Synthesis and Characterization of AIE-Active B–N-Coordinated Phenalene Complexes

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Abstract
Organoboron compounds provide a new line to tune the electronic structures of π-conjugated molecules, which is critical to the development of new organic semiconductor materials. In this work, we demonstrate the synthesis of two novel boron–nitrogen (B–N) coordinated phenalene complexes (BNP-PX and BNP-PA) by employing BN phenalene (BNP) as the acceptor unit and phenoxazine/phenylphenazine groups as the donors. Based on single-crystal X-ray analysis, both BNP-PX and BNP-PA possess highly twisted conformations with the dihedral angles of 76.6° and 70.5°, respectively. The photophysical properties of BNP-PX and BNP-PA are elucidated through UV-vis absorption, fluorescence spectroscopy, and theoretical calculations. In addition, BNP-PX exhibits a large Stokes shift (8,033 cm⁻¹) and excellent aggregated-induced emission behavior. The red organic light-emitting diode device was fabricated based on compound BNP-PX, manifesting its promising application in organic optoelectronic devices.

Key words donor–acceptor, BN-coordinated compounds, large Stokes shift, AIE effect, OLED device

Introduction

π-Conjugated molecules consisting of electron donor (D) and acceptor (A) units have attracted considerable attention due to their enhanced polarizability, narrow energy gap, and high carrier mobility, which render them actively used in organic semiconductor devices. In particular, the D–A type molecules have made significant progress in the exploitation of organic light-emitting diodes (OLEDs). Nevertheless, most of the π-conjugated luminophores exhibit weak emission behavior in their aggregated states due to the notorious aggregation-caused emission quenching, which limits the development of efficient OLED devices. Toward this end, aggregation-induced emission (AIE) has emerged as an effective strategy to achieve high emission in concentrated solution or even in the solid state. For instance, the carbon-rich tetraphenylethene and its derivatives have been widely explored to develop high-performance OLEDs. Despite the progress made in recent years, the bottom-up synthesis of AIE-active boron–nitrogen (B–N) containing luminogens remains a challenge.

B–N-doped polycyclic aromatic hydrocarbons (PAHs) exhibit broad absorption and intense fluorescence which can be used as efficient emitters. In addition, the BN-coordinated unit (B–N) and the C–C unit are also recognized as isoelectronic and isosteric (Figure 1a). Unlike the nonpolar covalent C–C bond, the B–N bond possesses a large dipole moment and a low bond dissociation energy (Figure 1a). Accordingly, a B–N unit can serve as a typical kind of Lewis acid/base pair, which has been utilized to synthesize π-conjugated systems with narrow band gaps, high electron affinity, and photochromic properties. For instance, with respect to the unstable phenalene (Figure 1b), upon replacing the C–C unit by a B–N unit, the resultant BN-doped phenalene (BNP) exhibits high ambient stability and intense fluorescence.

Herein, we demonstrate the synthesis of two novel D–A phenalene derivatives (BNP-PX and BNP-PA; Figure 1c) by...
employing BNP as the building block. The phenoxazine and phenylphenazine groups in BNP-PX and BNP-PA not only serve as electron donors but also lead to the highly twisted geometrical conformations, which render the spatial separation of their HOMO and LUMO. Compared to the parent BNP, the frontier orbital energy gaps of BNP-PX and BNP-PA can be increased by the introduction of the phenoxazine and phenylphenazine substituents. In addition, BNP-PX demonstrates the largest Stokes shift (8,033 cm⁻¹) among all the reported B—N coordinated complexes,¹² and exhibits excellent AIE behavior with a quantum yield (Φ) of 0.54 in the solid state. We further fabricated a red OLED device based on BNP-PX, revealing its promises in organic optoelectronic devices.

Results and Discussion

The synthetic routes toward BNP-PX and BNP-PA are depicted in Scheme 1. First, the Buchwald–Hartwig coupling of 8-(benzyloxy)-5-bromoquinoline (3) with phenoxazine (1) was performed to afford 10-(8-(benzyloxy)quinolin-5-yl)-10H-phenoxazine (4) in 65% yield. The treatment of 4 with 2 equivalents of 1,4-cyclohexadiene provided 5-(10H-phenoxazin-10-yl)quinolin-8-ol (6) and the crude product was used without purification in the next step. Subsequently, compound 6 was reacted with trifluoromethanesulfonic anhydride (Tf₂O) to afford 5-(10H-phenoxazin-10-yl)quinolin-8-yl trifluoromethanesulfonate (8) in 97% yield over two steps (Scheme 1).¹³ Next, Pd-induced cyclization of 8 in toluene at 60 °C in the presence of alkynyl(triaryl)borates provided the target compound 10-(1,1,2-triphenyl-1H-1λ⁴,10λ⁴-[1,2]azaborinino-[5,6,1-j]quinino-lin-6-yl)-10H-phenoxazine (BNP-PX) in 91% yield. Following a similar synthetic strategy, (E)-5-(8-(2-(diphenylboraneyl)-2-phenylvinyl)quinolin-5-yl)-10-phenyl-5,10-dihydrophenazine (BNP-PA), in which the substituent phenoxazine in BNP-PX was replaced by a phenylphenazine unit, was successfully synthesized starting from compound 3 over four steps (Scheme 1).¹⁴ The targeted compound BNP-PX was purified by silica column chromatography and then recrystallized in chloroform/methanol (CHCl₃/MeOH), while BNP-PA was obtained by precipitation in MeOH followed by recrystallization in CHCl₃/MeOH. Compounds BNP-PX and BNP-PA were fully characterized by high-resolution mass spectrometry (HRMS; Figures S39, S40) and ¹H, ¹³C, ¹¹B as well as 2D NMR measurements (Figures S28-S38).

Single crystals of compounds BNP-PX and BNP-PA were obtained by slow diffusion of a chloroform/methanol mixed solution. BNP-PX crystallizes in the monoclinic space group P2₁/c and shows an edge-on twisted geometry (Figure 2a, b). Due to the different rotation angles between the BNP and phenoxazine group (R1), two different conformational isomers (BNP-PXa and BNP-PXb in Figure 2a, b) are found in the solid state of BNP-PX. The bond length of B1–N1 (1.642 Å in BNP-PXa and 1.643 Å in BNP-PXb; Figure 2a, b)
is a typical B–N coordination bond (1.6–1.7 Å),\(^{5a,15}\) which is similar to that of reported BNP (Figure S1).\(^{11}\) Besides, the dihedral angles of C11–N1–B1–C10 in BNP-PXa and BNP-PXb are 7.3° and 1.7° (Figure 2a, b), respectively, indicating the nearly planar geometry of the BNP core. Interestingly, the dihedral angles between the BNP and phenoxazine group (C4–C5–N2–C30) in BNP-PXa and BNP-PXb are 76.6° and 68.0° (Figure 2a, b), respectively. As shown in Figure 2d, BNP-PX displays a slipped stack mode with a π–π stacking distance of 3.17 Å (BNP-PXa) and 3.45 Å (BNP-PXb), respectively, which are shorter than the sum of the van der Waals radii (3.60 Å).\(^{16}\) Similar to BNP-PX, BNP-PA also stacks in the monoclinic space group P21/c and adopts a twisted geometry (Figure 2c). Although the size of the phenylphenazine group (R2) is comparable to that of the phenoxazine group (R1), only one conformation (Figure 2c) was found in the single-crystal structure of BNP-PA. This is possibly due to the existence of an additional phenyl unit in R2, which increases the rotational energy between the R2 and BNP. The bond length of B1–N1 (1.638 Å) in BNP-PA is slightly shorter than those of BNP and BNP-PX. Moreover, the dihedral angle of C7–C6–N2–C41 in BNP-PA is 70.5° (Figure 2c), and there is no obvious π–π interaction in the stacking mode of BNP-PA (Figure 2e).

The UV-vis absorption and fluorescence spectra of BNP-PX and BNP-PA in anhydrous toluene solution are presented in Figure 3a. BNP-PX displays a maximum absorption peak at 424 nm, with a bathochromic shift of 7 nm compared with BNP (Figure S52 and Table S3). Based on the time-dependent density functional theory (TD-DFT) calculations, this absorption peak of BNP-PX can be attributed to the HOMO–1–LUMO transition (Figure S60) and belongs to the local excitation (LE) from the core of BNP according to the corresponding orbital plots (Figure S57). In addition, a weak shoulder absorption at a longer wavelength of BNP-PX (450 nm; Figure 3b) was also observed, which is owing to the intramolecular charge transfer (ICT) from the donor phenoxazine group to the acceptor BNP on the basis of measured negative solvatochromic effect\(^{(5a,17)}\) (Figure S41 and Table S2) and TD-DFT calculations (the HOMO–LUMO transition; Figures S60 and S57). The blue shift of the absorption peak with the increased polarity of the solvent (Figure S41) suggests that the ground state of BNP-PX is more polar than its excited state, which is consistent with the molecular donor–acceptor (D–A) structure.\(^{(5a,17)}\) For compound BNP-PA, a similar absorption peak at \(\lambda_{\text{max}} = 424\) nm was observed. According to the TD-DFT calculations, this peak can be assigned to the HOMO–1–LUMO transition (Figure 3a) and also belongs to the LE from the BNP. In addition, there is a broad absorption from 500 to 700 nm for BNP-PA (maximum peak at 581 nm; Figure 3b), because of the ICT effect from the donor phenylphenazine group to the acceptor BNP based on the negative solvatochromic effect\(^{(17)}\) investigation (Figure S42) and TD-DFT calculations (the
HOMO—LUMO transition; Figures S61 and S58). BNP-PA displays a stronger HOMO—LUMO absorption than BNP-PX (Figure 3a, b), this is due to the strong electron-donating character of the sp³-hybridized phenylphenazine group than that of the phenoxazine unit. Moreover, the weak HOMO—LUMO absorptions of BNP-PA and BNP-PX are also observed in different solvents (Figures S41 and S42), which are well supported by the TD-DFT calculations. The fluorescence spectra of BNP-PX show a maximum emission peak at 643 nm (excited at 424 nm) with a Stokes shift of 8,033 cm⁻¹ in toluene (Figure 3c), exhibiting the largest Stokes shift among all the reported B-N-coordinated complexes.¹² However, two maximum peaks (around 460 and 525 nm) with an additional shoulder (around 675 nm) in the emission spectra of BNP-PX in dichloromethane (DCM), THF, and DMF were observed (Figure S43), this is likely attributable to the existence of the twisted ICT.¹⁸ For compound BNP-PA, the maximum emission peak at 518 nm can be observed in toluene (excited at 424 nm). Moreover, BNP-PA demonstrated a positive solvatochromism of the emission spectra (Figure S44), which may due to the fact that the interaction of BNP-PA with different polar solvents is mostly stabilized by the local excited states (as predicted by the TD-DFT calculations).¹⁹ In addition, no emission spectra of BNP-PA was observed after excitation at ca. 600 nm in different solvents (Figure S45), indicating that the emission spectra of BNP-PA (Figure 3c) mainly came from the second excited state (the HOMO-1—LUMO excitation, which was predicted by TD-DFT calculations). The solution quantum yield (QY) of BNP is estimated to be
increasing the fractions of water. These results strongly suggest a typical solvent-dependent AIE character for BNP-PX. In contrast, there was no AIE response for BNP and BNP-PA under the same conditions (Figures 3f, S50, and S51). According to the concentration-dependent absorption and fluorescence spectra (Figure S47), there is no obvious excimer formation of BNP-PX under high concentrations. According to the temperature-dependent absorption and fluorescence spectra (Figure S48), the intensity of the HOMO–LUMO absorption and the maximum emission peak of BNP-PX increased with temperature. Thus, we consider that the unique AIE response for BNP-PX might be caused by a restriction of intramolecular motion mechanism, where the free rotational motion of the phenoxazine group in BNP-PX is limited in the aggregated state, resulting in the cut off of nonradiative transition and intense luminescence. In addition, BNP-PX showed similar solvent-dependent AIE behavior in the THF–hexane solvent (Figure S49).

The electrochemical behaviors of BNP-PX and BNP-PA in anhydrous DCM were investigated by means of cyclic voltammetry (CV) as depicted in Figure 3d. BNP-PX displayed a reversible reduction process at the half-wave potential of −1.88 V vs. Fc+/Fc (Figure 3d). In addition, one reversible, one quasi-reversible, and one irreversible oxidation processes were observed with a half-wave potential at 0.38, 0.87, and 1.28 V vs. Fc+/Fc (Figure 3d), respectively. For BNP-PA, one quasi-reversible reduction process was identified with a half-wave potential at −2.06 V vs. Fc+/Fc (Figure 3d). Moreover, BNP-PA exhibited one reversible and one irreversible oxidation processes with a half-wave potential at −0.28 and 0.52 V vs. Fc+/Fc (Figure 3d), respectively. However, under high potential (>0.8 V vs. Fc+/Fc), the CV curves of BNP-PA became complex owing to its low electrochemical stability (Figure S54). Accordingly, the LUMO energy levels are

![Figure 3](image-url)  ![Figure 4](image-url)

**Figure 3** (a) UV-vis absorption spectra of BNP-PX and BNP-PA in toluene (concentration: 1 × 10⁻⁵ M). (b) The locally enlarged UV-vis spectra. (c) Fluorescence spectra of BNP-PX and BNP-PA in toluene (concentration: 1 × 10⁻⁵ M). (d) Cyclic voltammograms of BNP-PX and BNP-PA measured in CH₂Cl₂ (0.1 M n-Bu₄NPF₆) at the scan rate of 0.1 V/s. (e) Fluorescence spectra of BNP-PX in THF–water mixtures (8.0 × 10⁻⁴ M, excited at 424 nm) with varied volumetric fractions (fₓw) of water. (f) The fluorescence intensity ratios (I/I₀) of BNP, BNP-PX, and BNP-PA in different fractions of water (fₓw is the fluorescence intensity of BNP, BNP-PX, and BNP-PA in THF), (g) The digital photo of BNP-PX in THF–water mixtures under UV light (8.0 × 10⁻⁴ M, excited at 365 nm).

**Figure 4** Calculated molecular orbitals and energy diagrams of (a) BNP-PX and (b) BNP-PA.
estimated to be −2.92 and −2.74 eV for BNP-PX and BNP-PA, respectively (Table S3). On the basis of their optical energy gaps obtained from their absorption edges, the HOMOs of BNP-PX and BNP-PA are derived to be −5.42 and −5.22 eV, respectively (Table S3). The HOMO and LUMO energy levels of BNP-PX and BNP-PA are obviously higher than that of BNP (HOMO: −6.06 eV; LUMO: −3.50 eV), manifesting the important role of the integrated donor moieties (phenoxazine and phenylphenazine groups). In addition, the experimental results are well supported by the DFT calculations (Figure 4 and Table S3). The HOMOs in BNP-PX and BNP-PA are mainly localized on the phenoxazine and phenylphenazine groups due to their electron-donating properties. In contrast, the LUMOs of BNP-PX and BNP-PA are fully localized over the BNP motif. In comparison with BNP (Figure S56), the frontier molecular orbitals of BNP-PX and BNP-PA are spatially separated, indicating their typical D–A configurations.5a,17

The thermal stability of BNP-PX was analyzed by the thermogravimetric analysis (TGA) method under a N2 atmosphere, as shown in Figure S55. At the beginning of the heating process (25–150 °C), the adsorbed water or residual organic solvent is released, resulting in a weight loss of −2.0%. At the temperature range of 150–280 °C, there is a weight loss of −3.0% occurred on the TGA curve, suggesting the decomposition of BNP-PX. Accordingly, BNP-PX exhibits a decomposition temperature Td (TD5%, corresponding to 5% weight loss) more than 280 °C, indicating its relatively good thermal stability. To evaluate the electroluminescence (EL) behavior of BNP-PX as the emitter in the host-guest and nondoped systems, vacuum-sublimated OLEDs with a configuration of indium tin oxide (ITO)/MoO3 (10 nm)/1,1’-bis[4-(di-p-tolylamino)phenyl]-cyclohexane (TAPC) (30 nm)/4,4’4”-tri(N-carbazolyl)-triphenylamine (TCTA) (5 nm)/emissive layer/1,3,5-tri(m-pyridin-3-ylphenyl)benzene (TmPyPB) (65 nm)/LiF (1 nm)/Al (100 nm) were fabricated, in which MoO3, TAPC, and TmPyPB worked as the hole-injection, hole-transporting, and electron-transporting layers, respectively (Figure 5a). In addition, TCTA and LiF were used as the exciton-blocking layer and the electron-injection layer, respectively.

![Image](attachment:image.png)

**Figure 5** (a) Schematic diagrams of the basic structures of the OLED device based on BNP-PX. (b) Current density–voltage–luminance (J−V−L) characteristics. (c) Current efficiency (CE)−luminance characteristics. (d) External quantum efficiency (EQE)−luminance characteristics.
As shown in Figure 5 (b, c), the turn-on voltage of the devices is around 6.0 V, and the maximum brightness is 317 cd/m². Varying the driving voltages of 6.0, 8.0, and 10.0 V, the devices show very small spectra shifts (Figure S62). The EL spectra and color coordinates of these devices show a small variation from low-to-high driving voltages, implying the efficient energy transfer from the host to the guest. Among the devices fabricated, the optimized device exhibits a maximum external quantum efficiency (EQE) of 0.6% and a maximum current efficiency of 1.0 cd/A (Figure 5d).

Conclusions

In conclusion, we report the synthesis of two novel BN-coordinated phenalene derivatives containing D-A structures (BNP-PX and BNP-PA). Single-crystal analysis together with the DFT calculations reveals that both BNP-PX and BNP-PA possess highly twisted geometries, which render the spatial separation of the HOMO and LUMO distributions. By introduction of the phenazine and phenylphenazine substituents, the frontier orbital energy levels of BNP-PX (HOMO: −5.42 eV; LUMO: −2.92 eV) and BNP-PA (HOMO: −5.22 eV; LUMO: −2.74 eV) are increased compared with the parent BNP (HOMO: −6.06 eV; LUMO: −3.50 eV). In addition, BNP-PX demonstrates excellent AIE effect and macroscopic observation of the AIE effect. The spectra and color coordinates of these devices show a small variation from low-to-high driving voltages, implying the efficient energy transfer from the host to the guest. Among the devices fabricated, the optimized device exhibits a maximum external quantum efficiency (EQE) of 0.6% and a maximum current efficiency of 1.0 cd/A (Figure 5d).

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Supporting Information

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References and Notes


(13) Synthetic procedure for compound BNP-PX: In a 50 mL one-necked flask, compound 8 (153.5 mg, 0.32 mmol), alkynylborate (120.9 mg, 0.35 mmol), DPEPhos (16.3 mg, 0.03 mmol) and Pd(n-allyl)Cl (17.2 mg, 0.047 mmol) were charged under argon atmosphere. After three times vacuum-argon operation, degassed toluene (10 mL) was added into the flask under argon. Then the mixture was stirred at 60 °C for 12 h. Afterwards, the reaction mixture was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel (CH2Cl2/iso-hexane = 1/1) to give product as red powder (167.8 mg, 91%).

(14) Synthetic procedure for compound BNP-PA: In a 50 mL one-necked flask, compound 9 (59.9 mg, 0.11 mmol), alkynylborate (49.8 mg, 0.14 mmol), DPEPhos (13.0 mg, 0.024 mmol) and Pd(n-allyl)Cl (14.4 mg, 0.039 mmol) were charged under argon atmosphere. After three times vacuum-argon operation, degassed toluene (5 mL) was added into the flask under argon. Then the mixture was stirred at 60 °C for 12 h. After cooling down to room temperature, anhydrous methanol (15 mL) was added directly for further characterization. 1H NMR (300 MHz, CD2Cl2) δ 8.96 (dd, J = 8.4, 1.6 Hz, 1H), 8.92–8.84 (m, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.6 Hz, 3H), 7.60–7.51 (m, 2H), 7.46 (d, J = 7.7 Hz, 3H), 7.38 (d, J = 1.7 Hz, 2H), 7.35 (s, 2H), 7.25–7.17 (m, 4H), 7.15 (d, J = 5.9 Hz, 3H), 7.12 (d, J = 2.7 Hz, 5H), 6.30 (t, J = 7.5 Hz, 2H), 6.21 (t, J = 7.5 Hz, 2H), 5.71–5.64 (m, 2H), 5.57–5.49 (m, 2H). 11B NMR (96 MHz, CD2Cl2) δ −5.37. 13C NMR (76 MHz, CD2Cl2) δ 150.8, 146.2, 140.9, 140.3, 137.8, 137.0, 136.4, 134.5, 134.5, 134.0, 133.5, 131.8, 131.6, 131.5, 129.3, 128.8, 128.6, 128.3, 127.7, 127.6, 126.6, 125.8, 125.3, 122.5, 121.9, 121.3, 113.2, 112.9. HRMS (APCI, m/z): calcd for C17H13BN3O− [M−H]− 651.2846, found 651.2845.


