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Efficient Thermally Activated Delayed Fluorescence of Functional Phenylpyridinato^{3/C6TC04994J} Boron Complexes and High Performance Organic Light-Emitting Diodes

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Abstract

A new series of functional phenylpyridinato boron complexes possessing thermally activated delay fluorescence (TADF) have been strategically designed and synthesized. These boron complexes utilize phenylpyridine as the electron acceptor (A) that links to carbazole or triphenyl amine as the electron donor (D) via a core boron atom, forming four-coordinate neutral boron complexes. The selection of boron to spatially separate donor and acceptor takes its advantage of facile functionalization. TADF properties of the resulting D-A functional materials in various solvents have been investigated via their emission spectra and associated relaxation dynamics. The results show that the operation of TADF is strongly solvent polarity dependent in fluid states, and several underlying mechanisms are discussed. OLEDs fabricated by **fppyBTPA** and **dfppyBTPA** shows EL efficiencies of up to (20.2%, 63.9 cd·A⁻¹, 66.9 lm·W⁻¹) and (26.6%, 88.2 cd·A⁻¹, 81.5 lm·W⁻¹), respectively, in which a nearly 27% EQE for the **dfppyBTPA** device is

among the most efficient TADF OLEDs so far.

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Introduction

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Efficient light emitting materials are an indispensable component in the fabrication of organic light emitting diodes (OLEDs) for flat-panel display and solid state lighting applications. It is notable that the heavy transition-metal of phosphorescent emitters are capable to induce fast intersystem crossing (ISC) between the singlet (S₁) and triplet (T₁) excited states, giving electroluminescence with internal quantum efficiencies (η_{int}) of nearly 100%.¹⁻⁴ Alternatively, there is a relatively new class of compounds, namely: thermally activated delayed fluorescence (TADF) emitters, which can also achieve unitary η_{int} without employment of the third-row transition-metal atoms.⁵⁻⁹ In general, TADF emitter can be enabled by reducing the spatial overlap between the HOMO and LUMO orbitals of molecules, for which the reduced electron exchange energy afforded the smaller energy gap between triplet (typically T₁) and singlet (S₁) states, defined as ΔE_{T-S} (T₁-S₁). The smaller $|\Delta E_{T-S}|$ facilitates the fast reverse intersystem crossing (RISC) from the non-emissive T₁ to the emissive S₁ excited state upon thermal activation, rendering effective harvest of triplet excitons to the singlet state for the generation of bright electroluminescence (fluorescence).

Bipolar molecules with suitable electron donor (D) and acceptor (A) entities are known to foster efficient TADF by virtue of the reduced orbital overlap between these individual constituents. Bearing this criterion in mind, many TADF molecules have been successfully constructed by combining D and A units in a way that the mutual orthogonality among them restricts their π -conjugation and, hence affords the smaller $|\Delta E_{T-S}|$. Typical donors comprise functional arylamine,¹⁰⁻¹² carbazole,¹³ phenoxazine,¹⁴⁻¹⁶ acridine¹⁷⁻¹⁹ and etc., while conventional acceptors contain carbonyl,²⁰ phosphine oxide,²¹⁻²⁴ sulfoxide or sulfone-containing units,²⁵⁻²⁹ triazine,^{30-³⁵ pyrimidine^{36, 37} and other heteroaromatic fragments for achieving the demanded bipolar and TADF properties. More recently, efficient TADF materials bearing a wide range of boron-containing acceptor such as phenoxaborin,³⁸ phenazaborin,³⁹ and}

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polycyclic organoboron compounds with either 1,4-oxaborine⁴⁰ or azaborine^{2/C6TC04994J} subunit,⁴¹ were reported. Of particularly interesting are the second class of organoboron compounds, for which the strong emissions with smaller Stokes shifts and narrow FWHMs were attributed to their extremely rigid π -conjugated framework.^{40, 41}

In this work, we report a new series of TADF boron complexes, including fppyBTPA and dfppyBTPA in which the electron-donating triphenylamine and the electronaccepting functional phenylpyridinato fragment are linked at the spiro-bridged, fourcoordinate boron atom.⁴² The (phenylpyridinato-N,C²⁷)boron unit (ppyB) and its analogues are known to be the excellent building blocks in assembling functional luminescent materials.⁴³⁻⁴⁶ This tricyclic ppyB entity is isostructural to the PrFB fragment, for which the hexagonal arranged phenyl cyclometalate is akin to that of the pentagonal arranged pyrrolide unit, PrFH = 2-(3,5-bis(trifluoromethyl)-1H-pyrrol-2yl)pyridine.⁴⁷ Moreover, the same ppyB unit is also related to the fluorene fragment, but the inherent difference in electronegativity between boron and nitrogen atom makes the ppyB fragment to possess greater degree of charge separation and suitable than fluorene to serve as a core atom in construction of TADF molecules. Intrinsically, these ppyB-containing compounds are different from that of the three-coordinate, boron compounds such as PXZ-Mes3B and TB-3PXZ,^{48,49} in which the three-coordinate boron fragment served as the electron accepting unit to foster the charge transfer. On the other hand, the choice of the coordinated phenylpyridinato boron complexes turns out to be highly critical, as it can substitute the lower energy empty p-orbital of boron fragment with the π^* -orbital of similar energy on the pyridyl unit, in serving as the electron acceptor. Equally important is the employment of more stabilized donor orbitals, such as 4-(9H-carbazol-9-yl)phenyl (PCz) and 9-phenyl-9H-carbazol-3-yl (CzP) fragments, for which the enlarged $|\Delta E_{T-S}|$ afforded the inefficient TADF. This has been shown in the relevant derivatives, e.g. fppyBCzP, fppyBPCz, dfppyBCzP and dfppyBPCz, for which results and discussion are also elaborated on the basis of both experimental and computational approaches. Moreover, our observation is in sharp contrast to the

closely related boron complex **ppyBTPA**,⁵⁰ for which severe device degradation



Results and discussion

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Synthesis and characterization. As for the preparation of desired D-A complexes, the intermediates. fppyBBr₂ and $dfppyBr_2$ were obtained from 2-(4fluorophenyl)pyridine (or 2-(2,4-difluorophenyl)pyridine) and BBr₃ through an electrophilic aromatic borylation catalyzed by ethyldiisopropylamine.⁵¹ The dibromide intermediates are stable and can be handled in air without decomposition. After then, treatment with the corresponding in-situ generated Grignard reagents afforded the desired functional boron compounds in 47-35% yields. Their synthetic protocol is depicted below:

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These boracyclic compounds were identified by mass spectrometry and NMR spectroscopies, together with the X-ray structural analysis of fppyBTPA (cf. electronic supporting information). The B-N and B-C distances of 1.624(2) and 1.610-1.623(2) Å are comparable to the relevant bond distances observed in boracycles.⁵²⁻⁵⁴ All samples exhibited adequate stability and solubility in common solvents, such as toluene, CH_2Cl_2 and acetonitrile.

Solution photophysics. The UV-Vis absorption and emission spectra of fppy and dfppy based boron complexes in different solvents at RT are shown in Figure 1 and Figure 2, while pertinent photophysical data are listed in Table 1. As can be seen, the lower energy absorption peaks for these complexes at ~350 nm have a large molar extinction coefficient in the order of ~ 1.5×10^4 M⁻¹cm⁻¹ (in toluene). Thus, this characteristic absorption can reasonably be assigned to a ligand-centered π - π * transition, of which the spectral features in terms of peak wavelength and profile are nearly independent of solvent polarity.

In stark contrast, all these complexes exhibit featureless emission in the visible range, of which the peak wavelength is strongly solvent dependent, being red shifted upon increasing the solvent polarity. For example, the emission maximum in **fppyBPCz** shifts from 485 nm (in toluene), 550 nm (in CH₂Cl₂) to 620 nm (in CH₃CN), which can be ascribed to the photo-induced inter-ligand charge transfer (CT, vide infra), resulting in a large change of dipole moment in the electronically excited state versus that of the ground state, and affording a notable red-shifted emission upon increasing solvent polarity, which is conventionally dubbed as the solvatochromism.^{55, 56} Similar behavior was observed for **fppyBCzP** and **fppyBTPA**. It is worth of noting that a non-negligible band at approx. 390 – 410 nm for **fppyBPCz** and **fppyBCzP**, and became obvious for

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fppyBTPA in CH₃CN due to its very weak CT emission. This short-wavelength emission is attributed to the localized excitation (LE) emission to distinguish it from the CT emission. This phenomenon is reminiscent of a number of compounds that exhibit nonadiabatic or twisted intramolecular charge transfer.^{57, 58} Similar dual emission has been observed recently by Adachi and co-workers on the dihydrophenazine-based emitters exhibiting TADF.59

We also performed the time-dependent density functional (TD-DFT) calculations to gain insight into the basic photophysical data for all titled boron complexes. As a result, the lowest lying singlet $S_0 \rightarrow S_1$ optical transition is ascribed to HOMO \rightarrow LUMO processes (see Tables S1–S6 in the Electronic Supporting Information (ESI)). Their frontier molecular orbitals are shown in Figure 3 (in toluene) and Figure S1–S6 of ESI. In Figure 3, the electron density distribution of LUMO is localized at fppy (or dfppy) moiety of all complexes, while the electron density distribution of HOMO is localized at TPA, PCz or CzP fragments of the respective compounds. It is worth of noting that the electron density distribution of boron atom is negligible in both HOMO and LUMO for these boron complexes, being within 0.18% to 0.59%. Therefore, the $S_0 \rightarrow S_1$ transition displays a large inter-ligand charge transfer (ILCT) character, for which the transition moment in oscillator strength is calculated to be near zero. Therefore, the ILCT can be treated as a nonadiabatic type of electron transfer in the excited state, giving rise to negligible ILCT absorption but prominent charge transfer emission.

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We then performed the transient photoluminescence decay dynamics of these compounds in various solutions. Figure 4 displays the PL decay profiles for **fppyBTPA** and dfppyBTPA in the degassed toluene and their corresponding lifetime data are listed in Table 1. Apparently, the emission decay for both TPA derivatives exhibited double exponential decay kinetics, consisting of a prompt and a long decay components, for which the time constants fitted to be 77 ns and 2.5 µs for **fppyBTPA** and 75 ns and 2.7 µs for dfppyBTPA, respectively. Under the assumption of preequilibrium between S₁ and T₁ states, the difference in energy ΔE_{T-S} can be derived according to the relationship between ΔE_{T-S} and S_1-T_1 equilibrium constant K_{eq} , which

is expressed as $\Delta E_{T-S} = -RTIn(K_{eq}/3)$ where K_{eq} can be deduced from the preexponential factors for prompt fluorescence versus delay fluorescence components. A factor of 3 stands for the triplet degenerate states.⁴⁷ ΔE_{T-S} was then deduced to be – 1.65 and -1.52 kcal/mol for fppyBTPA and dfppyBTPA in toluene, respectively. As shown in Table 1, dfppyBCzP exhibits similar double exponential decay kinetics in toluene (31 ns, 2.6 μ s), for which ΔE_{T-S} is calculated to be -2.36 kcal/mol. Interestingly, the rest of boron complexes fppyBCzP, fppyBPCz and dfppyBCzP show solely single exponential decay kinetics in toluene (see Table S7). For a tentative rationalization, increasing (decreasing) the HOMO (LUMO) energy level for donor (acceptor) should stabilize the charge transfer state, such that ΔE_{T-S} is expected to be smaller due to the greater charge separation. As elaborated in the cyclic voltammetry measurement, the oxidation potential was measured to be in the order of BTPA < BCzP < BPCz and the reduction potential shows the order fppy > dfppy. The combination of these two factors gives the monotonous order of the free energy for the charge transfer:

fppyBPCz > dfppyBPCz > fppyBCzP > dfppyBCzP > fppyBTPA > dfppyBTPA

As a result, charge transfer for dfppyBTPA, fppyBTPA and dfppyBCzP is more exergonic than that for fppyBPCz, dfppyBPCz and fppyBCzP. Due to the reduced charge transfer character, $|\Delta E_{T-S}|$ for the last three boron compounds may be too large to be thermally accessed in toluene, resulting in insufficient TADF character.

In the more polar solvents such as CH₂Cl₂ and CH₃CN, as shown in Table S7, even dfppyBTPA and fppyBTPA did not show typical TADF decay behavior, i.e., the double exponential decay kinetics. Instead, the emission decay could be well fitted by a single exponential decay component and the resulting data are listed in Table S7. For a tentative rationalization, recent experimental evidence in the literature has supported the involvement of triplet local excited states (LE) from the donor or acceptor units, other than the triplet charge-transfer (CT) in the reverse intersystem crossing (RISC). Therefore, RISC may not occur between ¹CT and ³CT but between ¹CT and ³LE.^{60, 61} This is attributed to the fact that the energy of the CT states is stabilized in the more polar environments such that they now lie below the ³LE that is unaffected by solvent

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polarity. This provides an extra decay pathway, i.e., internal conversion, from ${}^{3}L^{2}$ to ${}^{3}L^{2}$. As a result, the ${}^{3}CT \rightarrow {}^{1}CT$ RISC rather inefficient due to the large energy gap in polar solvent, making ${}^{3}CT$ an effective triplet reservoir for **dfppyBTPA** and **fppyBTPA**.

Photophysics in thin solid film. Photophysical measurements of these boron complexes doped (with a doping concentration of 8 wt.%) in a large-triplet-energy host mCPCN [9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile] or DPEPO [bis[2-(diphenylphosphino)phenyl]ether oxide],⁶²⁻⁶⁶ have also been performed. Pertinent photophysical data are listed in Table 2. Figure 5a depicts all photoluminescence spectra (measured at RT) doped at 8 wt.% in the mCPCN host. The featureless PL spectra in the mCPCN host are similar to their emission spectra in the toluene solution, except for a ~20 nm blue shift in the doped film for all samples due perhaps to the restricted relaxation of the surrounding media and hence less stabilization in the solid film.^{67, 68} Also, similar to that in solutions, the emission wavelength is mainly determined by the type of the donor units (TPA, CzP, PCz) connected to the ppyB acceptor, i.e., with PL peak wavelengths being descending in the order of **fppyBTPA/dfppyBTPA > fppyBCzP/dfppyBCzP > fppyBPCz/dfppyBCz.** It is generally consistent with the strength of electron-donating capability of different donor units:

TPA > CzP > PCz

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and the strength of intramolecular charge-transfer characteristics, as supported by the electrochemical results (cf. ESI). Meanwhile the number of fluoro atom substitution on the ppyB acceptor (dfppy vs. fppy) has minor effects on emission wavelengths. Blue emitting compounds **fppyBPCz/dfppyBPCz** and **fppyBCzP/dfppyBCzP** doped into DPEPO host with an exceedingly larger singlet/triplet energies exhibit emission spectra/wavelengths similar to those in the mCPCN host (see Table 2 and ESI). As listed in Table 2, 8 wt.% of **fppyBTPA** and **dfppyBTPA** in mCPCN host show high PL quantum yields (PLQYs, Φ) of 72% and 95%, respectively, while all other compounds (bearing PCz and CzP donors) exhibit much lower PLQYs of only 6-19% in either mCPCN or DPEPO host.

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From the difference in the onset wavelengths of both fluorescence and phosphorescence of all samples in the doped films (see Fig. S12 in ESI) fppyBTPA/dfppyBTPA show very close onset positions in both fluorescence and phosphorescence spectra, suggesting very small ΔE_{T-S} for favoring the RISC, while **fppyBPCz/dfppyBPCz** and **fppyBCzP/dfppyBCzP** show relatively large ΔE_{T-S} (~ -3.69 to -10.2 kcal/mol)) not so favoring for RISC in both mCPCN and DPEPO hosts. Indeed, the room-temperature transient PL characteristics of all samples at 8 wt.% in the mCPCN shown in Figure 5b (and those of fppyBPCz/dfppyBPCz and fppyBCzP/dfppyBCzP in the DPEPO host, cf. ESI) indicate that **fppyBTPA/dfppyBTPA** in mCPCN exhibit distinct delayed fluorescence along with the initial prompt fluorescence, while all other compounds in either mCPCN or DPEPO host hardly show (or show very weak) delayed fluorescence and behave more like conventional fluorescent emitters.

fppyBTPA and **dfppyBTPA** show very close onset positions in both fluorescence and phosphorescence spectra in doped films (see Figure S12 in ESI). This suggests a very small ΔE_{T-S} , which makes unreliable estimation of their ΔE_{T-S} from the spectral onsets. Thus, for **fppyBTPA** and **dfppyBTPA**, we had instead characterized their ΔE_{T-S} from the activation energies of their temperature-dependent RISC rate constants k_{risc} . Figures 6a and 6b depict transient PL profiles of fppyBTPA and dfppyTPA (8 wt.% concentration) in the mCPCN host at different temperatures, respectively. Significant dependence of the decay rates of the delayed components on the temperature can be seen. Following the analysis method showed in literature,^{13, 69} the k_{risc} at different temperatures are extracted and are depicted as a function of the reciprocal of the temperature in Figures 6c and 6d, from which the ΔE_{T-S} for **fppyBTPA** and **dfppyBTPA** are estimated to be -0.60 kcal/mol (-26 meV) and -0.74 kcal/mol (-32 meV), and listed in Table 2. These results confirm very small ΔE_{T-S} values of **fppyBTPA** and **dfppyBTPA**, which are among the smallest ΔE_{T-S} values ever reported for TADF materials.

Transient PL profiles of fppyBTPA/dfppyBTPA can be fitted by two exponential decay components as: $I(t) = B_1 \exp(-t/\tau_0) + B_2 \exp(-t/\tau_d)$, where B_1 and B_2 are preexponential factor, and τ_p and τ_d are the observed lifetimes of the prompt and delayed

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decay components. Extracted (τ_p , τ_d) for **fppyBTPA/dfppyBTPA** are (48 ns, 2.0^D µs) and τ_p (46 ns, 2.4 μ s), respectively (Table 2). The emission quantum yields Φ_p and Φ_d for the prompt and delayed fluorescence components, respectively, can further be derived by $\Phi_p = \Phi \cdot B_1 \cdot \tau_p / (B_1 \cdot \tau_p + B_2 \cdot \tau_d)$ and $\Phi_d = \Phi \cdot B_2 \cdot \tau_d / (B_1 \cdot \tau_p + B_2 \cdot \tau_d)$.⁷⁰ Determined (Φ_p, Φ_d) for fppyBTPA/dfppyBTPA in mCPCN are (38%, 34%) and (50%, 45%), respectively (Table 2), clearly indicating significant contribution of delayed fluorescence for these two emitters.

OLED performance. The boron complexes fppyBTPA/dfppyBTPA with significant delayed fluorescence and high PLQYs were applied for electroluminescent (EL) studies using the common device architecture of: glass substrate/ITO anode/PEDOT:PSS (70 nm)/TAPC (15 nm)/mCP (5 nm)/mCPCN doped with TADF dopants (4-75 wt.%; 20 nm)/3TPYMB (50 nm)/LiF (0.5 nm)/Al (100 nm). Indium tin oxide (ITO), poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), LiF, and AI were used the anode, hole-injection layer, electron-injection layer and cathode, as respectively.⁶²⁻⁶⁵ Both di-[4-(N,N-ditolylamino)phenyl]cyclohexane (TAPC) and N,Ndicarbazolyl-3,5-benzene (mCP) constituted the hole-transport layers (HTL), while mCPCN was served as the host of emitting layer (EML) and tris-[3-(3pyridyl)mesityl]borane (3TPYMB) employed as the electron-transport layer (ETL).62-65 Details of device fabrication and material characterization (molecular structures and energy levels of materials used in OLEDs) can be found in the supporting information.

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With a same device structure, devices with different doping concentrations (from 4 to 75 wt.%) were tested (with detailed EL characteristics of these devices being shown in supporting information). Figure 7a-7d shows EL characteristics of OLEDs with optimized fppyBTPA/dfppyBTPA doping concentrations at 8 wt.% and 25 wt.%, respectively, while performance parameters of both devices are summarized in Table 3. The EL spectra are similar to PL spectra in doped films, indicating pure EL from either fppyBTPA or dfppyBTPA. These devices in general exhibit a rather low turn-on voltage of ~2.5 V and low operation voltage (e.g., ~3-4 V for a brightness of 100 $cd \cdot m^{-2}$). The

optimized dfppyBTPA device based shows EL efficiencies of up to (26.6%, 88.2°cd⁰Å^{019/C6TC04994J} 81.5 lm·W⁻¹), superior to (20.2%, 63.9 cd·A⁻¹, 66.9 lm·W⁻¹) of the **fppyBTPA** device, due to superior PLQY of dfppyBTPA. Having a nearly 27% of EQE, the present dfppyBTPA device is among the most efficient TADF OLEDs.^{48, 49} Such an EQE is certainly beyond the theoretical limit of a conventional fluorescent emitter and clearly indicates effective recycling and utilization of the triplet excitons formed during the EL process, through the effective TADF (or reverse intersystem crossing) process. Overall, results here clearly demonstrate that linking electron-donating and the electron-accepting fragments through the spiro-bridged, four-coordinate boron atom provide a flexible and powerful design for TADF emitters capable of high PLQYs and high EL efficiencies.

Preliminary stability tests had been conducted on fppyBTPA and dfppyBTPA devices. Currently, operational lifetimes (defined as the time for the brightness to drop to 50% of initial brightness) of these devices are not satisfactory, i.e. only minutes to tens of minutes (under an initial brightness of 200-250 cd·m⁻², see Figure S20 of ESI). Nevertheless, it already showed a significant improvement compared to the boron complex represented by ppyBTPA,⁵⁰ for which severe and rapid device degradation occurred even under standard OLED current-voltage-luminance characterization conditions and afforded extremely low efficiency. Hence, the electron withdrawing fluoro substituent on ppy fragment of boron complexes appears to improve the stability of the as-fabricated OLEDs relative to those of **ppyBTPA**.

Conclusion

In summary, we report the design and synthesis of a new series of four-coordinated boron complexes anchoring with both electron donating and accepting units. Due to the electron deficiency and saturated atomic character, the boron atom has negligible contribution to the lower lying electronic transition and hence creates spatial separation between donor and acceptor moieties. Among the titled boron complexes the underlying ICT characters and TADF properties have been investigated via steadystate and time-resolved measurements, together with computational approach.

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OLEDs based on **fppyBTPA** and **dfppyBTPA** have been fabricated successfull^{9,0} which^{9,0} corroad and exhibit a rather low turn-on voltage of ~2.5 V and low operation voltage, e.g., ~3-4 V for a brightness of 100 cd·m⁻². The performances of **dfppyBTPA** based OLEDs (26.6%, 88.2 cd·A⁻¹, 81.5 lm·W⁻¹) are among the most efficient TADF OLEDs so far. Moreover, our observation is in sharp contrast to the closely related boron complex **ppyBTPA**,⁵⁰ for which severe and rapid device degradation occurred even under standard OLED current-voltage-luminance characterization conditions and afforded extremely low efficiency. Hence, the electron withdrawing fluoro substituent on the ppy fragment of boron complexes has obviously improved the stability of the as-fabricated OLEDs

relative to those of **ppyBTPA**. Our results thus broaden the horizon for boron based D-A complexes as emerging TADF materials that are able to harvest the triplet excitons efficiently.

Experimental Section

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General Procedures. All reactions were conducted under nitrogen atmosphere unless otherwise noted. All solvents were dried over appropriate drying agents and distilled prior to use. Commercially available reagents were used without further purification. 4-Bromo-triphenylamine was obtained from monobromination of triphenylamine using *N*-bromosuccinimide.⁷¹ 3-Bromo-9-phenylcarbazole was synthesized from Ullmann coupling using 3-bromocarbazole and iodobenzene in presence of Cul,⁷² while 9-(4-bromophenyl)carbazole was obtained from the coupling of carbazole and 1-bromo-4-iodobenzene.⁷³ Reactions were monitored by pre-coated TLC plates (0.20 mm with fluorescent indicator F₂₅₄). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. ¹H NMR spectra were obtained in CDCl₃ and calibrated using residual CHCl₃ (δ = 7.24 ppm) as an internal reference. Elemental analysis was carried out with a Heraeus CHN-O-Rapid Elemental Analyzer. Thermal analysis was performed using a Seiko Instrument TG/DTA320 thermogravimetric analyzer under nitrogen at a

heating rate of 15 °C/min. Differential scanning calorimeter (DSC) was conducted using a Seiko Instrument DSC220C, with a heating and cooling rate of 10 °C /min.

Preparation of borane dibromide complexes fppyBBr₂ and dfppyBBr₂. To a solution of 2-(4-fluorophenyl)pyridine (3.6 g, 20 mmol) in 50 mL of CH₂Cl₂, 60 mL of 1 M solution of BBr₃ in CH₂Cl₂ (60 mmol) was slowly added at 0 °C, followed by addition of ethyldiisopropylamine (3.7 mL, 20 mmol). The mixture was warmed up to RT and stirred for 12 hours. After then, the mixture was washed with saturated K₂CO₃ solution and water (three times), and the organic layer was dried over Na₂SO₄, and concentrated to dryness. The crude product was rinsed with hexane to afford air-stable, colorless 2-(4-fluorophenyl)pyridine boron dibromide **fppyBBr₂** (3.7 g, 53%). The corresponding 2-(2,4-difluorophenyl)pyridine derivative **dfppyBBr₂** was synthesized in an analogous manner in 30% yield.

Characterization of **fppyBBr**₂: ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm) 8.91 (d, J = 6.0 Hz, 1H), 8.15 (t, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.73 (dd, J = 8.4, 6.0 Hz, 1H), 7.55-7.49 (m, 2H), 7.08 (t, J = 8.4 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃, 298K) δ (ppm) -105.18 (1F).

Characterization of **dfppyBBr**₂: ¹H NMR (400 MHz, d₆-acetone, 298K) δ (ppm) 9.12 (d, *J* = 6.0 Hz, 1H), 8.58 (t, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.95 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H); ¹⁹F NMR (376 MHz, d₆-acetone, 298K) δ (ppm) –104.03 (1F), –112.92 (1F).

Preparation of fppyBTPA. To a solution of **fppyBBr**₂ (0.50 g, 1.5 mmol) in THF (10 mL) at 0 °C, was slowly added a Grignard reagent, which was *in-situ* generated from 4bromotriphenylamine (1.0 g, 3.2 mmol), Mg chip (0.23 g, 9.6 mmol) and trace amount of I₂ in THF (15 mL) and stirred at RT for 12 hours. The solution was evaporated to dryness, and the residue was dissolved into CH_2Cl_2 , washed with H_2O , dried over MgSO₄ and concentrated. The resulting product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and hexane (v/v = 1/5), followed by recrystallization from mixed CH_2Cl_2 and hexane to afford **fppyBTPA** $(0.432)^{/C6TC04994J}$ g, 42%) as a light yellow solid.

Characterization of **fppyBTPA**: ¹H NMR (400 MHz, d₆-acetone, 298K) δ (ppm) 8.68 (d, *J* = 5.9 Hz, 1H), 8.40-8.33 (m, 2H), 8.16 (t, *J* = 4.2 Hz, 1H), 7.67 (t, *J* = 5.9 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.23-7.18 (m, 8H), 7.13-7.07 (m, 5H), 6.98-6.92 (m, 12H), 6.88 (d, *J* = 8.6 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 166.4(*C*-F), 163.9, 157.3, 148.1(4C), 145.4 (2C), 144.2, 140.6, 133.7 (4C), 131.8, 129.0 (8C), 123.8 (8C), 123.6 (4C), 122.0 (4C), 121.5 (2C), 117.8, 117.3, 117.1, 113.8, 113.5; ¹⁹F NMR (376 MHz, d₆-acetone, 298K) δ (ppm) –111.18 (1F); MS (EI) *m/z*: calcd for C₄₇H₃₅BFN₃: 671.3; found: 671.4 [M⁺]; anal. calcd for C₄₇H₃₅BFN₃: C, 84.05; H, 5.25; N, 6.26; found: C, 83.68; H, 5.69; N, 6.16.

Preparation of dfppyBTPA. Following the procedure described for **fppyBTPA**, reaction of **dfppyBBr**₂ (0.40 g, 1.1 mmol) and the *in-situ* generated Grignard reagent afforded **dfppyBTPA** (0.36 g, 47%) as a light yellow solid.

Characterization of **dfppyBTPA**: ¹H NMR (400 MHz, d₆-acetone, 298K) δ (ppm) 8.73 (d, *J* = 6.4 Hz, 1H), 8.42 (t, *J* = 7.6 Hz, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 6.4 Hz, 1H), 7.23-7.18 (m, 9H), 7.10 (d, *J* = 8.4 Hz, 4H), 6.98-6.92 (m, 13H), 6.88 (d, *J* = 8.4 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 166.7(*C*-F), 164.2(*C*-F), 157.6, 144.2, 141.0 (4C), 141.0, 134.2 (8C), 131.9, 126.0 (4C), 125.7 (8C), 123.2 (2C), 120.1 (2C), 119.5 (4C), 118.2, 117.4, 117.2, 114.3, 114.0, 110.0 (4C); ¹⁹F NMR (376 MHz, d₆acetone, 298K) δ (ppm) –107.05 (1F), –114.28 (1F); MS (EI) *m/z*: calcd for C₄₇H₃₄BF₂N₃: 689.3; found: 689.4 [M⁺]; anal. calcd for C₄₇H₃₄BF₂N₃: C, 81.86; H, 4.97; N, 6.09; found: C, 81.77; H, 5.04; N, 6.11.

Preparation of fppyBPCz and dfppyBPCz. Following the procedure described for both **fppyBTPA** and **dfppyBTPA**, the reactions with the *in-situ* generated Grignard reagent from 9-(4-bromophenyl) carbazole afforded **fppyBPCz** and **dfppyBPCz** in 35-45% yields.

Characterization of **fppyBPCz**: ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm) 8.67 (d, J = 5.2

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Hz, 1H), 8.18-8.07 (m, 6H), 7.95 (dd, J = 7.1, 3.4 Hz, 1H), 7.55-7.36 (m, 17H), 7.28-7.24/C6TC04994J (m, 5H), 7.11 (t, J = 8.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 166.7 (C-F), 164.2, 157.7, 144.2, 141.1, 141.0 (4C), 135.6 (2C), 134.2 (4C), 131.9, 126.1 (4C), 125.7 (4C), 123.2 (4C), 121.9 (2C), 120.1 (4C), 119.5 (4C), 118.2, 117.4, 117.2, 114.3, 114.0, 110.1 (4C); ¹⁹F NMR (376 MHz, CDCl₃, 298K) δ (ppm) –107.94 (1F); MS (EI) m/z: calcd for C₄₇H₃₁BFN₃: 667.2; found: 667.4 [M⁺]; anal. calcd for C₄₇H₃₁BFN₃: C, 84.56; H, 4.68; N, 6.29; found: C, 84.62; H, 4.84; N, 6.30.

Characterization of **dfppyBPCz**: ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm) 8.52 (d, J = 5.76 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.08 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 6.6 Hz, 1H), 7.22-7.17 (m, 8H), 7.07-7.03 (m, 10H), 6.96-6.91 (m, 7H), 6.74 (t, J = 9.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 157.4 (C-F), 148.4 (C-F), 144.3, 144.2, 141.7, 141.5, 141.0 (4C), 135.8 (4C), 134.2 (2C), 126.2 (4C), 126.1 (4C), 125.7 (4C), 125.6 (4C), 123.2 (4C), 122.3, 120.3 (2C), 120.1, 119.7, 119.5, 113.1, 110.0 (4C); ¹⁹F NMR (376 MHz, CDCl₃, 298K) δ (ppm) -106.37 (1F), -115.00 (1F); MS (EI) m/z: calcd for C₄₇H₃₀BF₂N₃: 685.3; found: 685.2 [M⁺]; anal. calcd for C₄₇H₃₀BF₂N₃: C, 82.34; H, 4.41; N, 6.13; found: C, 82.59; H, 4.27; N, 6.21.

Preparation of fppyBCzP and dfppyBCzP. Following the procedure described for both fppyBTPA and dfppyBTPA, the reactions with the in-situ generated Grignard reagent from 3-bromo-9-phenylcarbazole afforded fppyBCzP and dfppyBCzP in moderate yields.

Characterization of **fppyBCzP**: ¹H NMR (400 MHz, d₆-acetone, 298K) δ (ppm) 8.83 (d, J = 5.6 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 8.29 (t, J = 8.0 Hz, 1H), 8.18-8.15 (m, 1H), 8.09 (s, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.65-7.57 (m, 9H), 7.48-7.43 (m, 3H), 7.35-7.28 (m, 6H), 7.24 (d, J = 8.0 Hz, 2H), 7.14-7.06 (m, 3H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 166.6 (C-F), 164.0, 157.4, 144.3 (2C), 140.7 (2C), 140.6 (2C), 140.0 (2C), 138.1 (2C), 131.8, 131.6 (2C), 129.7 (4C), 126.95, 126.90 (4C), 125.2 (2C), 124.4 (2C), 123.7 (2C), 123.1 (2C), 121.6, 120.2 (2C), 119.4 (2C), 117.9, 117.3, 117.1, 113.7, 113.5, 109.4 (2C), 109.1 (2C); ¹⁹F NMR (376 MHz, d₆-acetone, 298K) δ (ppm) –111.27 (1F); MS (EI) m/z:

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calcd for C₄₇H₃₁BFN₃: 667.3; found: 667.4 [M⁺]; anal. calcd for C₄₇H₃₁BFN₃: C, 84.56; H, 4.73; N, 6.35.

Characterization of **dfppyBCzP**: ¹H NMR (400 MHz, d₆-acetone, 298K) δ (ppm) 8.91 (d, *J* = 5.6 Hz, 1H), 8.46-8.39 (m, 2H), 8.07 (s, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.75 (t, *J* = 5.6 Hz, 1H), 7.67-7.63 (m, 4H), 7.59 (d, *J* = 8.0 Hz, 4H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.36-7.30 (m, 7H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, 298K) δ (ppm) 158.4 (*C*-F), 144.4 (*C*-F), 140.7 (2C), 140.4 (2C), 139.9 (2C), 138.2 (2C), 135.9, 131.72 (2C), 131.68, 131.3, 131.0, 129.6 (4C), 126.93 (4C), 126.89 (2C), 125.9, 125.1 (2C), 124.50 (2C), 124.47, 123.8 (2C), 123.1, 121.9, 121.8, 120.2 (2C), 119.3 (2C), 118.2 (2C), 109.4 (2C), 108.9 (2C); ¹⁹F NMR (376 MHz, d₆acetone, 298K) δ (ppm) –107.22 (1F), –114.39 (1F); MS (EI) *m/z*: calcd for C₄₇H₃₀BF₂N₃: 685.3; found: 685.4 [M⁺]; anal. calcd for C₄₇H₃₀BF₂N₃: C, 82.34; H, 4.41; N, 6.13; found: C, 82.46; H, 4.26; N, 6.20.

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Photophysical Measurements. Steady-state absorption and emission spectra in solution were recorded with a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively.⁷⁴ Thin films for photophysical characterization were prepared by thermal evaporation on quartz substrates at 1-2 Å/sec in a vacuum chamber with a base pressure of $<10^{-6}$ torr. Absorption spectra were characterized by a UV-vis-NIR spectrophotometer (UV-1650 PC, Shimadzu). Photoluminescence (PL) spectra, photoluminescence quantum yields (PLQYs), and phosphorescence spectra were characterized by a spectrofluorimeter (FluoroMax-P, Horiba Jobin Yvon Inc.). PLQYs of thin films or dilute solutions were determined using this spectrofluorimeter equipped with a calibrated integrating sphere. During the PLQY measurements, the integrating sphere was purged with pure and dry nitrogen to keep the environment inert. The selected monochromatic excitation light was used to excite samples placed in the calibrated integrating sphere. By comparing the spectral intensities of the monochromatic excitation light and the PL emission, the PL quantum yields were Phosphorescence spectra of thin films or dilute solutions were determined.

conducted at 77 K (the liquid nitrogen temperature) by the spectrofluorometer equipped with a microsecond flash lamp as the pulsed excitation source. A 10-ms delay time was inserted between the pulsed excitation and the collection of the emission spectrum. Time-resolved PL (PL decay curves) was measured by monitoring the decay of the intensity at the PL peak wavelength using the time-correlated single-photon counting technique with a fluorescence lifetime system (FluoroCube, Horiba Jobin Yvon Inc.) and nanosecond pulsed light excitation from a UV light-emitting diode (300 nm). The samples were placed in a vacuum cryostat chamber with the temperature control.

Computational method. All the calculations were performed with the Gaussian 09 program package. The geometry optimization of ground states for the six boron complexes was simulated with density functional theory (DFT) at the B3LYP/6-31g(d) levels. The calculated optical absorptions were performed with the time-dependent density functional theory (TD-DFT) method. The solvent effect was based on the polarizable continuum model (PCM), which was implemented in the Gaussian 09 program. We also adopted the Mulliken population analysis (MPA) to obtain the electron density distribution of every atom in each molecular orbital. Additionally, upon performing the TD-DFT calculation we were able to access the assignment and corresponding percentage of the frontier orbitals for HOMO \rightarrow LUMO (or HOMO-1 \rightarrow LUMO, HOMO \rightarrow LUMO+1, etc.) excitation processes.

OLED Fabrication and Characterization. OLEDs were fabricated on the ITO-coated glass substrates with multiple organic layers sandwiched between the transparent bottom indium-tin-oxide (ITO) anode and the top metal cathode. The PEDOT:PSS layer was prepared by spin coating from the as-purchased aqueous dispersion of PEDOT: PSS (Clevios, Heraeus Co.), followed by annealing on a hot plate at 130 °C for 15 min. under ambient conditions. Other material layers were deposited by vacuum evaporation in a vacuum chamber with a base pressure of <10⁻⁶ torr. All organic materials used in experiments (except for the TADF emitters and the mCPCN host

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developed by ourselves) were purchased from Lumtec, Inc. All compounds were subjected to temperature-gradient sublimation under high vacuum before use. The deposition system permits the fabrication of the complete device structure in a single vacuum pump-down without breaking vacuum. The deposition rate of organic layers was kept at ~0.1 - 0.2 nm/s. The doping was conducted by co-evaporation from separate evaporation sources with different evaporation rates. The active area of the device is 1 x 1 mm², as defined by the shadow mask for cathode deposition. The current-voltage-brightness (I-V-L) characterization of the light-emitting devices was performed with a source-measurement unit (SMU) and a Si photodetector calibrated with a spectroradiometer (DMS 201, AUTRONIC-MELCHERS GmbH). EL spectra of devices were collected by a calibrated CCD spectrograph.

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Figure 1. Absorption and emission spectra of **fppyBTPA**, **fppyBPCz**, and **fppyBCzP** in solid (black), and in toluene (red), CH₂Cl₂ (blue), and CH₃CN solution (green) at 298 K.

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Figure 2. Absorption and emission spectra of **dfppyBTPA**, **dfppyBPCz**, and **dfppyBCzP** in solid (black), and in toluene (red), CH₂Cl₂ (blue), and CH₃CN solution (green) at 298 K.

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Figure 3. The frontier molecular orbitals (HOMO and LUMO) of (a) **fppyBTPA**, (b) **fppyBPCz**, (c) **fppyBCzP**, (d) **dfppyBTPA**, (e) **dfppyBPCz**, and (f) **dfppyBCzP** in toluene. Notation "B" indicates the electron density distribution at boron atom in each orbital. The Mulliken population analysis (MPA) in Gaussian 09 program was applied to obtain the electron density distribution in each molecular frontier orbital.

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Figure 4. The fluorescence decay of (a) **fppyBTPA** and (b) **dfppyBPTPA** (black line) in degassed toluene at 298 K. IRF: instrument response function (red line). Fitting curve (blue line).

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Figure 5. (a) PL spectra and (b) transient PL profiles (measured at RT) of all doped samples at 8 wt.% in mCPCN host.

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Figure 6. (a), (b) Transient PL profiles of fppyBTPA and dfppyBTPA (8 wt.% concentration) in the mCPCN host, respectively, at different temperatures. (c), (d) Extracted k_{risc} as a function of the reciprocal of the temperature.

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Figure 7 (a) EL spectra and (b) current-voltage-luminance (I-V-L) characteristics, (c) external quantum efficiencies (EQEs), and (d) power efficiencies of **fppyBTPA** and **dfppyBTPA** devices. The doping conc. for **fppyBTPA** and **dfppyBTPA** are at 8 wt.% and 25 wt.%, respectively. The 1931 CIE (x,y) coordinates for the **fppyBTPA** and **dfppyBTPA** devices are (0.27,0.54) and (0.26,0.58), respectively.

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Table 1. Selected	photophy	sical properties	s of all boron	complexes in	toluene at RT.
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Compound	СТ	PLQY [%]	T [nc] ^[b] (nro over factor)	ΔE_{T-S}
	[nm]			[kcal/mol]
fppyBTPA	529	11.6 ^[a] , 56.4 ^[b]	76.8 (0.9798); 3369.6 (0.0202)	-1.65
fppyBPCz	456	29.4 ^[b]	29.6 (–)	
fppyBCzP	485	31.9 ^[b]	27.7 (–)	
dfppyBTPA	535	19.9 ^[a] , 100.0 ^[b]	75.3 (0.9752); 2697.1 (0.0248)	-1.52
dfppyBPCz	488	16.0 ^[a] , 39.2 ^[b]	23.1 (–)	
dfppyBCzP	486	17.5 ^[a] , 44.4 ^[b]	31.6 (0.9819); 2576.1 (0.0181)	-2.36

[a] measured in aerated solution. [b] measured in degassed solution. [c] (–) indicates that the emission can be fitted solely by a single exponential decay kinetics.

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Table 2. Selected photophysical properties of all boron complexes in mCPCN and DPEPO hosts (with a doping concentration of 8 wt.%, except for an additional test on 25 wt.% dfppyBTPA).

Emitter	Host	λ _{PL, max} ^(a) [nm]	Φ ^(b) [%]	Es ^(c) [eV]	<i>Ε</i> _Τ ^(d) [eV]	∆ <i>E</i> ⊤-s ^(e) [kcal/mol]	τ _p ^(f) [ns]	τ _d ^(f) [μs]	Φ _p ^(g) [%]	Φ _d ^(g) [%]
fppyBTPA	mCPCN	494	72	~2.90	~2.90	–0.60 ^e	48	2.0	38	34
fppyBPCz	mCPCN	426	15.7	3.25	2.92	-7.61	10.4			
	DPEPO	420	6.0	3.35	2.92	-9.92	16.6			
fppyBCzP	mCPCN	450	15.5	3.11	2.87	-5.53	11.4	0.29	14.7	0.8
	DPEPO	456	16.6	3.25	2.92	-7.61	15			
dfppyBTPA (8 wt.%)	mCPCN	490	95	~2.92	~2.92	-0.74 ^{e)}	46	2.4	50	45
dfppyBTPA (25 wt.%)	mCPCN	508	100	~2.73	~2.73	-0.53 ^{e)}	51	2.4	62	38
dfppyBPCz	mCPCN	432	15.5	3.13	2.88	-5.77	9.4			
	DPEPO	427	7.0	3.40	2.96	-10.2	17.7			
dfppyBCzP	mCPCN	455	15.0	3.12	2.94	-4.15	9.8			
	DPEPO	456	19.4	3.14	2.98	-3.69	11			

a. fluorescence peak maximum; b. photoluminescence quantum yield; c. singlet energy calculated from the onset of the fluorescence; d. triplet

energy calculated from the onset wavelength of the 77K phosphorescence; e. ΔE_{T-S} of **fppyBTPA** and **dfppyBTPA** were obtained from the activation energy of temperature-dependent k_{risc} while ΔE_{T-S} of other compounds were obtained from onsets of fluorescence and phosphorescence spectra; f. lifetime of the prompt and delayed photoluminescence; g. quantum yield of the prompt and delayed fluorescence.

Table 3. EL parameters of the fppyBTPA and dfppyBTPA based OLED devices (with a doping concentration of 8 wt.% and 25 wt.%, respectively).

Device	Conc.		EQE [%]	Current efficiency [cd·A ⁻¹]	Power efficiency [lm·W ⁻¹]
fppyBTPA	8 wt.%	Peak	20.2	63.9	66.9
		at 100 cd·m ⁻²	15.5	49.1	28.5
dfppyBTPA	25 wt.%	Peak	26.6	88.2	81.5
		at 100 cd·m ⁻²	25.3	83.9	59.9

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TOC Illustration:



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