construct highly efficient pure blue or nearultraviolet electroluminescence emitters.³⁸⁻⁴¹ We have reported a blue OLED based on a TAZ derivative with a maximum EQE of 6.8% and CIE coordinates of (0.158, 0.043) and the extra singlets are attributed to the triplet-polaron interaction (TPI) induced upconversion from triplet to singlet.³⁸ In this work, triazole derivatives as the acceptors and phenanthroimidazole derivatives as the donors were firstly exploited to construct two highly efficient donor-acceptor (D-A) type blue emitters, TAZ-PPI and 4NTAZ-PPI. Besides, the ICT effect is weakened by the introduction of the benzene ring between phenanthroimidazole and triazole units. The EL performance can be greatly improved by changing the structure design of triazole derivatives linked with phenyl or naphthalene. Notably, the PLQY of 4NTAZ-PPI in the pristine film is 60%, and that of TAZ-PPI is 67%. Non-doped organic devices based on 4NTAZ-PPI and TAZ-PPI exhibited EQEs of 7.3% and 5.9%, and CIE coordinates of (0.149, 0. 131) and (0.149, 0.130) at a luminance of 1000cd m⁻², respectively. More

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[†] Electronic Supplementary Information (ESI) available: TGA, DSC, CV curves, transient decay curves, additional electroluminescence data of the OLED devices, NMR and other characterization. See DOI: 10.1039/x0xx00000x

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importantly, these devices demonstrated negligible efficiency **2.** Experimental Section roll-offs.



Synthesis of 2-(4'-(4,5-diphenyl-4H-1,2,4-triazol-3-yl)-[1,1'biphenyl]

-4-yl)-1-phenyl-1H-phenanthro[9,10-d] imidazole (TAZ-PPI)

TAZBr (0.55 g, 1.46 mmol), PPIB (0.8 g, 1.61 mmol), potassium carbonate (1.8 g, 13 mmol), tetrahydrofuran (30 mL), deionized water (16 mL) and Pd(PPh₃)₄ (0.084 g, 0.073 mmol) were placed in a 100 ml round-bottom flask. The mixture was stirred at 70 °C for 36 h under an argon atmosphere. After the reaction is over, extract with dichloromethane for several times, dry organic solution with anhydrous MgSO₄. The residue was purified via column chromatography by using dichloromethane/ethyl acetate (3:1, v/v) mixture as eluent. A white power was obtained. (0.58 g, Yield: 60%). ¹H NMR (500 MHz, CDCl₃) δ 8.80 (d, J = 8.3 Hz, 1H), 8.74 (d, J = 7.9 Hz, 1H), 7.87 - 7.74 (m, 1H), 7.74 - 7.62 (m, 6H), 7.51 (m 15H), 7.43 -7.35 (m, 1H), 7.35 – 7.31 (m, 3H), 7.22 (d, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl_3) δ 154.92, 154.35 , 141.16 , 135.39, 130.34, 130.01, 129.67, 129.61, 129.13, 128.82, 128.38, 127.91, 126.93, 126.82, 126.41, 124.19, 123.09, 120.91. MS(m/z) calculated for $C_{47}H_{31}N_5$: 665.26; Found [M]⁺ 665.24. Elem. Anal. Calcd (%) for C₄₇H₃₁N₅: C, 84.79, H, 4.69, N, 10.52. Found: C,84.74; H, 4.65; N, 10.50

Synthesis of 2-(4'-(4-(naphthalen-1-yl)-5-phenyl-4H-1,2,4-triazol-3yl)-[1,1'-biphenyl]-4-yl)-1-phenyl-1H-phenanthro[9,10-d] imidazole(4NTAZ-PPI)

The synthesis process of 4NTAZ-PPI was similar to the detailed method of TAZ-PPI. The residue was purified via column chromatography by using dichloromethane/ethyl acetate (3:1, v/v) as eluent to give 4NTAZ -PPI as a yellowish white solid (0.57 g, Yield: 55%). ¹H NMR (500 MHz, CDCl₃) δ 8.79 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.73 – 7.61 (m, 6H), 7.60 – 7.52 (m, 5H), 7.44 (m, 11H), 7.33-7.22 (m, 3H), 7.17 (m, 3H) ¹³C NMR (151 MHz, CDCl₃) δ 155.72, 155.19, 141.07, 134.21, 131.88, 131.80, 130.58, 130.26, 129.86, 129.59, 129.07, 128.61, 128.37, 128.31, 128.10, 127.36, 126.84, 126.70, 126.36, 125.41, 124.16, 123.07, 122.04, 120.89. MS (m/z) calculated for C₅₁H₃₃N₅: 7, 85.57, H, 4.65, N, 9.78. Found: C, 85.58; H, 4.59; N, 9.76.

3. Results and discussion

Synthesis and characterization of compounds

The synthetic scheme and molecular structures of TAZ-PPI and 4NTAZ-PPI are depicted in Scheme 1. The synthesis of PPIBr and PPIB were according to previous reports.^{30,42} The last target molecules were synthesized by the Suzuki cross-coupling reaction with good yields. Those chemical structures were confirmed by mass spectrometry and NMR. The synthetic details can be seen in the supporting information and experimental section.

Thermal stability and electrochemical properties



Figure 1. TGA curves of 4NTAZ-PPI and TAZ-PPI.

The thermal stability of TAZ-PPI and 4NTAZ-PPI were characterized by thermal gravimetric analysis (TGA) (Figure 1) and differential scanning calorimetry (DSC) under a nitrogen atmosphere (Figure S1). The two compounds exhibited extremely high decomposition temperature (T_d , corresponding to 5% weight loss) of 491°C due to the bulky and rigid skeleton of two molecules. As shown in Figure S1, no distinct glass transition temperatures (T_g) were observed for the two compounds, indicating that the thermal morphology is stable in

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the solid film. From those thermal analysis data, both compounds display outstanding thermal stability, which is conducive to get devices with remarkable performance.

Furthermore, electrochemical properties of TAZ-PPI and 4NTAZ-PPI were measured by cyclic voltammetry (CV) and the results are shown in Figure S2. The oxidation potentials of TAZ-PPI and 4NTAZ-PPI are determined to be 1.17 and 1.18 V, which correspond to the HOMO levels of -5.97 and -5.98 eV, respectively. The reduction potentials of TAZ-PPI and 4NTAZ-PPI are -2.08 and -2.17 V, which correspond to the LUMO levels of -2.72 and -2.63 eV, respectively.

Photophysical properties

To further understand the basic photophysical properties of TAZ-PPI and 4NTAZ-PPI, the normalized UV–vis absorption and photoluminescence (PL) spectra in dichloromethane (DCM) and pristine films are displayed in Figure 2. TAZ-PPI shows almost the same absorption and PL spectra as those of 4NTAZ-PPI. The absorption band centred at 288 nm can be ascribed to the π – π * transition of triazole moiety⁴⁰ and the absorption at 347 nm and 368 nm belong to the π – π * transition of PPI group.³¹ The optical band gap of TAZ-PPI and 4NTAZ-PPI were estimated to be 2.92 eV based on the onset of absorption. The PL spectra of DCM solution show an emission maximum at 436 nm for the two compounds. Moreover, the emission peak only has a red-shifted of 14 nm to 450 mining pristine films, indicating that ICT effect is weakened to some extend due to the rigidly twisted molecular conformation. The solvation effect was tested to further investigate the excited state properties of the two molecules. The PL spectra of 4NTAZ-PPI shift 24 nm from 420 nm in low polar solvent n-hexane to 444 nm in high-polarity acetonitrile. TAZ-PPI exhibits 19 nm bathochromic variations from 421 nm in n-hexane to 440 nm in acetonitrile. The shift of emission peak in PL spectra of the two compounds is not remarkable and vibration fine structure exists in low polarity solution, indicating mainly localized excited states (LE) characteristic of the lowest excited state S₁ for the two compounds. In addition, the dipole moments (μ_e) of the excited states of 4NTAZ-PPI and TAZ-PPI are estimated by the Lippert-Mataga model. For the two compounds, the plot of the Stokes shift $(v_a - v_f)$ versus the solvent polarity function f was drawn. The result shows μ_e is 10.2 D and 8.9 D for 4NTAZ-PPI and TAZ-PPI, respectively. These values are little larger than that of conventional LE emitters such as anthracene (approximately 4.0-6.0 D) while much smaller than the typical CT molecule DMABN with μ_e = 23 D,⁴³ indicating that the excited states of both compounds are mainly LE state (Figure S3). Further, the dipole moment of 4NTAZ-PPI is a bit greater than TAZ-PPI, which indicates the excited state of 4NTAZ-PPI retains a slight CT component.





Importantly, the PLQYs of both compounds were 73% in THF solution. 4NTAZ-PPI and TAZ-PPI exhibited high PLQYs of 60% and 67% in the film, respectively. The transient PL decay spectra of 4NTAZ-PPI and TAZ-PPI in THF solution were measured (Figure S4). Both compounds show short fluorescent lifetimes of approximately 1.5 ns in the THF solvent, and there is no delayed fluorescence. Thus, the radiative transition rate (K_r) was estimated to be near 5.0×10^8 s⁻¹ for both of them. The S₁ (E_{S1}) and T₁ (E_{T1}) energy levels were estimated by recording fluorescence and phosphorescence spectra at 77 K in THF solution (Figure S6). The E_{S1} was determined to be 2.88

and 2.91 eV for 4NTAZ-PPI and TAZ-PPI from the fluorescence spectra, respectively. According to the first vibrational phosphorescent peak, the T₁ of both compounds were obtained to be 2.27 eV. Therefore, the energy bandgap (ΔE_{ST}) between S₁ and T₁ were estimated to be 0.61 and 0.64 eV for 4NTAZ-PPI and TAZ-PPI, respectively, which is not conducive to the effective reverse intersystem crossing (RISC) from T₁ to S₁ states. Fluorescence and phosphorescence (at 77 K) spectra of 4NTAZ-PPI and TAZ-PPI pristine films were also measured, as shown in Figure S7. Similar results as

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the THF solvent (at 77 K) are acquired. Detailed photophysical properties are listed in Table 1.

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Table 1 Photophysical data and energy levels of 4NTAZ-PPI and TAZ-PPI.

Compound	λ_{abs}	λ_{PL}	Eg	S_1	T ₁	номо	LUMO	PLQY	τ	κ _r	κ _{nr}
	(nm)ª	(nm)⁵	(eV) ^c	(eV) ^d	(eV) ^d	(eV) ^e	(eV) ^e	(%) ^b	(ns)ª	10 ⁸ (s ⁻¹) ^f	10 ⁸ (S ⁻¹) ^f
4NTAZ-PPI	284,338,363	450	2.92	2.88	2.27	-5.98	-2.63	60	1.5	5.00	1.85
TAZ-PPI	284,338,363	450	2.92	2.91	2.27	-5.97	-2.72	67	1.5	5.03	1.86

^aMeasured in dilute DCM solution at room temperature. ^bMeasured in a thin film. ^cOptical band-gap calculated from the absorption spectra onset in THF solution. ^dEstimated from fluorescent and phosphorescent spectra at 77 K in THF solution. ^eMeasured by CV measurement. ^fCalculated from the equation: $\kappa_r = \phi/\tau$; $\tau=1/(\kappa_r + \kappa_{nr})$, meased in THF solution.

Density functional theory (DFT) calculations

To better understand the relationship between the structure and properties of the two compounds. We carried out density functional theory calculations by using the B3LYP/6-31G (d, p) method of the Gaussian 09 program package. Optimized molecular geometries can be seen in Figure 3, TAZ-PPI and 4NTAZ-PPI adopted highly twisted biphenyl units to regulate the molecular conjugation, which is in favour of preventing the inter-molecular π - π stacking. The highest occupied molecular orbitals (HOMO) are mainly located on the donor unit (PI) and the biphenyl bridge for the two molecules. The lowest unoccupied molecular orbital (LUMO) of TAZ-PPI is predominantly delocalized on the triazole and adjacent phenyl ring, whereas the

LUMO of 4NTAZ-PPI dominantly concentrates on the naphthyl ring. It can be seen that the electron-cloud spatial distributions between HOMO and LUMO for naphthyl-based 4NTAZ-PPI is more separated than that of phenyl-based TAZ-PPI. In addition, the nearly full spatial separation between HOMO and LUMO for 4NTAZ-PPI is favorable to the effective transport of carriers, while the orbitals overlap for TAZ-PPI is propitious for the radiative transition.^{27,28} The calculated results of the energy levels of first-ten singlet and triplet excited states are summarized (Figure S8). The S₁ of both compounds were obtained to be 3.3 eV and The T₁ was calculated to be 2.15 and 2.57 eV for 4NTAZ-PPI and TAZ-PPI by DFT calculation, respectively.



Figure 3. Optimized geometries, the HOMO and LUMO orbitals distributions of (a) TAZ-PPI (b) 4NTAZ-PPI.

Electroluminescence properties

The balanced carrier injection and transport are very important to obtain excellent device efficiencies. Figure S9 shows the current density versus voltage characteristics of the hole-only (HOD) and electron-only devices (EOD).³⁰ The carrier mobility can be calculated from the J^{1/2}-V curves of single-carrier devices according to the space charge limited current (SCLC) model (Figure S10, Supporting Information). The electron and hole mobilities were calculated to be 1.6×10^{-5} cm² V⁻¹s⁻¹ and 1.1×10^{-6} cm² V⁻¹s⁻¹ for TAZ-PPI, 1.4×10^{-5} cm² V⁻¹s⁻¹ and 1.0×10^{-6} cm² V⁻¹s⁻¹ for TAZ-PPI. The results suggest TAZ-PPI and 4NTAZ-PPI have good holes and electrons transporting capabilities. Additionally, both compounds transport electrons better than holes, which is attributed to the good electron transporting property of triazole groups. Further, the carrier

transport properties of 4NTAZ-PPI are slightly better than that of TAZ-PPI.

The non-doped OLEDs were fabricated with the optimized device structure of ITO/MoO₃(3 nm)/TCTA(40 nm) /TAZ-PPI or 4NTAZ-PPI (20 nm)/TPBI (40 nm)/LiF (1 nm)/AI (100 nm), where ITO (indium tin oxide) is the anode, MoO_3 is the hole injecting layer, TCTA (tris(4-carbazoyl-9-ylphenyl)amine) acts as the hole transporting layer (HTL), 4NTAZ-PPI and TAZ-PPI are the emitting layers and TPBI (1,3,5-tris-(N-phenylbenzimidazol-2-yl)benzene) plays the role of electron transporting layer. The device structure along with the HOMO/LUMO levels of organic materials are shown in Figure 4 (a).

The non-doped device based on 4NTAZ-PPI exhibits blue emission with a maximum EQE of 7.3 % and CIE coordinates of (0.149, 0.131). The EL spectrum has an emission peak at 460 nm and the maximum power efficiency (PE) and current efficiency (CE) reach 6.3 Im W⁻¹ and 8.0 cd A⁻¹, respectively. Compared with 4NTAZ-PPI, the maximum

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EQE of the TAZ-PPI based device is 5.9 % and maximum PE, CE up to 6.1 lm W⁻¹ and 6.7 cd A⁻¹, respectively. The EL spectrum shows blue emission with a peak at 460 nm and the corresponding CIE coordinates of (0.149, 0.130). The EL spectra almost remain unchanged as driving voltage increases from 5 to 8.5 V for all devices (Figure S11), which demonstrated the excellent spectra stability of the EL process. Interestingly, although 4NTAZ-PPI has lower PLQY in film , the EQE of the 4NTAZ-PPI-based device is a little higher than that of the TAZ-PPI-based device. The slightly superior charge mobility of 4NTAZ-PPI is considered to be an influencing factor. 4NTAZ-PPI and TAZ-PPI based devices show very small efficiency rolloff and remain EQEs of 7.0 % and 5.5% at the luminance of 1000 cd $EQE_{max} - EQE_{1000}$ m⁻², respectively. Further, according to $\eta_{roll-off} =$ EQEmax the efficiency roll-offs $(\eta_{roll-off})$ of non-doped 4NTAZ-PPI and TAZ-PPI devices at 1000 cdm⁻² were 4.1% and 6.8%, respectively.⁴⁴ The performance of devices based on 4NTAZ-PPI is comparable to those of the reported high-efficiency blue devices.

The electrically excited singlet exciton ratios were obtained in the range of 60-40% and 44-30% for 4NTAZ-PPI and TAZ-PPI, respectively, which greatly exceeded the theoretical limitation of 25% from the spin statistics for fluorescent OLEDs assuming the outcoupling efficiency is 20-30%.¹⁷ This means that there exist extra ways to create singlet excitons. Presently, the proposed different ways to create singlet excitons converted from triplets include: TADF, TTA, hybridized local and charge transfer (HLCT),⁴⁵ and etc. A small energy gap between singlet and triplet (ΔE_{ST}), generally smaller than 0.30 eV, is the primary feature of TADF materials. In our case, the energy bandgap (ΔE_{ST}) between S₁ and T₁ were estimated to be 0.61 and 0.51 eV for 4NTAZ-PPI and TAZ-PPI pristine films, respectively,

which is not conducive to the effective reverse intersystem-crossing (RISC) from T_1 to S_1 states. The energy of two this restrictions lies slightly above that of the singlet exciton, $(E(S_1) \leq 2E(T_1))$, which facilitates TTA mechanism.⁴⁶⁻⁴⁸ However, for TAZ-PPI and 4NTAZ-PPI compounds, the energy of two triplet excitons is much higher than that of the singlet exciton according to the experimental and theoretical results (Figure S7 and Figure S8). In addition, the EL intensities of the devices linearly increase as the current density increases (Figure S12), together with no delayed fluorescence in the transient PL decay measured at 77 K (Figure S5). These results suggest TTA are not dominant mechanism. Time-dependent DFT calculations were performed and the results indicate that there is no large energy gap (over 0.5 eV) between T_1 and T_n for the compounds which is the prerequisite of HLCT (Figure S8).45 The solvatochromic effect (Figure S3) also indicates HLCT has the undominant contribution to the emission of the devices. In view of the above results, it can be inferred that TADF, TTA and HLCT are not the main mechanism of converting triplet to singlet excitons in this work. As previously reported, some blue OLEDs with much higher singlet ratios than 25% and without observable delayed fluorescence may have the TPI process^{38,39}. The TPI process does not need the spin-flip. Moreover, TPI can occur circularly, that is TPI can continuously convert triplet to singlet, which may induce much higher singlet ratio in OLEDs. TPI can also happen at high current density. Therefore, one advantage of the TPI mechanism is that the efficiency roll-off of the OLEDs are not remarkable. So, according to the negligible efficiency roll-offs, we conjectured that the extra singlets here were attributed to the TPI mechanism. The deeper study about the TPI mechanism of the triazole cored D-A type emitters needs to be further performed.



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 Figure 4. (a) The device structure of 4NTAZ-PPI and TAZ-PPI. (b) The characteristic curves of current density-voltage-luminescence (J-V-L). (c) The curves of CE and PE versus luminance. View Article Online

 (d) The EL spectra of non-doped OLEDs based TAZ-PPI and 4NTAZ-PPI, the inset shows EL spectra of the OLEDs.
 DOI: 10.1039/D1TC01079D

 Table 2 Device performances of the devices based on 4NTAZ-PPI and TAZ-PPI.

Emitter	V _{on}	L _{max}	CE (cd A ⁻¹) ^b	PE (Im W ⁻¹) ^c	EQE	λ _{EL}	CIE	Ref
4NTA7-PPI	3.0	20210	8.0	6.3	7.3	460	(0.149.0.131)	This Work
TAZ-PPI	3.0	14750	6.7	6.1	5.9	460	(0.149.0.130)	This Work
IP-PPI	2.7	14600	4.49	4.49	4.86		(0.153,0.09)	[6]
pCzphAnBzt	3.5	5162	7.73	5.51	6.75	456	(0.15, 0.12)	[23]
m-PO-ABN	3.6	-	5.2		5.9	448	(0.148, 0.099)	[24]
CzAnTAZ	3.4	58679	13.0	11.7	7.96	468	(0.16, 0.25)	[27]
4NDTPA-TAZ	2.8	11006	_	_	6.3	426	(0.158,0.038)	[39]
TPATZ	3.1	4970	2.41	2.20	5.92	430	(0.155, 0.047)	[40]
PCZTZ	3.2	3113	2.85	_	6.57	408	(0.17, 0.07)	[41]
PPI-2BI	3.0	6228	4.98	4.82	4.63	452	(0.158, 0.124)	[49]

^aTurn-on voltage at 1 cd m⁻². ^bMaximum current efficiency. ^cMaximum power efficiency. ^dMaximum EQE.

4. Conclusions

In summary, we successfully designed and synthesized two novel highly efficient D-A type blue emitters, 4NTAZ-PPI and TAZ-PPI. They exhibit excellent thermal stability with the T_d of 491°C and PLQYs in the pristine film exceeding 60%. Besides, all non-doped devices show negligible efficiency roll-off at high current densities. Non-doped electroluminescent devices employing 4NTAZ-PPI as emitters has a maximum external quantum efficiency of 7.3% and CIE coordinates of (0.149, 0.131) at luminance of 1000cd m⁻². The results are comparable to the reported non-doped blue fluorescent OLEDs. The strategy proposed here to connect triazole derivatives as the acceptors and phenanthroimidazole derivatives as the donors has shown the great potential to obtain high-performance organic blue emitters.

Conflicts of interest

The authors declare that they have no conflict of interest.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (grant nos. 21875083, 51925303 and 91833304), the program "JLUSTIRT" (grant no. 2019TD-33) and the China Postdoctoral Science Foundation (No. 2020TQ0117).

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View Article Online DOI: 10.1039/D1TC01079D

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