Synthesis and Luminescent Properties of 1,4,5-Triphenylimidazole–Phenothiazine Fluorophores

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Abstract

Two blue donor-acceptor fluorophores with 1,4,5-triphenylimidazole as the electron-transporting unit and phenothiazine as the hole-transporting unit were synthesized by grafting 1,4,5-triphenylimidazole moieties onto 3- and 3,7-position of the phenothiazine core and characterized by spectroscopic methods. Their thermal stability, photophysical, electrochemical and electroluminescence properties were systematically investigated. These compounds exhibit good thermal stability and show blue emission in dichloromethane solution and thin solid films. The solution-processed doped devices were fabricated by using these fluorophores as the emitting dopant in 1,3-bis(*N*-carbazolyl)benzene host, in which the device fabricated from the fluorophore containing two 1,4,5-triphenylimidazole moieties exhibited blue emission with a luminance of 648 cd/m² and external quantum efficiency of 1.48%.

1. Introduction

Organic electroluminescence diodes (OLEDs) are becoming one of the leading technologies for full-color displays and environment-friendly light source due to the thinness, high brightness, wider viewing angle, lower power consumption, higher color gamut, faster response speed, better flexibility, wider operating temperature range and lower cost ^[1–6]. Over the last decades, great development of the light-emitting materials and device structures for high-performance OLEDs has been made in both scientific research and commercial applications ^[7–15]. Generally, OLED light-emitting materials can be divided into two main types according to their chemical and photophysical properties: small molecule light-emitting materials and polymeric light-emitting materials ^[16–23]. Compared with polymeric light-emitting materials, small molecule luminescent materials are easier to synthesize and purify, and their structure can be fine-tuned through appropriate molecular design. OLEDs based on small molecules can be fabricated either by vacuum deposition method or by solution spin-coating method ^[24–26]. Among the small-molecule luminescent materials, luminescent materials with high photoluminescence quantum (Φ_{PL}) and excellent charge transport characteristics can effectively improve the electroluminescence (EL) efficiency ^[17, 27].

Phenothiazine (PTZ) and its derivatives are a class of electron-rich aromatic heterocyclic compounds containing nitrogen and sulfur atoms, which have been widely used in various optoelectronic applications due to their unique optical, electronic properties, flexibility of functionalization, low cost, and commercial availability ^[28–30]. In the field of organic semiconductor materials for optoelectronics, phenothiazine (PTZ) has been commonly used as a strong electron donating group. It is well-known that anthracene has high fluorescence efficiency, but it is easy to crystallize, thus the OLEDs based on the simple structural anthracene derivatives usually exhibited low performance. Unlike anthracene with a planar conformation, PTZ core is a butterfly conformation that could restrain the formation of ground state aggregates and excimers, making PTZ a well-known building block for OLEDs ^[31, 32]. Due to the strong electron donating ability of phenothiazine, the D–A or D– π –A type emitters based on phenothiazine have been designed and synthesized for OLEDs. Kwon and co-workers ^[33] designed and synthesized two isomeric D–A fluorescent molecules based on phenothiazine–quinolone framework, 2-(4-phenyl-2-quinolyl)-10-

methylphenothiazine (**2PQMPT**) and 3-(4-phenyl-2-quinolyl)-10-methylphenothiazine (**3PQMPT**), for green organic light-emitting diodes, and it was found that the device performances of the isomer **3PQMPT** (25020 cd/m² of $L_{\max}$, 2.50% of $EQE_{\max}$) were superior to that of the isomer **2PQMPT** (10590 cd/m² of $L_{\max}$, 1.06% of $EQE_{\max}$). Ahn et al. [34] reported a new fluorescent emitter **PhBBPP** (3,7-bis(1-(biphenyl-4-yl)-1H-benzo[d]imidazole-2-yl)-10-phenyl-10H-phenothiazine) with D–A type structure, and the optimized non-doped OLED device used **PhBBPP** as emitting layer showed a luminous efficiency of 12.1 cd/A, and an external quantum efficiency (EQE) of 4.0%. Recently, Zhao and co-workers [35] reported three new bipolar molecules containing phenothiazine and phenanthroimidazole moieties, **PI-PTZ** (10-butyl-3-(phenanthroimidazol-2-yl)phenothiazine), **PPI-PTZ** (10-butyl-3-((4-(tert-butyl)phenyl)phenanthroimidazol-2-yl)phenothiazine) and **PPI-PTZ-PPI** (10-butyl-3,7-bis((4-(tert-butyl)phenyl)phenanthroimidazol-2-yl)phenothiazine), and the optimized doped device based on **PPI-PTZ-PPI** exhibited a maximum brightness of 30,180 cd/m², a maximum external quantum efficiency (EQE) of 4.0% and a maximum current efficiency of 10.65 cd/A.

The twisted 1,4,5-triphenylimidazole as an acceptor could cause a wider band-gap and lead to deeper blue emission than the planar and rigid phenanthroimidazole acceptor, and the twisted 1,4,5-triphenylimidazole could also hamper the tight π – π intermolecular interactions. Therefore, it was often used to construct blue-emitting materials [36, 37]. Based on the structural feature of 1,4,5-triphenylimidazole, in this work, we have synthesized two blue D–A fluorophores containing 1,4,5-triphenylimidazole as the electron-acceptor and phenothiazine as the electron-donor by grafting 1,4,5-triphenylimidazole moieties onto 3- and 3,7-position of the phenothiazine core to investigate the effect of the number of electron-acceptors on the optoelectronic properties of the materials.

2. Experimental

2.1. Materials and methods

Phenothiazine, 1-bromobutane, benzyl and 4-*tert*-butylaniline were obtained from Energy Chemical (China). All the other reactants and solvents were obtained from commercial sources. All organic solvents used in this study were dried with the suitable desiccants and freshly distilled prior to the relevant reactions.

The NMR spectrum was measured on Bruker 500. The mass spectrum was recorded using a Bruker Esquire 3000 mass spectrometer. Thermogravimetric analysis (TGA) was performed on Shimadzu thermal analyzer in Japan. The UV-vis absorption spectrum was recorded on a Shimadzu UV-2550 spectrometer. The cyclic voltammogram was performed on an electrochemical analyzer (CHI Instruments 760 B). At room temperature, using Edinburgh instrument FLS920 integrating sphere and Xe lamp, the quantum yield of photoluminescence was measured by the absolute method. At room temperature, the Edinburgh instrument FLS920 was used with a microsecond flash lamp as the excitation source

(repetition frequency 90 Hz), and the photoluminescence decay lifetime was measured by a time-correlated single photon counting spectrometer.

The synthesis process of the intermediates, 10-butyl-10*H*-phenothiazine-3-carbaldehyde and 10-butyl-10*H*-phenothiazine-3,7-dicarbaldehyde, were described in our previous paper [35].

2.2. Synthesis and characterization of the compounds

10-Butyl-3-(1-(4-(tert-butyl)phenyl)-4,5-diphenyl-1*H*-imidazol-2-yl)-10*H*-phenothiazine (PTZ-PIM): In a 250 mL three-necked flask, benzil (0.82 g, 3.90 mmol), 4-*tert*-butylaniline (0.64 g, 4.29 mmol), 10-butyl-10*H*-phenothiazine-3-carbaldehyde (1.00 g, 3.53 mmol) and CH₃COONH₄ (4.08 g, 52.93 mmol) were dissolved in 50 mL of glacial acetic acid, and then it was stirred at 120°C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into ice water and filtered to obtain a yellow solid. The crude product was purified by silica gel chromatography using dichloromethane/petroleum ether (1:3, v/v) to obtain a pale yellow solid (1.90 g, 89%). m.p. > 240°C. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.59 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.25–7.15 (m, 8H, Ar-H), 7.12 (d, *J* = 7.7 Hz, 3H, Ar-H), 7.08 (s, 1H, Ar-H), 7.03 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.95 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.8 Hz, 2H, Ar-H) 3.78 (t, *J* = 7.0 Hz, 2H, N-CH₂), 1.76–1.70 (m, 2H, -CH₂-), 1.45–1.37 (m, 2H, -CH₂-), 1.29 (s, 9H, -C(CH₃)₃), 0.92 (t, *J* = 7.5 Hz, 3H, -CH₃). ¹³C NMR (126 MHz, CDCl₃, δ, ppm): 151.7, 138.1, 134.5, 134.3, 131.1, 130.7, 128.3, 128.2, 128.0, 127.8, 127.5, 127.2, 126.6, 126.1, 115.3, 114.7, 34.8, 31.2, 20.1, 13.9. HRMS: Calcd. for C₄₁H₃₉N₃S, 606.2937 [M+H]⁺; Found: 606.2937. Anal. Calcd. for C₄₁H₃₇N₃S: C, 81.28; H, 6.49; N, 6.94. Found: C, 81.43; H, 6.46; N, 6.91.

10-Butyl-3,7-bis(1-(4-(tert-butyl)phenyl)-4,5-diphenyl-1*H*-imidazol-2-yl)-10*H*-phenothiazine (PIM-PTZ-PIM): In a 250 mL three-necked flask, benzil (1.86 g, 8.85 mmol), 4-*tert*-butylaniline (1.44 g, 9.65 mmol), 10-butyl-10*H*-phenothiazine-3,7-dicarbaldehyde (1.00 g, 3.21 mmol) and CH₃COONH₄ (9.30 g, 0.12 mol) were dissolved in 60 mL of glacial acetic acid, and then the reaction mixture was stirred at 120°C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into ice water and filtered to obtain a white solid. The crude product was purified by silica gel chromatography using dichloromethane/petroleum ether (1:1, v/v) to obtain a pale white solid (2.15 g, 70%). m. p. > 250°C. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.57 (d, *J* = 7.1 Hz, 3H, Ar-H), 7.39 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.7 Hz, 3H, Ar-H), 7.28 (d, *J* = 8.6 Hz, 5H, Ar-H), 7.25–7.14 (m, 12H, Ar-H), 7.11 (d, *J* = 7.8 Hz, 3H, Ar-H), 7.00 (s, 2H, Ar-H), 6.94 (d, *J* = 8.6 Hz, 3H, Ar-H), 6.61 (d, *J* = 8.7 Hz, 1H, Ar-H), 3.72 (t, *J* = 7.2 Hz, 2H, N-CH₂-), 1.71–1.61 (m, 2H, -CH₂-), 1.43–1.36 (m, 2H, -CH₂-), 1.29 (s, 18H, -C(CH₃)₃), 0.91 (t, *J* = 7.5 Hz, 3H, -CH₃). ¹³C NMR (126 MHz, CDCl₃, δ, ppm): 168.3, 151.8, 147.2, 146.1, 144.4, 135.3, 134.3, 131.1, 130.7, 130.6, 128.6, 128.3, 128.1, 127.9, 127.8, 127.5, 127.3, 126.6, 126.1, 125.8, 123.9, 119.8, 114.5, 47.1, 34.7, 34.4, 31.4, 31.3, 28.7, 24.5, 20.0, 13.8. HRMS: Calcd. for C₆₆H₆₁N₅S, 956.4720 [M+H]⁺; Found: 956.4720. Anal. Calcd. for C₆₆H₆₁N₅S: C, 82.89; H, 6.43; N, 7.32. Found: C, 83.03; H, 6.45; N, 7.30.

3. Results And Discussion

3.1. Synthesis

The synthetic routes of **PTZ-PIM** and **PIM-PTZ-PIM** were shown in Scheme 1. These compounds were synthesized by a facile multicomponent reaction of the monoaldehyde or dialdehyde of 10-butyl-10*H*-phenothiazine with benzyl, 4-*tert*-butylaniline and ammonium acetate in acetic acid medium in good yields (70% yield), in which the key intermediates, 10-butyl-10*H*-phenothiazine-3-carbaldehyde and 10-butyl-10*H*-phenothiazine-3,7-dicarbaldehyde, were prepared through Vilsmeier-Haack formylation of 10-butyl-10*H*-phenothiazine [35]. The final compounds **PTZ-PIM** and **PIM-PTZ-PIM** were purified on a silica gel column to obtain pure solid products, and were characterized by NMR (^1H and ^{13}C), high-resolution mass spectrometry and elemental analysis. Both compounds are soluble in common organic solvents, such as toluene, dichloromethane, chloroform, ethyl acetate, acetone, tetrahydrofuran and DMF.

3.2. Photophysical, electrochemical properties and thermal stabilities of the compounds

In their absorption spectra, the stronger absorption bands at 260 nm for **PTZ-PIM** and 272 nm for **PIM-PTZ-PIM** were attributed to the $\pi-\pi^*$ transitions of the phenothiazine units, while the weak absorption bands at 375 nm for **PTZ-PIM** and 392 nm for **PIM-PTZ-PIM** could be assigned to the intramolecular charge transfer (ICT) transitions from phenothiazine cores to imidazole units [35]. The moderately intense absorption bands located in range of 280 – 360 nm could be the $\pi-\pi^*$ transitions of imidazole and the substituted benzene rings [38]. Compared with **PTZ-PIM**, the absorption spectrum of **PIM-PTZ-PIM** was red-shifted due to more conjugation of A–D–A type structure for **PIM-PTZ-PIM** than that of A–D type structure for **PTZ-PIM**. The optical absorption edges (λ_{onset}) of **PTZ-PIM** and **PIM-PTZ-PIM** in dichloromethane solution were estimated to be at ca. 443 nm and 461 nm, the corresponding optical band gaps of **PTZ-PIM** and **PIM-PTZ-PIM** were about 2.80 eV and 2.69 eV, respectively, from the equation: $E^{\text{opt}} = 1241/\lambda_{\text{onset}}$.

As shown in Fig. 1, **PTZ-PIM** and **PIM-PTZ-PIM** exhibited strong blue emission with a maximum peak at 459 nm and 476 nm in dilute chloromethane solution, while their PL spectra in thin solid films were obviously blue-shifted, and the maximum emission peaks of **PTZ-PIM** and **PIM-PTZ-PIM** in thin solid films were observed at 443 nm and 469 nm, respectively. The presence of the butterfly conformational PTZ core and the twisted 1,4,5-triphenylimidazole units in **PTZ-PIM** and **PIM-PTZ-PIM** could efficiently limit π -conjugation and inhibit the intermolecular aggregations, which could cause the blue-shifts of their PL spectra in thin solid films than that in dilute chloromethane solution. In addition, the fluorescence quantum yields (Φ_f) of **PTZ-PIM** and **PIM-PTZ-PIM** in dichloromethane solutions (1.0×10^{-6} mol/L) were measured to be 18.49% and 28.92%, respectively, at room temperature under air atmosphere, and their decay lifetimes (τ) were measured to be 5.6 and 5.8 ns, which belong to typical fluorescent materials.

In order to investigate the influence of solvent polarity on the PL spectra of the compounds, the steady-state fluorescence spectra of **PTZ-PIM** and **PIM-PTZ-PIM** were measured in different polar solvents (1.0×10^{-5} mol/L) (Fig. 2). Compared with the PL spectra of **PTZ-PIM** in different solvents, from low polarity

toluene to high polarity DMF, the PL spectrum of **PIM-PTZ-PIM** in toluene, dichloromethane, tetrahydrofuran and dimethylformamide exhibits obvious solvatochromic effects, and the emission band of **PIM-PTZ-PIM** is obviously red-shifted from 452 nm in toluene to 477 nm in DMF, and the total redshift of 25 nm was observed. For **PTZ-PIM**, its emission peak is located at 452 nm in toluene and red-shifted to 458 nm in DMF. As the solvent polarity increases, the emission peak of **PTZ-PIM** was only red-shifted 8 nm. The results were indicated that **PIM-PTZ-PIM** has a more obvious charge transfer characteristic.

The thermal stabilities of **PTZ-PIM** and **PIM-PTZ-PIM** were measured by thermogravimetric and differential thermal analyses (TG-DTA) under nitrogen atmosphere (Fig. 4). As shown in Fig. 4, **PTZ-PIM** and **PIM-PTZ-PIM** show excellent thermal stability, and they exhibit higher thermal decomposition temperatures (corresponding to a 5% weight loss) of 365°C for **PTZ-PIM** and 378°C for **PIM-PTZ-PIM**. From their differential thermal analyses, their glass transition temperatures are 226°C and 202°C, respectively.

The electrochemical properties of **PTZ-PIM** and **PIM-PTZ-PIM** were investigated by cyclic voltammetry. The cyclic voltammograms of the compounds are shown in Fig. 5. The first oxidation potentials (E_{ox}) of **PTZ-PIM** and **PIM-PTZ-PIM** were about 1.11 and 1.12 V, respectively. Under the same condition, the measured Fc/Fc^+ potential was 0.52 V. Thus, the HOMO energy levels of **PTZ-PIM** and **PIM-PTZ-PIM** were calculated to be -5.39 and -5.40 eV^[39, 40], and the LUMO energy levels of **PTZ-PIM** and **PIM-PTZ-PIM** were calculated to be -2.59 and -2.71 eV, respectively.

3.3. Theoretical calculation

The optimized molecular geometries and the HOMO and LUMO density maps of **PTZ-PIM** and **PIM-PTZ-PIM** were calculated by the density functional theory (DFT) calculation at B3LYP/6-31G(d) level (Fig. 6). From their optimized molecular geometries, it was found that these compounds exhibit a highly distorted configuration, which could effectively inhibit the intermolecular aggregations and weaken the $\pi-\pi$ intermolecular interactions. For **PTZ-PIM**, the dihedral angles of 17.0° between the imidazole ring and the adjacent benzene ring of the phenothiazine unit, 40.1° between the benzene ring substituted at the N-1 position of the imidazole ring and the imidazole ring, and 24.9° and 3.3° between the benzene rings substituted at the 4-position and 5-position of the imidazole ring and the imidazole ring were observed, respectively. For **PIM-PTZ-PIM**, the dihedral angles between the imidazole rings and the adjacent benzene rings of the phenothiazine unit, between the benzene rings substituted at the N-1 position of the imidazole rings and the imidazole rings, and between the benzene rings substituted at the 4-position and 5-position of the imidazole rings and the imidazole rings were 7.3(7.5)°, 37.7(40.5)°, 26.9(24.9)° and 1.7(2.2)°, respectively.

From their electron distributions of the molecular orbitals, the electron distributions in their HOMOs are almost centralized on the whole molecules except for the benzene rings at the N-1 position of the imidazole rings, and the electron distributions are somewhat more abundant on the phenothiazine cores. In their LUMOs, the electron distributions are concentrated in the whole molecules, but the majority of

electron densities distributed on 1,4,5-triphenylimidazole units, and only small part of them located on the phenothiazine cores. In addition, the calculated HOMO/LUMO energy levels of **PTZ-PIM** and **PIM-PTZ-PIM** are -4.37/-1.34 and -4.26/-1.45 eV, respectively.

The data of photophysical, electrochemical and thermal properties of **PTZ-PIM** and **PIM-PTZ-PIM** are listed in Table 1.

Table1. Photophysical, thermal and electrochemical properties of the compounds

Compound	^a UV-vis (nm)	^a PL/ ^b PL (nm)	T _d (°C)	T _g (°C)	^a Φ _f (%)	^a τ (ns)	E _{ox} (V)	E ^{opt} (eV)	HOMO/LUMO (eV)
PTZ-PIM	260, 291, 319, 375	459/443	365	226	18.49	5.6	1.11	2.80	-5.39/-2.59
PIM-PTZ-PIM	272, 323, 392	476/469	378	202	28.92	5.8	1.12	2.69	-5.40/-2.71
^a Measured in dichloromethane solution. ^b Measured in thin solid films.									

3.4. Electroluminescence investigation

To investigate the electroluminescent properties of the compounds, the doped devices with a configuration as ITO/PEDOT:PSS (30 nm)/mCP:**PTZ-PIM** or **PIM-PTZ-PIM** (x wt%, 25 nm)/TPBi (35 nm)/Liq (2 nm)/Al (150 nm) were fabricated, in which the PEDOT:PSS (30 nm) layer and the emitting layer mCP:**PTZ-PIM** (x wt%, 25 nm) or **PIM-PTZ-PIM** (x wt%, 25 nm) were spin-coated, and other layers are made by evaporation. The device structure and the energy levels of the materials are depicted in Fig. 7.

The doped devices based on **PTZ-PIM** and **PIM-PTZ-PIM** exhibited the turn-on voltage from 5.6 to 6.4 V. Among the compounds, the device based on **PIM-PTZ-PIM** exhibited the best performances with a maximum current efficiency (CE_{max}) of 2.45 cd/A, a maximum power efficiency (PE_{max}) of 1.48 lm/W, a maximum brightness (L_{max}) of 648 cd/m² and a maximum external quantum efficiency (EQE_{max}) of 1.48% at 15 wt% doping concentration. From Table 2, it was found that the devices based on **PTZ-PIM** showed poor EL performances in comparison to that of **PIM-PTZ-PIM**, which was consistent with the higher photoluminescence quantum yield of **PIM-PTZ-PIM** in solution than that of **PTZ-PIM**. The device based on **PTZ-PIM** exhibited the best EL performances with 1.37 cd/A of CE_{max}, 0.68 lm/W of PE_{max}, 638 cd/m² of L_{max} and 1.13% of EQE_{max} at 20 wt% doping concentration.

Table 2
EL performances of **PTZ-PIM** and **PIM-PTZ-PIM**.

	Concentration	V _{on} (V)	EL _{max} (nm)	L _{max} (cd/m ²)	LE _{max} (cd/A)	PE _{max} (lm/W)	EQE _{max} (%)
PTZ-PIM	5 wt%	6.4	449	283	0.44	0.19	0.36
	10 wt%	6.4	450	348	0.84	0.38	0.69
	15 wt%	6.0	452	435	0.78	0.39	0.64
	20 wt%	5.6	452	638	1.37	0.68	1.13
	25 wt%	5.5	455	652	1.29	0.47	0.90
PIM-PTZ-PIM	5 wt%	6.2	465	404	1.36	0.89	0.89
	10 wt%	6.4	469	460	2.26	1.44	1.44
	15 wt%	5.8	469	648	2.45	1.48	1.48
	20 wt%	5.8	470	647	1.91	1.24	1.24

4. Conclusions

Two blue D–A fluorophores, **PTZ-PIM** and **PIM-PTZ-PIM**, were synthesized by grafting 1,4,5-triphenylimidazole moieties onto 3- and 3,7-position of the phenothiazine core and characterized by NMR, high-resolution mass spectrometry and elemental analysis. These compounds exhibit strong blue emission and good thermal stability. The doped devices based on **PIM-PTZ-PIM** had better EL performances than that of **PTZ-PIM** because of more conjugation of A–D–A type structure for **PIM-PTZ-PIM** than that of A–D type structure for **PTZ-PIM**, which was consistent with the higher photoluminescence quantum yield of **PIM-PTZ-PIM** in solution than that of **PTZ-PIM**. The doped device fabricated from **PIM-PTZ-PIM** exhibited a maximum brightness of 648 cd/m², a maximum current efficiency of 2.45 cd/A and a maximum external quantum efficiency of 1.48% at 15 wt% doping concentration.

Declarations

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

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2. Conflicts of interest/Competing interests (include appropriate disclosures)

We declare that there are no conflicts of interest/competing interests.

3. Ethics approval (include appropriate approvals or waivers)

Not applicable

4. Consent to participate (include appropriate statements)

Not applicable

5. Consent for publication (include appropriate statements)

Consent for publication was obtained from all participants.

6. Availability of data and material (data transparency)

The data supporting the results of this article are included within the manuscript.

7. Code availability

Not applicable

8. Authors' contributions

Tianzhi Yu developed the idea of the study, participated in its design and coordination and helped to draft the manuscript. Long Qian and Hongyan Yang contributed to the acquisition and interpretation of data. Yuling Zhao and Yongchun Guo did some testing works.

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Schemes

Scheme 1 is available in the Supplemental Files section

Figures

Figure 1

The UV–vis absorption and photoluminescence spectra in Dichloromethane solution (1.0×10^{-5} mol/L) and thin solid film of **PTZ-PIM** and **PIM-PTZ-PIM**.

Figure 2

The photoluminescence spectra of **PTZ-PIM** (A) and **PIM-PTZ-PIM** (B) in different solvents (1.0×10^{-5} mol/L).

Figure 3

The photoluminescence spectra of **PTZ-PIM** (A) and **PIM-PTZ-PIM** (B) in different concentrations of dichloromethane solution.

Figure 4

Thermogravimetric and differential thermal (inset) analyses of **PTZ-PIM** and **PIM-PTZ-PIM** under nitrogen atmosphere (heating rate: 10 °C/min).

Figure 5

Cyclic voltammograms of ferrocene, **PTZ-PIM** and **PIM-PTZ-PIM** (scan rate: 10 mV/s; solvent: chloroform).

Figure 6

The optimized molecular geometries and the calculated HOMO and LUMO density maps of **PTZ-PIM** and **PIM-PTZ-PIM** at the B3LYP/6-31G(d) level.

Figure 7

Schematic diagram of the OLED device configuration (a), the relative HOMO/LUMO energy levels of the materials investigated in this work (b) and structures of PEDOT, mCP and TPBi.

Figure 8

(A) Current density–voltage–luminance (J – V – L) characteristics and (B) current/power efficiency–luminance (CE/PE – L) curves of the devices based on **PTZ-PIM** with different dopant concentrations.

Figure 9

(A) Current density–voltage–luminance (J – V – L) characteristics and (B) current/power efficiency–luminance (CE/PE – L) curves of the devices based on **PIM-PTZ-PIM** with different dopant concentrations.

Supplementary Files

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- [Scheme1.png](#)