In Situ Generation of Red-Emissive AIEgens from Commercial Sources for Nondoped OLEDs

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⁎ Supporting Information

ABSTRACT: Luminescent materials with red emission are promising materials for optoelectronic devices and biological sciences. However, their synthesis is often complicated. In this work, we developed a facile approach to generating red-emissive luminogens with aggregation-induced emission (AIE) characteristics from commercially available reactants. The new compounds, abbreviated PN-BTZ-Cz and DP-BTZ-Cz, were prepared by coupling 4,7-dibromobenzothiadiazole with (1-naphthyl)phenylamine or diphenylamine followed by the reaction of the monobromo-substituted compounds with carbazole. Although all of the reactants were non-AIE-active, PN-BTZ-Cz and DP-BTZ-Cz showed AIE characteristics. This suggested that the AIE chromophores were generated in situ through the reactions. PN-BTZ-Cz and DP-BTZ-Cz were soluble in common organic solvents and showed red emission with high fluorescence quantum yields of 42.2 and 38.3% in the film, respectively. They were thermally and morphologically stable, as revealed by their high decomposition temperature (up to 327 °C) and glass-transition temperature (up to 120 °C). Nondoped organic light-emitting diodes with a configuration of ITO/HATCN/TAPC/PN-BTZ-Cz or DP-BTZ-Cz/Bphen/Liq/Al were fabricated using these compounds as emitting layers, which emitted red electroluminescence at a low turn-on voltage (down to 2.8 V) with a maximum external quantum yield of up to 2.7% and a small efficiency roll-off.

INTRODUCTION

Organic fluorescent materials with red emission have found extensive applications in optoelectronics and biological sciences. As their emission color belongs to one of the three primary ones, they are also important for full-color display and white light devices. However, compared to many efficient green and blue emissive materials, only a few luminesophores exhibit strong red emission.12 To date, many systems are developed to create red emitters, including lanthanide/transition-metal complexes, conjugated polymers, and organic small molecules.3 Long-wavelength and even near-infrared emission could be easily achieved in the organic light-emitting diodes (OLEDs) of organometallic complexes with their outstanding electroluminescence (EL) efficiencies (3−24%) of their OLEDs.3 However, their air and moisture stability and high cost are of concern. Organic polymers, on the other hand, possess good solution processability and provide a more cost-effective approach for mass production. However, their relatively low quantum yield and exciton annihilation caused by their kinks are severe problems waiting to be solved. Thus, organic small molecules offer the most promising opportunity for creating new luminescent materials, thanks to their easy color tunability by changing or modifying their chemical structures through molecular engineering.5 To synthesize red luminophores, introduction of large π-conjugation and strong intramolecular donor–acceptor interaction is often needed to decrease the band gap, both of which, however, will greatly increase the intermolecular π−π interactions. It is known that strong intermolecular π−π interaction is detrimental to fluorescence emission, which is also the main cause of the aggregation-caused quenching (ACQ) effect commonly observed in traditional luminophores with planar structures.5,7 Although many strategies such as the incorporation of steric bulky groups at the molecular level or doping with host matrix at the device level can partially address the ACQ problem, new problems such as complicated synthetic procedure and poorer

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charge transportation emerge. The devices fabricated using composites also suffer from high cost of mass production, performance degradation caused by phase separation upon heating, and complexity of technology due to addition of dopants. Thus, it is much desirable to develop nondoped light-emitting systems.4

In 2001, Tang and co-workers8 observed that some propeller-shaped luminogens showed no fluorescence or dim emission in solution but bright emission in the aggregate state. They termed this interesting phenomenon as aggregation-induced emission (AIE). Various mechanisms have been proposed to explain the AIE effect. Among them, the most commonly accepted interpretation is the restriction of intermolecular motions (RIM), including the restriction of intermolecular rotation and the restriction of intermolecular vibration.9 Take tetraphenylethylene (TPE), a typical AIE unit, as an example; its four phenyl rings serve as rotors and play a key role in relaxing the exciton energy through the nonradiative channel in dilute solution. When TPE molecules are aggregated, the rotors are restricted from undergoing any motions. This blocks the nonradiative channels to allow TPE to emit intensely in the aggregate state. Because AIEgens show strong emission in the solid state, they are promising materials for fabricating nondoped organic OLEDs.10,11 Unfortunately, most of the AIEgens prepared so far exhibit emission at short wavelength. This is because that AIEgens generally adopt a twisted molecular conformation to show low conjugation. This makes it difficult for them to show long-wavelength emission. Nevertheless, through elaborate efforts, some red AIEgens have been reported and some of them have been found to show very good device performances.

For example, in 2011, Li et al.12 synthesized a thermally stable AIE compound, namely, T2BT2, through embellishing a donor (D)−π−acceptor (A) core (Figure 1). A multilayered OLED built from it showed an EL maximum at approximately 590 nm (Table 1). In 2012, Zhao et al.13 reported a red lumiphore, abbreviated TTPBTTD, by attaching three TPE units to the 4,7-di(thiophen-2-yl)benzo-2,1,3-thiadiazole core. The nondoped OLED fabricated from it radiated a red light at 650 nm with a high efficiency of 3.7%. In 2015, Tang et al.14 developed a red emitter, called TTB, with bifunctional properties of high hole transportation and strong solid-state light emission. An EL device using TTB as a hole-transporting layer and an emitting layer exhibited good performance with external efficiency of up to 3.5%. Somanathan et al.15a designed a class of luminophores with typical strong electron-donating phenothiazine and electron-accepting α-cyanostilbene with end-capped naphthalene, namely, PTNAA, in 2017. The PTNAA-based device showed a broad emission peaked at 615 nm with an external efficiency of 7.13% and an AIE effect. The same group reported15b an emitter consisting of two terminal attachments of a push–pull moiety separated by a biphenyl free rotor, called BPPTA. Its nondoped device showed a maximum brightness of 21 673 cd m−2 at 16 V. From the structures shown in Figure 1, we can see that the D−π−A−π−D structure is a common way to construct red emitters to expand the π-conjugation of the whole molecules, and the introduction of typical AIE units such as TPE and cyanostilbene can endow the molecules with AIE property reliably. Unfortunately, these luminogens are not easy to synthesize because of a complicated structure, which is a big shortcoming for mass production. Furthermore, the design strategy of these red-emissive AIEgens is still limited, whereas a typical AIE unit is needed mostly to guarantee the AIE characteristics.

Recently, our group4 developed a simple method to produce efficient near-infrared AIEgens by Buchwald–Hartwig coupling of 4,7-dibromobenzo[c][1,2,5]thiadiazole (BT-2Br) with tetraphenylethene-substituted arylamines (Scheme 1). A nondoped OLED using one of the AIEgens was fabricated, which emitted at 684 nm with a large radiance of ∼5800 mW Sr−1 m−2 and an impressive external quantum efficiency (EQE) of 1.73%. Although the molecular design is interesting and the
The synthetic procedure is much simpler than that of many of previously developed systems, presynthesis of the AIEgen-containing reactants is required. This thus motivates us to explore a more efficient molecular design and facile synthesis method to produce efficient red-emissive AIEgens for nondoped OLED application.

In this work, we developed a facile approach to construct red AIEgens from non-AIE reactants. The coupling of BT-2Br with 1 equivalent of commercially available (1-naphthyl)-phenylamine or diphenylamine followed by end-capping of the resulting monobromo-substituted compounds with carbazole generated the desirable products, abbreviated PN-BTZ-Cz and DP-BTZ-Cz, respectively. Although PN-BTZ-Cz and DP-BTZ-Cz possess no typical AIE building blocks such as TPE and silole, they show AIE activity. Like other AIEgens, they are weakly emissive in solutions but show bright red emission at 616 and 624 nm in the film state with high photoluminescence (PL) quantum yields of 42.4 and 38.3%, respectively.

Nondoped OLEDs using them as emitting layers were fabricated, which showed low turn-on voltages of 2.8 and 3.0 V with maximum EQEs of 2.7 and 2.1%, respectively.

**RESULTS AND DISCUSSION**

The synthetic routes to PN-BTZ-Cz and DP-BTZ-Cz are shown in Scheme 1, and the detailed procedures are given in the Experimental Section. The structures of the intermediates and final products were characterized by $^1$H NMR, $^{13}$C NMR, and high-resolution mass spectroscopy techniques with satisfactory results (see Figures S1−S12 in the Supporting Information).

In these molecules, the arylphenylamino group served as an electron donor, whereas the benzo[1,2,5] thiadiazole core (BTZ) served as a strong electron acceptor. The carbazole moiety, on the other hand, served dual functions. In one way, it acted as an electron donor but with a weaker effect than that of the phenyl(naphthyl)amino (PN) and diphenylamino (DP) groups. In another way, it endowed PN-BTZ-Cz and DP-BTZ-Cz with a more twisted structure to reduce the likelihood of emission quenching in the solid state by the ACQ effect. Both
molecules showed good solubility in common organic solvents, such as dichloromethane (DCM), chloroform, tetrahydrofuran, and toluene, but were insoluble in water.

We then studied the photophysical properties of the new molecules. Figure 2 shows the UV−vis absorption spectra and PL spectra of PN-BTZ-Cz and DP-BTZ-Cz in dimethyl sulfoxide (DMSO), and Table 2 summarizes the results. The UV−vis spectrum of PN-BTZ-Cz peaked at 470 nm and originated from the intramolecular charge transfer from the PN units to the central BTZ core (Figure 2A). The UV−vis spectrum of DP-BTZ-Cz resembled that of PN-BTZ-Cz. When the dilute DMSO solutions of PN-BTZ-Cz and DP-BTZ-Cz were photoexcited, red emission at 600 and 614 nm with low absolute fluorescence quantum yields ($\Phi_F$) of 3.2 and 4.3% was observed, respectively (Figure 2B). In the solid state, PN-BTZ-Cz emitted at 616 nm with a high $\Phi_F$ of 42.4%. The increase in $\Phi_F$ from solution to the solid state suggests that the molecule is AIE-active. DP-BTZ-Cz emitted at 624 nm when aggregated accompanied by a high $\Phi_F$ of 38.3%. Compared with PN-BTZ-Cz, the less twisted structure of DP-BTZ-Cz may make it suffer stronger intermolecular interactions in the solid state to result in redder emission.

To gain deeper insight into the PL properties of the molecules, the fluorescence decays of PN-BTZ-Cz and DP-BTZ-Cz in DMSO and the solid state were studied. The data is summarized in Table 2. The mean lifetime of PN-BTZ-Cz in the solid state (14.95 ns) was longer than that in solution (12.13 ns), which was in agreement with the $\Phi_F$ measurement and the AIE characteristics of the molecule.

According to the simplified relationship among $\Phi_F$, radiative decay rate ($k_r$), and nonradiative decay rates ($k_{nr}$), i.e., $\Phi_F = k_r / (k_r + k_{nr})$, and fluorescence lifetime ($\tau$) equals $1 / (k_r + k_{nr})$ in quantum chemical calculations, $k_r$ and $k_{nr}$ were calculated to be $2.69 \times 10^7$ and $5.56 \times 10^7$ s$^{-1}$ in solution and $2.84 \times 10^7$ and $3.85 \times 10^7$ s$^{-1}$ in the solid state, respectively. Clearly, the large decrease in the nonradiative decay rate leads to the $\Phi_F$.

### Table 2. Photophysical and Thermal Properties of PN-BTZ-Cz and DP-BTZ-Cz

| Compound      | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) | $\tau$ (ns) | $\Phi_F$ (%) | $T_d$ (°C) | HOMO (eV) | LUMO (eV) |
|---------------|-----------------------|---------------------|-------------|---------------|------------|-----------|-----------|
| PN-BTZ-Cz     | 470                   | 600, 614            | 12.13, 14.95| 3.2, 42.4     | 326.5      | −5.33     | −3.08     |
| DP-BTZ-Cz     | 466                   | 614, 624            | 14.00, 16.03| 4.3, 38.3     | 282.6      | −5.31     | −3.06     |

$\lambda_{abs}$ = absorption maximum, $\lambda_{em}$ = emission maximum, $\tau$ = fluorescence lifetime; $\Phi_F$ = photoluminescence quantum yield; $T_d$ = temperature for 5% weight loss measured by thermogravimetric analysis (TGA); HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital measured and calculated by cyclic voltammetry (CV); soln = in DMSO solution.
enhancement in the solid state. Similar results were obtained for DP-BTZ-Cz, and the calculated $k_r$ and $k_{nr}$ were $2.72 \times 10^7$ and $4.42 \times 10^7$ s$^{-1}$ in solution and $2.39 \times 10^7$ and $3.85 \times 10^7$ s$^{-1}$ in the solid state, respectively.

The AIE characteristics of the molecules were further confirmed by studying their emission behaviors in DMSO/H$_2$O mixtures. Taking PN-BTZ-Cz as an example, addition of a small amount of water ($\leq 40\%$) into its dilute solution had weakened its PL intensity (Figure 3A). As PN-BTZ-Cz possesses an electron donor and acceptor in its structure, the enhancement of the polarity of the solvent medium upon water addition may strengthen the twisted intramolecular charge transfer (TICT) effect, resulting in emission annihilation. The PL intensity increased swiftly at a water fraction of 50\% (Figure 3B). Due to its poor solubility in water, aggregates of PN-BTZ-Cz should be readily formed in aqueous mixture with high water fraction. According to the RIM mechanism of the AIE phenomenon, the intramolecular motion is very active in pure DMSO but is restricted in the aggregate state because of the physical constraints. Therefore, the loss of excited-state energy through the nonradiative relaxation pathway is prevented to enable PN-BTZ-Cz to show strong PL. Surprisingly, the emission became weak again as the water fraction increased. This may be ascribed to (1) the domination of the TICT effect over the AIE effect on the light emission process and (2) the aggregate size effect.\textsuperscript{19,20} As the PL drop due to the TICT effect is obvious only at low water fraction, the first factor is less likely to be the main reason for such observation. On the other hand, dynamic light scattering analysis showed that the aggregate size in 50\% water fraction was 500 nm, which decreased to 60 nm in 95\% water fraction. Aggregates with smaller sizes showed lesser luminogenic molecules inside, resulting in their comparatively weaker emission than that of the larger ones. The emission behaviors of DP-BTZ-Cz were similar to those of PN-BTZ-Cz with a more obvious decrease in the PL intensity at a water fraction higher than 60\% (Figure 3C,D).

To demonstrate that the PL drop in the DMSO/H$_2$O mixture with low water fraction is due to the TICT effect or that the present molecules are TICT-active, their optical properties in different solvents were investigated. As shown in Figure 4A,B, the solvent exerted a little influence on the absorption of the molecules and the UV–vis spectra measured in different solvents were basically the same and peaked at a similar wavelength. However, the PL changed dramatically with solvent. PN-BTZ-Cz emitted a strong yellow light in a nonpolar solvent such as hexane. When the solvent was changed from relatively polar ones, such as DCM and THF, to those with high polarity, such as acetone and methanol, the emission wavelength gradually red-shifted. Meanwhile, the PL intensity decreased with increasing solvent polarity. The PL spectrum in methanol was basically a straight line parallel to...
the abscissa. A similar phenomenon was also observed in DP-BTZ-Cz, and its PL maximum shifted from 570 nm in hexane to 620 nm in acetone. Similarly, DP-BTZ-Cz exhibited almost no fluorescence in methanol. The high sensitivity of light emission from PN-BTZ-Cz and DP-BTZ-Cz to solvent polarity clearly demonstrated the TICT characteristics of the molecules.

To further study the photophysical properties of PN-BTZ-Cz and DP-BTZ-Cz, theoretical calculations were carried out. Their molecular conformations were optimized by the density function theory (DFT) using the Gaussian 09 suite of programs. The optimized molecular geometries shown in Figure 5 suggested that both molecules adopted twisted conformations with similar torsion angles of around 60° between the BTZ unit and the carbazole moiety. The phenyl ring and the naphthalene ring of the arylamino unit of PN-BTZ-Cz were also twisted out of the central BTZ core with torsion angles of 68° and 83°, respectively. A similar case was also observed in DP-BTZ-Cz, and the torsion angle between both phenyl rings of the unit and the central BTZ core was about 70°. The twisted conformation of the two molecules not only provides a free space for the intramolecular motions of the phenyl rings in dilute solution but also prohibits close intermolecular packing in the solid state to endow PN-BTZ-Cz and DP-BTZ-Cz with typical AIE characteristics. The highest occupied molecular orbitals (HOMOs) of both molecules were distributed on the donor fraction and the phenyl ring of BTZ. The lowest unoccupied molecular orbitals (LUMOs), on the other hand, were mainly distributed on the central BTZ moiety and the nitrogen atom of the arylamino unit. Such an orbital distribution endows the molecules with an intramolecular charge transfer character. The calculated HOMO and LUMO energy levels were −5.16 and −2.42 eV for PN-BTZ-Cz and −5.15 and −2.45 eV for DP-BTZ-Cz, respectively. Besides using DFT calculation, cyclic voltammetry (CV) measurements were also used to determine the HOMO and LUMO energy levels of the emitters. As shown in Figure 6, PN-BTZ-Cz and DP-BTZ-Cz exhibited a similar quasi-reversible oxidation process with onset potentials of 0.93 and 0.91 V. The energy levels of the HOMO and the LUMO were calculated from the onset oxidation potential (E\text{onset}) and the optical band gap (E\text{g}) using the following equations: HOMO = −(4.4 + E\text{onset}) eV and LUMO = (HOMO + E\text{g}) eV, where E\text{g} = 1240/\lambda\text{onset} and \lambda\text{onset} is the onset absorption wavelength. The energy levels of the molecules suggest that they possess good electron-transporting properties, and the narrow band gap of PN-BTZ-Cz and DN-BTZ-Cz, on the other hand, was consistent with their red emission. The thermal properties of PN-BTZ-Cz and DP-BTZ-Cz were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen at a heating rate of 10 °C min\textsuperscript{−1}. As shown in Figure 7A, PN-BTZ-
Cz and DP-BTZ-Cz lose 5% of their weight at high temperatures of 327 and 283 °C, suggestive of good thermal stability for film fabrication by vapor deposition. The DSC curves of the molecules recorded during the heating scan showed signals associated with their glass transition at 119.6 and 95.8 °C, respectively, indicating their high morphological stability.

The good optical and thermal properties of the present AIEgens encourage us to study their EL performance. OLEDs of PN-BTZ-Cz (devices a and b) and DP-BTZ-Cz (devices c and d) with a configuration of indium tin oxide (ITO)/hexaazatriphenylenehexacarbonitrile (HATCN) (5 nm)/1,1-bis[4-bis(4-methylphenyl)aminophenyl]cyclohexane (TAPC) (50 or 55 nm)/4,4′,4″-tris(carbazol-9-yl)-triphenylamine (TCTA) (5 nm)/emitting layer (EML) (20 nm)/4,7-diphenyl,1,10-phenanthroline (Bphen) (55 nm)/Liq (2 nm)/Al were fabricated. In these devices, the neat film of PN-BTZ-Cz or DP-BTZ-Cz served as an emitting layer (EML). On the other hand, HATCN worked as a hole-injection layer, TAPC worked as a hole-transport layer, TCTA was used as an electron-blocking layer, and Bphen was used as an electron-transport layer. The performances of the devices are shown in Table 3.

Table 3. EL Performances of PN-BTZ-Cz and DP-BTZ-Cz

| device | V_on (V) | EL_max (nm) | L_max (cd m⁻²) | CE_max (cd A⁻¹) | CIE (x,y) at 5 V | EQE_max (%) | roll-off (%) |
|--------|---------|-------------|----------------|----------------|----------------|-------------|-------------|
| a      | 2.8     | 631         | 2566           | 2.72           | (0.631, 0.368) | 2.68 (1.55) | 42.2        |
| b      | 2.8     | 632         | 2536           | 2.33           | (0.626, 0.372) | 2.20 (0.64) | 70.9        |
| c      | 3.0     | 642         | 1581           | 1.56           | (0.646, 0.352) | 2.10 (1.21) | 37.6        |
| d      | 3.0     | 644         | 1644           | 1.68           | (0.642, 0.357) | 2.10 (1.18) | 43.8        |

*V_on = turn-on voltage at 10 cd m⁻², EL_max = electroluminescence maximum, L_max = maximum luminance, CE_max = maximum current efficiency, EQE_max = maximum external quantum efficiency with value at 1000 cd m⁻² shown in the parentheses.*

Figure 7. (A) TGA and (B) DSC thermographs of PN-BTZ-Cz and DP-BTZ-Cz recorded under nitrogen at a heating rate of 10 °C min⁻¹.

Figure 8. (A) Current density–voltage–luminance and (B) external quantum efficiency–luminance curves of nondoped OLED devices based on PN-BTZ-Cz (devices a and b) and DP-BTZ-Cz (devices c and d). Configuration: ITO/HATCN (5 nm)/TAPC/TCTA*/PN-BTZ-Cz or DP-BTZ-Cz (20 nm)/Bphen (55 nm)/Liq (2 nm)/Al. *50 nm (devices a and c) and 55 nm (devices b and d). Inset in (B): photos of devices a and c.

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CONCLUSIONS

In summary, two simple unsymmetrical AIEgens (PN-BTZ-Cz and DP-BTZ-Cz) were prepared from commercially available, non-AIE reactants through a facile synthetic route. These molecules showed red emission with high solid quantum yields of 42.4 and 38.3%. They were thermally and morphologically stable, and nondoped OLEDs using the neat films of these AIEgens as emitting layers exhibited red electroluminescence with maximum EQEs of 2.7 and 2.1%. Compared with the doped systems, the nondoped ones show a lower turn-on voltage, a smaller roll-off, and a lesser complexity in the fabrication process.23 This work hopefully will give more hints for molecular structure design for red or even near-infrared OLEDs and provide a promising strategy to fabricate OLEDs with better efficiency and stability.

EXPERIMENTAL SECTION

Materials and Characterization. Diketopyrrolopyrrole, 9,9-diisopropoxybiphenyl (Ru Phos), and solvents were all purchased from J&K, Sigma, Meryer, and AIEgen Biotech and used as received without further purification. The materials were distilled using sodium as a drying agent and benzophenone as an indicator under nitrogen prior to use. Diisopropoxybiphenyl (Ru Phos) was purchased from J&K, Sigma, Meryer, and AIEgen Biotech and used as received without further purification. The materials were distilled using sodium as a drying agent and benzophenone as an indicator under nitrogen prior to use. Diisopropoxybiphenyl (Ru Phos) was purchased from J&K, Sigma, Meryer, and AIEgen Biotech and used as received without further purification.

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Synthesis of 1. N-Phenyl-1-naphthylamine (420 mg, 1.92 mmol), 4,7-dibromo-2,1,3-benzothiadiazole, cesium carbonate (Cs2CO3), tris(dibenzylideneacetone)-dipalladium(0) (Pd2(dba)3), 2-dicyclohexylphosphino-2′-diphenylphosphino-1,1′-binaphthyl (RPuPhos), and solvents were all purchased from J&K, Sigma, Meryer, and AIEgen Biotech and used as received without further purification. The materials were distilled using sodium as a drying agent and benzophenone as an indicator under nitrogen prior to use. Diisopropoxybiphenyl (Ru Phos) was purchased from J&K, Sigma, Meryer, and AIEgen Biotech and used as received without further purification.

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Synthesis of 1. N-Phenyl-1-naphthylamine (420 mg, 1.92 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (1.69 g, 5.75 mmol), Pd2(dba)3 (87 mg, 0.096 mmol), RuPhos (90 mg, 0.192 mmol), and Cs2CO3 (1.56 g, 4.80 mmol) were added into a 100 mL two-necked round-bottom flask with 30 mL of distilled toluene. The mixture was then heated under reflux and under nitrogen for 24 h. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane (DCM). The organic phase was washed with saturated NaCl solution and dried with anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using the DCM/hexane mixture (1:6, v/v) as eluent. Orange-red solid of 1 was obtained in 50.6% yield (420 mg).1H NMR (400 MHz, CDCl3, 25 °C, δ (ppm): 7.95–7.87 (t, 2H, J = 8 Hz), 7.83–7.77 (d, 1H, J = 8 Hz), 7.61–7.55 (d, 1H, J = 8 Hz), 7.50–7.40 (q, 2H, J = 8 Hz), 7.36–7.27 (q, 2H, J = 8 Hz), 7.25–7.18 (t, 2H, J = 8 Hz), 7.08–7.00 (t, 1H, J = 8 Hz), 6.96–6.90 (d, 2H, J = 8 Hz), 6.84–6.78 (d, 1H, J = 8 Hz).13C NMR (100 MHz, CDCl3, 25 °C, δ (ppm): 154.0, 149.3, 147.6, 142.8, 139.6, 134.5, 131.8, 128.5, 125.4, 123.1, 122.3, 121.9, 120.6, 106.0. MS (MALDI-TOF): m/z 432.9875 (M+, calc 432.3390).

Synthesis of PN-BTZ-Cz. PN-BTZ-Cz was synthesized from 1 (420 mg, 0.97 mmol), carbazole (488 mg, 2.91 mmol), Pd2(dba)3 (44.5 mg, 0.049 mmol), RuPhos (45.4 mg, 0.098 mmol), and Cs2CO3 (792 mg, 2.43 mmol) in 20 mL toluene using procedures similar to those for 1. The crude product was purified by silica-gel column chromatography using the DCM/hexane mixture (1/3, v/v) as eluent. Orange-red solid of 1 was obtained in 50.6% yield (420 mg).1H NMR (400 MHz, CDCl3, 25 °C, δ (ppm): 8.20–8.14 (d, 2H, J = 8 Hz), 8.10–8.04 (d, 1H, J = 8 Hz), 7.98–7.92 (d, 1H, J = 8 Hz), 7.89–7.82 (d, 1H, J = 12 Hz), 7.62–7.58 (d, 1H, J = 8 Hz), 7.55–7.48 (t, 2H, J = 8 Hz), 7.45–7.35 (m, 4H), 7.30–7.26 (m, 4H), 7.19–7.15 (d, 2H, J = 8 Hz), 7.13–7.04 (m, 4H).13C NMR (100 MHz, CDCl3, 25 °C, δ (ppm): 152.4, 150.4, 147.6, 142.9, 140.7, 139.8, 134.6, 130.2, 127.9, 126.9, 125.8, 125.2, 123.0, 122.4, 122.0, 119.8, 119.6, 119.2, 109.5. MS (MALDI-TOF): m/z 518.1612 (M+, calc 518.6380).

Synthesis of 2. Compound 2 was synthesized from diphenylamine (1.0 g, 6.0 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (5.2 g, 17.8 mmol), Pd2(dba)3 (270.7 mg, 0.3 mmol), RuPhos (276.0 mg, 0.6 mmol), and Cs2CO3 (4.8 g, 15.0 mmol) in 50 mL distilled toluene using procedures similar to those for 1. The crude product was purified by silica-gel column chromatography using the DCM/hexane mixture (1/6, v/v) as eluent. Orange solid, yield 70.3% (1.6 g).1H NMR (400 MHz, CDCl3, 25 °C, δ (ppm): 7.73 (s, 2H), 7.70–7.66
(d, 1H, J = 8 Hz), 7.30–7.24 (m, 4H), 7.13–7.00 (m, 7H). 13C NMR (100 MHz, CDCl3, 25 °C), δ (ppm): 146.8, 139.3, 131.9, 128.7, 123.7, 123.2, 122.5. MS (MALDI-TOF): m/z 383.0051 (M+, calcd 382.2790).

**Synthesis of DP-BTZ-Cz.** DP-BTZ-Cz was synthesized from 2 (200 mg, 0.52 mmol), carbazole (132 mg, 0.78 mmol), Pd(dba)2 (24 mg, 0.026 mmol), RuPhos (24 mg, 0.052 mmol), and Cs2CO3 (340 mg, 1.3 mmol) in 30 mL distilled toluene using procedures as described above. The crude product was purified by silica-gel column chromatography using the DCM/hexane mixture (1/5, v/v) as eluent. Orange-red solid; yield 40.8% (100 mg). 1H NMR (400 MHz, CDCl3, δ (ppm): 8.25–8.12 (d, 1H, J = 8 Hz), 7.71–7.67 (d, 1H, J = 8 Hz), 7.47–7.28 (m, 10H), 7.21–7.12 (m, 6H). 13C NMR (100 MHz, CDCl3, δ (ppm): 147.0, 140.6, 140.4, 128.8, 128.3, 125.5, 125.2, 126.1, 123.5, 123.4, 123.1, 121.1, 120.2, 120.0, 119.8, 119.6. MS (MALDI-TOF): m/z 468.1457 (M+, calcd 468.1409).

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02372.

1H NMR, 13C NMR spectra, and high-resolution mass spectra of compound 1, compound 2, FN-BTZ-Cz, and DP-BTZ-Cz (PDF)

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Notes
The authors declare no competing financial interest.

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