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PII: S1566-1199(19)30153-3

DOI: https://doi.org/10.1016/j.orgel.2019.03.044

Reference: ORGELE 5182

To appear in: Organic Electronics

Received Date: 23 January 2019

Revised Date: 12 March 2019

Accepted Date: 24 March 2019

Please cite this article as: Y. Jia, S. Wu, Y. Zhang, S. Fan, X. Zhao, H. Liu, X. Dong, S. Wang, X. Li, Achieving non-doped deep-blue OLEDs by applying bipolar imidazole derivatives, *Organic Electronics* (2019), doi: https://doi.org/10.1016/j.orgel.2019.03.044.

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Achieving non-doped deep-blue OLEDs by applying bipolar

imidazole derivatives

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Abstract: In this work, we designed and synthesized two novel bipolar deep-blue emitting materials, 2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-1 (4(tri-fluoromethyl) phenyl)-1H-phenanthro[9,10-d] imidazole (CzB-FMPPI) and 9-(4'-(4,5-diphenyl-1 (4-(trifluoromethyl) phenyl)-1*H*-imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-9*H*-carbazole (CzB-FMPIM). Among them, carbazole and phenanthroimidazole are bridged linkage by the biphenyl ring and act as electron-donating part. The CF₃-substituted phenyl ring applies as strong electron-withdrawing moiety. The exhibit highly twisted molecular configuration of two compounds efficiently shorten π -conjugation and inhibit intermolecular interaction, resulting in superior thermal stability and deep blue emission. High decomposition temperature of 431 °C and 414 °C, glass transition temperature of 150 °C and 135 °C for CzB-FMPPI and CzB-FMPIM, respectively, had been achieved. As a consequence of breaking the conjugation of phenanthroimidazole chromophore, CzB-FMPIM achieves a 8 nm blue-shifted emission compared with CzB-FMPPI. CzB-FMPPI exhibits a higher relative fluorescence quantum yield of 92.5% than 83.3% of CzB-FMPIM. Moreover, bipolar property was observed in both compound and homogeneous amorphous films were deposited and applied in the non-doped deep-blue OLEDs. The devices based on two emitters showed maximum luminance of 6667 cd/m^2 and 3084 cd/m^2 , maximum EQE of 4.10% and 3.17%,

respectively. Commission International de l'Éclairage (CIE) coordinates of CzB-FMPIM based device achieved (0.15, 0.07) which is extremely close to the NTSC standard blue CIE (0.14, 0.08).

Keywords: Bipolar, Deep-blue emission, Twisted configuration, Phenanthroimidazole, Non-doped OLEDs.

1. Introduction

Organic light emitting diodes (OLEDs)^[1] have already been applied in several fields due to their preeminent advantages.^[2-5] However, the great potential prospect in the full-color flat-panel display and solid-state lighting^[6,7] make it still a hot field and attracts scientists' attention from worldwide. To fulfil the full-color display, three basic colors (RGB) are crucial. In recent years, a lot of efforts have been devoted to achieve highly efficient green, red and blue emitters with outstanding color purity and stability. So far, the green and red emitters have already met the needs for practical application.^[8-12] Nevertheless, excellent blue emitters are still on the pursuing list in terms of efficiency and stability.^[13-15] In particular, deep-blue emitter ^[16, 17] is of great significance and play a key role in OLEDs devices because of its multi-function, such as efficiently decreasing the power consumption, increasing the color gamut and being utilized to be a host for other long-wavelength emitters.^[18-20]

In the long term of developing ideal materials for OLEDs, phosphorescent and thermally activated delayed fluorescent (TADF) emitters are welcome among the researchers. OLEDs devices based on these materials theoretically could harvest all excitons to emit photons, thereby achieve a high external quantum efficiency (EQE). ^[2, 3, 21-23] However, to realize commercialization, the barriers stand in front of phosphorescent material is the high cost caused by transition metal complexes, server efficiency roll-off and poor stability. ^[24, 25] The requirement for TADF-based OLEDs is the host-guest doping system to reduce triplet-triplet annihilation and weaken the efficiency roll-off at high voltage, but this will give rise to complicated device fabrication technique and raising the cost. Thus, blue fluorescent emitters are still considered as the competitive candidates for stable non-doped OLEDs devices.

Constructing bipolar molecules is one of the effective ways to develop highly

efficient deep-blue emitting materials. Chun-Sing Lee's group lately reported a series of bipolar blue emitting materials, in which the best non-doped OLEDs performance based on TPAPOPPI shows an EQE_{max} of 6.69% and CIE coordinates of (0.152, 0.095).^[4] Zuolun Zhang had demonstrated a non-doped OLEDs device using mTPE-DPI as emitting layer achieved EQE of 3.69% with CIE coordinate of (0.15, 0.14). ^[26] Lei Wang's group showed a DPACPhTPI-based non-doped device exhibits CIE of (0.156, 0.047), and a EQE of 3.5%. ^[27] C. Huang's group got a high EQE of 5.8% for non-doped OLEDs based on CPBPMCN with CIE of (0.15, 0.08). [28] Generally, bipolar material could transport both holes and electrons, so that achieve a better balanced charge carriers and broaden exciton recombination region, consequently improve the device performance. The strategy to construct bipolar materials is to introduce electron donors and electron acceptors into the molecules.^{[29,} ^{30]} Nevertheless, the intramolecular charge transfer (ICT) between D and A will lower photoluminescence quantum yields (PLQYs) and lead to a red-shift emission. Therefore, it is absolutely imperative to choose appropriate donors and acceptors to regulate the ICT aiming at getting ideal deep-blue bipolar emitters. Carbazole unit is usually selected as donor originating from its moderate electron-donating properties, good carriers transporting ability, and good thermal stability.^[31] Phenanthroimidazole is also regarded as an ideal building block in designing a blue emitting material owing to the high thermal stability and bipolar transporting properties. Meanwhile, the ICT could be alleviated by modifying appropriate Donor or Acceptor on Phenanthroimidazole moiety.^[32]

Based on the ideas above, we designed and synthesized the molecule CzB-FMPPI and CzB-FMPIM. In which, carbazole and phenanthroimidazole serves as electron-donating unit. The CF₃-substituted phenyl ring applies as strong electron-withdrawing moiety and could also trigger blue shifted emission. ^[33, 34] The carbazole and phenanthroimidazole are bridged linkage by the biphenyl with moderate twist angle, maintaining molecular conjugation and high PLQYs. Furthermore, compared to CzB-FMPPI, CzB-FMPIM fulfils deeper blue emission by breaking the conjugation of phenanthroimidazole chromophore, but at the cost of thermal stability

to some extent. The two compounds CzB-FMPPI and CzB-FMPIM exhibit good thermal stability with glass transition temperature (T_g) of 150 °C and 135 °C, decomposition temperature (T_d) of 431 °C and 414 °C, respectively. What's more, both compounds have bipolar properties demonstrated by single-carrier devices and reorganization energy calculation. The non-doped OLEDs devices based on two emitters showed maximum luminance of 6667 cd/m² and 3084 cd/m², CIE coordinates of (0.15, 0.12) and (0.15, 0.07), maximum EQE of 4.10% and 3.17%, respectively. Comprehensively speaking, the overall performance of the devices based on the both compounds are comparable to the non-doped deep-blue OLEDs with CIEy≈0.1 reported to date. ^[14, 35, 36]

2. Experimental section

2.1 Material

All the reagents and solvents used in this paper were purchased from manufacturers without further processing. THF was freshly distilled from sodium/benzophenone under argon (Ar) atmosphere before use.

2.2 Genernal procedures

¹H and ¹³C NMR measurements were conducted on a Bruker ACF400 (400 MHz) spectrometer. High resolution mass spectra (HRMS) data were obtained on a Bruker MicrOTOF-Q II. Absorption spectra and Photoluminescence spectra were recorded on a Thermo Evolution 300 UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Fluorescence quantum yield (Φ_f) was determined by using quinine sulfate solution in 0.01 M H₂SO₄ ($\Phi_f = 0.54$) as a reference. DSC measurement was studied on a TA Q20 instrument operated at a heating rate of 10 °C/min from 25 °C to 350 °C in N₂. TGA was recorded on a METTLER TOLEDO TGA/DSC1 Thermogravimetric Analyzer at the heating rate of 10 °C /min from 30 °C to 800 °C in N₂. The transient PL spectrum was performed by FLS980 fluorescence spectrometer. X-ray diffraction spectra were recorded on a Rigaku Miniflex 600 with 2 θ range of 3°-20°, scanning at a rate of 1°/min. crystallography of CzB-FMPPI was collected at the temperature of 113 K on a Rigaku XtaLAB P200 diffractometer equipped with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The

structure was solved with the SHELXL-97 program, and the refinement was performed by a full-matrix least-squares technique based on F^2 with the SHELXL-97 program 2.3 *OLEDs fabrication and characterization*

ITO-coated glasses with a sheet resistance of 30 Ω per square were used as substrates. Before device fabrication, the ITO glass substrates were cleaned with deionized water, isopropanol, acetone and ethanol in succession, and then dried with nitrogen and treated with oxygen plasma for 5 min. ITO glass substrates were spin-coated with a layer of PEDOT: PSS (~40 nm) colloidal solution on the ITO side at 3000 rpm, followed with baking at 140°C for 20 min, and then transferred into a thermal evaporation system with a pressure of 7×10^{-4} Pa. Then, all organic functional layers were sequentially deposited onto the ITO substrates at a rate of 0.3-1.0 Å/s. Finally, 1 nm LiF and 100 nm Al were deposited onto the substrate at the rate of 0.2 Å/s and 10 Å/s, respectively. The thicknesses and deposition rates of film were controlled by a quartz crystal thickness monitor. The EL spectra, luminance of device, and CIE coordinates were measured with Konicaminolta CS-2000. The current-voltage characteristics were recorded using a Keithley 2400 SourceMeter under ambient atmosphere.

2.4 Synthesis and characterizations



Scheme 1. Molecular structures and synthetic routes of CzB-FMPPI and CzB-FMPIM The molecular structure and synthetic routes were shown in Scheme 1. Firstly,

9-(4-bromophenyl)-9*H*-carbazole was prepared by classical Ullmann reaction, then reacted with boric acid esters to get the (4-(9*H*-carbazol-9-yl) phenyl) boronic acid.^[37] 2-(4-bromophenyl)-1-(4-(trifluoromethyl) phenyl)-1*H*-phenanthro[9,10-*d*] imidazole and 2-(4-bromophenyl)-4,5-diphenyl-1-(4-(trifluoromethyl) phenyl)) phenyl)-1*H*-imidazole were prepared by a method previously reported.^[38] The final compounds were successfully prepared by Suzuki cross-coupling reaction. The target compounds were fully characterized by NMR and HRMS. Detailed reaction procedures are shown in supporting information.

3. Result and discussion

3.1 X-ray crystal structure and packing mode



Fig. 1 single crystal structure (a) and packing fromat (b) of CzB-FMPPI.

The molecular structure and intermolecular interaction were investigated by X-ray crystal diffraction. The single crystal of CzB-FMPPI was prepared by slow volatilization of dichloromethane. (Crystal data of CzB-FMPPI has been submitted to the Cambridge Crystallographic Data Centre and the CCDC deposition number is: 1891230). The single crystal structure and packing pattern are displayed in Fig. 1. The data of CzB-FMPPI crystal are summarized in Table S1. As shown in Fig. 1a. The

CzB-FMPPI exhibits a twisted steric configuration with dihedral angles of 42.28° plane and adjacent benzene 87.89° between carbazole ring, between phenanthroimidazole plane and the side benzene ring, 50.12° between the phenanthroimidazole plane and the adjacent benzene ring, and 38.73° between the bridging biphenyl group, respectively. The packing details are demonstrated in Fig. 1b. Two neighboring parallel carbazole can be observed to have a certain extent overlap with a rather long distance of 3.388 Å, indicating a weak π - π intermolecular interaction might exist. The carbazole chromophore is also perpendicular to the benzene ring linked with the $-CF_3$ group, a rather weak edge-to-face intermolecular interaction with CH/ π distance about 2.8 Å could be found. Moreover, the hydrogen on carbazole is bonded with the phenanthroimidazole by a N/H interaction (d = 2.631 Å). The biphenyl group mainly has a certain distance (d ≈ 2.8 Å) with phenanthroimidazole plane, besides, also a comparable distance with carbazole plane. To sum up, the molecule was successfully synthesized to be a twisted configuration. Such twist structure suppressed strong π - π intermolecular interaction in some extent, which may decrease aggregation induced fluorescence quenching in film state.^[39] The CzB-FMPPI is promising to apply in a non-doped OLEDs as emitter.

3.2 optical properties



Fig. 2 Normalized UV-Vis spectra and PL spectra of CzB-FMPPI and CzB-FMPIM in dilute DMF and in neat film

The UV-vis and photoluminescence spectrum of CzB-FMPPI and CzB-FMPIM in DMF and films were recorded to study their photophysical properties (Fig. 2). Both two compounds have similar absorption profile. The peak at 294 nm could be assigned to n- π^* transition of carbazole. ^[40, 41] The absorption band around 340 nm may originate from π - π^* transition between substitute benzene ring and the imidazole unit. ^[42]The unique shoulder-peak at 365nm of CzB-FMPPI is generated by the n- π^* transition of phenanthroimidazole chromophore. ^[42]



Fig. 3 The lifetime measurement of CzB-FMPPI (a) and CzB-FMPIM (b) in degassed THF by using time-correlated single photon counting method

As shown in the photoluminescent spectrum (Fig. 2), both compounds exhibit strong blue emission with maximum emission peak at 423 nm and 415 nm in dilute DMF solution, and at 440 nm and 415 nm in neat film for CzB-FMPPI and CzB-FMPIM, respectively. Compared with CzB-FMPPI, CzB-FMPIM exhibit a 8 nm blue-shift in solution, which could be attributed to the small π -conjugation backbone of noncoplanar 1,4,5-triphenyl-1*H*-imidazole. Meanwhile, this noncoplanar structure of CzB-FMPIM also inhibits the intermolecular stacking in solid state, hence reduce the aggregation caused fluorescence quenching. The relative fluorescence quantum yield of CzB-FMPPI and CzB-FMPIM were investigated in THF to be 92.5% and 83.3%

using quinine sulfate (0.01 M dilute H_2SO_4 , $\Phi_f = 0.54$)^[43] as a standard.

To verify whether the TADF process contributes to the PL spectrum, transient PL decay curve in 10⁻⁶ M degassed THF were investigated by time-correlated single photon counting method. Both spectra reveal a mono-exponential PL decay with a short lifetime of 1.41 ns for CzB-FMPPI and 1.44 ns for CzB-FMPIM, respectively (Fig. 3). As it was known, TADF molecules usually exhibit two-exponential lifetime: a fast PL decay for nanoseconds and a delayed fluorescence decay for hundreds of microseconds. ^[15] This phenomenon indicates that no triplet excitons contribute to PL decay by thermally activated reverse intersystem crossing (RISC).

Subsequently, combined with PLQYs and transient PL lifetimes. the radiative rate constants (k_f) and nonradiative rate constants (k_{nf}) were calculated to investigate the excited state nature. The data are displayed in Table S3. The k_f is 12-fold higher than its k_{nf} for CzB-FMPPI (6.54×10^8 /S, 0.53×10^8 /S), 5-fold higher for CzB-FMPIM (5.76×10^8 /S, 1.15×10^8 /S). The higher k_f rate indicate that the radiative process is predominant in light emission, as a result obain high PLQYs.

3.3 Thermal properties and morphology

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were studied. As shown in Fig. S1, the T_d and T_g for CzB-FMPPI are 431 °C and 150 °C, which are higher than 414 °C and 135 °C of CzB-FMPIM, respectively. The better thermal stability of CzB-FMPPI could be attributed to its larger rigidity of phenanthroimidazole chromophore.



Fig. 4 X-ray diffraction spectra of ITO, CzB-MOPPI and CzB-FMPIM thin film on ITO substrate

To study the film property of the compound in solid state, the X-ray diffraction (XRD) spectrum was performed as shown in Fig. 4. All films were prepared by vacuum deposition. Both compounds exhibit featureless pattern compare to ITO substrate before and after annealing for 24 h at 90 °C. Such character implies these compounds are capable of forming homogeneously amorphous films during thermal deposition.^[44, 45]

3.4 Electrochemical properties

Photoelectron yield spectroscopy was employed to estimate the HOMO (the highest occupied molecular orbital) of two compounds (Fig. S2). The HOMO of CzB-FMPPI is -5.62 eV and CzB-FMPIM is -5.87 eV, respectively. The LUMO (the lowest unoccupied molecular orbital) of CzB-FMPPI (-2.36 eV) and CzB-FMPIM (-2.54 eV) were calculated by uniting HOMO energy level with optical band gap (E_g). Herein, the optical band gaps were determined by the λ_{onset} of absorption spectrum. Details are summarized in the Table 1.

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Compound	$T_{\rm d}/T_{\rm g}$	$\lambda_{ m abs}{}^a$	$\lambda_{\rm em}{}^a$	$\lambda_{em}^{\ b}$	$arPhi_{ m f}^{~c}$	HOMO^d	$LUMO^d$	E_g^{e}	$ au^f$	
	(□)	(nm)	(nm)	(nm)	(%)	(eV)	(eV)	(eV)	(ns)	
CzB-FMPPI	431/150	294, 343, 364	423	440	92.5	-5.62	-2.36	3.16	1.41	_
CzB-FMPIM	414/ 135	294,331	415	<mark>415</mark>	83.3	-5.87	-2.54	3.33	1.44	_

Table 1 Basic properties of CzB-FMPPI and CzB-FMPIM

^{*a*} Absorption and PL: measured in 10⁻⁵ M DMF. ^{*b*} Absorption and PL: measured in neat film. ^{*c*} Photoluminescent quantum yield (PLQY) measured using quinine sulfate as standard. ^{*d*} Measured by photoelectron yield spectroscopy. ^{*e*} Optical band gap determined from the absorption onset in DMF. ^{*f*} Prompt PL lifetime in THF

3.5 Theoretical calculation

Density functional theory (DFT) calculation at B3LYP/6-31G(d) level was carried out to get a deeper understanding of the electronic properties. The electron-cloud distributions of frontier molecular orbitals are demonstrated in Fig. 5. Interruption of phenanthroimidazole conjugated plane has no effect on HOMO and LUMO distributions of the two compounds. The HOMO nearly spread on the whole molecules except the N1-connected benzene ring with trifluoromethyl. While the LUMO mainly locate on the biphenyl and N1-connected benzene ring, as well as a

little residue on phenanthroimidazole. Both LUMO and HOMO occupied on imidazole cycle, this might contribute to the electronic dual nature of imidazole. Bonding different chromophores on the two nitrogen atoms in imidazole ring will lead to different bipolar properties: it is a weak electron donor when bonding with a strong acceptor and a weak acceptor otherwise. ^[46, 47]The Large HOMO-LUMO overlap is responsible for their high fluorescence quantum yield. ^[48] The HOMO energy levels were calculated to be -5.27 eV and -5.27 eV, LUMO energy levels were -1.54 eV and -1.46 eV for CzB-FMPPI and CzB-FMPIM, respectively.



Fig. 5 DFT calculated HOMO (upper) and LUMO (bottom) of CzB-FMPPI (a) and

CzB-FMPIM (b)

The reorganization energy calculation was also conducted to study the bipolar properties of the compounds. Detailed data were summarized in Table S2. The hole reorganization energy was defined to be 0.182 eV and 0.222 eV, while the electron reorganization energy were 0.462 eV and 0.468 eV for CzB-FMPPI and CzB-FMPIM, respectively. Such results indicate both compounds are capable of transporting hole and electron, which could contribute to good device performance. However, the hole reorganization energy of two compounds are smaller than the electron reorganization energy, implying both compounds perform better hole transport ability. Besides, CzB-FMPPI shows a lower hole reorganization energy than CzB-FMPIM, suggesting CzB-FMPPI own superior hole tansport ability.

3.6 Carrier transporting characteristics

To further study the charge transporting capacity of two compounds, single

carrier devices with structure of ITO/NPB (10 nm)/(CzB-FMPPI or CzB-FMPIM) (30 nm)/NPB (10 nm)/Al (100 nm) (hole-only device) and ITO/TPBi (10 nm)/(CzB-FMPPI or CzB-FMPIM) (30 nm)/TPBi (10 nm)/LiF (1 nm)/Al (100 nm) (electron-only device) were fabricated. As displayed in Fig.6, all of the devices show high current density at low operated voltages, indicating that both compounds are capable of transporting electrons and holes. In addition, the hole-only devices exhibit a higher current density than electron-only device at a relatively high voltage. Such characteristics agrees with the reorganization energy calculation. Besides, the curves of CzB-FMPPI reveal a smaller current-density difference between single carrier devices at high voltage, implying the balance of charge carrier mobility. It is assumed that the CzB-FMPPI-based blue OLEDs should possess the better performance. The ohmic conduction regime in low applied voltage and space-charge limited conduction regime in high applied voltage could be observed for both compounds in Figure 6, suggesting a good Ohmic (or quasi-Ohmic) contact between the organic layer and the metal electrode.



Fig. 6 Current density versus voltage characteristics of single carrier devices of CzB-FMPPI (a) and

CzB-FMPIM (b)

3.7 Electroluminescence investigations

Non-doped OLEDs devices are fabricated with a simple structure of ITO/PEDOT:PSS (40 nm)/NPB (25 nm)/(CzB-FMPPI/CzB-FMPIM) (30 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm) to evaluate their EL performance. The device structure and materials energy level are displayed in Fig. 7. ITO was anode, PEDOT:PSS was hole injection layer fabricated by spin coating, NPB was hole-transporting layer, TPBi was electron-transporting layer, LiF/Al act as electron injection layer and cathode. The energy level diagrams and device structure are displayed in Figure 5b. Key device parameters are summarized in table 2.



Fig. 7 a) the device structure; b) energy level diagrams of the materials used in OLEDs; c) molecular structures of the compounds used in device

Compound	$V_{ m on}{}^a$	CE_{max}^{b}	L_{max}^{c}	EQE^{d}	$\lambda_{\mathrm{EL}}^{e}$	CIE^{f}
	(V)	(cd/A)	(cd/m^2)	(%)	(nm)	(x, y)
CzB-FMPPI	4.0	3.17	6667	4.10	441	0.15, 0.12
CzB-FMPIM	3.6	1.55	3084	3.17	425	0.15, 0.07

Table 2 Non-doped OLEDs device performances based on CzB-FMPPI	and CzB-FMPIM
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^a Turn-on voltage recorded at the luminance of 1 cd m². ^b Maximum luminous efficiency. ^c Maximum luminance. ^d

Maximum external quantum efficiency. ^e Maximum peak of EL spectra. ^f Measured at 8 V.

As shown in the table 2, the device based on CzB-FMPIM has a lower turn on

voltage (V_{on}) of 3.6 V (recorded at the luminance of 1 cd/m²) than 4.0 V of device based on CzB-FMPPI. Presumably, such phenomenon might be attributed to the low electron-injection barrier of 0.16 eV from TPBi to emitting layer. What's more, the non-doped device based on CzB-FMPPI demonstrate a bigger maximum luminance (L_{max}) of 6667 cd/m², a better maximum CE (current efficiency) of 3.17 cd/A than that of 3084 cd/m², 1.55 cd/A for non-doped device based on CzB-FMPPI. The result might benefit from the higher PLQY and radiative relaxation rate of CzB-FMPPI. The external quantum efficiency (EQE) value are estimated to be 4.10 % and 3.17 % for devices based on CzB-FMPPI and CzB-FMPIM, respectively.



Fig. 8 a) Current density-voltage-luminance curves; b) Current density-current efficiency curves; c) the plots of current density versus EQE; d) Normalized electronluminance spectrum of the devices, inset EL spectra at 5V, 8V, 10V, and 12V.

Apparently, as shown in Fig. 8d, both non-doped devices exhibit deep-blue emission at the wavelength of 441 nm and 425 nm for CzB-FMPPI and CzB-FMPIM, respectively. The former emission peak is the same as its PL emission in film, indicating the EL emission is from the emitting layer. In the meantime, the broadened

emission at long wavelength could be generated from excimer or exciplex.^[49, 50] The CIE coordinates of two devices based on CzB-FMPPI and CzB-FMPIM are (0.15, 0.12) and (0.15, 0.07), in which the lower CIE_y for CzB-FMPIM-based device is consistent with the original design idea. Not only the CIE coordinates are extremely close to the NTSC standard blue, but also their emission spectra are also stable along with the voltage increasing from 5 V to 12 V (Fig. 8d). what's more, the devices based on CzB-FMPIM suffers a more severe efficiency roll-off than CzB-FMPPI, that's because the hole injection barrier between NPB and CzB-FMPIM (0.57 eV) is bigger than that of CzB-FMPPI and NPB (0.32 eV), bigger hole injection barrier would block the hole from transporting to emissive layer at high voltage, leading to a severe efficiency roll-off.

In order to verify whether TADF or HLCT process contribute to the high EL performance, first we measured the fluorescence and phosphorescence curves of two compounds in toluene (shown in Fig. S4), the ΔE_{sT} are calculated to be 0.57 and 0.70 eV based on the onset of FL and Phos. curves for CzB-FMPPI and CzB-FMPIM, respectively. The ΔE_{ST} of two emitters are so much bigger than sufficiently small S-T energy gap (<0.2 eV) to efficiently active the RISC process in TADF mechanism.^[51] The big HOMO-LUMO overlap of two emitters in the DFT calculation (Fig. 5) also could not meet the requirement of reducing ΔE_{ST} to support a TADF process. ^[15] In fact, the transient fluorescence of two compounds in degassed tetrahydrofuran (Fig. 3) exhibit single exponential PL decay without any delayed fluorescence, which is featureless from typical TADF emitters.^[51]On the contrary, it might be the integration of HLCT state.^[30] So, we studied the FL of two emitters in different solvents, the absorption and fluorescence spectrum of two compounds are shown in Fig. S5. In the low-polar solvent like hexane, both compounds show a LE-like character because of the shoulder peak caused by their vibrational fine structure. The FL of CzB-FMPPI and CzB-FMPIM all demonstrate an obvious solvatochromic shift, indicating a typical CT feature of their emissive state. ^[32, 52] To better understand the solvatochromic effect, the Stokes shift $(v_a - v_f)$ versus the orientation polarizability f (ε , n) was fitted in more solvents according to the Lippert-Mataga model (Fig. S5c, f).^[53]

Both compounds show two independent linear relationships, indicating two different excited states happened in the emissive progress. The excited state dipole moment μ_e are calculated to be 10.0 and 8.9 D in low-polarity solvents, 22.7 and 21.2 D in high-polarity solvents for CzB-FMPPI and CzB-FMPIM, respectively. The small μ_e can be attributed to the LE-based HLCT state, whereas the large μ_e can be treated as the CT-dominated HLCT state. In which, the μ_e of CzB-FMPPI is bigger than that of CzB-FMPIM in low-polar solvents, implying the radiation transition rate and fluorescence quantum yield of former compound is higher than the latter one, leading to a better EL performance of CzB-FMPPI than that of CzB-FMPIM. Such results are coincidence with the experiments above.

4. Conclusion

In conclusion, two novel bipolar deep-blue emitters CzB-FMPPI and CzB-FMPIM were successfully synthesized and systematically investigated. In comparison with CzB-FMPPI, CzB-FMPIM realized a deeper blue emission through decrease the conjugation area of phenanthroimidazole chromophore. Both compounds exhibited high fluorescence quantum yield, good thermal stability and bipolar properties. Their distinct properties were all ascribed to their diverse twisted molecular configuration, which accord with our prospection. What's more, the non-doped OLEDs devices based on these two molecules showed deep blue emission. Especially CzB-FMPIM-based OELDs presented CIE coordinates of (0.15, 0.07), which is extremely close to the NTSC standard blue. The maximum luminance of OLEDs devices are 6667 cd/m² and 3084 cd/m², maximum EQE of 4.10% and 3.17% for CzB-FMPPI and CzB-FMPIM, respectively. We believe that these experimental data will provide the guideline for future molecule design and achieving highly-efficient deep-blue OLEDs.

Acknowledgements

This work is supported by the National Key Research and Development Program of China (2016YFB0401303), the National Natural Science Foundation of China (No. 21676188) and the Key Projects in Natural Science Foundation of Tianjin (16JCZDJC37100). The calculation in this work was supported by high performance

computing center of Tianjin University, China.

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Two donor-acceptor type deep blue fluorescent materials were firstly designed and synthesized.

Compounds exhibit high fluorescence quantum yield, good thermal stability and bipolar properties.

Non-doped good-performance deep-blue OLED devices with CIE of (0.15, 0.07) were achieved.