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Blue emitters with various electron-donors attached to the 9-phenyl-9-phosphafluorene oxide (PhFIOP) moiety and their thermally activated delayed fluorescence (TADF) behavior†

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A series of luminescent molecules have been developed through attaching various electron-donors to the 4- and/or 6-positions of the 9-phenyl-9-phosphafluorene oxide (PhFIOP) moiety. Furthermore, their photophysical, thermal, electrochemical and electroluminescent properties have been characterized in detail. Critically, it has been found that introducing two electron-donors to the 4- and 6-positions of the PhFIOP moiety can furnish a smaller singlet-triplet energy gap (ΔE_{ST}) than the analogues with a single electron-donor at the 4-position of the PhFIOP moiety. Hence, PhFIOP-based emitters with two phenoxazine and two acridine moieties as electron-donors can show thermally activated delayed fluorescence (TADF) behavior with a high reverse inter-system crossing constant (k_{RISC}) in the order of 10^6 s⁻¹. In contrast, TADF features cannot be observed in PhFIOP-based emitters with only one electron-donor. In addition, these luminescent molecules can also exhibit high photoluminescence quantum yields (PLQYs) ranging from 70% to 90% in doped films, which results in excellent electroluminescence (EL) performance. To validate this idea, monochromatic OLED devices have been fabricated and the results show a maximum current efficiency (η_1) of 55.6 cd A^{-1} , a power efficiency (η_2) of 49.2 lm W $^{-1}$, and an external quantum efficiency ($\eta_{\rm ext}$) of 27.3%. Moreover, blue EL emission has also been achieved with CIE (0.17, 0.14) as well as high EL efficiencies of 18.7 cd A^{-1} , 15.6 lm W^{-1} , and 21.9%, respectively. Thus, these PhFIOP-based emitters will enrich the structural diversity of APO-type TADF molecules with high EL efficiency.

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Introduction

Recently, a remarkable breakthrough in the development of organic light-emitting molecules, the so-called thermally activated delayed fluorescence (TADF) materials, have attracted researchers' interests. 1-5 Compared with traditional fluorescent materials, the generated triplet excitons can be harvested by a reverse intersystem crossing (RISC) process induced by a sufficiently small singlet-triplet energy gap (ΔE_{ST}), thus the TADF materials can achieve 100% exciton utilization efficiency.⁶⁻¹⁵ Meanwhile, due to the lack of precious metal ions, TADF

Aryl phosphine oxide (APO) units are widely applied in organic optoelectronic molecules due to their excellent electron injection/transport capability. 4,31-36 For example, Rajamalli's team has reported a kind of non-doped green organic lightemitting diodes (OLEDs) with the triphenylphosphine oxide as an electron-acceptor, showing an external quantum efficiency $(\eta_{\rm ext})$ over 7.2%, a current efficiency $(\eta_{\rm L})$ of 28.3 cd ${\rm A}^{-1}$, and a power efficiency (η_P) of 23.0 lm W⁻¹.³⁷ Besides, APO-type groups are also commonly introduced into novel organic ligands to construct efficient phosphorescent complexes as well as new efficient host materials. 38-43 With so many excellent

materials are more cost-effective and environmentally friendly than phosphorescent complexes. 16,17 Besides, they also possess an excellent electroluminescence efficiency comparable to that of phosphorescent complexes. 18-20 It has been reported that the construction of a donor-acceptor (D-A) structure is a facile way to prepare TADF luminescent molecules. 21-30 Thus, the enrichment of the structure of different donor/acceptor groups is of great importance for the construction of efficient TADF molecules.

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reports, APO-type moieties show great potential for the construction of TADF molecules. Therefore, it is essential to enrich the structural diversity by chemical modifications. Yasuda's team from Kyushu University has introduced the oxygen atom as a bridge-linked atom into the triphenylphosphine group and achieved a maximum η_{ext} of 12.3%.⁴ This proves that this approach by locking the two benzene rings of triphenylphosphine can enhance the rigidity of the molecular structure, reduce the non-radiative decay of the molecule, and thus improve the electroluminescence (EL) efficiency. Inspired by this method, more APO-based emitters with improved rigidity have been reported. 32,42,44-49

Among the APO-type moieties, the 9-phenyl-9-phosphafluorene oxide (PhFIOP) group can possess inherent advantages of a highly rigid structure to furnish improved opto-electronic properties. Recently, we have introduced electron-donors to the 2- and 8-positions of the PhFIOP unit to construct new green TADF emitters showing high electroluminescence (EL) efficiencies of 23.3%, 83.7 cd A^{-1} , 59.1 lm W^{-1} for η_{ext} , η_{L} , and η_{P} , respectively, indicating its great potential for developing highly efficient TADF emitters. 50 Unfortunately, TADF emitters with the PhFIOP unit as an electron-acceptor are very scarce, especially blue emitters which are important for full-color displays. Furthermore, construction of a PhFIOP unit involves tedious synthetic processes and very sensitive reagents. So, developing new PhFIOP-based TADF emitters which can be synthesized conveniently is very necessary. Based on the aforementioned content, a series of new PhFIOP-based blue TADF emitters have been synthesized conveniently via successive nucleophilic aromatic substitution (S_NAr) reactions between dibenzothiophene dioxides and PhPH₂-KOH under very mild reaction conditions. Furthermore, various electron-donors have been introduced to the 4- and/or 6-positions of the PhFIOP moiety to optimize their TADF behaviors. Encouragingly, these new PhFIOP-based TADF emitters can show impressive blue EL performances. Obviously, this research can provide crucial information for developing novel PhFIOP-based TADF emitters for OLED applications.

Experimental

General information

Commercial materials are used directly in the reaction without pretreatment, and all reactions were carried out in a nitrogen atmosphere using Schlenk techniques. All the reactions are monitored by thin-layer chromatography (TLC) sheets from Merck In. The products are separated and purified by column chromatography and preparative TLC plates which are conducted using silica gel from Shanghai Qingdao (300-400 mesh). The ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra of all compounds are obtained using a PerkinElmer Lambda 950 spectrophotometer and Edinburgh Instruments FLS920 fluorescence spectrophotometer at room temperature, respectively. 1H, 13C, and 31P NMR spectra are obtained using a Bruker Avance 400 or 600 MHz NMR spectrometer, and CDCl₃ is selected as the solvent. Thin film spectra and lifetimes of TADF emitters are measured using an Edinburgh FLS920 fluorescence spectrometer. Absolute photoluminescence quantum yields (PLQYs) of solution samples and doped films are obtained using an integrating sphere. Fast atom bombardment mass spectrometry (FAB-MS) spectra are obtained on a Finnigan MAT SSQ710 system. Cyclic voltammetry measurements are carried out at a scan rate of 100 mV s⁻¹ on a Princeton Applied Research model 2273A potentiostat through a threeelectrode configuration with a glassy carbon working electrode, a Pt-sheet counter electrode, and a Pt-wire reference electrode in the electrolyte of 0.1 M [Bu₄N]PF₆ in degassed CH₃CN. All potentials are quoted with reference to the ferrocene/ferrocenium (Fc/Fc⁺) couple as an internal calibrant.

Synthesis

Preparation details of the key intermediate compounds, 4-bromodibenzo[b,d]thiophene-5,5-dioxide, 4,6-dibromodibenzo-[b,d]thiophene-5,5-dioxide, PhSO-o-Oz, PhSO-o-Ad, PhSO-o-Cz, PhSO-o-2Oz, PhSO-o-2Ad, and PhSO-o-2Cz, followed the reported literature 51-55 and their synthetic details are presented in the ESI.†

Specific procedure for the synthesis of PhFIOP-based emitters

FIOP-o-Oz. Under a nitrogen atmosphere, PhSO-o-Oz (1.0 equiv., 0.10 g, 0.21 mmol), phenylphosphine (2.0 equiv., 0.02 g, 0.42 mmol), and KOH (3.0 equiv., 0.03 g, 0.63 mmol) are added to a solution of DMSO (5 mL) and then the mixture is stirred for 12 h at 50 °C. After the reaction, the reaction mixture is cooled to room temperature and then H₂O₂ (2 mL) is added dropwise. After stirring for 2 h, water (20 mL) is added, and then the reaction mixture is extracted with CH2Cl2 (30 mL) three times and dried with anhydrous Na₂SO₄. After evaporation to dryness, the residue is purified by column chromatography over silica gel using AcOEt/petroleum ether (1:2, v:v) as the eluent with a high yield of 80%. The product is obtained as a white solid.

FIOP-o-Ad. PhSO-o-Ad (1.0 equiv., 0.10 g, 0.20 mmol), phenylphosphine (2.0 equiv., 0.02 g, 0. 40 mmol), KOH (3.0 equiv., 0.02 g, 0.60 mmol) and DMSO (5 mL) are added into 10 mL Schlenk tubes in a nitrogen atmosphere and stirred vigorously for 12 h at 50 °C. When the reaction is finished, the reaction mixture is cooled to room temperature and H2O2 (2 mL) is added dropwise. After stirring for 2 h, water (20 mL) is added, and then the reaction mixture is extracted with CH₂Cl₂ (30 mL) three times and dried with anhydrous Na₂SO₄. After evaporation to dryness, the residue is purified by column chromatography over silica gel using AcOEt/petroleum ether (1:2, v:v) as the eluent with a high yield of 83%. FIOP-o-Ad appears as a white solid.

FIOP-o-Cz. Under a nitrogen atmosphere, PhSO-o-Cz (1.0 equiv, 0.10 g, 0.20 mmol), phenylphosphine (2.0 equiv, 0.02 g, 0.40 mmol), and KOH (3.0 equiv, 0.02 g, 0.60 mmol) are added into DMSO (5 mL) and then the mixture is heated to 50 °C and stirred for 12 h. After the reaction is accomplished, the reaction mixture is cooled to room temperature and H₂O₂ (2 mL) is added dropwise. After stirring for 2 h, water (20 mL) is added, and then the reaction mixture is extracted with CH₂Cl₂ (30 mL) three times and dried with anhydrous Na₂SO₄.

After evaporation to dryness, the residue is purified by column chromatography over silica gel using AcOEt/petroleum ether (1:2,v:v) as the eluent with a high yield of 82%. The product is obtained as a white solid.

FIOP-o-2Oz. Under a nitrogen atmosphere, PhSO-o-2Oz (1.0 equiv, 0.10 g, 0.14 mmol), phenylphosphine (4.0 equiv, 0.06 g, 0.56 mmol), and KOH (3.0 equiv, 0.02 g, 0.42 mmol) were added into a solution of DMSO (5 mL) and then the mixture is stirred for 12 h at 50 °C. The reaction mixture was cooled to room temperature after the reaction and H₂O₂ (4 mL) was added dropwise. After stirring for 2 h, water (20 mL) is added to the system, and then the reaction mixture is extracted with CH₂Cl₂ (40 mL) three times and dried with anhydrous Na₂SO₄. After evaporation to dryness, the residue is purified by column chromatography over silica gel using CH2Cl2/petroleum ether (2:1, v:v) as the eluent with a yield of 54%. The product is a white solid.

FIOP-o-2Ad. PhSO-o-2Ad (1.0 equiv., 0.10 g, 0.13 mmol), phenylphosphine (4.0 equiv., 0.06 g, 0.52 mmol), and KOH (3.0 equiv., 0.02 g, 0.39 mmol) are added to a solution of DMSO (5 mL) in a nitrogen atmosphere and then the mixture is stirred for 12 h at 50 °C. After the reaction, the reaction mixture is cooled to room temperature and H2O2 (4 mL) is added dropwise. After stirring for 2 h, water (20 mL) is added, and then the reaction mixture is extracted with CH2Cl2 (40 mL) three times and dried with anhydrous Na₂SO₄. After evaporation to dryness, the residue is purified by column chromatography over silica gel using CH₂Cl₂/petroleum ether (2:1, v:v) as the eluent with a yield of 52%. The product is obtained as a white solid.

FIOP-o-2Cz. Under a nitrogen atmosphere, PhSO-o-2Cz (1.0 equiv., 0.10 g, 0.14 mmol), phenylphosphine (4.0 equiv., 0.06 g, 0.56 mmol), and KOH (3.0 equiv., 0.02 g, 0.42 mmol) are added to a solution of DMSO (5 mL) and then stirred for 12 h at 50 °C. The system is cooled to room temperature after the reaction is accomplished and H₂O₂ (4 mL) is added dropwise. After stirring for 2 h, water (20 mL) is added, and then extracted with CH2Cl2 (40 mL) three times and dried with anhydrous Na₂SO₄. After evaporation to dryness, the residue is purified by column chromatography over silica gel using CH₂Cl₂/petroleum ether (2:1, v:v) as the eluent with a yield of 51%. FIOP-o-2Cz also appears white.

FIOP-*o***-Oz.** ¹H NMR (400 MHz, CDCl₃, δ): 7.91–7.88 (m, 2H), 7.79 (dt, I = 8.0, 4.0 Hz, 2H), 7.73–7.59 (m, 3H), 7.46–7.26 (m, 7H), 7.20 (td, J = 8.0, 4.0 Hz, 2H), 6.76-6.56 (m, 6H), 5.82(dd, J = 7.6, 1.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃, δ): 145.82, 145.74, 144.05, 143.02, 142.80, 141.77, 141.56, 139.53, 138.70, 134.34, 133.80, 133.51, 132.22, 131.87, 131.18, 131.07, 130.51, 130.43, 130.04, 129.94, 129.81, 128.29, 128.17, 123.37, 123.24, 121.35, 121.25, 120.44, 120.34, 115.52, 113.35; ³¹P NMR (162 MHz, CDCl₃, δ): 34.93; FAB-MS (m/z): 533 [M]+; anal. calcd for C₃₆H₂₄NO₂P: C, 81.04; H, 4.53; N, 2.63. Found: C, 81.12; H, 4.48; N, 2.71.

FIOP-*o***-Ad.** ¹H NMR (400 MHz, CDCl₃, δ): 7.92–7.89 (m, 2H), 7.84 (dt, J = 8.0, 4.0 Hz, 2H), 7.74-7.67 (m, 2H), 7.64 (t, J =7.6 Hz, 1H), 7.50-7.34 (m, 7H), 7.31-7.27 (m, 2H), 7.23 (dd, J = 8.0, 2.0 Hz, 2H), 7.00 (td, J = 8.0, 1.6 Hz, 2H), 6.94 (td, J = 8.0, 1.6 Hz), 6.95 (td, J = 8.0, 1.6 Hz), 6.95 (td, J = 8.0, 1.6 Hz), 6

1.2 Hz, 2H), 6.18 (dd, J = 8.0, 1.2 Hz, 2H), 1.69 (s, 6H); ¹³C NMR (101 MHz, CDCl₃, δ): 140.99, 140.91, 133.75, 133.47, 131.89, 131.87, 131.23, 131.12, 131.03, 130.68, 130.59, 130.13, 130.05, 129.95, 129.89, 129.78, 128.34, 128.21, 126.37, 125.25, 121.32, 121.22, 120.65, 120.36, 120.27, 114.15, 42.77, 36.07, 31.24; ³¹P NMR (162 MHz, CDCl₃, δ): 35.01; FAB-MS (m/z): 559 [M]⁺; anal. calcd for C₃₉H₃₀NOP: C, 83.70; H, 5.40; N, 2.50. Found: C, 83.65; H, 5.49; N, 2.53.

FIOP-*o***-Cz.** ¹H NMR (400 MHz, CDCl₃, δ): 8.17 (d, J = 8.0 Hz, 2H), 7.91 (t, J = 8.0 Hz, 2H), 7.75 (t, J = 8.0 Hz, 2H), 7.70 (t, J =7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.49– 7.39 (m, 6H), 7.36–7.30 (m, 5H), 7.19 (dt, J = 7.6, 4.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃, δ): 145.91, 142.79, 142.58, 141.99, 141.78, 140.84, 138.41, 137.48, 133.75, 133.54, 131.96, 131.04, 130.45, 130.04, 129.79, 129.51, 128.33, 126.60, 126.05, 123.52, 121.37, 121.27, 120.46, 120.35, 120.25, 120.12, 109.89; ³¹P NMR (162 MHz, CDCl₃, δ): 34.95; FAB-MS (m/z): 517 [M]⁺; anal. calcd for C₃₆H₂₄NOP: C, 83.54; H, 4.67; N, 2.71. Found: C, 83.44; H, 4.72; N, 2.67.

FIOP-*o***-2Oz.** ¹H NMR (400 MHz, CDCl₃, δ): 8.14 (d, J = 7.6 Hz, 6H), 7.98 (dd, I = 7.6, 2.0 Hz, 3H), 7.76 (td, I = 8.0, 1.2 Hz, 3H), 7.73-7.67 (dt, J = 8.0, 4.0 Hz, 6H), 7.49-7.46 (m, 4H), 7.45-7.38(m, 12H), 7.35-7.27 (m, 12H), 7.24-7.15 (m, 5H), 7.03 (td, J =8.0, 2.0 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃, δ): 145.47, 145.41, 143.90, 142.57, 142.43, 139.24, 139.22, 139.00, 138.45, 137.86, 136.51, 135.72, 134.18, 133.66, 132.66, 132.13, 132.06, 130.86, 130.79, 130.73, 130.23, 129.32, 129.02, 128.63, 128.21, 127.68, 127.60, 125.28, 123.35, 123.07, 121.40, 121.28, 120.65, 120.37, 115.37, 113.48, 113.19; ³¹P NMR (162 MHz, CDCl₃, δ): 35.70; FAB-MS (m/z): 790 [M]⁺; anal. calcd for C₅₄H₃₅N₂O₃P: C, 82.01; H, 4.46; N, 3.54. Found: C, 82.10; H, 4.53; N, 3.49.

FIOP-*o***-2Ad.** ¹H NMR (400 MHz, CDCl₃, δ): 7.97 (dd, J = 7.6, 2.0 Hz, 2H), 7.81-7.66 (m, 6H), 7.43 (dd, J = 8.0, 4.0 Hz, 2H), 7.25–7.08 (m, 7H), 7.02 (td, J = 7.9, 3.2 Hz, 2H), 6.73–6.51 (m, 12H), 5.72 (d, J = 4.0 Hz, 4H), 1.25 (s, 12H); ¹³C NMR (151 MHz, $CDCl_3$, δ): 145.71, 145.66, 142.64, 142.50, 141.78, 139.25, 139.06, 136.31, 135.89, 133.64, 132.73, 131.94, 131.64, 131.42, 131.00, 130.93, 130.79, 130.15, 130.01, 129.06, 128.58, 128.25, 127.82, 127.73, 126.52, 126.27, 125.12, 125.06, 120.66, 120.54, 120.39, 120.32, 114.32, 114.07, 35.97, 31.12; ³¹P NMR (162 MHz, CDCl₃, δ): 35.64, FAB-MS (m/z): 843 $[M]^+$; anal. calcd for $C_{60}H_{47}N_2OP$: C, 85.49; H, 5.62; N, 3.32. Found: C, 85.57; H, 5.58; N, 3.26.

FIOP-*o***-2Cz.** ¹H NMR (400 MHz, CDCl₃, δ): 7.98 (dd, I = 7.6, 2.0 Hz, 2H, 7.80 (dt, J = 8.0, 2.0 Hz, 4H), <math>7.75 (td, J = 8.0, 1.2 Hz,2H), 7.49 (dd, J = 7.2, 4.0 Hz, 2H), 7.47–7.40 (m, 4H), 7.25–7.17 (m, 6H), 7.10 (td, J = 8.0, 2.0 Hz, 2H), 6.98-6.90 (m, 9H), 6.09(dd, J = 7.6, 1.6 Hz, 4H); ¹³C NMR (151 MHz, CDCl₃, δ): 145.69, 145.63, 142.67, 142.53, 140.72, 140.58, 139.26, 138.39, 138.20, 137.26, 135.71, 135.22, 133.71, 132.78, 132.25, 131.91, 131.59, 131.21, 131.14, 131.03, 130.87, 130.66, 130.63, 130.55, 129.59, 129.06, 128.89, 128.25, 127.88, 127.79, 126.89, 126.80, 126.40, 126.03, 125.89, 125.32, 123.56, 123.39, 120.59, 120.40, 120.32, 120.29, 120.16, 120.00, 110.09, 109.81; ³¹P NMR (162 MHz, CDCl₃, δ): 35.90; FAB-MS (m/z): 758 [M]⁺; anal. calcd for C₅₄H₃₅N₂OP: C, 85.47; H, 4.65; N, 3.69. Found: C, 85.52; H, 4.58; N, 3.74.

Results and discussion

Synthesis and structural characterization

Synthetic strategies for the PhFIOP-based emitters are summarized in Scheme 1 and details of the synthetic methods for

intermediates are provided in the ESI.† In order to synthesize target molecules, aromatic boron with electron-donors need to be prepared first by Ullman and Suzuki cross-coupling reactions. The synthesis of the target molecules starts from 4-bromodibenzo[b,d]thiophene and 4,6-dibromodibenzo[b,d]thiophene,

Scheme 1 Synthesis of the PhFIOP-based emitters.

followed by oxidation and Suzuki cross-coupling with aromatic borons with electron-donors to obtain the precursors PhSO-o-Oz, PhSO-o-Ad, PhSO-o-Cz, PhSO-o-2Oz, PhSO-o-2Ad, and PhSO-o-2Cz. Then, they undergo successive nucleophilic aromatic substitution (S_NAr) reactions with PhPH₂-KOH under very mild reaction conditions and then oxidation with H₂O₂ at room temperature to obtain the final product. FIOP-o-Oz, FIOP-o-Ad, and FIOP-o-Cz of the D-A structure with a single electron-donor can be synthesized in high yields of around 80%, while FIOP-o-2Oz, FIOP-o-2Ad, and FIOP-o-2Cz of the D-A-D structure containing two electron-donors show slightly lower yields of around 50%, probably due to the higher steric hindrance in the orthopositions of the P=O center. It is worth mentioning that this method of constructing a PhFIOP moiety is very mild without the use of sensitive organometallic reagents and in higher yields than the conventional strategy,56-58 which provides a new idea for the synthesis of PhFIOP-based emitters.

The chemical structures of these PhFIOP-based emitters have been characterized. According to the NMR spectra of these compounds, there appears all the characteristic signals of the corresponding groups, which confirms the accuracy of the synthesis (Fig. S1-S6, ESI†). From the ¹H NMR spectra, a set of signals at ca. 6.60 ppm to 5.80 ppm and ca. 7.16 ppm to 7.01 ppm are ascribed to the phenoxazine units of FIOP-o-Oz and FIOP-o-2Oz, respectively. The singlet peak at 1.69 ppm is attributed to the methyl groups of the acridine unit in FIOP-o-Ad. Similarly, the singlet peak signal at 1.25 ppm belongs to the acridine units in FIOP-o-2Ad. The characteristic peak signals of the carbazole moiety in FIOP-o-Cz appears at ca. 7.19 ppm. Due to the structural similarity, the ³¹P NMR spectra of all the emitters show a distinct characteristic signal around 35.00 ppm, which are assigned to the PhFIOP group.

Thermal and photophysical properties

Thermal properties of the PhFIOP-based emitters are characterized via thermogravimetric analysis (TGA) under a nitrogen flow and the data are summarized in Table 1. All these emitters possess excellent thermal stability with a high thermal decomposition temperature ($T_{\rm d}$) ranging from 321 to 424 °C, which is important for the preparation of OLEDs. At the same time, due to the improved structural rigidity of the emitters containing two electron-donors, their thermal decomposition temperature is significantly higher than that with one electron-donor.

From their TGA curves (Fig. S7, ESI†), it should be noted that the weight-loss of FIOP-o-Oz and FIOP-o-Cz should probably result from their sublimation, and thus their T_d may be even higher than the data revealed by their TGA curves. However, as for FIOP-o-Ad and FIOP-o-2Ad, they seem to begin to decompose at a lower temperature because of the less rigidity of the acridine groups.

Fig. 1 shows the UV-vis absorption spectra of the PhFIOPbased emitters in toluene at 293 K and the corresponding data are included in Table 1. The UV spectra suggest that all these emitters exhibit two absorption peaks at ca. 350 nm and ca. 400 nm. The high-energy absorption band is attributed to $\pi \to \pi^*$ transitions in the electron-donor and electron-acceptor, while the low-energy absorption band should be ascribed to intramolecular charge-transfer transition. It is noteworthy that the absorption spectral profile does not change obviously after introduction of the second electron-donor, probably due to the insignificant effect on the electron transition of these PhFIOP-based emitters. However, by varying the electrondonating abilities of the electron-donor, their absorption spectra can exhibit obvious differences (Fig. 1).

In order to gain insight into the absorption behavior of these PhFlOP-based emitters, key frontier molecular orbitals (MOs) based on the ground states (S₀) have been obtained by theoretical calculation (Fig. 2). From the MO diagram, it can be noticed that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are clearly separated, and the HOMOs are mainly located on the π orbitals of the electron-donors, while LUMOs are mainly distributed in the π^* orbitals of the PhFIOP unit. Hence, the electron transition process with the lowest energy exhibits an obvious intramolecular charge transfer (CT) feature, so the lowenergy absorption band of these PhFlOP-based emitters should be induced by the intramolecular CT transition. Among all the electron-donors, the phenoxazine group possesses the strongest electron-donating ability to facilitate a CT transition. Therefore, FIOP-o-Oz and FIOP-o-2Oz can show the intramolecular CT absorption band with the lowest energy-level, indicated by their absorption onset at ca. 410 nm. Owing to the much weaker electron-donating ability of the carbazole moiety, FIOP-o-Cz and FIOP-o-2Cz should show the intramolecular CT absorption band with the highest energy-level, indicated by their absorption onset at the shortest wavelength ca. 370 nm.

Table 1 Photophysical and thermal data of these PhFIOP-based emitters

Compound	Absorption ^a λ_{abs} (nm)	Emission λ_{em} (nm) solution ^b /film ^c	PLQY solution d /film e	$T_{\mathbf{d}}^{f}(^{\circ}\mathbf{C})$
FIOP-o-Oz	286(4.46), 299(4.40), 331(4.45), 396(3.65)	496/495	90.2%/93.3%	363
FIOP-o-Ad	286(4.45), 298(4.32), 340(3.54), 376(2.00)	455/453	80.4%/80.0%	352
FIOP-o-Cz	295(4.38), 315(4.28), 328(4.29), 341(4.27), 373(3.03)	400/405	82.1%/81.2%	321
FIOP-o-2Oz	284(4.55), 291(4.48), 302(4.45), 328(4.55), 392(3.68)	497/503	73.2%/65.6%	415
FIOP-o-2Ad	284(4.53), 292(4.46), 344(3.53), 378(2.18)	451/456	93.3%/96.5%	397
FIOP-o-2Cz	287(4.37), 294(4.45), 327(4.15), 341(4.13), 379(3.13)	403/418	69.84%/73.31%	424

^a Measured at a concentration of ca. 10^{-5} M in toluene at room temperature, and $\log \varepsilon$ values are presented in parentheses. ^b Measured in toluene at 293 K. ^c Measured in the doped mCP film (doping ratio: 10 wt %) at 293 K. ^d Absolute PLQY in toluene measured with an integrating sphere at room temperature. ^e Absolute PLQY in the doped mCP film (doping ratio: 10 wt %) measured with an integrating sphere at 293 K. ^f T_d is the decomposition temperature.

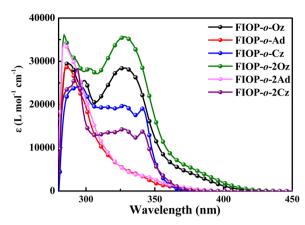


Fig. 1 UV-vis absorption spectra of these PhFIOP-based emitters measured in toluene at 293 K.

With a stronger electron-donating ability than carbazole moiety, the acridine unit can afford a lower energy-level for the intramolecular CT absorption band to FIOP-o-Ad and FIOP-o-2Ad, showing absorption onset at a longer wavelength ca. 380 nm. From Fig. 2, we can see that both mono- and di-substituted emitters with the same electron-donor can display very similar HOMO and LUMO patterns to furnish their similar absorption spectral profile (Fig. 1).

Photoluminescence (PL) spectra of these PhFIOP-based emitters are recorded in toluene and in the doped 1, 3-bis(Ncarbazolyl)benzene (mCP) film (doping ratio: 10 wt%) at 293 K, respectively (Fig. 3). The PhFIOP-based emitters exhibit different emission wavelengths due to the various electron-donating abilities of the electron-donors. The sky-blue emission wavelength of FIOP-o-Oz and FIOP-o-2Oz is 496 nm due to the strong electron-donating ability of the phenoxazine moiety. As for FIOP-o-Cz and FIOP-o-2Cz, owing to the weaker electron-donating ability of the carbazole group, they show emission maximum at ca. 400 nm, showing a blue-shift effect compared with that of the blue-emitting FIOP-o-Ad and FIOP-o-2Ad (ca. 450 nm) possessing an acridine unit with a stronger electron-donating feature (Fig. 3). Clearly, the emission wavelengths of these PhFlOP-based emitters exhibit good consistence with the energy-levels of their intramolecular CT absorption bands. Hence, it seems that their emission can exhibit an intramolecular CT feature which has been indicated by the structureless PL spectral profiles shown in Fig. 3. From the PL spectra in toluene, it is obvious that the PhFIOP-based emitters containing one or two electron-donors exhibit similar emission behavior. The PL spectra in the doped mCP film are consistent with those in toluene. However, the emission wavelength of FIOP-o-2Cz in doped film has a slight red shift compared with that in the solution, which may be due to the fact that more rigid planar carbazole units can induce stronger molecular interaction resulting in red-shifted emission. It should be noted that these PhFIOP-based blue emitters show PLQYs ranging from 65% to 90% both in degassed toluene and doped films due to the rigid PhFIOP unit which can restrain the nonradiative decay processes. Especially for FIOP-o-Oz and FIOP-o-2Ad, they achieve high PLQYs of 90.2% and 93.3% in toluene, respectively.

TADF behaviors

In order to characterize the TADF behavior of these PhFIOPbased emitters, both the transient decay curves in the doped mCP film (doping ratio: 10 wt%) (Fig. 4) together with those at different temperatures in degassed toluene (Fig. 4, inset) have been obtained. For FIOP-o-2Oz and FIOP-o-2Ad, two decay processes are observed in their transient PL decay curves, in both doped mCP film and degassed toluene. The prompt decay shows short lifetimes in the order of nanosecond (29.6 ns for

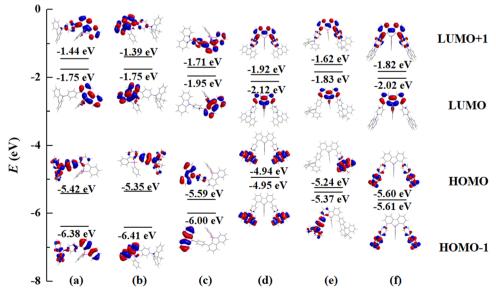


Fig. 2 MO patterns (isocontour value = 0.030) for the PhFIOP-based emitters based on their optimized S₀ geometries. (a) FIOP-o-Oz, (b) FIOP-o-Ad, (c) FIOP-o-Cz, (d) FIOP-o-2Oz, (e) FIOP-o-Ad, and (f) FIOP-o-2Cz.

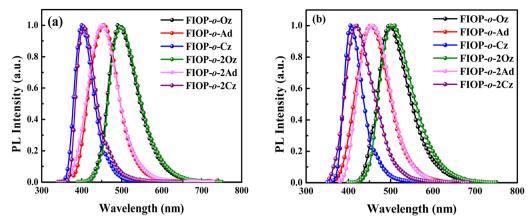


Fig. 3 PL spectra of these PhFIOP-based emitters. (a) Measured in toluene at 293 K, and (b) measured in the doped mCP film (doping ratio: 10 wt %) at 293 K.

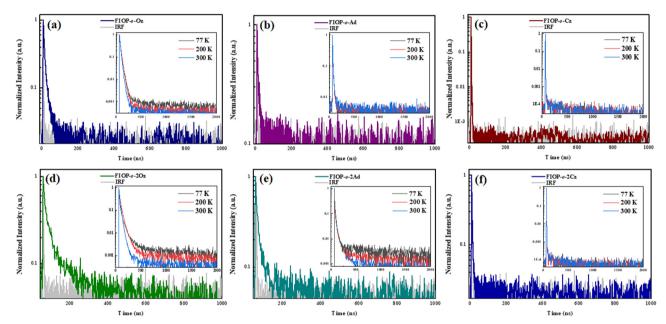


Fig. 4 Transient PL decays for these PhFIOP-based emitters doped in the mCP film (doping ratio: 10 wt %). The inset shows the temperature dependence of transient PL decay in degassed toluene. (a) FIOP-o-Oz, (b) FIOP-o-Ad, (c) FIOP-o-Cz, (d) FIOP-o-2Oz, (e) FIOP-o-2Ad, and (f) FIOP-o-2Cz. IRF: the instrument response functions of the light source.

FIOP-o-2Oz and 12.6 ns for FIOP-o-2Ad), while the delayed decay has a lifetime more than ten times that of the prompt decay (170 ns for FIOP-o-2Oz and 180 ns for FIOP-o-2Ad) (Table 2). At the same time, the lifetime of the delayed decay decreases with the increase of temperature, which also reflects the obvious TADF feature. Unfortunately, FIOP-o-Oz, FIOP-o-Ad, FIOP-o-Cz and FIOP-o-2Cz do not exhibit obvious TADF behavior.

To further interpret the TADF behavior of these PhFIOPbased emitters, natural transition orbital (NTO) patterns for $S_0 \rightarrow S_1$ excitations based on their optimized S_1 geometries have been obtained (Fig. 5). For the PhFIOP-based emitters that contain one electron-donor, they all possess a large $\Delta E_{\rm ST}$ (0.406 eV for FIOP-o-Oz, 0.302 eV for FIOP-o-Ad and 0.420 eV for

FIOP-*o***-Cz**), which is unfavorable to exhibit TADF behavior. This result is consistent with the transient PL decays. After introduction of the second electron-donor, the torsion angle between the electron-donor and electron-acceptor becomes larger, which promotes the separation of the HOMO and LUMO to achieve a smaller ΔE_{ST} . As for **FIOP-***o***-2Oz**, the results from the theoretical calculations show that the hole and particle orbitals are well separated. In addition, the calculated $\Delta E_{\rm ST}$ of FIOP-o-2Oz is 0.003 eV with a larger twisting angle between its electron-donor and electron-acceptor (79.48°) compared with FIOP-o-Oz (65.90°). These results indicate that FIOP-o-2Oz will exhibit a typical TADF behavior, and the same is true for FIOP-o-2Ad. However, FIOP-o-2Cz possesses poor separation between its hole and particle orbitals together with a large

Table 2	TADE data of these Phelop-based emitters

Compound	S ₁ ^a (eV)	${{\operatorname{T}_{1}}^{a}} (\operatorname{eV})$	$\frac{\Delta E_{\mathrm{ST}}^{b}}{\mathrm{(eV)}}$	$ au_{\mathrm{PF}}^{}^{}}$ (ns)	τ _{DF} ^c (μs)	$\Phi_{ ext{PF}}^{}^{}$	$\Phi_{ ext{DF}}^{}d} \ ig(\%ig)$	${k_{ m PF}}^e \ \left(10^7 \ { m s}^{-1} ight)$	$k_{ m DF}^{\ \ e} \ (10^5 { m s}^{-1})$	$k_{\rm ISC}^f (10^6 { m s}^{-1})$	$k_{ m RISC}^{\ f} (10^6 { m s}^{-1})$
FIOP-o-Oz	2.86	2.54	0.32	14.2				•			
FIOP-o-Ad	3.02	2.66	0.36	8.7							
FIOP-o-Cz	3.26	3.04	0.22	7.9							
FIOP-o-2Oz	2.62	2.53	0.09	29.6	0.17	27.9	37.0	0.9	21.7	5.4	5.1
FIOP-o-2Ad	2.89	2.71	0.18	12.6	0.18	46.9	46.1	3.9	25.6	19.0	4.9
FIOP-o-2Cz	3.22	2.88	0.34	3.2							

^a Experimental data were determined from the onsets of the fluorescence and phosphorescence (77 K) spectra (Fig. S8, ESI) in the doped mCP film Experimental data were determined from the onsets of the hubrescence and phosphorescence (7/ K) spectra (Fig. S8, ES1) in the doped mCP film (doping ratio: 10 wt%). b $\Delta E_{\rm ST} = E_{\rm S1} - E_{\rm T1}$. c The prompt fluorescence lifetime ($\tau_{\rm PF}$) and delayed fluorescence lifetime ($\tau_{\rm DF}$) were measured in the doped mCP film at 293 K. d The prompt fluorescence quantum yields ($\Phi_{\rm PF}$) and delayed fluorescence quantum yields ($\Phi_{\rm DF}$) were estimated according to the prompt and delayed proportions in transient decay curves. e The rate constants of PF and DF ($k_{\rm PF}$ and $k_{\rm DF}$) evaluated according to experimental data: $k_{\rm PF} = \Phi_{\rm PF}/\tau_{\rm PF}$ and $k_{\rm DF} = \Phi_{\rm DF}/\tau_{\rm DF}$. f The rate constants of intersystem crossing and reverse ($k_{\rm ISC}$ and $k_{\rm RISC}$) are further estimated according to $k_{\rm ISC} = \Phi_{\rm DF}/t_{\rm PF} + \Phi_{\rm DF}$) and $k_{\rm RISC} = k_{\rm DF}/t_{\rm RISC} + k_{\rm PF}/t_{\rm RISC} + k_{\rm PF}/t_$

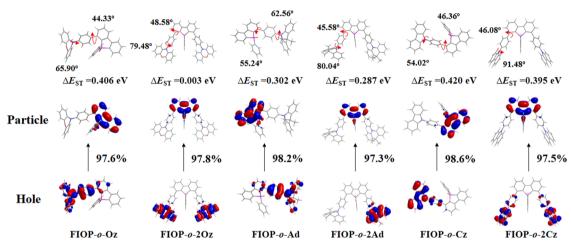


Fig. 5 NTO patterns (isocontour value = 0.030) for $S_0 \rightarrow S_1$ excitations based on the optimized S_1 geometries, together with the S_0 geometry showing the twisting angle between the donor and the acceptor.

 $\Delta E_{\rm ST}$ (0.395 eV), which should be detrimental to show a TADF effect. Furthermore, the $\Delta E_{\rm ST}$ of these PhFIOP-based emitters are also measured experimentally and the data are listed in Table 2. Clearly, the ΔE_{ST} of **FIOP-o-2Oz** and **FIOP-o-2Ad** is just 0.09 eV and 0.18 eV, respectively, while the data associated with other emitters are obviously much larger (Table 2). This result is consistent with the theoretical calculations. Besides, both FIOP-o-2Oz and FIOP-o-2Ad have a high k_{RISC} in the order of 10⁶ s⁻¹, which is another key parameter to determine the TADF behavior. This high k_{RISC} indicates the presence of an efficient reverse intersystem crossing process within FIOP-o-2Oz and **FIOP-***o***-2Ad**, promoting their TADF behavior effectively.

Electrochemical properties

The electrochemical properties of these PhFIOP-based emitters are characterized by cyclic voltammetry (CV), using ferrocene as the internal standard. This series of emitters all exhibit apparent oxidation and reduction processes (Table 3 and Fig. S9, ESI†). In the cathodic scan, the reduction process with potential ranging from ca. -1.6 V to -1.7 V can be attributed to the reduction of the PhFIOP moiety. Meanwhile, the electrondonors contribute to the emergence of an obvious reversible

Table 3 Redox properties of these PhFIOP-based emitters

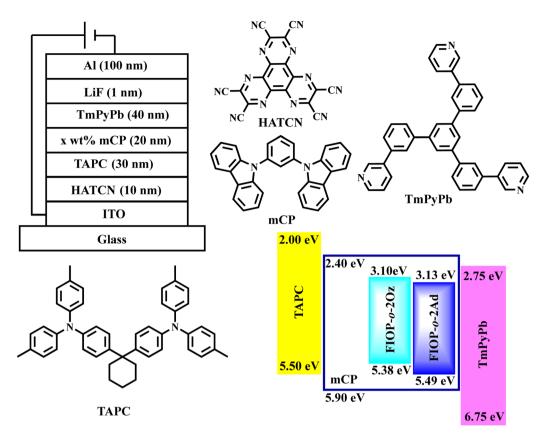
Compound	$E_{\mathrm{pa}}\left(\mathbf{V}\right)$	$E_{\mathrm{pc}}\left(\mathbf{V}\right)$	E_{HOMO}^{b} (eV)	E_{LUMO}^{c} (eV)	$E_{\rm g}^{\ { m CV}d}$ (eV)
FIOP-o-Oz	0.53^{a}	-1.61^{a}	-5.34	-3.19	2.15
FIOP-o-Ad	0.74^{a}	-1.56^{a}	-5.54	-3.24	2.30
FIOP-o-Cz	1.03^{a}	-1.75^{a}	-5.83	-3.05	2.78
FIOP-o-2Oz	0.58^{a}	-1.70^{a}	-5.38	-3.10	2.28
FIOP-o-2Ad	0.69^{a}	-1.67^{a}	-5.49	-3.13	2.36
FIOP-o-2Cz	1.02^{a}	-1.62^{a}	-5.82	-3.18	2.64

^a Reversible. The value was set as $E_{1/2}$. ^b $E_{\rm HOMO} = -(4.8 + E_{\rm pa})$ eV. ^c $E_{\rm LUMO} = -(4.8 + E_{\rm pc})$ eV. ^d CV energy gap $E_{\rm g}^{\rm CV} = {\rm LUMO-HOMO}$.

oxidation process during the anodic scan. For FIOP-o-Ad/FIOPo-2Ad and FIOP-o-Cz/FIOP-o-2Cz, they have oxidation potentials $(E_{\rm pa})$ from ca. 0.7 V to 1.0 V, which is ascribed to the oxidation of acridine and carbazole units, respectively. However, the oxygen atom makes the phenoxazine group more susceptible to oxidation, so the E_{pa} of **FIOP-***o***-Oz**/**FIOP-***o***-2Oz** is lower than that of other emitters.

Electroluminescence ability

To investigate the EL performance of these two TADF emitters, multilayer OLED devices were fabricated with the structure of



Dopant Devices and doping level A1 (6 wt%), A2 (8 wt%), A3 (10 wt%) FIOP-o-2Oz FIOP-o-2Ad B1 (6 wt%), B2 (8 wt%), B3 (10 wt%)

Fig. 6 Device structure of the vacuum-evaporated OLEDs together with the energy-level diagram and molecular structures of the materials employed in the fabricated OLEDs.

ITO/HATCN (10 nm)/TAPC (30 nm)/x-wt% Emitter: mCP (20 nm)/ TmPyPb (40 nm)/LiF (1 nm)/Al (100 nm) (Fig. 6). 1,4,5,8,9,11-Hexaazatriphenylenehexacarbonitrile (HATCN) and 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) were used as the holeinjection layer and hole-transporting material, respectively. mCP serves as the host material and 1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPb) acts as the electron-transporting layer, whereas LiF and Al are used as the election-injection layer and cathode, respectively.

When a suitable voltage is applied to the OLEDs, the device based on FIOP-o-2Oz exhibits sky-blue EL with a maximum wavelength located at 500 nm. As for the device of FIOP-o-2Ad, blue emission with a maximum EL wavelength at 444 nm is achieved (Fig. 7a). It is worth highlighting that this is the first blue TADF emitter based on the PhFIOP acceptor reported so far, demonstrating the great potential in the construction of new TADF molecules. In addition, their EL spectra are well consistent with the PL spectra of the emitters in the mCP films, indicating that the EL signal is from the PhFIOP-based emitters. Current density-voltage-luminance (*J-V-L*) characteristic and relationship of efficiency-luminance of the devices are depicted in Fig. 7 and in the ESI† (Fig. S10 and S11). The key EL data are listed in Table 4.

As can be observed in Table 4, all devices possess a low turnon voltage at ca. 3.0 V, which indicates the reasonableness of the device structure. With the doping concentration at 8 wt%, the devices achieve the optimal EL performance. The device based on FIOP-o-2Oz achieves the maximum luminance of 14139 cd m⁻² at 18.5 V, with the maximum η_L of 55.6 cd A⁻¹, $\eta_{\rm P}$ of 49.2 lm W⁻¹, and $\eta_{\rm ext}$ of 27.3%. When **FIOP-***o***-2Ad** is employed as the guest emitter, the optimized device **B2** reaches the maximum luminance of 6273 cd m⁻² at 18.0 V, the maximum $\eta_{\rm L}$ of 18.7 cd ${\rm A}^{-1}$, $\eta_{\rm P}$ of 15.6 lm ${\rm W}^{-1}$, and $\eta_{\rm ext}$ of 21.9% with blue emission at CIE (0.17, 0.14). The EL efficiency of the devices is slightly inferior when the doping concentration is 6 wt% or 10 wt%, but still at a high level overall. To our best knowledge, among the blue TADF emitters reported to date, the EL efficiencies of these emitters are obviously at a high level. 59-61 These results indicate that all these PhFIOP-based emitters possess excellent potential for EL applications. The reason for the high EL properties may be due to their high PLQYs (65.6% for FIOP-o-2Oz and 96.5% for FIOP-o-2Ad). In addition, the superior EL performance of FIOP-o-2Oz can be attributed to the high horizontal orientation ratio (Θ ca. 80%) of its transition dipole (Fig. S12, ESI†), which can result in a high $\eta_{\rm ext}$ of 27.3%. Encouragingly, both optimized devices A2 and B2

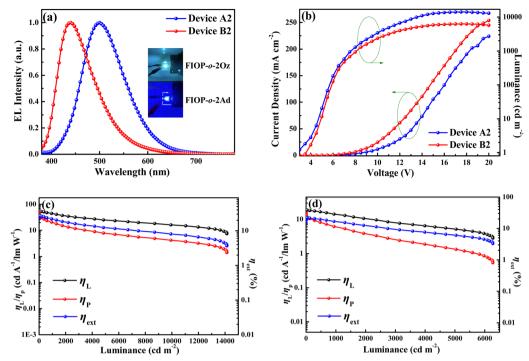


Fig. 7 (a) EL spectra of device **A2** and device **B2**. (b) Current density-voltage-luminance (J-V-L) characteristics for the optimized devices. Relationship between EL efficiencies and luminance of (c) device A2, and (d) device B2.

Table 4 EL Performance of the monochromatic OLEDs

Device	Dopant	$V_{\text{turn-on}}$ (V)	Luminance L_{max}^{a} (cd m ⁻²)	η_{ext} (%)	$\eta_{\rm L} \left({\rm cd} \ {\rm A}^{-1} \right)$	$\eta_{\rm P} \left({ m lm} \ { m W}^{-1} \right)$	$\lambda_{\max}^{d} (nm)$
A1	FIOP-o-2Oz (6.0 wt%)	3.0	13129(18.0)	$22.5(5.0)^a$	45.8(5.0)	37.3(4.0)	500 (0.22, 0.40)
	,		,	21.9^{b}	44.6	25.7	, ,
				18.3 ^c	37.4	16.2	
A2	FIOP-o-2Oz (8.0 wt%)	3.0	14139(18.5)	27.3(5.0)	55.6(5.0)	49.2(3.5)	500 (0.23, 0.40)
				26.3	53.4	30.7	
				20.4	41.4	17.8	
A3	FIOP-o-2Oz (10.0 wt%)	3.0	9252(18.5)	18.3(4.5)	37.3(4.5)	35.9(3.5)	500 (0.23, 0.40)
				16.2	32.9	15.2	
				13.7	28.0	10.2	
B1	FIOP-o-2Ad (6.0 wt%)	3.5	5023(18.0)	10.1(6.5)	8.6(6.5)	5.7(5.5)	444 (0.16, 0.14)
				9.8	8.4	4.6	
				8.4	7.2	2.8	
B2	FIOP-o-2Ad (8.0 wt%)	3.5	6273(18.0)	21.9(5.0)	18.7(5.0)	15.6(4.0)	444 (0.17, 0.14)
				21.2	18.1	10.4	
				15.3	13.0	5.3	
B3	FIOP-o-2Ad (10.0 wt%)	3.5	5631(17.5)	18.1(4.0)	15.5(4.0)	15.3(3.5)	444 (0.16, 0.15)
				15.8	13.4	8.4	
				10.6	9.1	3.6	

^a Maximum EL efficiency, corresponding driving voltage in brackets. ^b EL efficiency at ca. 100 cd m⁻². ^c EL efficiency at ca. 1000 cd m⁻². ^d Maximum emission wavelength and CIE color coordinates at 10 V.

possess relatively low efficiency roll-offs. For device A2, the $\eta_{\rm ext}$ remains 26.3% at 100 cd A⁻¹ and 20.4% at 1000 cd A⁻¹, corresponding to roll-offs of 3.7% and 25.3%, respectively. Furthermore, device B2 also exhibits low efficiency roll-offs of 3.2% at 100 cd A^{-1} and 30.1% at 1000 cd A^{-1} . Apparently, the efficiency roll-off of these devices is also at a favorable level compared with the reported results. 62,63 This is due to the fact that these PhFIOP-based emitters possess a large k_{RISC} (10⁶), which inhibits the triplet-involved annihilation in the devices.

These promising EL data illustrate the important potential of the PhFIOP unit in the construction of efficient TADF molecules.

Conclusions

A series of blue emitters based on the 9-phenyl-9-phosphafluorene oxide (PhFIOP) moiety have been synthesized through a convenient and novel strategy with high yields and their photophysical, thermal, electrochemical and EL properties were also intensively investigated. The results illustrate that the emitters containing two electron-donors are more likely to exhibit TADF behavior than those containing one electrondonor. Among them, emitters coupled with two phenoxazine and two acridine units as electron-donors show obvious TADF behavior with a k_{RISC} in the order of 10^6 s⁻¹. Inspired by the high PLQYs ranging from ca. 70% to 90% in the doped film, their OLED devices are also prepared. The sky-blue devices achieved a maximum luminance of 14139 cd m⁻² at 18.5 V, with a maximum η_L of 55.6 cd A⁻¹, an η_P of 49.2 lm W⁻¹, and an $\eta_{\rm ext}$ of 27.3%. Moreover, blue emission with CIE (0.17, 0.14) is also accomplished, together with high EL efficiencies of 18.7 cd A^{-1} , 15.6 lm W^{-1} , and 21.9% for maximum η_L , η_P and $\eta_{\rm ext}$, respectively. Excitingly, this is the first reported blue TADF emitter based on the PhFIOP moiety as an acceptor with high EL efficiency. These encouraging results not only illustrate the great potential of the PhFIOP group for the construction of efficient TADF molecules, but also enrich a variety of novel emitters based on aryl phosphine oxide (APO) moieties.

Author contributions

Xi Chen: contributed to the synthesis of target molecules, performed photophysical testing, conducted device optimization and data curation, and writing-original draft. Siqi Liu: contributed to the thermal stability measurement. Yuling Sun: contributed to the synthesis of key intermediates. Daokun Zhong: contributed to the synthesis of key intermediates. Zhao Feng: contributed to the cyclic voltammetry measurement. Xiaolong Yang: contributed to the theoretical calculation. Bochao Su: revised the manuscript. Yuanhui Sun: revised the manuscript. Guijiang Zhou: contributed to the implementation of this work. Bo Jiao: contributed to the implementation of this work. Zhaoxin Wu: contributed to the implementation of this work.

Conflicts of interest

There are no conflicts to declare.

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