1. Introduction

Boron, a versatile element with an empty p_z-orbital, tends to form electron-deficient multiatom networks in three-coordination and trigonal-planar geometry, arousing fascinating characteristics when being introduced into the organic optoelectronic molecules. Boron-containing molecules with strong electron-accepting triarylboron moiety have received considerable attention, because they are potential materials for a number of photonic and optoelectronic applications, such as nonlinear optic molecules, anion sensing probes, electron-transporting materials, fluorescent dyes, and thermally activated delayed fluorescent compounds. However, borane derivatives are rarely used as electron-accepting species to construct bipolar host materials for phosphorescent organic light-emitting diodes (PhOLEDs), probably due to the high activity of the empty boron p_z-orbital in binding any Lewis bases, although almost all the other requirements of host materials can be fulfilled. High thermal stability, solvent solubility, solution processability, and triplet energy are achieved simultaneously. With the thus-designed boron-containing bipolar molecules as host materials, the solution-processed PhOLEDs exhibit high device performances, which are comparable to the vacuum-processed counterparts, showing high external quantum efficiencies up to 18.5% and 14.5% in blue and white PhOLEDs, respectively. These results demonstrate the great potential of the star-shaped and symmetry-breaking borane derivatives in solution-processable organic optoelectronic devices.

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Star-Shaped Boron-Containing Asymmetric Host Materials for Solution-Processable Phosphorescent Organic Light-Emitting Diodes

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Boron-containing compounds have attracted considerable attention because of their electron-accepting properties, and they are widely used in a variety of fields. However, due to the essential requirement to protect the empty p_z-orbital of the boron atom using large steric hindrance or rigid groups, borane derivatives generally show poor solubility and are rarely reported as acceptor units to construct bipolar host materials for phosphorescent organic light-emitting diodes (PhOLEDs). Here, a combined star-shaped and asymmetric donor–acceptor molecular design strategy to improve the solubility and fine tune the optical and electronic properties of boron-containing materials is presented. High thermal stability, solvent solubility, solution processability, and triplet energy are achieved simultaneously. With the thus-designed boron-containing bipolar molecules as host materials, the solution-processed PhOLEDs exhibit high device performances, which are comparable to the vacuum-processed counterparts, showing high external quantum efficiencies up to 18.5% and 14.5% in blue and white PhOLEDs, respectively. These results demonstrate the great potential of the star-shaped and symmetry-breaking borane derivatives in solution-processable organic optoelectronic devices.

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(LUMO) energy levels to support balanced and efficient carrier injection and transportation during the operation of PhOLEDs, and 3) high thermal stability and good miscibility with the guest molecules for stable amorphous and uniformly doped films through vacuum thermal evaporation and upon heating.

To prepare stable triarylboranes that free of chemical attack, steric hindrance around the boron center has been recognized as a useful way to protect the empty $p_z$ orbital of boron atom in constructing applicable optoelectronic molecules. In 2012, by combining bulky dimesityl borane and rigid carbazole, Wu and co-workers first reported the boron-containing host materials for blue and white PhOLEDs, achieving the corresponding external quantum efficiencies (EQEs) of 16.5% and 15.7% in vacuum-deposited devices. [14] In 2016, Liao and co-workers used also the bulky dimesityl borane as acceptor (A) but more rigid spirotacridine-9,9'-fluorene as donor (D) to design boron-based bipolar host materials for blue PhOLEDs with high EQE up to 25.1%. [15] Very recently, they linked the dimesityl borane to the N-atom of bicarbazole and thus obtained boron-containing host material showed a maximum EQE of 16.7% in blue PhOLEDs. [16] In spite of these high device performances reported recently, the development of boron-based host materials lags far behind in comparison to that of the other types of host molecules. Even more tragically, the bulky steric hindrance and rigid groups employed to kinetically prevent the attack of nucleophiles generally lead to the poor solubility of the boron-containing compounds in solvents; this inevitably prohibits their applications in solution-processed devices, although the solution processing in fabricating devices has widely recognized advantages than the vacuum thermal deposition technology and is in great demand for low-cost and large-area production of optoelectronic devices in commercial manufacture. [11, 17, 18]

Here, we aim to address this intrinsic obstacle by combining the star-shaped and asymmetric molecular design strategies together to improve the solubility and fine tune the optical and electronic properties of the boron-containing D–A molecules with an acceptor core of bulky tetramethylphenyl borane and varied peripheral donors of carbazole and diphenylamine (Scheme 1). It is well known that star-shaped molecules are promising candidates for solution-processable optoelectronic devices; meanwhile, the asymmetric materials could finely modulate the photophysics and electrochemistry properties by increasing the number of the conformers and amount of energy for crystallization to favor the stability improvement of amorphous film. [20] Since carbazole is a weak donor and diphenylamine is a strong one, the competition and cooperation of the different number and types of donors in the star-shaped symmetry-breaking D–A molecular architecture would significantly modify the molecular structures and optoelectronic properties of asymmetric molecules. Indeed, good solubility and high stability were observed in these asymmetric star-shaped boron-containing D–A molecules; high $E_T$ and suitable HOMO and LUMO qualify them as solution-processable bipolar host materials for blue PhOLEDs. Impressively, the solution-processed PhOLEDs using asymmetric host materials of DNP hcZB and NP hDcZB exhibit comparable device performances to those of vacuum-fabricated devices, showing low turn-on voltage of 3.5 V, high EQEs of 18.4% and 18.5% for blue PhOLEDs, and of 10.7% and 14.5% for white PhOLEDs in simplified device structures.

2. Result and Discussion

2.1. Molecular Design and Synthesis

The boron-containing star-shaped D–A molecules of TNPhB, DNPhCZB, NPhDCzB, and TCzB (Scheme 1) were designed to have the same electron-withdrawing core of triarylborane with tetramethylphenyl propeller arrangements, which effectively shields the boron $p_z$-orbital from attack by Lewis bases or nucleophiles and facilitates the forming of amorphous films through solution-processing. Then, carbazole or diphenylamine, which has been extensively applied in PhOLEDs with high $E_V$ and hole-transport properties, [21] were introduced symmetrically or asymmetrically as the electron-donating moiety to the three branches of the triarylborene core. Based on the facilely prepared tris-brominated triarylborene core, these compounds in white powders were efficiently synthesized in high yields (72–88%) through one or two steps of classical Suzuki coupling reactions (Scheme S1, Supporting Information). [22] Detailed synthetic route and systematic characterizations through $^1$H/$^13$C NMR spectroscopy and high resolution mass spectrum are given in Figures S1–S4 in the Supporting Information. Owing to the star-shaped molecular architecture, all the compounds exhibit good solubility (>30 mg mL$^{-1}$) in common organic solvents (Table S1, Supporting Information), and these asymmetric molecules of DNP hcZB and NP hDcZB demonstrate even higher solubility (>150 mg mL$^{-1}$) than the symmetric compounds due to the effects of asymmetric architectures, which
could increase the number of the conformers with weaker intermolecular interaction.

2.2. Thermophysical and Photophysical Properties

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) reveal that these boron-containing compounds have good thermal stability with high decomposition temperatures ($T_d > 416 \, ^\circ C$), glass-transition temperatures ($T_g > 158 \, ^\circ C$), and melting temperature ($T_m > 213 \, ^\circ C$) owing to the stable triarylborane core with triple protection of tetramethylphenyl and peripheral aromatic carbazole and diphenylamine branches (Figure S5, Supporting Information). Impressively, higher $T_g$, $T_m$, and $T_d$ were observed in asymmetric molecules compared to the HOMO energy level. $E_g$ calculated by the absorption edge technique in solid film; $d$)Triplet energy ($E_t$) measured from phosphorescent spectrum at 77 K with a delay time of 5 ms; $e$LUMO energy level estimated by adding $E_t$ to the HOMO energy level.

Table 1. Photophysical and electrochemical properties of the boron-containing D–A molecules.

| Compound   | $T_d/T_m$ [°C] | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | $E_{opt}^{\pi\pi}$ [eV] | $E_{opt}^{\pi\pi}$ [eV] | $E_{opt}^{\pi\pi}$ [eV] | $E_{opt}^{\pi\pi}$ [eV] |
|------------|----------------|----------------------|---------------------|------------------------|------------------------|------------------------|------------------------|
| TNPhB      | 416/158\(^{a}\) | 310, 338             | 302, 330            | 3.32                   | 467                    | 408                    | -5.34                  | -2.02                  |
| DNPhCzB    | 453/161\(^{a}\) | 298, 334             | 295, 333            | 3.31                   | 467                    | 412                    | -5.35                  | -2.04                  |
| NPhDCzB    | 448/274\(^{a}\) | 298, 334             | 295, 333            | 3.30                   | 468                    | 415                    | -5.40                  | -2.10                  |
| TCzB       | 416/213\(^{a}\) | 298, 334             | 295, 333            | 3.45                   | 403                    | 396                    | -5.66                  | -2.21                  |

$^{a}$Subscript: $d$Optical bandgap ($\omega E_{opt}$) calculated by the absorption edge technique in solid film; $h$Triplet energy ($E_t$) measured from phosphorescent spectrum at 77 K with a delay time of 5 ms; $e$LUMO energy level estimated by adding $E_t$ to the HOMO energy level.
spectra in thin films than in CH$_2$Cl$_2$ (Figure 1b). This could be due to the characteristic property of boron-containing D–A molecules, exhibiting small dipole moments at ground states for almost unchanged absorption bands in different solvents and solid states but large dipole moments at excited states to response significantly to the molecular state change.[24,25]

From the onset thresholds of the absorption spectra in solid films, the optical band gaps ($\text{opt} E_{g}$) of TNPhB, DNPhCzB, NPhDCzB, and TCzB were identified to be as wide as 3.32, 3.31, 3.30, and 3.45 eV, respectively. From the time-resolved phosphorescence spectra (Figure S9, Supporting Information) measured at 77 K in CH$_2$Cl$_2$, the lowest triplet excited states ($T_1$) energy ($E_T$) of these molecules were evaluated to be as high as 2.77, 2.80, 2.87, and 2.90 eV for TNPhB, DNPhCzB, NPhDCzB, and TCzB, respectively. To our delight, the $E_T$ of all these compounds are successfully designed to be higher than that of the popular blue phosphorescent emitter of bis[2-(4,6-difluorophenyl) pyridinato-C$_2$N] (picolinato) iridium (III) (FIrpic).[26] To experimentally confirm the efficient energy transfer from the boron-containing host material to FIrpic, both steady-state and time-resolved photoluminescent investigations were performed (Figure 2). Under the irradiation of 330 nm UV-light to excite the host molecules, the composite films with 5 wt% doped FIrpic show only the characteristic emission bands of the dopant without the apparent luminescent peaks of the host materials. Moreover, the emission lifetimes of the host materials doped by 1 wt% FIrpic are reduced remarkably in comparison to that of the dopant-free films, presenting direct evidence for the direct energy transfer from the host to the guest molecules. Thus, we would conclude that these star-shaped boron-containing compounds are potentially good host materials for blue PhOLEDs capable of providing effective confinement of the triplet excitons on the guest of FIrpic and preventing back energy transfer from the guest to the host molecules for high device performances.

2.3. Electrochemical and Computational Investigations

The electrochemical properties of the star-shaped boron-containing D–A molecules were investigated by cyclic voltammetry (CV) using tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte and ferrocene as the internal standard.[27] From the onset of the oxidation wave, the HOMO energy levels of TNPhB, DNPhCzB, NPhDCzB, and TCzB were measured to be $-5.34$, $-5.35$, $-5.40$, and $-5.66$ eV, respectively. With the aid of their optical band gaps, their LUMO energy levels were estimated to be $-2.02$, $-2.04$, $-2.10$, and $-2.21$ eV, respectively. These experimentally measured frontier orbital energy levels are well in line with those theoretically predicted by the density functional theory (DFT) calculations, demonstrating the highest HOMO in TNPhB and lowest LUMO in TCzB due to the stronger electron-donating property of diphenylamine than that of carbazole (Figure 3). Impressively, the asymmetric molecules of DNPhCzB and NPhDCzB can inherit both the high HOMO from TNPhB and low LUMO from TCzB, resulting in the lowest bandgap in NPhDCzB. It should be also noted that these HOMO and LUMO energy levels are close to those of the widely used hole-transporting and electron-transporting materials, suggesting their good potentials in optoelectronic device applications.

Further, from the frontier orbital isosurfaces, the acceptor of triarylborane core dominates the LUMO, while the HOMO is
determined mainly by the peripheral donors of diphenylamine or carbazole in these star-shaped D–A molecules, demonstrating the separated frontier orbital distributions for the typical bipolar character.[28] When diphenylamine and carbazole coexist on the peripheral branches asymmetrically in DNPhCzB and NPhDCzB, HOMO tends to be dominated by diphenylamine due to its stronger electron-donating ability, leading to their close HOMO energy levels to that of TNPhB (Figure 3).

The interaction modes of carbazole and diphenylamine with the triarylborane core should be different, because higher electrostatic potential (ESP) was observed on carbazole moieties, although ESP distributions still delocalize on the whole molecular architectures due to the extension of \( \pi \)-conjugation in these star-shaped D–A molecules. The less negative ESP values on diphenylamine could be due to its better electronic communication between the triarylborane core to delocalize more efficiently its electrons on the acceptor. This efficient electron communication should be also an important reason for the much lower bandgaps of the diphenylamine-containing molecules.

From the spin density distributions (Figure S11, Supporting Information), carbazole and diphenylamine tend to dominate the \( T_1 \) state. In contrast, the \( T_1 \) of NPhDCzB was codetermined by diphenylamine and triarylborane. Therefore, superior \( E_T \) of the triarylborane core, higher than that of carbazole and diphenylamine, can be inferred according to the fact that the lowest \( E_T \) moiety determines the \( T_1 \) of the whole molecule. Such high \( E_T \) of the triarylborane core could be due to its non-conjugated central C–B bond with highly twisted bulky tetramethylphenyl propeller substituents, resulting in the limited conjugation length along the boron-containing core. This observation suggests that our triarylborane core is highly attractive as high-performance acceptor unit for the design of bipolar host materials with high \( E_T \) for blue PhOLEDs.

2.4. Solution-Processed PhOLEDs Hosted by the Star-Shaped Boron-Containing D–A Molecules

In light of the high solubility, stability, and \( E_T \) as well as suitable frontier orbital energy levels of these star-shaped boron-containing D–A molecules, we used them as host materials for the FIrpic-based blue PhOLEDs fabricated through solution-processing under the simplified device configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonic acid) (PEDOT:PSS) (80 nm)/boron-containing molecule: 1,1-bis[di-4-tolylamino]phenyl] cyclohexane (TAPC) (x wt%): 15 wt% FIrpic (35 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al

Figure 3. Theoretical (black) and experimental (red) energy levels of TNPhB, DNPhCzB, NPhDCzB, and TCzB, as well as the isosurfaces of the frontier orbitals and electrostatic potential (ESP). The potential energy range is \(-0.03–0.03\) H \( q^{-1} \) for all surfaces shown, where red indicates areas with dense electron density, yellow for normal, and blue areas suggest less electron density.
In these devices, PEDOT:PSS and 8-hydroxyquinolino-lato-lithium (Liq) serve as the hole- and electron-injecting layer, respectively; FIrpic as the blue lighting phosphorescent guest, TNPhB, DNPhCzB, NPhDCzB, and TCzB as the hosts, and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) as the hole-blocking and electron-transporting material. The incorporation of TAPC in the host material can, to some extent, improve the morphology of the spin-coated film (Figure S6, Supporting Information) and increase the hole-transport properties of the emitting layers. Efficient exothermic energy transfer from the host to the guest molecules was verified by both the photoluminescent (Figure S12, Supporting Information) and electroluminescent spectra (Figure 4b; Figure S13, Supporting information) of the FIrpic-doped emitting layer. Only the characteristic emission bands of FIrpic were observed with a small peak of TAPC-induced excimer emission around 580 nm [29] in all the host–guest composite films without any emissions of host molecules at different contents of TAPC (Figure S13, Supporting information). Time-resolved emission decay curves of FIrpic exhibit monoexponential decay behavior (Figure S13, Supporting Information), indicating the well confinement of excitons on FIrpic and efficient energy transfer from the host to guest.[30] Furthermore, the short emission lifetime of FIrpic around 1.0 µs would be helpful to alleviate the triplet state involved quenching effects in the emitting layer; this is favorable for the high-performance devices.[24] Therefore, at the optimized TAPC content (Table S2, Supporting Information), the blue PhOLEDs hosted by the star-shaped boron-containing bipolar host materials reach the maximum current efficiencies (CE) of 31.8, 38.9, 38.5, and 32.8 cd A⁻¹, power efficiencies (PE) of 20.0, 30.5, 30.2, and 25.8 lm W⁻¹, and EQEs of 15.6%, 18.4%, 18.5%, and 15.8% at turn-on voltages (V_on) of 3.8, 3.5, 3.5, and 3.5 V for TNPhB, DNPhCzB, NPhDCzB, and TCzB, respectively (Figure 4c,d).

Figure 4. a) Device configuration and energy level diagram of the materials used in the spin-coated blue PhOLEDs based on host materials of TNPhB, DNPhCzB, NPhDCzB, and TCzB. b) Electroluminescent spectra at 7.0 V. c) Current density–voltage (open symbols) and luminance–voltage (solid symbols) curves, d) Efficiency–current density curves.
Supporting Information). The maximum CEs of the white-emitting PhOLEDs (WA–WD) are 14.2, 27.9, 37.0, and 28.7 cd A$^{-1}$; their maximum PEs reach 5.1, 12.5, 19.4, and 15.0 lm W$^{-1}$; and, their maximum EQEs are 5.8%, 10.7%, 14.5%, and 11.0%, respectively (Figure 5a,b). Again, better device performances were observed in the asymmetric host molecules of DNPhCzB and NPhDCzB.

### Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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### Table 2. Device performances of the solution-processed blue (BA–BD) and white (WA–WD) PhOLEDs hosted by the boron-containing D–A molecules.

| Device | Hosta) | Guest | $V_{on}$ [V] | CE [cd A$^{-1}$] | PE [lm W$^{-1}$] | EQE [%] | CIE |
|--------|--------|-------|--------------|-----------------|-----------------|--------|-----|
| BA     | TNPhB  | Flrpic| 3.8          | 31.8            | 20.0            | 15.6   | (0.21, 0.34) |
| BB     | DNPhCzB| Flrpic| 3.5          | 38.9            | 30.5            | 18.4   | (0.20, 0.35) |
| BC     | NPhDCzB| Flrpic| 3.5          | 38.5            | 30.2            | 18.5   | (0.21, 0.34) |
| BD     | TCzB   | Flrpic| 3.5          | 32.8            | 25.8            | 15.8   | (0.22, 0.34) |
| WA     | TNPhB  | Flrpic, Ir(bt)$_2$acac | 6.7 | 14.2   | 5.1   | 5.8   | (0.44, 0.43) |
| WB     | DNPhCzB| Flrpic, Ir(bt)$_2$acac | 5.1 | 27.9   | 12.5  | 10.7  | (0.41, 0.44) |
| WC     | NPhDCzB| Flrpic, Ir(bt)$_2$acac | 5.6 | 37.0   | 19.4  | 14.5  | (0.41, 0.44) |
| WD     | TCzB   | Flrpic, Ir(bt)$_2$acac | 4.6 | 28.7   | 15.0  | 11.0  | (0.41, 0.44) |

a)With 20 wt% TAPC; b) With 10 wt% TAPC; c) With 30 wt% TAPC.

3. Conclusion
In summary, we have developed a series of novel star-shaped boron-containing D–A molecules based on an electron-withdrawing triarylborane core and three peripheral electron-donating branches of carbazole and diphenylamine in symmetric or asymmetric molecular architecture to address the intrinsic dilemma of boron-containing compounds in the improvements of stability and solubility. With the combined effects of star-shaped and asymmetric molecular design strategies, considerably good solubility, high stability, amorphous morphology, bipolar transporting characteristic, and high triplet energy were realized in these star-shaped and symmetry-breaking borane derivatives. Consequently, with these facilely prepared molecules as host materials, high-performance solution-processed blue and white PhOLEDs were fabricated successfully, exhibiting maximum CEs up to 38.9 and 37.0 cd A$^{-1}$, PEs up to 30.5 and 19.4 lm W$^{-1}$, and EQEs up to 18.5% and 14.5%, respectively. Our strategy, which overcomes the intrinsic difficulties of borane derivatives in solution processing for the first time, demonstrates the great potential of the star-shaped asymmetric boron-containing D–A molecules in solution-processed organic optoelectronic devices.
The authors declare no conflict of interest.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

boron-containing materials, host materials, organic light-emitting diodes, solution processing

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