

Aggregation-Induced Emission and Efficient Solid-State Fluorescence from Tetraphenylethene-Based N,C-Chelate Four-Coordinate Organoborons

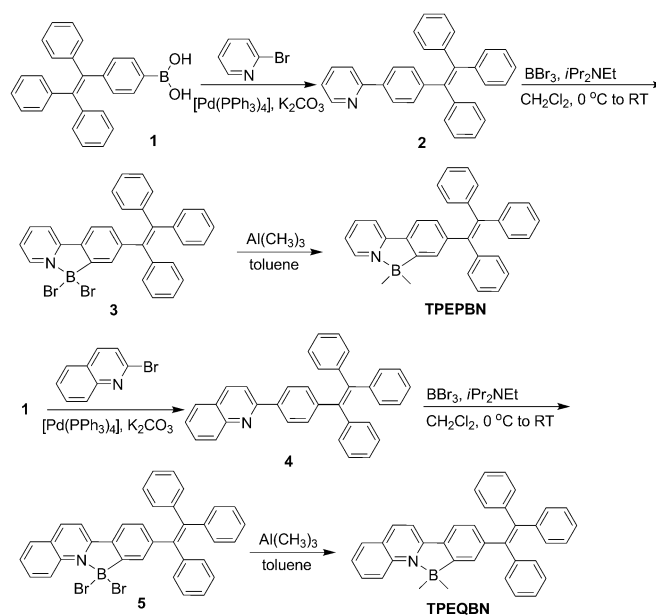
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Organoborons have attracted considerable research attention due to their unique electronic structure and interesting optical property derived from the intrinsic $p_{\pi}-\pi^*$ conjugation between the vacant p_{π} orbital of the boron atom and the π^* orbital of the π -conjugated framework.^[1] The strong Lewis acidity of boron atom also enables it to bond Lewis basic substrates or nucleophilic species and allows the formation of diverse organoborons which can be used to address specific issues.^[2] So far, various tailored boron compounds including three- and four-coordinate organoborons have been studied.^[3] Among them, those with efficient solid-state fluorescence are of particular interest for their practical applications in optoelectronic devices, such as organic light-emitting diodes.^[4] However, many famous organoborons, such as borondipyrrromethene (BODIPY) dyes, are only emissive in dilute solutions and their fluorescence is quenched severely in the aggregate state.^[5] Thereby, really robust ones are still rare.

Many efforts have been devoted to exploring new solid-state emissive organoborons from BF_2 complexes, some of which have shown enhanced emission in solid films than in solutions.^[6] Their solid-state emission efficiencies, however, are not so high, leaving much room for improvement. Tetraphenylethene (TPE) is an interesting propeller-like luminogen with peculiar emission behavior. It fluoresces faintly in

solutions but can emit strongly upon aggregate formation, presenting a novel characteristic of aggregation-induced emission (AIE).^[7,8] Recent studies have revealed that molecular melding of TPE with conventional planar chromophores that suffer from aggregation-caused quenching is a feasible approach to efficient solid-state emitters with excellent emission efficiencies.^[9] Inspired by the AIE motif of TPE, in this work, we designed two novel boron compounds containing the TPE moiety and N,C-chelate. Their synthesis and photophysical properties are presented.

The synthetic routes to TPE-based N,C-chelate four-coordinate organoborons are illustrated in Scheme 1. Detailed



Scheme 1. Synthetic routes to the N,C-chelate four-coordinate organoborons based on TPE.

procedures and characterization data are given in the Experimental Section. Briefly, Suzuki couplings of 4-(1,2,2-triphenylvinyl)phenylboronic acid (**1**) with 2-bromopyridine and 2-bromoquinoline yielded compounds **2** and **4**,^[9c] respectively; this was followed by an electrophilic aromatic borylation reaction^[10] with tribromoborane (BBr_3) under basic conditions with *N,N*-diisopropyl-*N*-ethylamine (iPr_2NEt) to afford pyridine- and quinoline-dibromoborane complexes (**3** and **5**)

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that are also stable in air and moisture. Without purification, subsequent treatments of **3** and **5** with trimethylaluminum (Me_3Al) generated the target N,C-chelate four-coordinate organoborons **TPEPBN** and **TPEQBN**, respectively, in moderate yields. Both products are stable to air and water. This is very important because hydrolysis often occurs in most four-coordinate organoborons with alkyl substituents attached at the boron atoms. Therefore, such organoborons are very rare.^[3,11] They dissolve readily in common organic solvents, such as THF, chloroform and dichloromethane, but are insoluble in methanol and water. Single crystals of **TPEPBN** and **TPEQBN** were grown from THF/ethanol mixtures and analyzed by X-ray diffraction crystallography. The crystal structures show that the whole molecules are highly twisted, whereas the pyridine and quinoline rings become coplanar with their neighboring phenyl rings due to the N,C-chelate with boron atoms (Figure 1). Thermal stability is an important issue for materials, and greatly impacts the stability and lifetime of most organic optical and electronic devices. **TPEPBN** and **TPEQBN** show high decomposition temperatures at 303 and 340 °C, respectively, recorded by thermogravimetric analysis (TGA, Figure S1 in the Supporting Information); this indicates they are thermally stable.

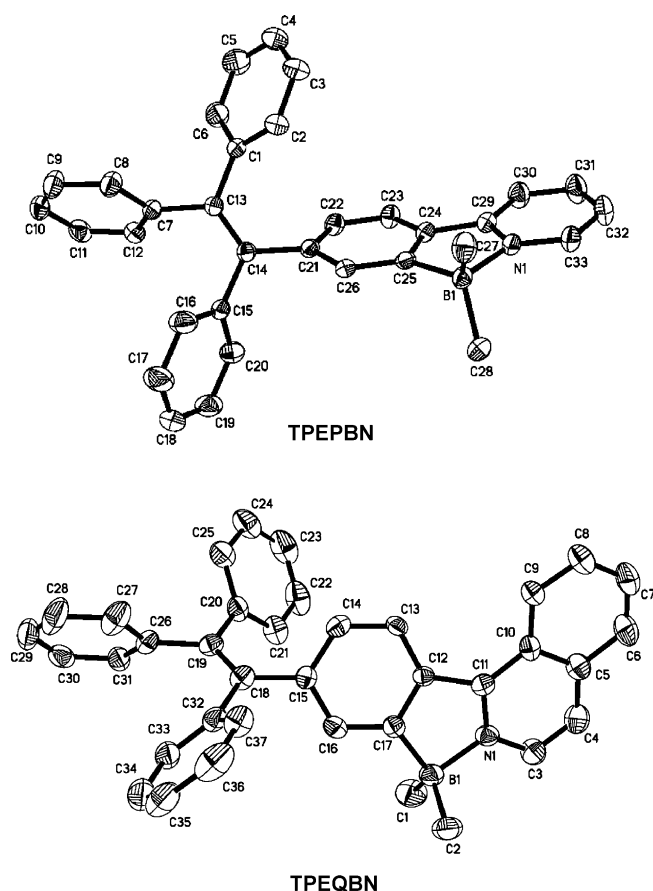


Figure 1. ORTEP drawings of **TPEPBN** and **TPEQBN** at the 50 % probability level. Hydrogen atoms are omitted for clarity.

The absorption spectra of **TPEPBN** and **TPEQBN** in THF solutions are shown in Figure 2A. **TPEQBN** absorbs lights at longer wavelength than **TPEPBN** due to the extended conjugation of quinoline relative to pyridine. The ab-

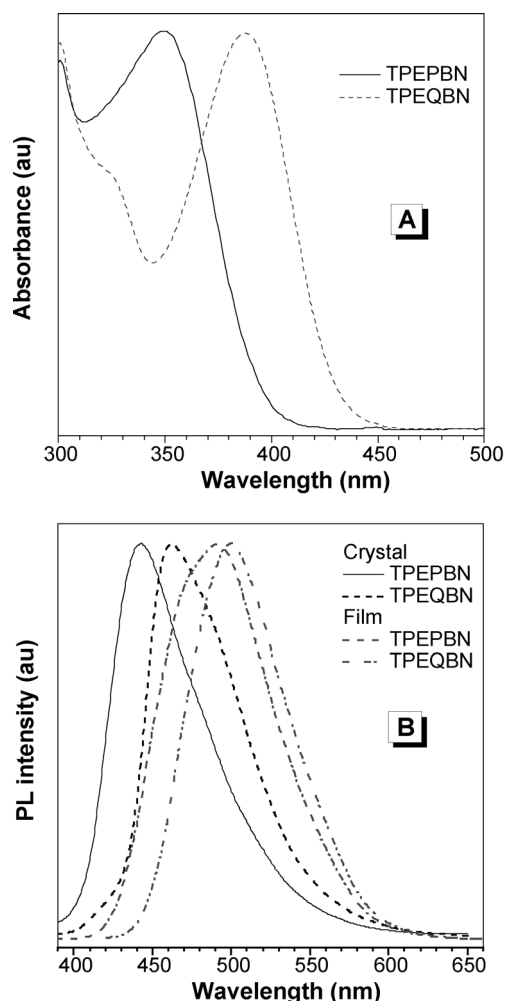


Figure 2. A) Absorption spectra of **TPEPBN** and **TPEQBN** in THF solution. B) PL spectra of **TPEPBN** and **TPEQBN** in crystals and films.

sorption maximum of **TPEQBN** is located at 388 nm, which is greatly red-shifted by 57 nm than that of **4**, a control luminogen without B·N coordination. **TPEPBN** shows faint emission without discernable peaks in dilute THF solution (10 μM) and its fluorescence quantum yield (Φ_F) is as low as 0.40 % because the active intramolecular rotation (IMR) process of phenyl rotors consumes the excited state energy (Table 1).^[7] **TPEQBN** shows slightly better emission at around 501 nm with a Φ_F value of 0.94 %. Even if the value is low, it is about 50-fold higher than that of **4** (0.019 %),^[12] demonstrating that the intramolecular B·N coordination has restricted the rotations of quinoline ring and its neighboring phenyl ring, and hence reduced the nonradiative decay of the excited state.

Although both **TPEPBN** and **TPEQBN** are weakly fluorescent in the solution state, they are highly emissive in the

Table 1. Optical properties of **TPEPBN** and **TPEQBN** in solution (soln.)^[a] and crystalline (cryst.) and amorphous^[b] (film) states.

| | λ_{abs} [nm] | | λ_{em} [nm] | | Φ_F [%] | |
|---------------|-----------------------------|-------|----------------------------|------|----------------------|---------------------|
| | soln. | soln. | cryst. | film | soln. ^[c] | film ^[d] |
| TPEPBN | 351 | – | 443 | 491 | 0.40 | 98 |
| TPEQBN | 388 | 501 | 462 | 500 | 0.94 | 99 |
| 4 | 331 | – | 445 | 471 | 0.019 | 20 |

[a] In THF solution (10 μM). [b] Film spin-coated on quartz plate. [c] Quantum yields (Φ_F) determined in THF solutions using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard. [d] Quantum yield of the amorphous film measured by integrating sphere.

aggregate state. Upon photoexcitation, the crystals of **TPEPBN** and **TPEQBN** show strong blue photoluminescence (PL) peaked at 443 and 462 nm, whereas their amorphous films radiate redder lights at 491 and 500 nm, respectively (Figure 2B). The hypsochromic shifts in the PL spectra of crystals relative to amorphous films were also observed from other TPE derivatives.^[9b, c, 12, 13] The solid-state Φ_F values of **TPEPBN** and **TPEQBN** are 98 and 99%, respectively, measured from their amorphous films by integrating sphere, which are remarkably enhanced in comparison with those in solutions, indicating that they are AIE active. The solid-state Φ_F values are also much higher than those of most boron compounds reported.^[6] The excellent solid-state PL efficiency coupled with tunable emission color in crystalline and amorphous states suggest both new organoborons are promising mechanochromic materials.^[13]

To further confirm the AIE nature of **TPEPBN** and **TPEQBN**, their PL spectra in THF/water mixtures were measured (Figure 3). It can be seen that the PL intensity of **TPEQBN** increases swiftly with the addition of a large amount of water into its THF solution. Since **TPEQBN** is insoluble in water, aggregates of **TPEQBN** are formed when the water fraction becomes high in the mixtures. The IMR process is restricted in condensed phase and radiative relaxation of the excited state is promoted, making the luminogens emit efficiently. Similar PL spectra were also recorded from **TPEPBN**. These results demonstrate that **TPEPBN** and **TPEQBN** are AIE active. Meanwhile, the emission intensity of both luminogens can be reversibly modulated by the dispersive and aggregate states of the molecules. Addition of THF and water alternately makes the luminogens emissive and weakly emissive (Figure 4).

To better understand the PL properties of the luminogens, their molecular packing patterns in the crystalline state were investigated. The arrangement of **TPEQBN** molecules is displayed in Figure 5 and that of **TPEPBN** is given in Figure S2 in the Supporting Information. As illustrated, all the **TPEQBN** molecules adopt a highly twisted conformation to fit to the crystalline lattice. This hampers the molecules to stack closely in a face-to-face fashion. Multiple C–H $\cdots\pi$ hydrogen bonds with distances in the range of 2.693–3.000 Å are formed between hydrogen atoms and aromatic rings. An additional π – π interaction (3.452 Å) is formed between phenyl and quinoline rings. All these weak interactions work collectively to restrict the IMR process,^[12, 14] and hence

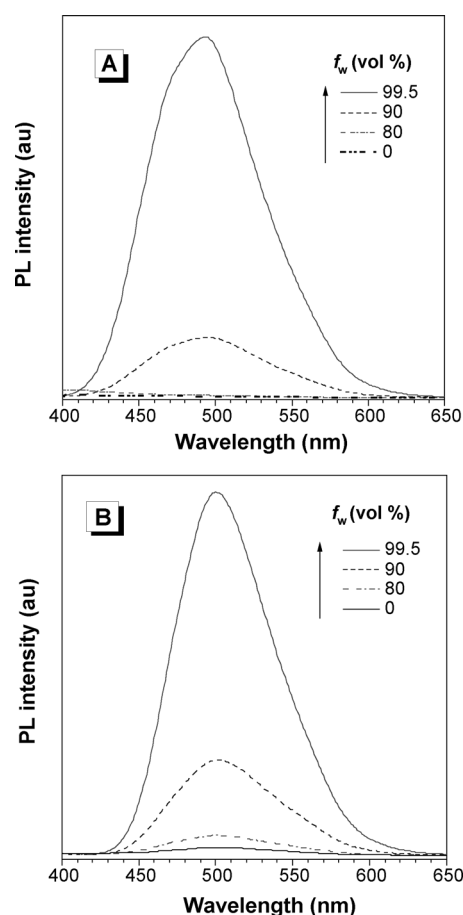


Figure 3. PL spectra of: A) **TPEPBN**, and B) **TPEQBN** in THF/water mixtures with different water fraction (f_w).

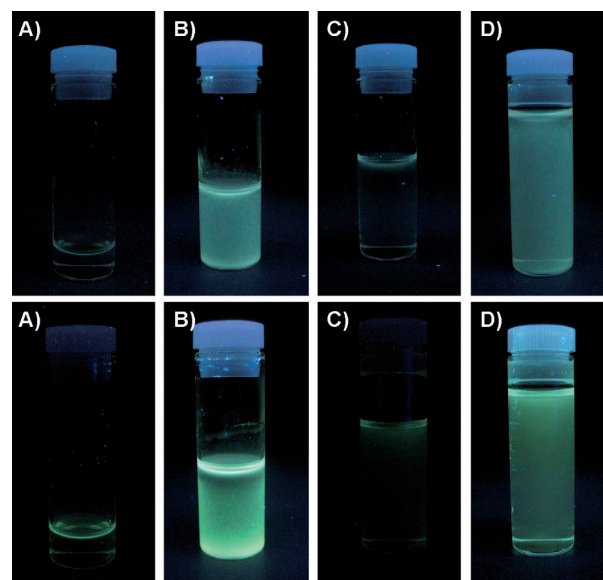


Figure 4. Photographs of **TPEPBN** (upper panels) and **TPEQBN** (lower panels): A) in THF; B) obtained with the addition of water into (A); C) obtained with the addition of THF into (B); D) obtained with the addition of water into (C), taken under the illumination of a UV lamp.

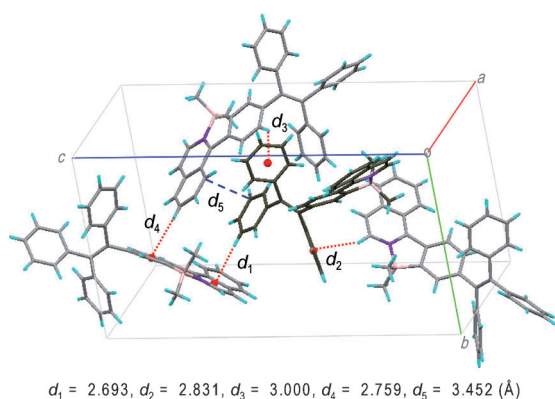


Figure 5. Molecular arrangement of **TPEQBN** in a unit cell, with indicated C–H... π hydrogen bonds (red dash) and π – π interaction (blue dash) between adjacent molecules.

promote radiative relaxation of the excited state, causing the molecules to fluoresce strongly. Without the constraint in crystalline lattice, the molecular conformation becomes planar in some measure in the amorphous state and thereby, close packing and stronger intermolecular interactions are induced. These factors should be responsible for the red-shifts in PL spectra in amorphous films relative to crystals.

The electronic structures and energy levels of **TPEPBN** and **TPEQBN** were investigated by theoretical calculation. The nonlocal density functional of B3LYP with 6-31G(d) basis sets was used for the calculation. The optimized structures and the orbital distributions of HOMO and LUMO energy levels are shown in Figure 6. The HOMOs of both

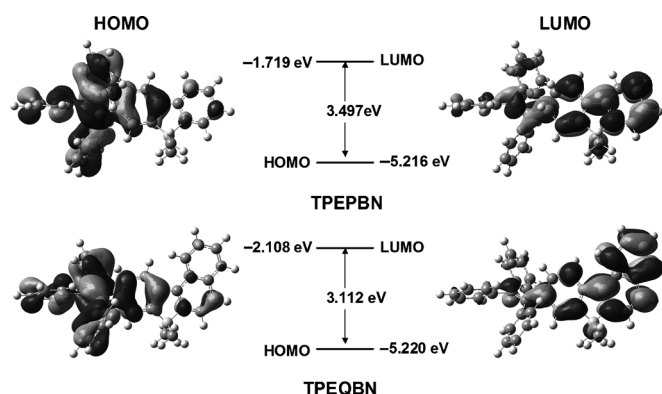


Figure 6. Molecular orbital amplitude plots and energy levels of HOMOs and LUMOs of **TPEPBN** and **TPEQBN** calculated by using B3LYP/6-31G(d) basis set with G09 program.

luminogens are dominated by the orbitals from the TPE moieties, whereas the LUMOs are located mainly on the orbitals from pyridine and quinoline rings. A significant dense electron cloud is distributed on the exocyclic B–C single bonds in the LUMOs of both luminogens, due to the p_π – π^* conjugation between p_π orbital of boron and π^* orbitals of the aromatic rings, leading to a low lying LUMO energy level. The calculated HOMO energy level of **TPEQBN** is

–5.220 eV, and is close to that of **TPEPBN** (–5.216 eV). The LUMO energy level of **TPEQBN** (–2.108 eV), however, is much lower than that of **TPEPBN** (–1.719 eV). The LUMO energy levels of both organoborons are lower than those of many silole derivatives, good electron transporters, indicating electron-injection and transport are favored.^[15]

The electrochemical property of **TPEPBN** and **TPEQBN** was investigated by cyclic voltammetry (CV). Similar CV curves with two reversible oxidation peaks at about 1.34 and approximately 1.54 V were detected (Figure 7). The onset

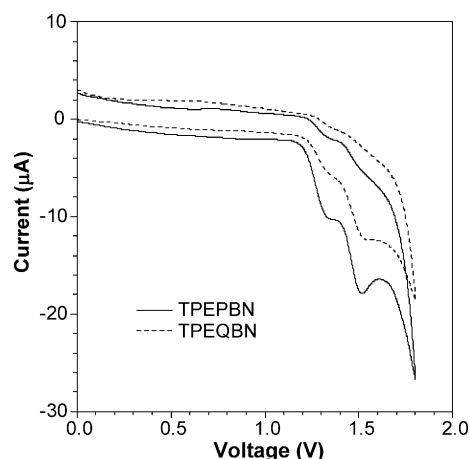


Figure 7. Cyclic voltammograms of the **TPEPBN** and **TPEQBN**, measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Scan rate: 100 mV s^{–1}.

potentials (E_{onset}) of **TPEQBN** and **TPEPBN** occurred at 1.23 and 1.19 V, respectively, from which the HOMO energy levels were determined to be –5.63 and –5.59 eV [$\text{HOMO} = -(4.4 + E_{\text{onset}})$]. The LUMO energy levels were obtained by subtraction of the optical band gap energies from the HOMO energy levels, and are equal to –2.59 and –2.83 eV, for **TPEPBN** and **TPEQBN**, respectively. The low LUMO value of **TPEQBN** is comparable to those of silole derivatives (e.g., –2.77 and –2.81 eV),^[16] indicating that **TPEQBN** is a potential electron transporter.

In summary, a practical approach to building organoborons that can function as efficient solid-state emitters is proposed. Two novel N,C-chelate four-coordinate organoborons with good thermal stability were synthesized and characterized. Due to the presence of the TPE moiety, both organoborons exhibit AIE characteristics and fluoresce efficiently in the aggregate state, with high Φ_F values approaching unity. The theoretical calculation and electrochemical studies reveal that they possess low-lying LUMO energy levels, evidencing that the introduction of B–N coordination into the π -conjugated framework can effectively lower the LUMO energy levels, and hence enhance the electron affinity. Further studies on the applications of these organoborons in electronic devices and anion sensors are in progress.

Experimental Section

Compound TPEPBN: BBR_3 (1.0 M in dichloromethane, 3.0 mL, 3.0 mmol) was added to a stirred solution of **2** (0.4 g, 1.0 mmol) and $i\text{Pr}_2\text{NEt}$ (0.13 g, 1.0 mmol) in dry dichloromethane (20 mL) at 0 °C. After being stirred at room temperature for 24 h, saturated K_2CO_3 aqueous solution was added to the reaction mixture. The reaction was poured into water and extracted with dichloromethane twice. The combined organic layers were washed with water, and then dried over magnesium sulfate. After filtration and solvent evaporation, the resulting crude product was added with toluene (20 mL) and Me_3Al (1.1 M in hexane, 2.0 mL, 2.2 mmol), and then stirred at room temperature for 0.5 h. The reaction was poured into water and extracted with dichloromethane twice. The combined organic layers were washed with water, and then dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography by using hexane/dichloromethane mixture as eluent. A pale yellow solid was obtained in 42% yield (0.19 g). ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 8.52 (d, 1H, J = 5.6 Hz), 8.07–8.03 (m, 1H), 7.98 (d, 1H, J = 8.0 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.45–7.39 (m, 3H), 7.28–7.21 (m, 14H), 7.10 (d, 1H, J = 6.8 Hz), 0.02 ppm (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 156.8, 145.6, 143.9, 143.8, 142.7, 141.8, 139.0, 132.6, 131.5, 131.4, 131.3, 128.4, 127.6, 126.3, 120.9, 120.6, 117.8, 8.8 ppm; HRMS: m/z 434.19 ($\text{M}^+ - \text{CH}_3$, calcd 434.2080); elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{28}\text{BN}$: C 88.20, H 6.28, N 3.12; found: C 88.09, H 6.18, N 3.04.

Compound TPEQBN: Pale yellow solid, yield 55%. ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 8.54 (d, 1H, J = 8.8 Hz), 8.30 (d, 1H, J = 8.8 Hz), 7.92 (d, 1H, J = 8.8 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.81–7.77 (m, 1H), 7.69 (d, 1H, J = 8.8 Hz), 7.57–7.53 (m, 1H), 7.33–7.30 (m, 1H), 7.25–7.23 (m, 1H), 7.12–7.07 (m, 13H), 6.98–6.94 (m, 2H), 0.05 ppm (s, 6H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 157.4, 146.2, 143.9, 143.8, 142.0, 141.7, 141.5, 140.0, 133.6, 132.2, 131.5, 131.4, 131.3, 131.2, 130.8, 128.7, 128.5, 127.7, 127.6, 127.4, 126.4, 126.1, 123.3, 121.5, 115.8, 9.0 ppm; HRMS: m/z 484.23 ($\text{M}^+ - \text{CH}_3$, calcd 484.2237); elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{30}\text{BN}$: C 88.98, H 6.05, N 2.80; found: C 88.85, H 5.92, N 2.63.

Crystal data for TPEPBN: $\text{C}_{33}\text{H}_{28}\text{BN}$, M_r = 449.37, monoclinic, $P2_1/c$, a = 12.734(2), b = 11.0252(18), c = 18.552(3) Å, β = 97.165(3)°, V = 2584.2(7) Å³, Z = 4, ρ_{calc} = 1.155 g cm^{−3}, μ = 0.066 mm^{−1} ($\text{MoK}\alpha$, λ = 0.71073), $F(000)$ = 952, T = 296(2) K, 14089 measured reflections, 4649 independent reflections (R_{int} = 0.0284), GOF on F^2 = 1.059, R_1 = 0.0675, wR_2 = 0.1700 (all data), $\Delta\rho$ 0.218 and −0.244 e Å^{−3}.

Crystal data for TPEQBN: $\text{C}_{37}\text{H}_{30}\text{BN}$, M_r = 499.43, orthorhombic, $P2_1(2)1(2)1$, a = 9.8722(14), b = 12.5757(17), c = 23.444(3) Å, V = 2910.6(7) Å³, Z = 4, ρ_{calc} = 1.140 g cm^{−3}, μ = 0.065 mm^{−1} ($\text{MoK}\alpha$, λ = 0.71073), $F(000)$ = 1056, T = 296(2) K, 9596 measured reflections, 5135 independent reflections (R_{int} = 0.0420), GOF on F^2 = 1.069, R_1 = 0.1130, wR_2 = 0.1881 (all data), $\Delta\rho$ 0.275 and −0.191 e Å^{−3}.

CCDC-854152 (TPEPBN) and -854153 (TPEQBN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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