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Highly efficient green organic light emitting diodes with

phenanthroimidazole-based thermally activated delayed

fluorescence emitters

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Abstract: Here, phenanthroimidazole moiety was firstly introduced to the construction of thermally activated delayed fluorescence (TADF) emitters, and two novel TADF emitters consisting of phenanthroimidazole as the acceptor group and phenazine the donor as group, 1-(4-(*tert*-butyl)phenyl)-2-(4-(10-phenylphenazin-5(10H)-yl)phenyl)-1H-phenanthro 9,10-d]imidazole (PPZTPI) and 1-phenyl-2-(4-(10-phenylphenazin-5(10H)-yl)phenyl)-1H-phenanthro[9,10-d]imidazo le (**PPZPPI**) were designed and synthesized. The highly twisted conformation between phenazine and phenanthroimidazole in the molecules results in effective spatial separation of the HOMO and LUMO and small singlet-triplet splittings. Both compounds possess obvious TADF features. Their crystallographic properties, electronic structures, thermal stabilities, photophysical properties, and energy levels are studied systematically. Organic light-emitting diode (OLEDs) using these two green TADF emitters demonstrate high external quantum efficiencies of 21.06% for **PPZPPI** and 20.52% for **PPZTPI**, respectively, which is comparable to the most of previously reported TADF OLEDs.

Introduction

Since the first organic light-emitting diode (OLED) was made by Tang¹, OLEDs have drawn great attention for their superior applications in displays and lighting. According to spin statistics, traditional fluorescent emitters could only harvest 25% of singlet excitons to produce light. In order to utilize the triplet excitons, researchers

developed precious-metal-based phosphorescent emitters to harvest both singlet and triplet excitons by heavy-atom effect.^{2, 3} Although phosphorescent OLEDs could achieve high efficiencies, high costs and the short operation lifetime of blue phosphorescent OLEDs limit their widespread application. Fortunately, in 2012, Adachi and co-workers reported nearly 100% internal quantum yield for pure organic thermally activated delayed fluorescence (TADF) molecules.⁴ TADF emitters could convert triplet excitons to singlet excitons through efficient reverse intersystem crossing (RISC), in which a small energy gap ($\Delta E_{ST} < 0.2 \text{eV}$) between the S₁ and T₁ states is required to accelerate the RISC process. Therefore, the TADF molecule could be designed with donor and acceptor moieties in twisted structures, which can effectively separate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and achieve a small ΔE_{ST} . Meanwhile, appropriate orbital overlap should be retained to promote the radiative transition.

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To date, different kinds of TADF molecules have been developed. Donor parts were mostly limited to aromatic amines, such as triphenylamine⁵, carbazole⁶, acridine⁷, phenoxazine⁸ and phenothiazine⁹. While there were a variety of acceptor moieties, including sulfone¹⁰, ketone¹¹, phosphine oxide^{12, 13}, triazine^{14, 15}, pyrimidine^{16, 17}, dicyanobenzene⁴, triarylboron¹⁸⁻²⁰ and some other electron deficient aromatic rings²¹⁻²⁴. Phenanthroimidazole is an ideal building block for organic light-emitting materials. It is a weak electron donor when an electron-withdrawing moiety is attached to the imidazole ring, but it shows electron withdrawing properties when linked with an electron donor. Ma et al.²⁵ reported a deep-blue molecule with phenanthroimidazole as a weak electron donor, it showed a CIE coordinates of (0.152, 0.077) and high EQE of 6.8%. Wang et al.²⁶ created a deep-blue emitter PPI-PPIPCz based on phenanthroimidazole with CIE coordinates of (0.15, 0.07) and high EQE of 8.1%, which also realized high-performance red, yellow and green phosphorescent devices using it as host. Our group reported a series of phenanthroimidazole-based bipolar host material^{27, 28}, and the corresponding green phosphorescent OLEDs showed a maximum EQE of 22.6%²⁹. There are still a lot of phenanthroimidazole derivatives for highly efficient blue emitters³⁰⁻³³ and host materials^{34, 35}, whereas

phenanthroimidazole have not been used in TADF materials. The main reason is that the energy gap between the singlet and triplet excited state of phenanthroimidazole is very large.²⁷

Recently, our group reported three donor-acceptor (D-A) type materials based on phenanthroimidazole and 9,9-diphenyl-9,10-dihydroacridine.³⁶ Although there was a great twist angle between the donor and acceptor, it exhibited a large ΔE_{ST} and not any TADF phenomenon. According to these, we introduced a strong donor phenazine instead, which led to a small ΔE_{ST} about 0.11eV and showed distinct TADF phenomenon. In this work, we designed and synthesized two novel TADF materials based phenanthroimidazole, on 1-(4-(tert-butyl)phenyl)-2-(4-(10-phenylphenazin-5(10H)-yl)phenyl)-1H-phenanthrof 9,10-d]imidazole (PPZTPI) and 1-phenyl-2-(4-(10-phenylphenazin-5(10H)-yl)phenyl)-1H-phenanthro[9,10-d]imidazo le (**PPZPPI**). Moreover, their crystallographic properties, electronic structures, thermal stabilities, photophysical properties, energy levels and device performances were investigated. Finally, the green TADF OLED device based on **PPZPPI** showed a maximum EQE of 21.06%. These results prove that phenanthroimidazole could be an excellent acceptor for the design of TADF materials.

Results and discussion

Synthesis and thermal properties

The synthetic routes and molecular structures are depicted in **Scheme 1**. 2-(4-bromophenyl)-1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole and 2-(4-bromophenyl)-1-phenyl-1*H*-phenanthro[9,10-*d*]imidazole were synthesized according to the literature³⁷. Due to the unstability of monosubstituted 5,10-dihydrophenazine under aerated conditions³⁸, the final products were synthesized in a one-pot reaction. The detailed synthetic methods and analysis are described in the Experimental section. The chemical structures of the compounds were confirmed by ¹H NMR, elemental analysis, mass spectrometry and single-crystal X-ray analysis. Before fabrication of the OLED devices, the two new compounds were further purified by repeated temperature-gradient vacuum sublimation.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to investigate the thermal properties of the two compounds under nitrogen atmosphere. As presented in Fig. 1 and Table 1, compounds **PPZTPI** and **PPZPPI** exhibit high decomposition temperatures (T_d , corresponding to 5% weight loss) of 430°C and 419°C, indicating their excellent thermal stability. In addition, they did not show any glass transition temperatures up to 250°C. The excellent thermal properties of the two compounds can be ascribed to their highly rigid and twisted structures.



Scheme 1. Synthetic routes and chemical structures of the materials: (a) $Na_2S_2O_4$, EtOH, H₂O; (b) $Pd(OAc)_2$, $[(t-Bu)_3PH]BF_4$, t-BuONa, toluene, 110°C.



Fig. 1. TGA curves of PPZTPI and PPZPPI.

Single-crystal structure

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We obtain the single crystal by slow evaporation of a solution of **PPZTPI** in a mixture of tetrahydrofuran and methanol. The crystal structure (**Fig. 2**) showed that

the phenazine group is orthogonal to its connected phenyl rings with a large dihedral angle of 89.8°. Such a twisted structure, arising from the steric repulsion by the hydrogen atoms in the phenyl and phenazine unit, results in effective spatial separation of the HOMO and LUMO and reduction of ΔE_{ST} . There were also large dihedral angles between the N-substituted benzene and phenanthroimidazole plane. Due to the twisted conformation, there are no close π - π stacking among **PPZTPI** fragments. Multiple intermolecular C-H··· π short contacts (see **Fig. S2**) are observed, which could lock intramolecular rotation and depress the nonradiative decay.



Fig. 2. Crystal structure (CCDC 1577557) of PPZTPI.

Theoretical calculations

To gain a better insight into the molecular configuration and electronic structures of these phenanthroimidazole based materials, we performed quantum chemical calculations using density functional theory (DFT) at the B3LYP/6-31G(d) level. **Fig. 3** shows the optimized structures, and the HOMO / LUMO distribution of the two compounds. The HOMO is mainly distributed on the donor phenazine moiety, and the LUMO is well spread over the acceptor phenanthroimidazole plane. The small spatial overlap between HOMO and LUMO indicates strong charge transfer transition and small electron exchange energy. On the other hand, the dihedral angles between the phenylene and the donor are 88.77° and 89.54°, respectively for **PPZTPI** and **PPZPPI**, which is consistent with the single-crystal. We next calculated the S₁ and T₁ excited energies using time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d) level in the gas phase based on the ground state geometries of compounds. The calculated ΔE_{ST} values of **PPZTPI** and **PPZPPI** are 0.01 eV and 0.008 eV, respectively, which is small enough for efficient TADF.



Fig. 3. HOMO and LUMO distributions, and calculated singlet (S_1) and triplet (T_1) energy levels

IOF (a) FFZIFI and (b) FFZFF	for (a)) PPZTPI	and (b)	PPZPPI
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Compound	Abs ^a (nm)	PL^a	Φ^{b}	$E_g^{\ c}$	$S_1/T_1^{\ d}$	S_1/T_1^e (eV)	HOMO/	T_d^{g}
		(nm)		(eV)	(eV)		$LUMO^{f}(eV)$	(°C)
PPZTPI	322, 364, 422	532	0.731	2.52	2.47/2.36	2.369/2.359	-4.73/-2.21	430
PPZPPI	328, 364, 423	531	0.990	2.51	2.48/2.36	2.327/2.319	-4.73/-2.22	419

Table 1. Physical properties of **PPZTPI** and **PPZPPI**.

a Measured in dilute toluene solution at room temperature.

b PLQY of these emitters doped into CBP films (5 wt%) under oxygen-free conditions at room temperature.

c Measured by the onset absorption wavelength of solution state.

d Obtained from the peak of fluorescence spectra and phosphorescence spectra of these emitters in 2-MeTHF at 77K.

e Calculated by TD-DFT at the B3LYP/6-31G(d) level.

f HOMO was determined from the onset of oxidation potentials with ferrocene as reference; LUMO was determined from E_g and HOMO level.

g Measured from TGA.

Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of the two compounds are measured in dilute toluene, as shown in **Fig. 4**. Key optical parameters are summarized in **Table 1**. The two compounds display similar absorption features in

toluene solution. The absorption bands in the range from 320 to 380 nm are attributed to the π - π * transition of the phenanthroimidazole moiety. In addition, the longer wavelength absorption peaks of the two compounds at around 420 nm are assigned to the intramolecular charge transfer (CT) transition. The energy gaps (E_{σ}) of **PPZTPI** and **PPZPPI** obtained from the onset of the absorption spectra are 2.52 eV and 2.51 eV, respectively. The peak wavelengths of the PL spectra of **PPZTPI** and **PPZPPI** in diluted toluene are 532 nm and 531 nm, respectively. In order to unveil the solvatochromic effect chromatically, the fluorescence of **PPZTPI** and **PPZPPI** in different polar solvents was measured, as shown in **Fig. S3**. As the solvent polarity increased, their fluorescence was red-shifted from blue to orange, suggesting the strong CT-state characteristic of the two compounds. Fig. S4 shows the PL spectra of the materials in doped films. The PL spectra of 5 wt% PPZTPI doped CBP film showed a peak at 527 nm, it was a slight blue-shift compare with the peak of 533 nm for **PPZPPI**. The blue shift resulted from the large size of tertiary butyl, which will avoid the intermolecular interaction between host and dopant. High PLQY values of 0.731 and 0.990 are obtained for **PPZTPI** and **PPZPPI**, which suggest that they will be potentially good emitters in OLEDs. The relative lower PLQY for **PPZTPI** should be attributed to the poor energy transfers from host to dopant.

To evaluate ΔE_{ST} values of the compounds, their fluorescence and phosphorescence spectra in 2-methyltetrahydrofuran (2-MeTHF) solutions were measured at 77 K. The fluorescence peaks of **PPZTPI** and **PPZPPI** at 77 K were 502 nm and 501 nm, which resulted in S₁ energy levels of 2.47 and 2.48 eV, respectively. And the phosphorescence peaks of **PPZTPI** and **PPZPPI** were found to be the same at 525 nm, and their corresponding T₁ energy levels were 2.36 eV. According to **Fig. 4**, the ΔE_{ST} values were estimated to be 0.11 eV for **PPZTPI** and 0.12 eV for **PPZPPI** in 2-MeTHF. The ΔE_{ST} values were low enough for the efficient RISC process.

In order to confirm the delayed fluorescence behavior of phenanthroimidazole based TADF emitters, the transient PL decay curves of both doped films were carried out at room temperature. As shown in **Fig. 5**, both the doped films of the compounds showed clear second-order exponential decays at 300 K. **PPZTPI** possess a short lifetime of 3.26 ns and a long lifetime of 126.5 μ s, and 3.0 ns and 118.0 μ s for **PPZPPI**. The short lifetime component was attributed to the relaxation from S₁ to S₀, and the delayed component should be assigned to the thermal up-conversion of excitons from T₁ to S₁, and then from S₁ to S₀. **PPZTPI** shows longer delayed lifetime than **PPZPPI** in the doped films, suggesting that the tertiary butyl blocks the intermolecular interaction between host and dopant and makes the excitons lasting longer time. The TADF property is further confirmed by the temperature dependent transient PL decay from 77K to 300K (see **Fig. S5**). With the temperature increasing, the ratio of the delayed component gradually increases and the delayed lifetime gradually decreases^{21, 39, 40}, which demonstrated the typical TADF characteristic of the two compounds. The detail kinetic parameters are summarized in **Table S2**.



Fig. 4. Absorption and PL spectra of PPZTPI and PPZPPI in dilute toluene at room temperature,

and their fluorescence and phosphorescence spectra at 77 K.



Fig. 5. Transient PL characteristics of **PPZTPI** and **PPZPPI** doped in CBP films (5 wt%) at 300 K.

Electrochemical properties

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The electrochemical properties and energy levels of the two compounds were

investigated by cyclic voltammetry using the conventional three electrode system. As shown in **Fig. 6**, **PPZTPI** and **PPZPPI** show well reversible oxidation behavior arising from phenazine unit. The onset voltages of these oxidation curves are the same, at -0.09 V versus the Ag/Ag^+ redox couple. The HOMO energy levels of **PPZTPI** and **PPZPPI** are estimated to be -4.73 eV with regard to ferrocene. The LUMO energy levels of **PPZTPI** and **PPZPPI** are calculated from HOMO level and E_g , and found to be -2.21 eV and -2.22 eV, respectively. It is worth noting that the stronger electron-donating group of phenazine makes the HOMO level much shallower,³⁶ which is not favorable for the hole transporting from the hole transporting layer or host.



Fig. 6. Cyclic voltammograms of PPZTPI and PPZPPI.

Electroluminescent devices

the electroluminescent (EL) То investigate properties of the two phenanthroimidazole based TADF emitters, multilayer OLEDs were fabricated with doped films as the emitting layer (EML). The device configuration was ITO/MoO₃ (10 nm)/TAPC (80 nm)/TCTA (10 nm)/EML (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm), in which ITO (indium tin oxide) was used as the anode, MoO_3 was used hole injection TAPC as layer, (4,4'-(cyclohexane-1,1-diyl)bis(*N*,*N*-di-*p*-tolylaniline)) was used as the hole transporting layer, TCTA (tris(4-(9H-carbazol-9-yl)phenyl)amine) was used as an exciton blocking PPZTPI PPZPPI doped CBP layer, or in (4,4'-di(9H-carbazol-9-yl)-1,1'-biphenyl) host was used as the EML, TmPyPB (1,3,5-tri(m-pyrid-3-yl-phenyl)benzene) was used as the electron transporting layer, LiF was used as electron injecting layer and Al was used as cathode. Fig. 7a shows the energy diagram of the materials. The doping concentration of emitters was fixed to be 5% in the EML after optimization of the control device efficiency. The devices show the highest EQE at a doping concentration of 5 wt%. As shown in **Fig. S6**, with the doping concentration increasing, both emitters exhibit slightly red-shifted EL spectra, which should be ascribed to the interaction between emitter and host under high doping concentration.



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Fig. 7. (a) Energy-level diagram of the materials used in the devices. (b) EL spectra at 100cd/m². (c) current density–voltage–luminance (J–V–L) characteristics. (d) EQE–luminance characteristics.

The current density–voltage–luminance (J–V–L) characteristics, external quantum efficiency (EQE) curves and EL spectra of these 5 wt% doped devices are shown in **Fig. 7**. Both of the devices turned on at a low turn-on voltage of 3.0 V. Their EL spectra are close to their PL spectra and there are no other emission peaks from host materials, which suggests the complete energy transfer from the host materials to the dopants. **PPZPPI** based device exhibited green electroluminescence with emission peak at 528 nm and CIE coordinates of (0.363, 0.572), with the maximum external quantum efficiency, current efficiency and power efficiency of 21.06%, 67.18 cd/A and 68.11 lm/W, respectively. **PPZTPI** based device showed similar green electroluminescence with emission peak at 528 nm and CIE coordinates of (0.359, 0.572).

0.575), with the maximum external quantum efficiency, current efficiency and power efficiency of 20.52%, 65.90 cd/A and 68.98 lm/W, respectively. These EQE of the devices exceed the theoretical limit of conventional fluorescent OLEDs, indicating efficient up-conversion from triplet excitons to singlet excitons. Meaningfully, the performance of both the devices was comparable to the most of previously reported TADF OLEDs.^{4, 5, 7, 11, 16, 18, 21, 41-46}

PPZPPI based device showed slightly lower efficiency roll-off, which was attributed to the short delayed lifetime and fast RISC and radiative rate. While the EQE is less than 10% at high brightness beyond 1000 cd/m² for both. Hole-only devices and electron-only devices were fabricated to study exciton transport and formation in the EML with the structure of ITO/MoO₃ (10 nm)/TAPC (80 nm)/TCTA (10 nm)/EML (30 nm)/TCTA (10 nm)/MoO₃ (10 nm)/Al (100 nm) and ITO/LiF (1 nm)/TmPyPB (40 nm)/EML (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm). As shown in Fig. S7, the current density of hole-only devices increase with the doping concentration of emitters in the emission layer and that of electron-only devices are opposite. The shallow HOMO cause holes to be almost trapped into and transported by emitter. Electron injection and transport are predominantly transported via the host, emitters capture more electron under high doping concentration and lead to a smaller current density. The efficiency roll-off at high brightness should be mainly attributed to unbalanced charge carriers and the direct combination of electron and hole on the dopant. Although **PPZTPI** has a lower PLQY than **PPZPPI**, **PPZTPI** based device also achieve relative high efficiency, which means the poor energy transfers from host to dopant has little effect to the performance. We anticipate that the device performance can further be improved by using optimized device structures with better hosts and carrier transporting materials.

Conclusion

In summary, we designed and synthesized two novel green TADF emitters (**PPZTPI** and **PPZPPI**) based on phenanthroimidazole derivatives in this work. The two compounds employ phenanthroimidazole as the acceptor unit and phenazine as the donor unit to form nearly vertical D-A structure. Both of these emitters possess obvious TADF features, good thermal stability, high PLQYs, a small ΔE_{ST} of around 0.1 eV and moderate delayed lifetimes. The OLEDs using **PPZTPI** and **PPZPPI** as the emitters achieve maximum EQE, PE and CE of 20.52%, 65.90 cd/A and 68.98 lm/W, respectively, and 21.06%, 67.18 cd/A and 68.11 lm/W, respectively. The results provide a promising opportunity for the design and construction of highly efficient TADF materials based on phenanthroimidazole derivatives.

Experimental section

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Materials and measurements

In our previous studies, most of the experimental conditions and equipment have been described.³⁶ All the reagents and solvents used for the syntheses and measurements were purchased from commercial suppliers and were used without further purification unless otherwise noted. ¹H NMR spectra was conducted on a Bruker-AF301 AT 400 MHz spectrometer. Mass spectra were recorded on a Bruker-Daltonics microflex LT/SH mass spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Thermogravimetric analyses (TGA) were undertaken using a PerkinElmer Instruments (Pyris1 TGA) under nitrogen atmosphere at a heating rate of 10°C/min from 30 to 600°C. The differential scanning calorimetry (DSC) was performed on a TA Q2000 DSC instrument under nitrogen at a heating rate of 10°C/min from 30 to 250°C. The glass transition temperature (T_{o}) was determined from the second heating scan. UV-Vis spectra were measured using a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). Photoluminescence (PL) spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. The transient PL decay curves were measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920). Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics). Cyclic voltammetry (CV) was performed on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional three electrode cell, which consisted of a platinum wire counter electrode, an

Ag/AgNO₃ (0.1 M) reference electrode and a Pt carbon working electrode of 2 mm diameter. Oxidations of all compounds were performed in dried dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. The solutions were purged with a nitrogen stream for 10 min before measurements.

Synthesis of 5,10-dihydrophenazine

A solution of sodium dithionite (17.4 g, 100 mmol) in water (200 mL) was added to a boiling solution of phenazine (1.8 g, 10 mmol) in ethanol (50 mL). The mixture was stirred and heated to reflux for 2 h. A white precipitate was collected by filtration and dried under reduced pressure to afford 5,10-dihydrophenazine (1.62 g, 8.9 mmol). This material was used in the next step without further purification. ¹H NMR (400 MHz, DMSO-*d*₆) δ [ppm]: 7.26 (s, 2H), 6.24-6.22 (m, 4H), 5.99-5.97 (m, 4H).

Synthesis

1-(4-(*tert*-butyl)phenyl)-2-(4-(10-phenylphenazin-5(10*H*)-yl)phenyl)-1*H*-phenanth ro[9,10-*d*]imidazole (PPZTPI)

А

mixture

2-(4-bromophenyl)-1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole (2.52 g, 5 mmol), 5,10-dihydrophenazine (1.62 g, 8.9 mmol), *t*-BuONa (0.96 g, 10 mmol), *tri-tert*-butylphosphonium tetrafluoroborate (87 mg, 0.3 mmol) and palladium acetate (33 mg, 0.15 mmol) was dissolved in dry toluene (50 mL), and purged three times by nitrogen/vacuum cycle. The reaction mixture was refluxed for 2 hours, and then bromobenzene (5 mL) was added by syringe. The reaction mixture was refluxed for another 10 hours. After cooling, petroleum ether (100 mL) was added to the cooled mixture and the solid was separated by filtration. The crude product was recrystallized from hexane and dichloromethane to produce yellow solid (1.77 g) in 52% yield. ¹H NMR (400 MHz, Benzene-*d*₆) δ [ppm]: 9.49 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51

of

of

(t, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.16-6.97 (m, 12H), 6.29-6.26 (m, 4H), 5.84-5.80 (m, 4H), 1.14 (s, 9H). MS (MALDI-TOF): calculated for C₄₉H₃₈N₄, 682.31; found 681.58, [M]⁺. Elemental analysis calculated (%) C₄₉H₃₈N₄: C 86.19, H 5.61, N 8.20; found: C 86.23, H 5.51, N 8.23.

Synthesis

of

1-phenyl-2-(4-(10-phenylphenazin-5(10*H*)-yl)phenyl)-1*H*-phenanthro[9,10-*d*]imid azole (PPZPPI)

PPZPPI was prepared with the similar procedure as that of **PPZTPI** but with 2-(4-bromophenyl)-1-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (2.24 g, 5 mmol) instead of

2-(4-bromophenyl)-1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole. The crude product was recrystallized from hexane and dichloromethane to produce yellow solid (1.72 g) in 55% yield. ¹H NMR (400 MHz, Benzene-*d*₆) δ [ppm]: 9.48 (d, *J* = 7.6 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30-7.25 (m, 2H), 7.16-6.88 (m, 12H), 6.29-6.27 (m, 4H), 5.85-5.80 (m, 4H). MS (MALDI-TOF): calculated for C₄₅H₃₀N₄, 626.25; found 625.96, [M]⁺. Elemental analysis calculated (%) C₄₅H₃₀N₄: C 86.24, H 4.82, N 8.94; found: C 86.33, H 4.73, N 8.87.

Computational details

The geometrical and electronic properties were computed using the Gaussian 09 program package. The ground-state geometry was optimized using density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31G(d). The singlet and triplet states were calculated by time-dependent density functional theory (TD-DFT) with the B3LYP functional at the same basis set level. Molecular orbitals were visualized using Gauss view 5.0 program.

Device fabrication and measurement

The carrier-injection material MoO_3 , lithium fluoride (LiF), and carrier-transporting material 4,4'-(cyclohexane-1,1-diyl)bis(N,N-di-p-tolylaniline) (TAPC). 3,3'-(5'-(3-(pyridin-3-yl)phenyl)-[1,1':3',1"-terphenyl]-3,3"-diyl)dipyridine (TmPyPB), exciton blocking material tris(4-(9H-carbazol-9-yl)phenyl)amine (TCTA) and host material 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP) were commercially available. Commercial ITO coated glass with a sheet resistance of 20 Ω per square was used as the substrate. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated with oxygen plasma for 5 min. MoO₃ was firstly deposited on the ITO substrate, followed by TAPC, TCTA, the emission layer, and TmPyPB. Finally, a cathode composed of LiF and aluminum was sequentially deposited onto the substrate in the vacuum of 2×10^{-6} Torr. For all of the OLEDs, the emitting areas were determined by the overlap of two electrodes as 0.09 cm^2 . The EL spectra, CIE coordinates and J-V-L curves of the devices were measured using a PHOTO RESEARCH SpectraScan PR655 photometer and a KEITHLEY 2400 SourceMeter constant current source. The efficiency values were calculated according to previously reported methods. All measurements were carried out at room temperature under ambient conditions.

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