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Synthesis and Photophysical Properties of Aryl-Substituted 2-Borylbenzaldimines and Their Extended π-Conjugated Congeners

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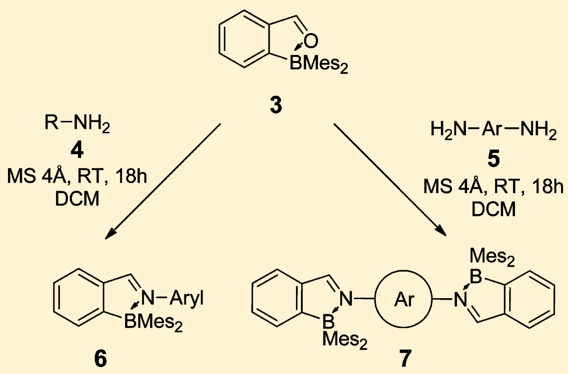
S *Supporting Information*

ABSTRACT: Novel *N*-aryl-substituted 2-borylbenzaldimines **6** and related systems with extended π-framework **7** based on two boryl-benzaldimine units linked by a spacer moiety were synthesized by condensation reactions of 2-(dimesitylboryl)benzaldehyde **3** with various amines **4** and diamines **5**. All compounds were completely characterized including X-ray diffraction, especially in view of Lewis acid–base B–O and B–N interactions. The electronic as well as the photophysical properties of bisimines **7** were determined using cyclic voltammetry, UV/vis, and fluorescence spectroscopy and quantum chemistry. These compounds feature large Stokes shifts and reversible reduction waves. Interestingly, UV irradiation experiments unfold enhanced photostability for compounds **7** with an extended π-skeleton. By use of 1,8-diaminonaphthalene we observed the formation of a hitherto unknown BN-heterocyclic compound **9** fused with a perimidine skeleton. Structural and energetic aspects were evaluated by high level quantum chemical methods (DFT and SCS-MP2-calculations).



INTRODUCTION

Organic π-conjugated materials[1] are of emerging interest for the design and development of organic optoelectronics such as organic light-emitting diodes (OLEDs)[2] and organic field-effect transistors (OFETs).[3] The incorporation of main group elements into π-conjugated frameworks was shown to be a versatile method for tuning the photophysical and electronic properties of these systems.[4] Four coordinate boron-containing π-conjugated compounds,[5] especially of the N,C-chelate type, have attracted interest because of their electronic and photophysical properties.[6,7] In particular, their photochromism has been extensively studied by the group of Wang, who used *N*-heteroaromatic rings, such as pyridine and indole, as the boron-coordinating subunit.[8,9] Imine-coordinating organoboron compounds were reported independently by Kawashima[10] and Gabbaï.[11] Kawashima used C_6F_5 substituents at the boron atom, whereas in the work of Gabbaï et al. mesityl substituents were employed. The latter work reports two examples with aliphatic substituents on the imine nitrogen. We became interested in the synthesis of more elaborate *N*-aryl-substituted imine–organoboron Lewis acid–base pairs with larger π-systems because the facile formation of the imine functionality should enable us to produce a variety of novel π-systems having potential for applications to organic electronics. To this end, it is crucial with regard to the chemical and photostability of the imine-coordinating boron compounds to study the substituent effects on B–N coordination and the resulting influences on the photophysical properties. Here we report the preparation and characterization of a series of *N*-aryl 2-borylbenzaldimines and their extended π-conjugated compounds with these BN-heterocycles as the terminating units. The impact of the π-spacers on the photophysical and electrochemical properties as well as on the photostability has been studied.

RESULTS AND DISCUSSION

Synthesis. Starting material for the synthesis of the imine derivatives **6a–c** and **7a–d** is the 2-dimesitylborylbenzaldehyde **3** (Scheme 1). Its preparation was previously described.[10,11]

In addition to the published data, we were able to obtain single crystals of the aldehyde **3** and to confirm the molecular structure by X-ray diffraction[12] (Figure 1). The molecular structure in the solid state reveals the coordination of the Lewis basic carbonyl oxygen atom to the Lewis acidic boron center (B–O: 1.645(2) Å, C=O: 1.2553(19) Å). The measured B–O distance is in line with the value of 1.66 Å determined by quantum chemical calculations.[11]

In order to get further insights into the bonding situation of **3**, Wiberg bond index[14] calculations using the NBO[15] approach as implemented in the GAUSSIAN 09 series of programs were

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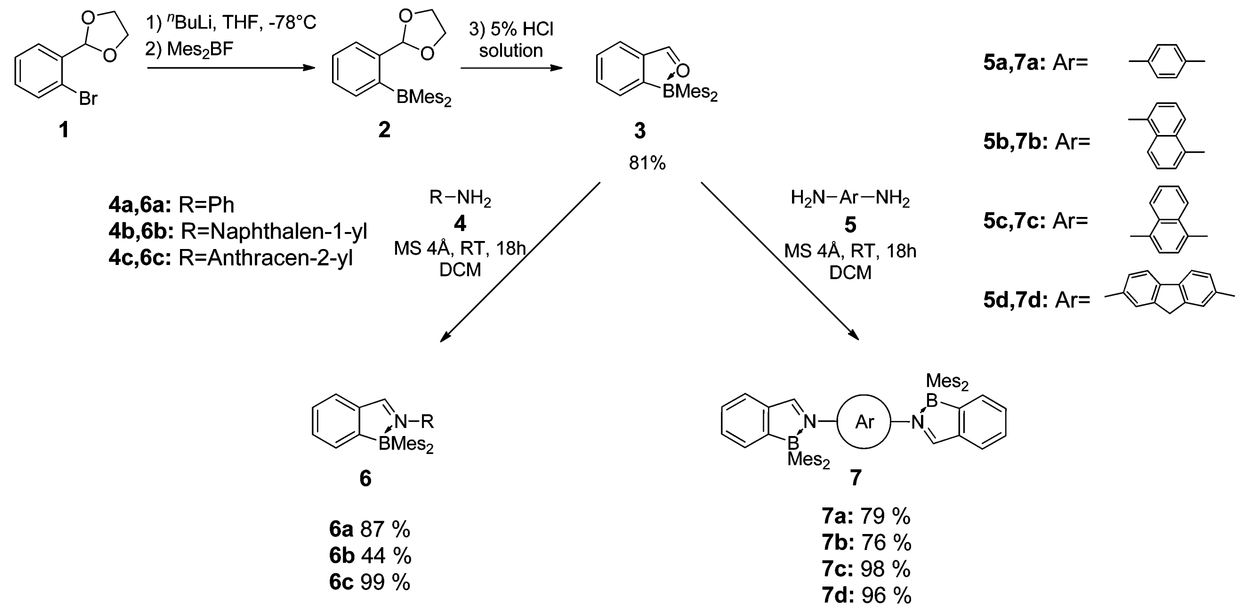
Scheme 1. Synthesis of Compounds 3, 6, and 7 by Condensation of Dimesitylboryl Benzaldehyde 3 with Amines 4 or Diamines 5



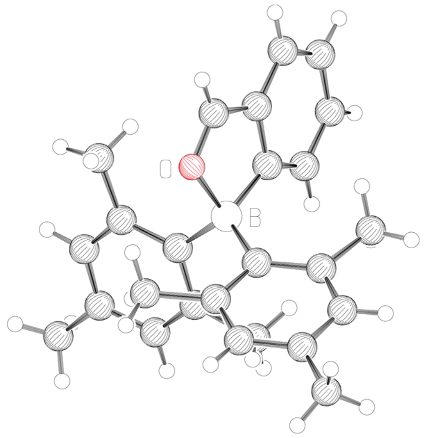
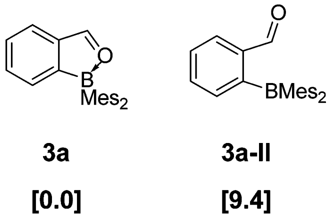


Figure 1. Molecular structure of compound **3** in the crystal (Schakal plot[13]).

performed.[16] The Wiberg bond index of the coordinating B−O interaction amounts to 0.489 (B−O) and for the C═O-bond to 1.48. For comparison, the isomer of **3-II** with no direct B−O coordination was also calculated. Here, the Wiberg bond index of the C═O bond has a value of 1.81, illustrating the severe electronic changes induced by the coordination of boron by oxygen in such compounds. This is well in line with the calculated energy difference between **3** and **3-II** of 9.4 kcal/mol (SCS-MP2/6-311+G(d,p)//B3LYP6-31G(d)[17]) (Scheme 2).

Scheme 2. Relative Energies for 3 and 3-II [kcal/mol] (SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE



The synthesis of the imine derivatives **6a−c** was accomplished by the condensation reaction of aldehyde **3** with various amines **4**/**5** (1.0−1.1 equiv) using molecular sieves (Scheme 1).[18] In addition to previous publications in which the preparation of *N*-alkylated compounds was reported, we were now able to synthesize fluorescent *N*-arylated BN-heterocycles **6a−c** for the first time by this method in moderate to excellent yield.[11] Such systems offer the additional possibility to extend the *π*-conjugation into the amine-derived part of the imino compound.

The structure of compound **6a** (crystal data were also obtained for **6b**; see the Supporting Information) was elucidated by X-ray crystallography (Figure 2). The lengths of the B−N and C═N bonds **6a** in the solid state were measured as 1.693(3) Å and 1.293(3) Å. The B−N bond length in **6a** is slightly elongated in comparison to the values reported in the literature (1.627(3) and 1.630(4) Å for *N*-alkylated compounds).[11] This might be attributed to the different electronic influences of the sterically more demanding aromatic substituents or spacer units at the nitrogen atom.

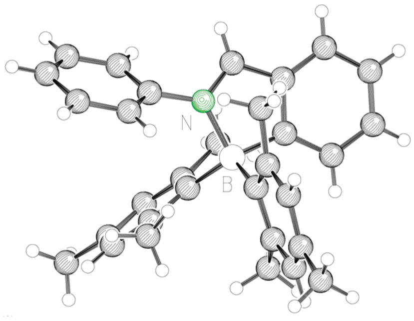
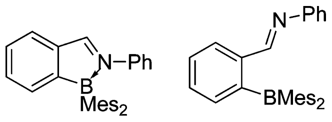


Figure 2. Molecular structure of **6a** in the crystal (Schakal plot).

The Wiberg bond indices for **6a** are calculated to 0.560(B−N) and 1.565(C═N), indicating the stronger B−N-interaction compared to the B−O-interaction in **3**. The noncoordinating structural isomer **6a-II** has a Wiberg bond index of 1.759 for the

C=N bond. Compound **6a-II** was found to be 10.7 kcal/mol higher in energy compared to **6a** (Scheme 3).

Scheme 3. Relative Energies of 6a and 6a-II [kcal/mol] (SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE)



6a **6a-II**

[0.0] **[10.7]**

For the preparation of the extended π-conjugated compounds **7** with various π-spacers, the aldehyde **3** and the corresponding diamines **5** were used in a 2−3:1 ratio (Scheme 1). In some cases, the use of an excess amount of aldehyde was necessary to prevent the formation of monocondensation products. Purification was performed by recycling GPC or recrystallization to obtain a series of the condensated compounds **7** in good to excellent yields. Compound **7a** is poorly soluble in various organic solvents, such as toluene, chlorinated solvents, or ethers, whereas **6a** can be dissolved as well in apolar as in various other solvents. Extending the π-skeleton going from **7a** to **7d** increases the solubility in solvents like benzene or toluene because of the growing apolar character of the molecule by extending the spacer moiety. While compound **6a** was found to decompose after a few hours (2−4) in benzene or dichloromethane solution, the extended congeners **7** could be stored in solution over days. The increasing chemical stability of compounds **7** in comparison to **6a** might be attributed to the sterically bulky dimesitylboryl subunits on both sides of the spacer in **7**. Therefore, the imine functionalities in **7** might be less accessible for decomposition reactions compared to the ones in **6a**.

We were able to obtain the molecular structures of compounds **7a** and **7b** by X-ray crystallography (for **7a**, see Figure 3). According to the crystal structure of **7a**, the lengths of the B−N and C=N bonds amount to 1.688(4) Å and 1.292(4) Å, respectively, which are comparable to those of compounds **6a** and **6b**. Wiberg bond indices for the B−N bonds were calculated for **7a** to 0.561 and **7b** to 0.557. For the C=N bonds, Wiberg indices of 1.549 and 1.560 were obtained (for Wiberg bond indices of other compounds, see the Supporting Information).

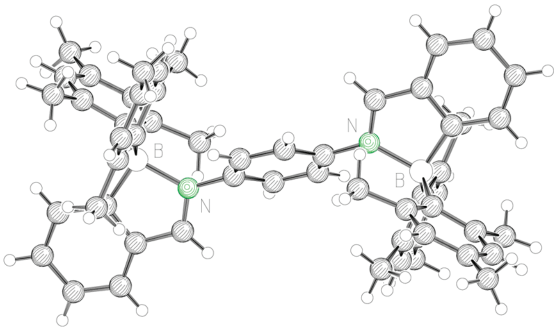
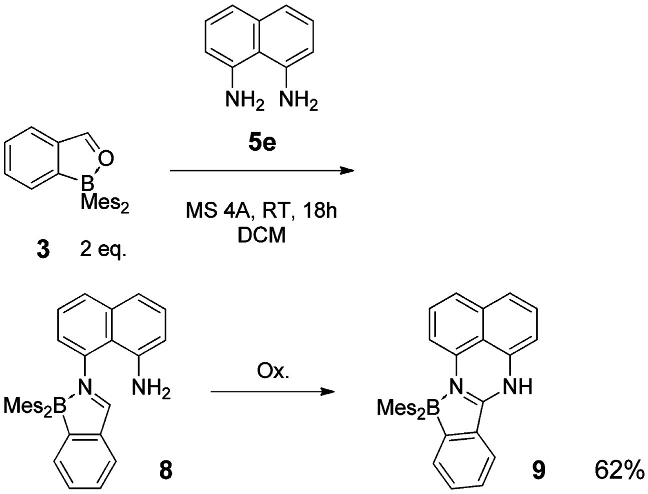


Figure 3. Molecular structure of **7a** in the crystal (Schakal plot).

An interesting reaction was observed when compound **3** was condensated with 1,8-diaminonaphthalene. After workup and recrystallization from dichloromethane, a perimidine derivate **9** was isolated in 62% yield (Scheme 4). Its structure was confirmed by X-ray analysis (Figure 4). This compound is assumed to be formed by the intramolecular cyclization of monocondensated product **8** followed by aerobic oxidation. According to the crystal structure of **9**, the B−N bond (1.658 Å) is slightly shorter than those of **6a** and **7a**. The bond lengths of the 6-membered ring formed amount to N1−C2 1.335(3) Å, C2−N2 1.328(3) Å, N2−C18 1.397(3) Å, C18−C19 1.418(4) Å, C19−C10 1.417(4) Å, and N1−C10 1.424(3) Å. NICS(0)[19] calculations (B3LYP/6-311+G(d)) give values of −7.1 and −7.4 ppm for the rings of the naphthalene subunit indicating aromatic character, whereas the NICS(0) value for the pyrimidine subunit is calculated to 7.7 ppm, a strong indicator for antiaromaticity.[20]

Scheme 4. Formation of Compound 9



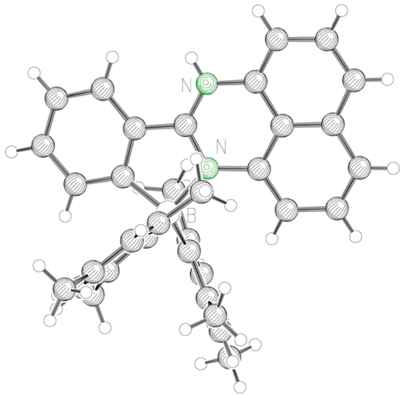


Figure 4. Molecular structure of compound **9** (Schakal plot).

Photophysical and Electrochemical Properties. UV/vis absorption and fluorescence spectra are shown in Figure 5. Table 1 provides the absorption and emission maxima and the quantum yields for **6a** and **7**. The UV/vis spectra of compounds **6a** and **7** show absorption maxima between 284 and 370 nm. The longest absorption band or shoulder (in **6a** ~350 nm and **7a** ~370 nm) can be attributed to the intramolecular charge transfer (ICT) transition from the mesityl to the *N*-benzylidenearylidene-2-amine part of the molecule (see below, quantum chemical calculations). All compounds show emissions in the region of 569 to 583 nm. The quantum yields for **6a** and **7** were found to range from 3% to 10%. Notably, these compounds exhibit large Stokes shifts in the range of 201−221 nm (9500−11100 cm^{-1}), which suggest the

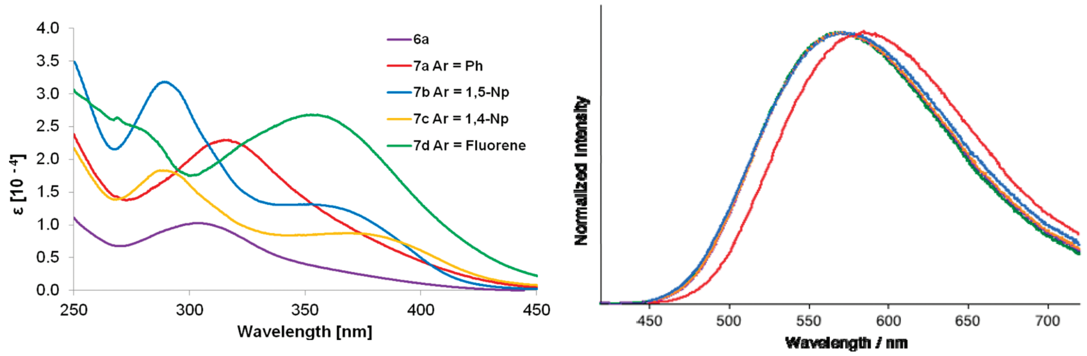
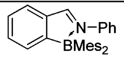
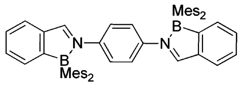
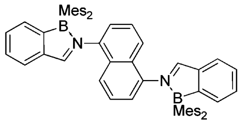
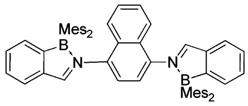
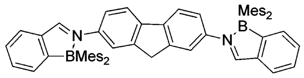
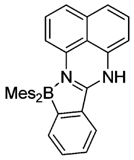


Figure 5. UV/vis (left) and fluorescence (right) spectra of compounds **6a** (purple) **7a** (red), **7b** (blue), **7c** (orange), and **7d** (green) in CH_2Cl_2 (for details, see the Supporting Information).

Table 1. Photophysical Data for Compounds 6a and 7a−d in CH_2Cl_2

Compound	Structure	λ_{abs} [nm]/ $\varepsilon \times 10^{-4}$ [$M^{-1}\cdot cm^{-1}$]	λ_{em} [nm]	Φ_f[a]
6a		304 / 1.16 350 (sh)	570	n.d.[b]
7a		317 / 2.23 370 (sh)	583	0.04
7b		289 / 2.98 351 / 1.20	572	0.04
7c		289 / 2.57 370 / 1.19	571	0.03
7d		325 (sh) 354 / 2.73	569	0.10
9		272 / 1.60 325 / 1.20 339 / 1.43	-	-

[a] Absolute fluorescence quantum yield determined by a calibrated integrating sphere system. [b] Could not be determined because the compound underwent a photoreaction during the measurement.

potential utility as fluorescence dyes.[21] For the pentacyclic **9**, the absorption maximum was found at 272 nm, while no fluorescence was observed.

NMR Experiments. To confirm the photochemical stability difference between systems **6a** and **7** we prepared NMR samples of both compounds, irradiated these with a UV lamp (366 nm, distance sample lamp: 3 cm), and measured proton NMR spectra after various irradiation periods. Figure 6 depicts the changes observed in the NMR spectra with time. Obviously, compound **7d** undergoes no structural change even after prolonged irradiation time, whereas new peaks appear in the spectra of the mono-BN-heterocyclic system **6a**, which decomposes completely within 4 h of UV irradiation. This is seen from the decreasing intensity of the mesityl signals at 2.18 and 2.04 ppm, while new signals arise.

Quantum Chemical Calculations. DFT calculations were carried out for **6a** and **7a−d** (B3LYP/6-31G(d)). Figure 7 depicts the Kohn−Sham HOMO and LUMO orbitals of **6a** and **7**. For all compounds **7**, the HOMO-1 and the HOMO are quasi-degenerate. They are each localized on one mesityl group of the two bismesityl boron subunits, while the LUMO is delocalized over the imine-containing π-conjugated skeleton. TD-DFT calculations (B3LYP/6-31G(d), td=(nstates=20)) indicate that the longest absorption bands for **6a** and **7a−d** are attributable to the HOMO−LUMO transitions (with contributions of the HOMO-1−LUMO-transitions in case of compounds **7**). Thus, these have the character of intramolecular charge-transfer transitions (ICT) from the mesityl group to the π-skeleton. Taking these similarities into consideration, the different photostabilities between **6a** and **7** may be attributable to the different

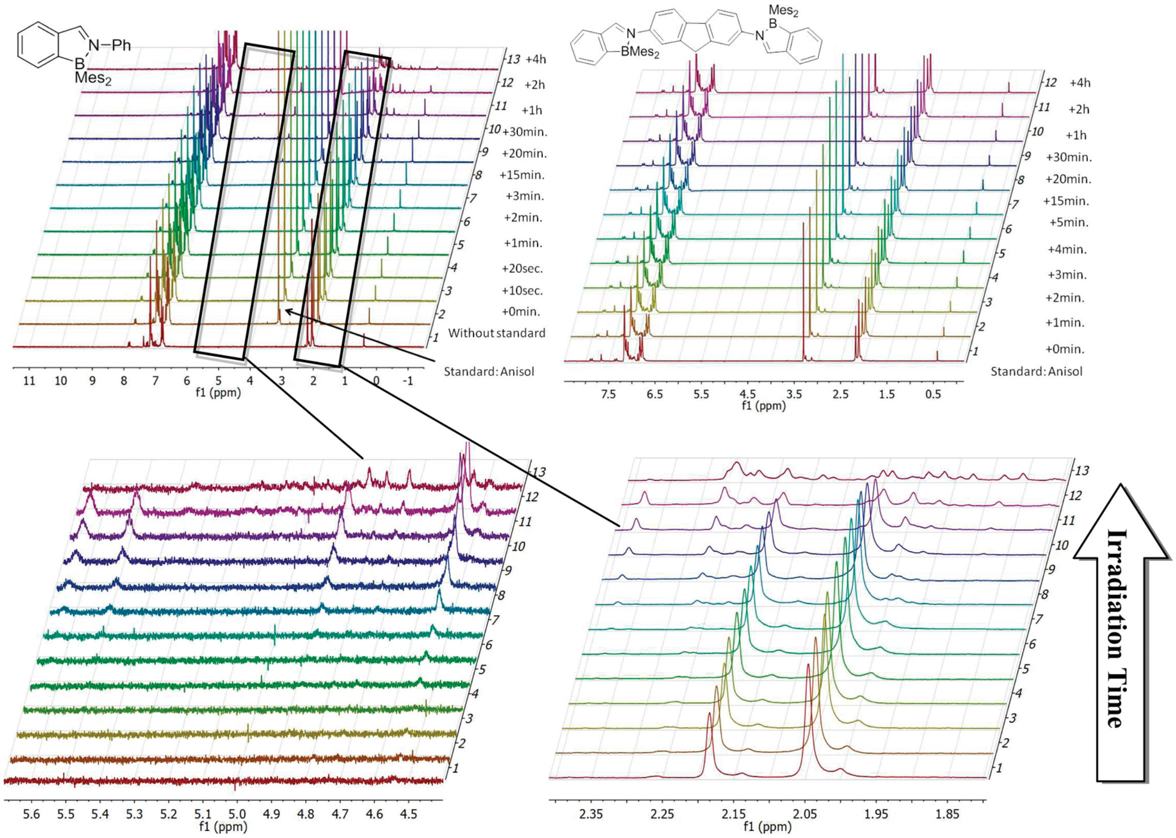


Figure 6. Time-dependent ^{1}H NMR spectra of **6a** (top/left) and **7d** (top/right, 8.0−0 ppm) after incremental periods of irradiation (with UV light (standard: anisole, solvent C_6D_6) and magnified spectra of **6a** region: 5.7−4.4 ppm (bottom/left) and 2.4−1.8 ppm (bottom/right).

degree of delocalization of the LUMO in **6a** compared to **7**. The considerably higher degree of delocalization in **7** might impede possible photorearrangement reactions, since here the energy might be dispersed over the spacer and the adjacent second BN-heterocyclic system.[9]

Table 2. Electrochemical Data for Compounds 7[a]

compd	E_{pc}[b,c] (V)	$E_{1/2}$[c] (V)
7a	−2.06	−1.98
7b	−2.18/−2.32	−2.14/−2.21
7c	−2.19/−2.50	−2.08/−2.38
7d	−1.88/−2.24	−1.96/−2.15

[a] In THF with $Bu_4N^+PF_6^-$, scan rate 100 mV s^{-1}. [b] Cathodic peak potential vs Fc/Fc^+. [c] Reduction potentials vs Fc/Fc^+

Cyclic Voltammetry. To assess the electrochemical properties of **7a**−**d**, cyclic voltammetric measurements were carried out. The results are summarized in Table 2, and the cyclic voltammograms are shown in Figure 8.

Reversible reduction waves were found in all cyclic voltammograms of **7**. Compound **7a** shows one ($E_{1/2}$ = −1.98 V) and **7b**−**d** two reversible reduction waves, respectively. In the latter cases, due to the large conjugated system, the generation of dianionic species seems to be reasonable. The change from the phenylene (**7a**) to the naphthyl spacer (**7b**) shifts the first reduction potential to more negative values ($E_{1/2}$ = −1.98 V for **7a** and $E_{1/2}$ = −2.14 V for **7b**). These values are comparable to those reported for the BN-coordinating thienylthiazoles dimers, which were suggested as electron-transporting materials.[6] Reversibility was also found at higher scan rates (0.2 V s^{-1}), demonstrating a fast redox process within the systems. In addition, we also studied the oxidation potential of **7a** as an example for molecules of type **7**. An irreversible oxidation process was observed in CH_2Cl_2 at 0.1 V s^{-1} scan rate, suggesting that the radical cation formed might be unstable under the measurement conditions.

Summary. In this work, we present the synthesis and characterization of novel imine-based BN-heterocycles, especially imines with *N*-aryl substituents **6** and related bisimines with extended π-conjugation **7**. The latter compounds contain a spacer moiety which interconnects two BN-heterocyclic systems. We observed that these molecules show enhanced chemical stability compared, e.g., to the phenyl derivative **6a** containing a single BN-heterocyclic unit. UV/vis and fluorescence and cyclic voltammetric measurements revealed that compounds of type **7** show large Stokes shifts and high electrochemical stability, which indicate their possible utility in organic optoelectonic materials, such as fluorescence dyes and semiconducting materials.[22] Furthermore, compounds **7** also do not undergo photoisomerization as it was previously observed in four coordinate boron compounds substituted with mesityl groups. The lack of photoisomerization reactions is advantageous for technical applications.[9] Additionally, we synthesized a novel pentacyclic molecule **9** containing a perimidine skeleton fused with a BN-heterocycle.

■ EXPERIMENTAL SECTION

Compounds **6** were synthesized by condensation reaction of dimesityl benzaldehyde **3**[11] with amines (1 equiv or small excess) in CH_2Cl_2.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene]-phenylamine (6a). A 1.11 g (3.13 mmol) portion of **3** was dissolved in 60 mL of dry CH_2Cl_2. Subsequently, 0.35 mL (3.19 mmol)

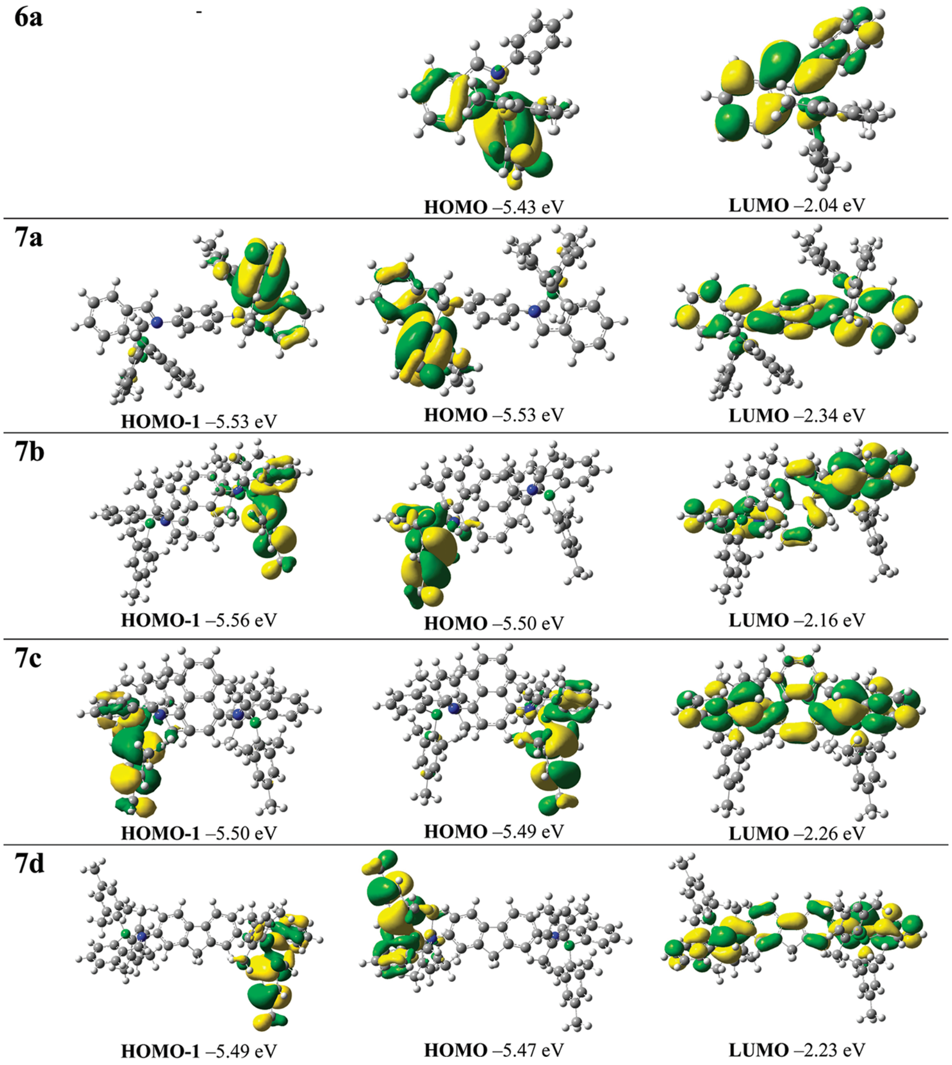


Figure 7. Photophysically relevant molecular orbitals with energies (in eV) of **6a** and **7a**−**d**: HOMO-1 (left), HOMO (center), LUMO (right) (B3LYP/6-31G(d), isocontour value 0.02) (for LUMO+1, excitation energies and oscillator strengths, see the Supporting Information).

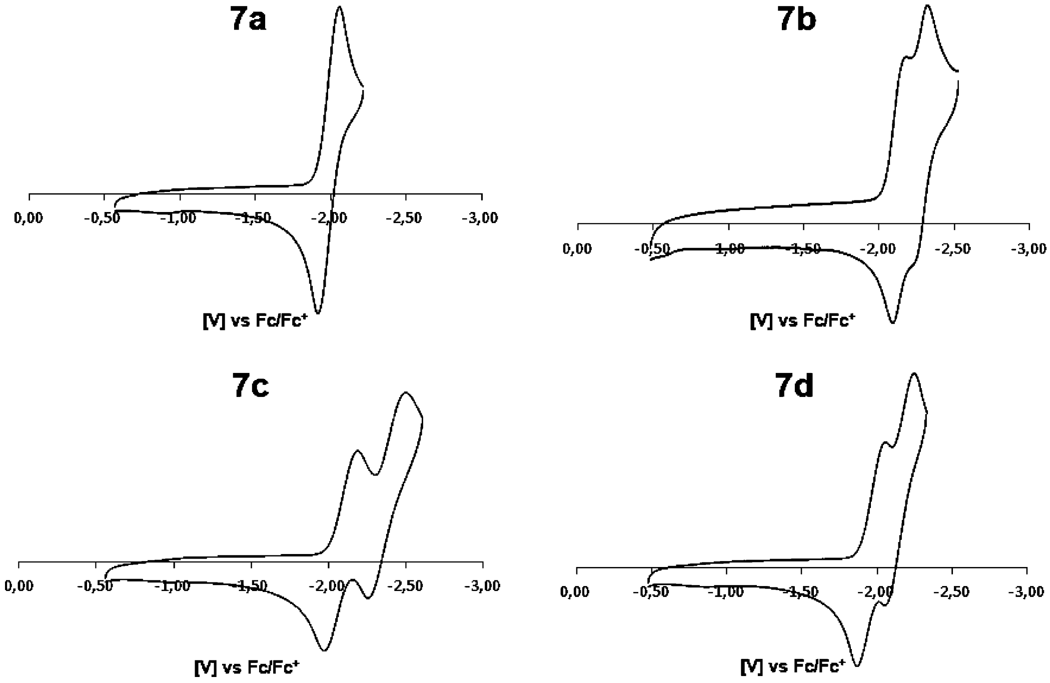


Figure 8. Cyclic voltammograms of compounds **7** (measured in THF, $Bu_4N^+PF_6^-$, scan rate 100 mV s^{-1}).

of aniline was added to the stirring mixture. The compound was purified by washing with pentane. Yellow crystals were obtained by recrystallization from CH_2Cl_2 to give 1.20 g (2.71 mmol, 87%) of compound **6a**. Mp: 170−171 °C. IR (neat): $\tilde{\nu}$ = 3017 cm^{-1} (w), 2970 (m), 2961 (m), 2920 (m), 2868 (w), 2849 (w), 1603 (s), 1595 (s), 1574 (m), 1537 (vs), 1491 (s), 1470 (s), 1443 (vs), 1412 (m), 1379 (m), 1358 (s), 1283 (w), 1261 (m), 1234 (m), 1202 (m), 1136 (m), 1113 (w), 1024 (m), 1015 (m). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 304 nm (32895 cm^{-1}, 1.16 × 10^{-4} M^{-1} cm^{-1}), 350 (28571 cm^{-1}, sh). Fluorescence (CH_2Cl_2): λ_{em} ($\tilde{\nu}$) = 570 nm (17544 cm^{-1}), λ_{exc} = 370 nm. ^{1}H NMR (C_6D_6, 300.13 MHz): δ = 2.05 ppm (s, 12H), 2.19 (s, 6H), 6.77 (bs, 4H), 6.79−6.85 (m, 4H), 7.00 (td, 1H, J = 7.2 Hz, J = 0.9 Hz, 1H), 7.10 (td, 1H, J = 7.2 Hz, J = 0.9 Hz, 1H), 7.26 (dt, J = 7.5 Hz, J = 0.9 Hz, 1H), 7.34 (s, 1H), 7.84 (d, J = 7.5 Hz, 1H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ = 21.0 ppm, 25.7, 125.2, 125.4, 126.3, 127.9, 128.3, 130.4, 131.8, 132.9, 134.2, 137.3, 141.3, 145.9, 170.0. ^{11}B NMR (C_6D_6, 128.15 MHz): δ = 8.37 ppm. HRMS(ESI): calcd for $C_{31}H_{32}BNNa$ 452.2521, found 452.2522. Anal. Calcd for $C_{31}H_{32}BN$ (429.40): C, 86.71; H, 7.51; N, 3.26. Found: C, 86.49; H, 7.50; N, 3.17. The X-ray crystal structure data of **6a** can be found in the Supporting Information.

[1-(2-(Dimesitylboranyl)phenyl)meth-(*E*)-ylidene]naphthalen-1-ylamine (6b). For the synthesis of compound **6b**, 0.35 g (1.00 mmol) of **3** was dissolved in 50 mL of dry CH_2Cl_2. Then 0.14 g (1.00 mmol) of 1-naphthylamine in 50 mL of dry CH_2Cl_2 was added, and the mixture was stirred for 18 h. The compound was purified by washing with hexane to give 0.21 g (0.44 mmol, 44%) of compound **6b** as colorless crystals. Mp: 196−197 °C. IR (neat): $\tilde{\nu}$ = 2976 cm^{-1} (w), 2959 (w), 2924 (m), 2916 (m), 2361 (m), 2342 (w), 2332 (w), 1597 (vs), 1574 (s), 1539 (vs), 1510 (m), 1466 (m), 1441 (vs), 1410 (m), 1395 (m), 1375 (s), 1360 (s), 1339 (w), 1304 (w), 1283 (w), 1263 (s), 1231 (m), 1209 (vs), 1186 (w), 1169 (m), 1161 (m), 1140 (s), 1107 (w), 1097 (w), 1086 (s), 1070 (w), 1053 (w), 1018 (s). ^{1}H NMR (C_6D_6, 300.13 MHz): δ = 2.16 ppm (bs, 6H), 2.18 (bs, 12H), 6.74 (bs, 4H), 6.99−7.18 (m, 4H), 7.24−7.27 (m, 2H), 7.33−7.39 (m, 1H), 7.43 (s, 1H), 7.49 (t, J = 8.4 Hz, 2H), 7.93 (t, J = 7.2 Hz, 2H). ^{13}C NMR (C_6D_6, 75.48 MHz): δ = 20.9 ppm, 25.7, 122.3, 124.2, 125.7, 125.9, 126.4, 126.6, 127.9, 128.3, 130.3, 132.5, 132.9, 134.3, 137.7, 141.6, 142.0, 171.8. ^{11}B NMR (C_6D_6, 96.29 MHz): δ = 11.34 ppm. HRMS(ESI): calcd for $C_{35}H_{34}BNH$ 480.2858, found 480.2858. Anal. Calcd for $C_{35}H_{34}BN$ (479.46): C, 87.68; H, 7.15; N, 2.92. Found: C, 87.06; H, 7.30; N, 2.85. The X-ray crystal structure data of **6b** can be found in the Supporting Information.

Anthracen-2-yl[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]amine (6c). A 0.35 g (1.00 mmol) portion of **3** was dissolved in 50 mL of dry CH_2Cl_2. Then, 0.20 g (1.02 mmol) of anthracen-2-amine in 100 mL of dry CH_2Cl_2 was added. To purify compound **6c**, the crude product was recrystallized from CH_2Cl_2 to give 0.53 g (0.99 mmol, 99%) as yellow crystals. Mp: 225−226 °C. IR (neat): $\tilde{\nu}$ = 3048 cm^{-1} (vw), 3019 (vw), 2974 (w), 2955 (w), 2914 (w), 2878 (vw), 2868 (vw), 2853 (vw), 1628 (vw), 1603 (s), 1574 (w), 1531 (vs), 1495 (vw), 1470 (w), 1443 (vs), 1408 (w), 1379 (w), 1366 (w), 1354 (w), 1335 (w), 1312 (vw), 1283 (vw), 1265 (w), 1223 (m), 1188 (w), 1171 (w), 1155 (w), 1140 (m), 1105 (w), 1080 (vw), 1024 (w), 1015 (m). ^{1}H NMR (C_6D_6, 300.21 MHz): δ = 2.15 ppm (s, 10H), 2.18 (s, 6H), 6.78 (bs, 4H), 6.89−6.97 (m, 1H), 7.02−7.07 (m, 1H), 7.12−7.16 (s, 1H), 7.20−7.23 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.58 (s, 1H), 7.57−7.58 (m, 1H), 7.69−7.72 (m, 2H), 7.90 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 2H). ^{13}C NMR (C_6D_6, 75.47 MHz): δ = 20.9 ppm, 25.7, 123.4, 123.9, 125.5, 126.0, 126.4, 126.6, 127.3, 128.4, 128.3, 128.4, 128.5, 128.7, 130.5, 130.6, 130.8, 131.8, 132.5, 132.6, 133.0, 134.3, 137.4, 141.4, 142.6, 170.0. ^{11}B NMR (C_6D_6, 96.29 MHz): δ = 10.26 ppm. HRMS(ESI): calcd for $C_{39}H_{36}BNH$ 530.3014, found 530.3005. Anal. Calcd for $C_{39}H_{36}BN$ (529.52): C, 88.46; H, 6.85; N, 2.65. Found: C, 88.09; H, 6.77; N, 2.57.

***N*,*N*′-Bis[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]benzene-1,4-diamine (7a).** A solution of 0.53 g (1.50 mmol) of compound **3** in 40 mL of dry CH_2Cl_2 was prepared. Then, 0.05 g (0.50 mmol) of *p*-phenylenediamine dissolved in 40 mL of dry CH_2Cl_2 was added slowly. The mixture was stirred for 48 h. Afterwards the crude product was heated to reflux in toluene and filtrated hot. To obtain single crystals, the solid was recrystallized from CH_2Cl_2 to give 0.30 g (0.39 mmol, 79%) as pale yellow crystals. Mp: > 300 °C. IR (neat): $\tilde{\nu}$ = 2974 cm^{-1} (w), 2959 (w), 2922 (w), 2913 (w), 1603 (s), 1578 (w), 1533 (vs), 1499 (m), 1470 (m), 1447 (s), 1412 (w), 1379 (w), 1356 (w), 1263 (w), 1229 (w), 1200 (vs), 1163 (w), 1142 (w), 1015 (m). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 317 nm (31546 cm^{-1}, 2.23 × 10^{-4} M^{-1} cm^{-1}), 370 nm (27027 cm^{-1}, sh). Fluorescence (CH_2Cl_2): λ_{em} ($\tilde{\nu}$) = 583 nm (17153 cm^{-1}), λ_{exc} = 370 nm. Φ_f: 0.04. ^{1}H NMR (THF-d_8, 399.65 MHz): δ = 1.73 ppm (s, 24H), 1.75 (s, 12H), 6.51 (bs, 8H), 6.95 (s, 4H), 7.23 (t, J = 8.0 Hz, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 8.83 (s, 2H). ^{13}C NMR (THF-d8, 100.40 MHz): δ = 21.0 ppm, 125.8, 126.3, 127.9, 130.7, 132.0, 133.5, 134.4, 138.6, 146.4, 173.0. ^{11}B NMR (THF-d_8, 128.15 MHz): δ = 10.02 ppm. HRMS(ESI): calcd for $C_{56}H_{58}B_2N_2Na$ 803.4679, found 803.4699. Anal. Calcd for $C_{56}H_{58}B_2N_2$ (780.70): C, 86.15; H, 7.49; N, 3.59. Found: C, 85.89; H, 7.44; N, 3.39. X-ray crystal structure data of **7a** can be found in the Supporting Information.

***N*,*N*′-Bis[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]naphthalene-1,5-diamine (7b).** A 0.71 g (2.00 mmol) portion of of **3** was dissolved in 20 mL of dry CH_2Cl_2. Subsequently, 0.16 g (1.00 mmol) of 1,5-diaminonaphthalene in 80 mL of dry CH_2Cl_2 was slowly added to the stirring mixture. After 18 h of stirring, the resulting yellow solid was washed with CH_2Cl_2 to give 0.64 g (0.76 mmol, 76%) as a light orange solid. Colorless crystals were obtained by recrystallization from dichloromethane. Mp: 295−296 °C. IR (neat): $\tilde{\nu}$ = 2970 cm^{-1} (m), 2961 (m), 2943 (m), 2934 (m), 2928 (m), 2920 (m), 2359 (vs), 2342 (vs), 1595 (vs), 1576 (m), 1533 (vs), 1506 (s), 1487 (w), 1466 (s), 1447 (vs), 1406 (vs), 1379 (s), 1358 (vs), 1325 (w), 1315 (w), 1267 (s), 1246 (m), 1219 (vs), 1206 (s), 1190 (m), 1177 (vs), 1159 (s), 1146 (s), 1109 (m), 1076 (m), 1063 (w), 1015 (vs). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 289 nm (34602 cm^{-1}, 2.98 × 10^{-4} M^{-1} cm^{-1}), 351 nm (28490 cm^{-1}, 1.20 × 10^{-4} M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{em} ($\tilde{\nu}$) = 572 nm (17483 cm^{-1}), λ_{exc} = 370 nm. Φ_f: 0.04. ^{1}H NMR (C_6D_6, 399.65 MHz): δ = 2.02 ppm (bs, 24H), 2.10 (bs, 12H), 6.65−6.71 (m, 11H), 6.97 (d, J = 8.4 Hz, 2H), 7.03 (t, J = 7.2 Hz, 3H), 7.22 (d, J = 7.2 Hz, 2H), 7.40 (s, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H). ^{13}C NMR (C_6D_6, 100.40 MHz): δ = 20.8 ppm, 24.8, 122.3, 122.4, 124.9, 125.8, 126.6, 128.4, 130.0, 130.1, 130.4, 130.5, 132.5, 133.1, 134.6, 137.6, 141.1, 141.9, 172.0. ^{11}B NMR (C_6D_6, 128.15 MHz): δ = 12.66 ppm. HRMS(ESI): calcd for $C_{60}H_{60}B_2N_2H$ 831.5016, found 831.5021.

***N*,*N*′-Bis[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]naphthalene-1,4-diamine (7c).** A 0.08 g (0.50 mmol) portion of 1,4-diaminonapthalene was dissolved in 20 mL of dry CH_2Cl_2. The mixture was slowly added to a solution of 0.35 g (1.00 mmol) of **3** in 80 mL of dry CH_2Cl_2. After addition, the solution was stirred for 17 h. Subsequently, the crude product was purified by recycling GPC (in toluene) to give 0.41 g (0.49 mmol, 98%) of **7c** as a yellow solid. Mp: 234−235 °C. IR (neat): $\tilde{\nu}$ = 2963 cm^{-1} (m), 2940 (m), 2920 (m), 2361 (m), 2340 (m), 1703 (w), 1601 (s), 1578 (m), 1535 (vs), 1445 (vs), 1412 (m), 1379 (m), 1358 (m), 1267 (m), 1233 (m), 1211 (vs), 1163 (m), 1144 (m), 1103 (w), 1059 (w), 1016 (m). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 289 nm (34602 cm^{-1}, 2.57 × 10^{-4} M^{-1} cm^{-1}), 370 nm (27027 cm^{-1}, 1.19 × 10^{-4} M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{em} ($\tilde{\nu}$) = 571 nm (17513 cm^{-1}), λ_{exc} = 370 nm. Φ_f: 0.03. ^{1}H NMR (C_6D_6, 399.65 MHz): δ = 2.09 ppm (bs, 12H), 2.12 (bs, 24H), 6.68 (bs, 8H), 6.80−6.83 (m, 2H), 7.00−7.07 (m, 4H), 7.12−7.16 (m, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.58 (s, 2H), 7.58−7.61 (m, 2H), 7.79 (d, J = 7.2 Hz, 2H). ^{13}C NMR (C_6D_6, 100.40 MHz): δ = 20.8 ppm, 25.4, 120.0, 122.5, 126.3, 126.4, 126.9, 128.6, 129.3, 129.9, 130.1, 130.4, 132.6, 133.0, 135.0, 137.7, 141.5, 142.6, 171.6. ^{11}B NMR (C_6D_6, 128.15 MHz): δ = 16.17 ppm. HRMS(ESI): calcd for $C_{60}H_{60}B_2N_2K$ 869.4575, found 869.4582. Anal. Calcd for $C_{60}H_{60}B_2N_2$ (830.75): C, 86.75; H, 7.28; N, 3.37. Found: C, 86.00; H, 7.42; N, 3.21.

***N*,*N*′-Bis[1-(2-(dimesitylboranyl)phenyl)meth-(*E*)-ylidene]-9*H*-fluorene-2,7-diamine (7d).** A 0.29 g (1.50 mmol) portion of 2,7-diaminofluorene was dissolved in 20 mL of dry CH_2Cl_2 and added slowly to a stirred solution of 1.07 g (3.00 mmol) of **3** in 80 mL of dry CH_2Cl_2. After 12 h, the reaction mixture was filtrated and the crude mixture was purified by GPC to give 1.25 g (1.44 mmol, 96%) as yellow crystals. Mp: 194–195 °C. IR (neat): $\tilde{\nu}$ = 2924 cm^{-1} (w), 2914 (w), 1605 (s), 1584 (s), 1557 (s), 1535 (s), 1514 (w), 1464 (s), 1433 s), 1416 (m), 1358 (m), 1333 (w), 1314 (w), 1306 (w), 1296 (w), 1263 (m), 1200 (s), 1175 (s), 1150 (s), 1111 (w), 1096 (w), 1038 (w), 1020 (w). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 325 nm (30769 cm^{-1}, sh), 354 (28249 cm^{-1}, 2.73 × 10^{-4} M^{-1} cm^{-1}). Fluorescence (CH_2Cl_2): λ_{em} ($\tilde{\nu}$) = 569 nm (17575 cm^{-1}), λ_{exc} = 370 nm. Φ_f: 0.10. ^1H NMR (C_6D_6, 399.65 MHz): δ = 2.14 ppm (s, 24H), 2.20 (s, 12H), 3.14 (s, 2H, CH_2), 6.81 (bs, 8H), 6.99–7.00 (m, 4H), 7.03–7.09 (m, 4H), 7.14–7.16 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 2H), 7.90–7.92 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (C_6D_6, 100.40 MHz): δ = 20.8 ppm, 25.6, 36.5, 119.8, 121.8, 124.1, 125.5, 125.7, 126.4, 128.4, 128.6, 129.3, 130.5, 131.7, 133.1, 127.8, 134.3, 137.3, 140.6, 141.4, 143.9, 144.9, 169.6. ^{11}B NMR (C_6D_6 128.15 MHz): δ = 9.29 ppm. HRMS(ESI): calcd for $C_{63}H_{62}B_2N_2Na$ 891.4992, found 891.5018. Anal. Calcd for $C_{63}H_{62}B_2N_2$ (868.80): C, 87.09; H, 7.19; N, 3.22. Found: C, 87.34; H, 7.46; N, 2.91.

2-[2-(Dimesitylboranyl)phenyl]-1*H*-perimidine (9). A 0.71 g (2.00 mmol) portion of compound **3** was dissolved in 20 mL of dry CH_2Cl_2. Then, 0.16 g (1.00 mmol) of 1,8-diaminonaphthalene in 20 mL of dry CH_2Cl_2 was added slowly. Recrystallization from CH_2Cl_2 afforded 0.31 g (0.62 mmol, 62%) as orange crystals. Mp: 270–271 °C. IR (neat): $\tilde{\nu}$ = 3530 cm^{-1} (vw), 3412 (w), 3163 (vw), 3103 (w), 3073 (w), 3065 (w), 3055 (w), 3017 (w), 2968 (w), 2918 (w), 2866 (w), 2857 (w), 2361 (w), 2342 (vw), 2326 (vw), 1643 (m), 1605 (s), 1576 (m), 1560 (m), 1537 (s), 1493 (m), 1472 (m), 1449 (m), 1412 (m), 1377 (m), 1369 (m), 1360 (m), 1327 (w), 1312 (m), 1277 (m), 1269 (m), 1236 (w), 1215 (w), 1200 (w), 1188 (w), 1169 (w), 1153 (m), 1138 (w), 1124 (w), 1103 (w), 1094 (w), 1076 (w), 1069 (w), 1049 (w), 1036 (m), 1016 (m). UV/vis (CH_2Cl_2): λ_{abs} ($\tilde{\nu}$, ε) = 272 nm (36765 cm^{-1}, 1.60 × 10^{-4} M^{-1} cm^{-1}), 325 nm (30770 cm^{-1}, 1.20 × 10^{-4} M^{-1} cm^{-1}), 339 nm (29499 cm^{-1}, 1.43 × 10^{-4} M^{-1} cm^{-1}). ^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 2.12 ppm (s, 12H), 2.17 (s, 6H), 6.67 (bs, 4H), 6.69–6.77 (m, 1H), 7.09–7.34 (m, 6H), 7.43 (td, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 8.49 (bs, 1H). ^{13}C NMR (CD_2Cl_2, 75.47 MHz): δ = 20.9 ppm, 25.2, 105.8, 114.0, 121.2, 122.3, 122.4, 125.6, 127.7, 128.8, 129.2, 130.0, 130.5, 133.2, 133.7, 134.3, 135.8, 138.4, 142.2. ^{11}B NMR (CD_2Cl_2, 96.29 MHz): δ = 4.25 ppm. HRMS(ESI): calcd for $C_{35}H_{33}BN_2H$ 493.2810, found 493.2796. Anal. Calcd for $C_{35}H_{33}BN_2$ (492.46): C, 85.36; H, 6.75; N, 5.69. Found: C, 85.23; H, 6.72; N, 5.61. The X-ray crystal structure data of **9** can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra for the new compounds; time-dependent spectra of NMR experiments; fluorescence measurements; graphics of the crystal structures showing thermal ellipsoids with 50% probability; optimized Cartesian coordinates (B3LYP/6-31G(d) and SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE energies for the calculated structures; details of TD-DFT calculations; Wiberg bond indices obtained from NBO calculations (B3LYP/6-311G(d,p)); NICS calculations (B3LYP/6-311+G(d,p)). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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