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Tuning electrical properties of phenanthroimidazole derivatives to construct multifunctional deep-blue electroluminescent materials

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Abstract: In this work, we introduce a n-type group, TPPO (triphenyl phosphine), to the N1-position of violet-blue fluorophore phenanthroimidazole (PI) and successfully develop one deep-blue (TPAPOPPI) and two violet-blue emitters (3-CzPOPPI and CzBPOPPI) for OLEDs (organic light-emitting diodes). With highly twisted linkage, the TPPO group shows negligible influences on their photophysical properties of the new materials and the materials inherit high efficient deep-blue and violet-blue emission of the PI unit and its C2-connected arylamine skeletons. Meanwhile, TPPO group can open a new channel to transport electron. The electron injection and transport abilities of the developed emitters are enhanced. Non-doped devices using the 3-CzPOPPI and the CzBPOPPI emitters exhibit EQE_{max} (external quantum efficiency) of 5.08% and 4.42% with CIE (Commission Internationale de l'Èclarage) coordinates of (0.156, 0.061) and (0.157, 0.071), respectively. Similar efficiencies and even deeper blue emissions (CIE_y) = 0.050 for **3-CzPOPPI** and 0.044 for **CzBPOPPI**) were observed in OLEDs with these emitters doped in 4,4'-bis(N-carbazolyl)-1,1'-biphenyl. **TPAPOPPI** is demonstrated to be a multifunctional deep-blue emitter and presents impressive performances when serving as non-doped (EQE_{max} = 6.69%, CIE: (0.152, 0.095)), doped (EQE_{max} = 6.61%, CIE: (0.154, 0.068)) as well as a high-performance host for yellow phosphorescent OLED. By doping a yellow phosphorescent dye (PO-01) into a **TPAPOPPI** host, a white OLED with a high EQE of 20.3% and a low driving voltage of 3.2 V (at 1,000 cd m⁻²).

Introduction

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In the past few decays, the advancement of electroluminescent material has greatly accelerated the development and commercialization of OLEDs (organic light-emitting diodes).¹⁻⁵ Especially, the emergence of phosphorescent⁵ (Ph) and thermally activated delayed fluorescent⁶ (TADF) materials enable an OLED to harvest all excitons for photon generation and achieve high EQE (external quantum efficiency) for both display and lighting applications.^{2,3,7,8} EOEs of state-of-the-art sky-blue and green PhOLED and TADF OLED have already surpassed 30%.⁹⁻¹² In terms of the red counterparts, an EOE of 24% was reported for PhOLED and a rapid progress from 8% to 14.5% was observed in a very short period for TADF OLED.^{6,13,14} Moreover, with optimized device structures, green and red OLED possessing practical lifetimes were also realized.¹⁵ The mature of these longer wavelength emitters makes it more urgent to develop high performance deep-blue emitters which can lower power consumption and widen color gamut of full-color displays and enhance color rendering index of lighting.^{1,3,15} Whereas, the nonradiative d-d transition of the core metal atoms and relatively low triplet energy level of common organic luminophores limited the development of deep-blue phosphorescent and TADF emitters.¹⁶⁻¹⁸ Besides, the popular host DPEPO for deep-blue phosphorescent and TADF emitters was reported to be unstable and not suitable for practical application.¹⁹ Host materials with high triplet energy (> 3 eV) and good electrical properties are still being explored.²⁰

Restricted by the spin statistics rule, OLEDs using fluorescent emitters can only achieve EQEs around 5%. Fortunately, with progresses of device fabricating technique, this demerit can be effectively remedied by using exciplex host,²¹ TADF host,²² TADF assistant dopant²³ or phosphorescent dopants²⁴. On the other hand, many deep blue fluorescent materials often have advantages in color purity, low efficiency roll-off at high luminance, as well as multifunctional (e.g as host).¹ They are thus considered as important complimentary materials to the high-efficiency phosphorescent and TADF emitters. To serve as a multifunctional material, the emitter should simultaneously have a deep-blue emission, high photoluminescent quantum yield (PLQY) in solid state, proper triplet energy (E_T) for sensitizing the dopant and excellent electrical properties to reduce device turn-on voltage (voltage at 1 cd m⁻², V_{on}) and driving voltages for improving power efficiency (PE) and to maintain good performance at high brightness. However, it is difficult to develop organic materials with simultaneously deep-blue emission and good carrier injection and transporting properties.^{25,26} It is because the intrinsically wide energy gaps of deep-blue emitters aggravate carrier injection barriers. A strong electron pull-push molecular system has been suggested to be a possible solution, but this strategy often sacrifices the color purity of

emitter.^{27,28} In many cases, to retain a deep-blue emission in solid state, deep-blue fluorophores often contain bulky groups to suppress intermolecular interaction and avoid excessive red-shifts in solid state.^{28,29} However, this strategy will impede carrier transport, especially for electron, resulting in higher V_{on} and lower PE in OLED.^{30,31}

TPPO (triphenyl phosphine) is a n-type group possessing excellent electron injection and transport abilities and is a common building block for electron transport materials and host materials.^{32–34} However, TPPO is rarely used in the design of emitters. This is because of its strong electron withdrawing ability may undermine the color purity of deep-blue emitters and the conjugation break in the P atom of TPPO group will lower the molecules' fluorescent yield.³⁵ In our molecular design (Scheme 1), the TPPO unit is attached to the N1 position of the phenanthroimidazole (PI) plane to form a nearly orthogonal linkage. In this way, we are aiming at using the highly twisted linkage to weaken conjugation between the two units effectively to minimize (ICT). The emission color is mainly dominated by the PI units and its C2-connected (No. 2 carbon atom in PI units, Scheme S2) arylamine skeleton. Moreover, in solid state, the bulky TPPO unit can prevent close packing of emitting center and avoid emission quenching. Meanwhile, the electron transporting properties of the TPPO may also enhance electrical performance of its constituting emitters. This idea is confirmed by analyzing their photophysical properties and electrical properties. In OLED using 3-CzPOPPI and CzBPOPPI as non-doped emitters, highly efficient violetblue emission with respectively EQE of 5.08 and 4.47% and CIE coordinates of (0.156, 0.061) and (0.157, (0.071) were obtained. When these materials are used as dopant emitters, similar EQE were achieved with deeper blue emission (CIE_v = 0.050 for **3-CzPOPPI** and 0.044 for **CzBPOPPI**). These performances are comparable to those of state-of-the-art violet-blue emitters.^{31,36-42} OLED using another molecule, **TPAPOPPI**, as non-doped emitter achieves an EQE of 6.69% with CIE coordinates of (0.152, 0.095). Besides, TPAPOPPI can also serve as a host for yellow phosphor PO-01(iridium(III) bis(4phenylthieno[3,2-c]pyridinato-N.C 2')acetylacetonate) and the vellow-emitting device achieve a decent EQE of 18.9%. A F/P (fluorescence and phosphorescence hybrid) white OLED with TPAPOPPI and PO-01 as emitters is shown to have a high EQE \approx 20% and shows very low operating voltages of 2.6, 3.2 and 4.6 V at 1, 1,000 and 10,000 cd m^{-2} .



Scheme 1 Chemical structure of the new compounds.

Experimental section

General information

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¹H NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer and mass spectra are measured with a PE SCFIEX API-MS spectrometer. A TA instrument TGAQ50 and a Perkin-Elmer DSC 7 thermal analyzer were used respectively to measure decomposition temperature (5% weight loss, T_d) and glass transition temperature (T_o). The tests were carried out at a heating rate of 10 °C minute⁻¹ and in nitrogen atmosphere. UV-vis absorption and photoluminescence (PL) spectra were obtained with a Shimadzu-1700 UV-vis scanning spectrometer and a Horiba Fluoromax-4 Spectrofluorometer, respectively. The absolute PLQY was measured with a LabsphereTM integrating sphere using a monochromatized Xe lamp (NewportTM) as an exciting source (at 360 nm). Time-dependent PL was recorded on an Edinburgh Instruments FLS980 spectrophotometer. Cyclic voltammetry (CV) was carried out in nitrogen-purged CH₂Cl₂ (positive scan) and DMF (Dimethylformamide, negative scan) solutions at room temperature using a CH1660 voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The measurements were carried out at a scan rate of 100 mV s⁻¹ with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum plate auxiliary electrode, and a Ag/AgCl reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc⁺: formal potential -4.8 eV). Molecular geometrical properties were optimized at the B3LYP/6-31g(d, p) level using the Gaussian 09 program package. The excited states analysis is then carried out at the TD-PBE0/6-31g(d, p) level.

Before device fabrication, pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω square⁻¹ were subjected to UV-ozone treatment for 20 min. All organic films were deposited at the rate of

 $0.5 \sim 1.0$ Å s⁻¹ by thermal evaporation in a deposition chamber with a base vacuum of 5×10^{-6} Torr. *J-V* (current density-voltage) characteristics were recorded with a Keithley 2400 Sourcemeter. Electroluminescence spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer.

Synthesis of compounds

All chemicals and solvents are received from commercial sources and used without further purification. Column chromatography was carried out using 400 mesh silica gel. **Scheme S1** in the ESI[†] presents the synthetic routes of the new compounds. Three steps of reactions are involved in the synthesis process. First, a Suzuki-coupling reaction and a "one-pot" reaction proceeded to form the corresponding arylamine substituted N1-(4-bromophenyl)-phenanthroimidazolyl intermediates. After that, a nickel catalyst C-P coupling reaction was applied to obtain the target products.⁴³ The products were isolated with moderate yields and their molecular structures were confirmed by¹H NMR, mass spectrometry (see ESI[†]).

Results and discussion

Thermal properties

Thermal properties of the new compounds were analyzed with TGA and DSC under N₂ protection, as shown in **Fig. 1** and **Table 1**. All of them exhibit high T_d s of over 480 °C and T_g s of them are equal or over 140 °C, which demonstrates that they are stable enough for thermal evaporation and their solid film should have good morphologic stabilities. It is found that the two carbazole derivatives (**3-CzPOPPI** and **CzBPOPPI**) show higher T_g than that of the triphenylamine derivative (**TPAPOPPI**). This should stem from the more rigid skeleton of carbazole than triphenylamine.

Table 1. Key physical data of the new compounds.	
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Compd	$T_{\rm d}$ (°C)	$T_{\rm g}$ (°C)	$E_{\rm g}^{\rm a}({\rm eV})$	HOMO ^b (eV)	LUMO ^b (eV)	$\lambda_{abs}^{c}(nm)$	$\lambda_{\rm PL}^{\rm c/d}$ (nm)	PLQY ^{e/d/f}
3-CzPOPPI	485	154	3.18	-5.47	-2.36	339	420/442	0.93/0.85/0.89
CzBPOPPI	506	165	3.19	-5.54	-2.51	342	420/434	0.91/0.80/0.80
TPAPOPPI	488	140	3.02	-5.31	-2.46	367	443/457	0.86/0.88/0.93

^aEstimated from absorption onset. ^bMeasured by cyclic voltammetry. ^cMeasured in THF (tetrahydrofuran) solution. ^dMeasured in neat film. ^eMeasured in hexane solution (10⁻⁶ M). ^fMeasured in doped film (10 *wt*% in CBP).



Fig. 1. a) TGA and b) DSC curves of the new compounds.

Photophysical properties

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Fig. 2 gives UV-Vis absorption and PL spectra of the new molecules (in THF solution) and key data are also listed in **Table 1**. The lowest absorption band for carbazole derivatives were located around 340 nm and a shoulder around 360 nm, which are ascribed to the π - π * transition of the PI unit and the C2-substituted carbazole moiety to PI core.³⁷ In the triphenylamine derivative, the absorption band around 360 nm dominates. This variation is originated from the stronger electron donation character of triphenylamine than carbazole. From their absorption onset, the optical bandgaps of the compounds were estimated to be 3.18, 3.19, and 3.02 eV for **3-CzPOPPI**, **CzBPOPPI** and **TPAPOPPI**, respectively. The PL emission peaks of the TPPO derivatives in THF solution locate at 420, 420, and 443 nm for **CzBPOPPI**, **3-CzPOPPI**, and **TPAPOPPI**, respectively, ranging from violet-blue to deep-blue emission (**Fig. 2b** and **Table 1**). Emission spectral profiles of the carbazole derivatives present fine vibration

features, while the triphenylamine derivative show structureless spectra. Comparing 3-CzPOPPI and **TPAPOPPI** with their analogues (with N1 position substituted by *tert*-butyl benzene) TPIBCz³¹ and TPA-BPI⁴⁴ ($\lambda_{PL,max}$ = 417 and 442 nm, respectively, Scheme S3), PL spectra of these new compounds show rather small red shifts, which imply that N1 substitution of TPPO has little influence (charge transfer) on the molecular radiative center (the PI unit and C2-substituents). Solvatochromic experiments give similar results. From nonpolar n-hexane to high polar acetonitrile solution (Fig. 3), carbazole derivatives present very small red shifts (10 and 9 nm for 3-CzPOPPI and CzBPOPPI) in emission peaks and remain fine structures in their spectral profiles. TPAPOPPI shows obvious bathochromic effect (63 nm, Table S1) and structureless PL profiles. In our previous reports^{31,44}, TPIBCz and TPA-BPI show similar solvatochromic effect in the same solutions (shifts 9 and 55 nm respectively) with these TPPO substituted compounds, further evidencing our N1-substitution strategy has negligible influence on the emission core of the molecules. Deposited on quartz substrates, PL spectra of the emitters peak at 442, 434, and 457 nm for **3-CzPOPPI**, CzBPOPPI, and TPAPOPPI, respectively. The relatively larger red shifts (22 nm) from solution to solid state of 3-CzPOPPI probably stems from its more planar molecular structure. High PLQYs of over 0.8 were observed in thin films of all compounds (Table 1), indicating they are promising candidates of deep-blue OLED emitters.



Fig. 2. (a) Absorption and (b) PL spectra in THF solution.



Fig. 3. PL spectra of the new compounds in different solvents.

Theoretical calculation

To better understand the structure-property relationships of the new compounds, ground state energyoptimized molecular structures and frontier orbitals were calculated with the Gaussian 09 program package on B3LYP/6-31g(d, p) level. As shown in **Fig. 4**, TPPO units have a nearly orthogonal dihedral (over 70°) angel with the PI units in all these compounds, which is consistent with our design. The HOMO of **3-CzPOPPI** distributes over the PI unit and C2-substituent while their LUMO centers on around the N1-connected benzene ring. This separate distribution indicates a bipolar nature of **3-CzPOPPI**. The HOMOs of **CzBPOPPI** and **TPAPOPPI** basically locate in the same segments but with emphasis on respectively the PI unit and the triphenylamine group. The LUMOs of these two molecules can spread from the N1-connected benzene ring to the C2-connected biphenyl group. This maybe because of the slightly smaller twist angel between TPPO unit and PI plane. Comparing the frontier orbital distribution of **TPAPOPPI** and TPA-BPI (see ref. 44), introducing TPPO units into the molecule will not change the HOMO property and can widen the LUMO distribution over the N1-connected benzene ring.



Fig. 4. Optimized molecular geometries and distributions of the molecular frontier orbitals (The blue, orange, red, grey and white ball represents the nitrogen, phosphor, oxygen, carbon and hydrogen atom, respectively.)

Electrochemical properties

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Using cyclic voltammetry, electrochemical properties of the three compounds were measured in CH₂Cl₂ and DMF solution for oxidation and reduction scans respectively (**Fig. 5**). The HOMO levels of them are determined to be -5.47, -5.54, and -5.31 eV for **3-CzPOPPI**, **CzBPOPPI** and **TPAPOPPI**, respectively. Comparing with TPA-BPI (HOMO: -5.31 eV), the very similar positive scan curves and the onset positions imply the donor part (triphenylamine) decided the HOMO level. This is further proved by the obvious different of oxidation curves and onset positions of carbazole derivatives. The slight shallower HOMO of **3-CzPOPPI** than **CzBPOPPI** can be attributed to the slightly longer conjugated length of **3-CzPOPPI** (**Fig. 4**). From the negative scan curves, LUMO levels of these molecules are deduced to be - 2.36, -2.51 and -2.46 eV for **3-CzPOPPI**, **CzBPOPPI** and **TPAPOPPI**, respectively. **CzBPOPPI** and **TPAPOPPI** show different scan curves and deeper LUMO levels than others, which may be because of their relative low twisting angles at N1-position and wider spread LUMOs. Comparing **TPAPOPPI** to TPA-BPI (LUMO: -2.39 eV), substitution of TPPO group deepens the LUMO level of the molecule by 0.07 eV, which is beneficial to electron injection in device.



Fig. 5. Cyclic voltammetry measurements of the new compounds and TPA-BPI.

Electrical properties

To evaluate electrical properties of **CzBPOPPI**, **3-CzPOPPI**, and **TPAPOPPI**, hole-only and electrononly devices were fabricated with the configuration of respectively ITO/NPB (10 nm)/one of the new compounds (70 nm)/NPB (10 nm)/Al (120 nm) and ITO/1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene (TPBi) (10 nm)/ one of the new compounds (70 nm)/TPBi (10 nm)/LiF (1 nm)/Al (120 nm). *J-V* curves of the device are shown in **Fig. 6**. All the three materials show bipolar properties and their hole transport abilities are better than that of electron. This should be originated from the good hole transporting abilities of the PI unit and its C2-substituted arylamine groups. Interestingly, **CzBPOPPI** shows poorest performance in both hole and electron transports. This may because of its largely twisting molecule structure (**Fig. 4**) which hinder effective molecular interaction and charge hopping. **TPAPOPPI** performs well in both transporting positive and negative carriers and we suppose the good hole transporting properties of the triphenylamine group and the relatively low LUMO level are the main reasons. Comparing the J-V curve of **TPAPOPPI** and **3-CzPOPPI** with their TPPO-free counterparts (TPA-BPI and TPIBCz), TPPO substituted derivatives show inferior hole conductivity but superior electron conductivity. This means substitution of TPPO group can enhance electron mobility of the material and endows the molecule with a better-balanced bipolar transport ability.



Fig. 6. Current density-voltage characteristics of the electron- and the hole-only devices.

Electroluminescent properties

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The three materials were first use as non-doped emitters in OLED, with a device structure of ITO/NPB (65 nm)/TCTA (4,4',4"-tris(carbazol-9-yl)-triphenylamine, 5 nm)/one of the new materials (25 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm). Here, NPB and TPBi are the hole and the electron transport layers respectively. TCTA is the exciton blocking layer. As the E_g (~ 3.0 eV) of NPB is relatively low and excitons may leak into it from the emitting layer. Inserting a TCTA layer, with its shallow LUMO (-2.20 eV) and larger Eg (~ 3.4 eV), electrons and excitons can be effectively blocked within the emitting layer.^{30,31,37} The device performances are presented in Fig. 7 and key data are summarized in Table 2. 3-CzPOPPI and CzBPOPPI show efficient violet-blue emission with CIE coordinates of (0.156, 0.061) and (0.157, 0.071), respectively. Decent performances were observed with high EQE of 4.44% and 4.13% at a practical luminance of 1,000 cd m⁻². Higher performance in the **3-CzPOPPI** based device is attributed to its better photophysical and electrical properties. In the TPAPOPPI-based device, a low Von of 2.8 V and a high EQE of 6.69% with CIE coordinates of (0.152, 0.095) were achieved. The maximum CE (current efficiency) and PE are determined to be 6.09 cd A⁻¹ and 5.94 lm W⁻¹, respectively. At 1,000 cd m^{-2} , high efficiency is maintained with an EQE of 6.10% and a CE of 5.27 cd A^{-1} . This performance is comparable to those of the state-of-the-art non-doped deep-blue OLED (CIE_v < 0.10).^{31,36-42} As shown in Fig. S4, the natural transition orbitals (NTOs) calculations of $S_0 \rightarrow S_1$ transition ("hole" to "particle") shows a clear feature of hybrid local and charge-transfer excited state and in the Lippert-Mataga model, the material present a LE-like (locally excited) excited state dipole movement in low polarity solvents and a CT character in high polarity solvents (Fig. S5 -S7 and Table S1).^{45,46} As only nanosecond scale signal is detected in the PL decay of **TPAPOPPI** and there is relatively large energy splitting of its first singlet

and triplet excited state (0.51 eV, **Fig. S3**), this high EQE should be ascribed to the contribution of extra singlet exciton generated from "hot" CT channels of hybrid locally and change transfer excited state.^{47,48} Specifically, reverse intersystem crossing may occur between S_1 and T_5 state as they both have CT (or HLCT) character and laid very close in energy (**Fig. S4 -S5**).



Fig. 7 a) Current density-voltage-luminescence characteristic curves, b) plots of current efficiencyluminance-power efficiency, c) luminance-EQE plots and d) EL spectra at 4 V of **3-CzPOPPI-**, **CzBPOPPI-** and **TPAPOPPI-**based non-doped OLEDs.

Emitter	$V_{\rm on}$ (V)	$\lambda_{\rm EL}$ (nm)	$CE^{g} (cd A^{-1})$	PE^{g} (lm W ⁻¹)	EQE ^g (%)	CIE ^h
3-CzPOPPI ^a	2.9	436	2.71, 2.35, 1.41	2.73, 2.39, 2.28	5.08, 5.00, 4.44	0.156, 0.061
CzPOBPPIª	2.9	440	2.94, 2.88, 2.47	2.64, 2.32, 1.47	4.47, 4.45, 4.13	0.157, 0.071
TPAPOPPIª	2.8	444	6.09,5.83, 5.27	6.37, 5.72, 3.68	6.67, 6.53, 6.10	0.152, 0.095
10 <i>wt</i> % 3-CzPOPPI ^b	3.5	432	1.95, 1.83, 1.61	1.73, 1.15, 0.72	4.93, 4.71, 4.15	0.158, 0.050
10 wt% CzPOBPPI ^b	3.5	432	1.76, 1.58, 1.36	1.58, 0.90, 0.54	5.62, 5.38, 4.82	0.157, 0.044
10 wt% TPAPOPPI ^b	3.4	432	4.33, 4.10, 3.59	3.89, 2.86, 1.69	6.61, 6.45, 5.62	0.154, 0.068
TPAPOPPI ^c	3.0	448	3.66, 3.60, 3.19	3.25, 1.89, 1.06	3.57, 3.52, 3.12	0.154, 0.117
5 <i>wt</i> % PO-01 ^d	2.5	564	57.3, 57.3, 54.1	60.0, 60.0, 53.4	18.9, 18.9, 17.8	0.500, 0.494

Table 2. EL performances of the fabricated devices.

W1 ^e	2.6	/	57.8, 57.1, 51.2	64.8, 59.3, 50.2	20.3, 19.2, 17.2	0.477, 0.468
W2 ^f	2.9	/	36.1, 35.8, 31.5	30.5, 26.1, 14.1	12.9, 12.8, 11.4	0.475, 0.455

^aDevice structure: ITO/NPB (65 nm)/TCTA (5 nm)/EML (25 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm). ^bDevice structure: ITO/MoO₃ (3 nm)/NPB (60 nm)/TCTA (10 nm)/EML(30 nm)/TmPyPB (25 nm)/LiF (1 nm)/Al (120 nm). ^cDevice structure: ITO/MoO₃ (3 nm)/ **TPAPOPPI** (120 nm)/LiF (1 nm)/Al (120 nm). ^dDevice structure: ITO/NPB (65 nm)/TCTA (5 nm)/ **TPAPOPPI**: PO-01 (5 wt%, 25 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm), ^eITO/NPB (65 nm)/TCTA (5 nm)/ **TPAPOPPI** (10 nm)/ **TPAPOPPI**: PO-01 (5 wt%, 15 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm). ^fDevice structure: ITO/MoO₃ (3 nm)/ **TPAPOPPI**: PO-01 (5 wt%, 15 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm). ^gDevice efficiency at maximum 100 and 1,000 cd m⁻², respectively. ^hMeasured at 1,000 cd m⁻².

Similar performance but better color purity was obtained when doping the materials in CBP (4,4'bis(N-carbazolyl)-1,1'-biphenyl). With a device configuration of ITO/MoO₃ (3 nm)/NPB (60 nm)/TCTA (10 nm)/CBP: one of new materials (10 *wt*% 30 nm)/TmPyPB (25 nm)/LiF (1 nm)/Al (120 nm), EQE up to 4.93, 4.68 and 6.61% were achieved (**Fig. 8**, **Fig. S8** and **Table 2**) with CIE coordinates of (0.158, 0.050), (0.157, 0.044) and (0.154, 0.068) for **3-CzPOPPI**, **CzBPOPPI** and **TPAPOPPI** respectively. This consistent efficiency trend with that of the non-doped devices indicates that close packing quenching of emitters is prevented by the bulky TPPO group and current induced quenching in device is reduced as an electron transport channel was established out of the emission core. The improved color purity is a reasonable result as the interactions of emitters are more effectively eliminated upon dispersion in the host and the non-polar environment provided by the CBP host may further shift the emission spectra toward the shorter wavelength side.



Fig. 8 a) Plots of current efficiency-luminance-EQE, b) EL spectra at 4 V of **3-CzPOPPI-**, **CzBPOPPI-** and **TPAPOPPI-**based doped OLEDs.

Motivated by its excellent photophysical and electrical properties and device performances, **TPAPOPPI** was further investigated as single layer OLED emitter and host for yellow phosphor PO-01. As shown in **Fig. 9a** and **Table 2**, the single layer deep-blue OLED (ITO/MoO₃ (3 nm)/ **TPAPOPPI** (120 nm)/LiF (1 nm)/Al (120 nm)) exhibits an impressive performance with EQE of 3.57% (maximum), 3.52% (at 100 cd m⁻²) and 3.12% (at 1,000 cd m⁻²). Low $V_{on} = 3$ V and good color index of (0.154, 0.117) were observed, which is comparable to reported most efficient single layer deep-blue OLED.^{49–53} When used as host for PO-01 (ITO/NPB (65 nm)/TCTA (5 nm)/ **TPAPOPPI**: PO-01 (5 *wt*%, 25 nm)/TPBi (30 nm)/LiF

(1 nm)/Al (120 nm), extremely low V_{on} of 2.5 V and EQE as high as 18.9% were achieved (**Fig. 9b** and **Table 2**), which demonstrates **TPAPOPPI** is an excellent host for PO-01.



Fig. 9 a) Plots of current efficiency-luminance-EQE of (a) single-layer deep-blue OLED and (b) yellow PhOLED (insets are EL spectra at 4 V). c) Plots of current efficiency-luminance-EQE of white OLEDs.

Finally, binary white OLEDs were fabricated using **TPAPOPPI** as blue fluorophore and PO-01 as yellow phosphor. In a device (W1) with the structure of ITO/NPB (65 nm)/TCTA (5 nm)/ **TPAPOPPI** (10 nm)/ **TPAPOPPI**: PO-01 (5 *wt%*, 15 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm), warm white emission (CIE: (0.477, 0.468)) and V_{on} of as low as 2.6 V were observed. As shown in **Fig. 9c**, the device exhibits a maximum CE, PE and EQE of 57.8 cd A⁻¹ and 64.8 lm W⁻¹ and 20.3%, respectively. Importantly, the luminances of 100, 1,000 and 10,000 cd m⁻² are achieved under bias of only 2.9, 3.2 and 4.6 V respectively. To demonstrate that **TPAPOPPI** has also good bipolar transporting properties, device W2 was fabricated with the structure of ITO/MoO₃ (3 nm)/ **TPAPOPPI** (70 nm)/**TPAPOPPI**: PO-01 (5 *wt%*, 50 nm)/LiF (1 nm)/Al (120 nm). As shown in **Fig. 9c** and **Table 2**, EQE_{max}, CE_{max} and PE_{max} of 12.9%, 36.1 cd A⁻¹ and 30.5 lm W⁻¹ were achieved. Driving by a bias of 7 V, a practical luminance of 1,000 cd m⁻² (EQE of 11.4%) can be achieved in device W2. These performances comparable to the best interlayer-free white OLED^{50,54-60} and demonstrate the good potential of **TPAPOPPI** as a multifunctional deep-blue emitter.

Conclusion

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In this work, we synthesized three deep-blue emitters **3-CzPOPPI**, **CzBPOPPI** and **TPAPOPPI**. As demonstrated by the spectroscopic experiments, CV measurements and single carrier device evaluations, the introduction of TPPO group with highly twisted linkage has negligible influences on the photophysical properties of molecules but open a new channel to facilitate electron injection and transport. Endowed by their excellent photophysical and electrical properties, highly efficient deep-blue and violet-blue OLED based on them were fabricated. Non-doped devices with **3-CzPOPPI** and **CzBPOPPI** as emitter exhibit EQE_{max} of 5.08 and 4.42% with CIE coordinates of (0.156, 0.061) and (0.157, 0.071).

Doped devices based on them achieve similar EQE but deeper blue emission (CIE_y of 0.050 for 3-CzPOPPI and 0.044 for CzBPOPPI). OLEDs using TPAPOPPI shows an EQE_{max} of 6.69% with CIE coordinates of (0.152, 0.095) for non-doped device and an EQE of 6.61% with CIE coordinates of (0.154, 0.068) in doped device, which is comparable to state-of-the-art deep-blue emitters. Besides, a binary white OLED with TPAPOPPI and PO-01 as emitters presents high EQE of 20.3% and shows a low operation voltage of 3.2 V at practical luminance of 1,000 cd m⁻². TPAPOPPI is demonstrated to be a promising multifunctional deep-blue emitter with good bipolar transporting properties.

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