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Triplet-Energy Control of Polycyclic Aromatic Hydrocarbons by BN Replacement: Development of Ambipolar Host Materials for Phosphorescent Organic Light-Emitting Diodes

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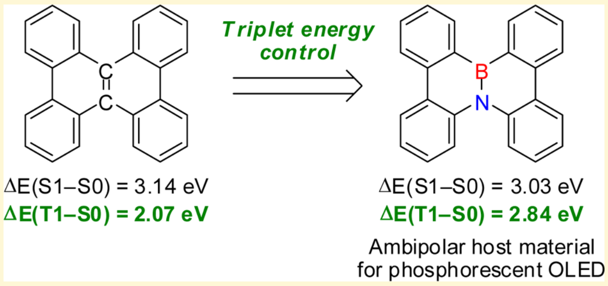
Ⓢ *Supporting Information*



ABSTRACT: In this work, we achieved the triplet-energy control of polycyclic aromatic hydrocarbons (PAHs) by replacing the Carbon–Carbon (CC) unit with a Boron–Nitrogen (BN) unit. Time-dependent density functional theory calculations suggested that the insertion of the BN unit may cause localization of the singly occupied molecular orbitals 1 and 2 (SOMO1/SOMO2) in the triplet state, which in turn can reduce the exchange interaction and dramatically increase the high singlet–triplet excitation energy (E_T). The PAH containing the BN unit, 4b-aza-12b-boradibenzo[*g,p*]chrysene, showed a large E_T value and ambipolar carrier-transport abilities. The introduction of a phenyl substituent on 4b-aza-12b-boradibenzo[*g,p*]chrysene slightly reduced the E_T values and the carrier-transport abilities, but increased the glass-transition temperatures. On the basis of these findings, we successfully built phosphorescent organic light-emitting diodes using the BN compounds as host materials, which exhibit a superior performance over the device using a representative host material, 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl, not only in terms of efficiency but also in terms of device lifetime. This study demonstrated the potential of BN-embedded polycyclic aromatics in organic electronics and showed a novel strategy to achieve triplet-energy control of aromatic compounds.

■ INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important class of materials that are used in organic electronics,[1] dyes,[2] batteries,[3] liquid-crystal displays,[4] and photoresponsive materials.[5] In particular, substantial efforts have been devoted to building organic field-effect transistors based on PAHs[6] because of their excellent charge-transport properties and redox stability. On the other hand, organic light-emitting diodes (OLEDs)[7] using PAHs as charge-transport materials have not received much attention.[8] This may be due to their small band gap (E_g) and/or to their poor morphological stability, which can reduce the efficiency and lifetime of devices.

Recently, a lot of studies focused on OLEDs using phosphorescent emitting materials (PHOLEDs), which can show much higher internal quantum efficiency than those using fluorescent ones because of capability of emission from the triplet exciton.[9] To achieve an optimum efficiency, ambipolar host materials with higher singlet–triplet excitation energy (E_T) than the phosphorescent emitting materials are required for the emitting layer.[9c,d] In this work, we explored the hypothesis that replacement of the CC unit of PAHs by an isoelectronic BN unit[10] would localize the singly occupied molecular orbitals (SOMO1 and SOMO2) in the triplet state (T1).[11] This in turn could suppress the exchange interaction between SOMOs in the T1 state and increase E_T. As shown in Figure 1, dibenzo[*g,p*]chrysene **1** was chosen as a PAH with a wide energy gap.[12] Time-dependent density functional theory (TD-DFT) calculations showed that the isoelectronic 4b-aza-12b-boradibenzo[*g,p*]chrysene **2** is characterized by a significant larger E_T (3.03 eV) than that of **1** (2.25 eV); in contrast, the singlet–singlet excitation energy (E_s) was found to be the same for both (E_S = 3.49 eV).[13] This finding can be explained if one

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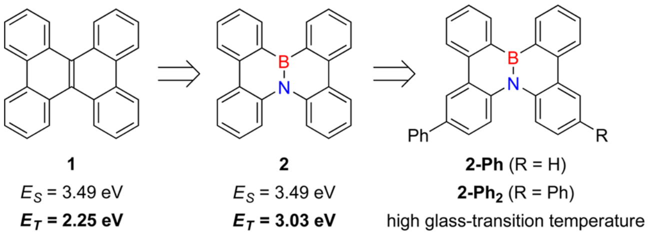


Figure 1. Design of ambipolar host materials for phosphorescent organic light-emitting diodes. Singlet−singlet and singlet−triplet excitation energies (E_S, E_T) at the ground-state (S0) structure were calculated with TD-DFT at the B3LYP/6-31G(d) level of theory.

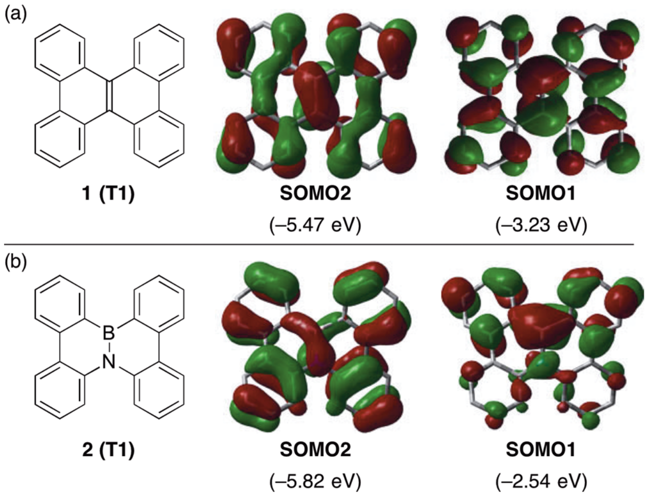


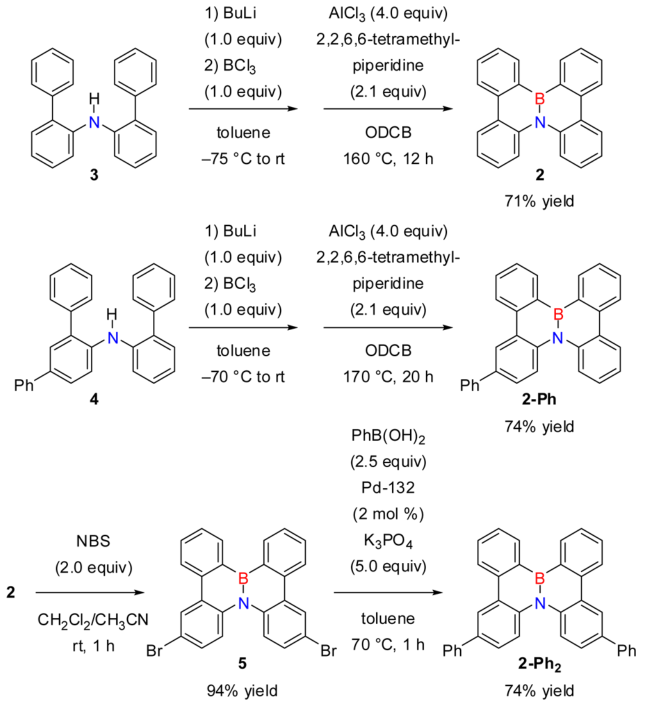
Figure 2. Singly occupied Kohn−Sham orbitals of **1** (a) and **2** (b) in the T1 state calculated at the UB3LYP/6-31G(d) level of theory. Orbital energies are shown in parentheses.

compares the localized SOMO1/SOMO2 of **2** in the T1 state with those of **1** (Figure 2). In particular, SOMO1 of **2** is localized on the boron atom, ortho and para positions to the boron atom, and meta position to the nitrogen atom; SOMO2 is localized on the nitrogen atom, meta position to the boron atom, and ortho and para positions to the nitrogen atom.[13] To achieve high glass-transition temperature (T_g), we have synthesized phenylated derivatives **2-Ph** and **2-Ph$_2$**. This allowed us to produce highly efficient PHOLEDs with a sufficiently long lifetime.

■ RESULTS AND DISCUSSION

Synthesis of 4b-Aza-12b-boradibenzo[*g*,*p*]chrysene Derivatives. The synthesis of the derivatives is illustrated in Scheme 1. 4b-Aza-12b-boradibenzo[*g*,*p*]chrysene **2** and mono-phenylated derivative **2-Ph** were synthesized under optimized conditions[14] from the corresponding diarylamines **3** and **4** via a tandem electrophilic arene borylation in 71% and 74% yield, respectively. The electrophilic bromination of **2** was accomplished by treatment with 2 equiv of *N*-bromosuccinimide (NBS) to give dibrominated derivative **5** in 94% yield. In the presence of 2 mol % dichlorobis(*p*-dimethylaminophenyldi-*tert*-butylphosphine)palladium(II) (Pd-132) and 5 equiv of K_3PO_4, the succeeding Suzuki−Miyaura coupling with phenylboronic acid smoothly took place to give coupling product **2-Ph$_2$** in 74% yield.

Scheme 1. Synthesis of 2, 2-Ph, and 2-Ph$_2$



Spectroscopic Measurements. To estimate E_S and E_T of **1** and **2**, a set of spectroscopic measurements was carried out as shown in Figure 3. The UV−visible absorption spectrum of **2**

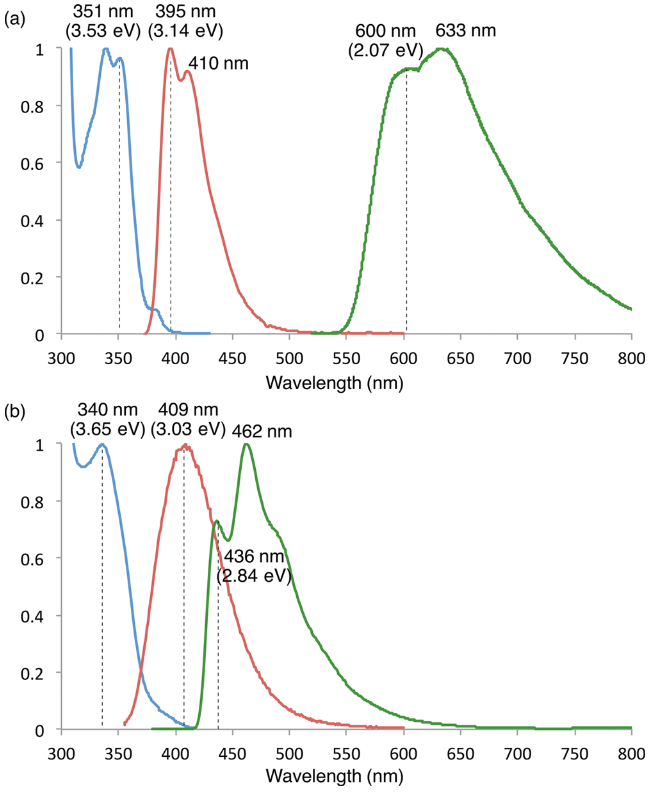


Figure 3. Standardized absorption spectra (blue line, 0.02 mM in CH_2Cl_2), fluorescence spectra (red line, 0.02 mM in CH_2Cl_2), and phosphorescence spectra (green line, saturated EtOH solution at 77 K) of (a) **1** and (b) **2**.

showed a relatively strong absorption band, corresponding to a $\pi-\pi^*$ transition, with a maximum at 340 nm (log ε = 4.06), to compare with that of **1** at 351 nm (log ε = 4.21). When the CC unit was replaced with the BN unit, a small blue shift in the UV−visible absorbance was observed, probably due to an insufficient double-bond character of the BN bond. The photoluminescence emissions of **1** and **2** showed vibronic fine structures at 395 and 410 nm and a maximum at 409 nm at room temperature, respectively. As predicted by the TD-DFT calculations, the BN replacement does not significantly change the fluorescence spectrum, but causes a remarkable blue shift in the phosphorescence spectrum. In particular, at 77 K the photoluminescence emissions of **1** and **2** showed maxima at 600 and 633 nm and at 436 and 462 nm, respectively. Thus, the combination of our experimental and computational data suggested that the replacement of CC unit with the BN unit hardly changes E_S, but significantly affects E_T through suppression of the exchange interaction between SOMOs.

Since **2** showed a high E_T value (2.84 eV), we compared its phosphorescence spectra with those of 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) and Ir(ppy)$_3$, which are considered in this work as a reference host material and a reference green dopant for PHOLEDs, respectively. As shown in Figure 4, **2** has a larger E_T than those of CBP and Ir(ppy)$_3$ (2.64 and 2.50 eV), confirming its potential as a host material for a PHOLED. Similarly, phenylated derivatives, **2-Ph** and **2-Ph$_2$**, also showed sufficiently large E_T values (2.70 and 2.69 eV).

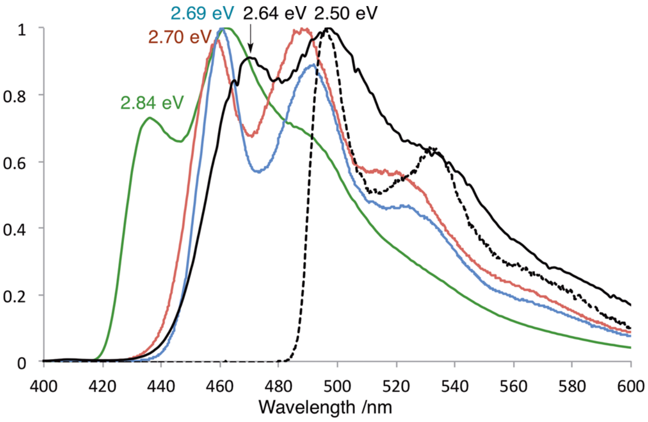


Figure 4. Standardized phosphorescence spectra of **2** (green line), **2-Ph** (red line), **2-Ph$_2$** (blue line), CBP (black line), and Ir(ppy)$_3$ (black dotted line) in EtOH at 77 K.

Charge Mobility and Photoelectron Spectroscopy Measurements. To perform the time-of-flight (TOF) measurements, we prepared films (thickness: 6.0−9.9 μm) of compounds **2**, **2-Ph**, and **2-Ph$_2$** and of the carbon analog **1** by vacuum deposition under 5.0 × 10^{-3} Pa. The carrier-transport properties of the films were then evaluated at room temperature and with electric fields of 5.0−5.8 × 10^5 V cm^{-1}. It was found that all the compounds containing the BN unit have ambipolar carrier-transport abilities (Table 1). In particular, the parent compound **2** showed the highest hole (4.1 × 10^{-4} cm^2 V^{-1} s^{-1}) and electron (2.3 × 10^{-3} cm^2 V^{-1} s^{-1}) mobility,[15] for example, 3 times larger than those of **1** (1.2 and 7.5 × 10^{-4} cm^2 V^{-1} s^{-1}, respectively). The ionization potentials (I_p) and optical band gaps (E_g) of the vacuum-deposited films were also determined. I_p of the parent compound **2** was estimated to be 6.01 eV, which is comparable to that of CBP. The introduction of one or two phenyl groups resulted in a lower I_p, 5.81 and 5.64 eV, respectively, possibly due to the expanded π-conjugation. For the same reason, **2** showed the highest E_g (3.29 eV), in agreement with the trend observed for E_T. Owing to their high T_g, all the derivatives form stable amorphous films, which were determined by X-ray diffraction analysis..

Phosphorescent Organic Light-Emitting Diodes. Since the compounds containing the BN unit showed promising ambipolar carrier-transport abilities and large E_T values, they were used as host materials, together with Ir(ppy)$_3$ as a green dopant, to build heterojunction PHOLEDs (Figures 5 and 6,

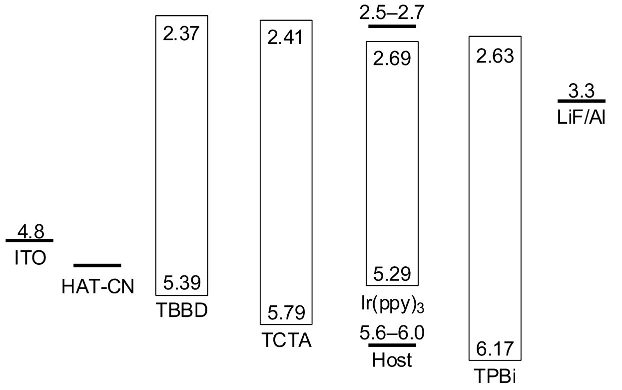


Figure 5. Energy diagram of the materials of PHOLEDs (in eV). The emissive layer consists of 10 wt % of Ir(ppy)$_3$ and 90 wt % of one of the five host materials. ITO = indium tin oxide. HAT-CN = dipyrazino[2,3-*f*:2′,3′-*h*]quinoxaline-2,3,6,7,10,11-hexacarbonit rile. TBBD = N^4,N^4,$N^{4\prime}$,$N^{4\prime}$-tetra([1,1′-biphenyl]-4-yl)-[1,1′-biphenyl]-4,4′-diamine. TCTA = tris(4-(9*H*-carbazoyl-9-yl)phenyl)amine. TPBi = 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene.

Table 1. Physical Properties of 2, 2-Ph, 2-Ph$_2$, 1, and CBP

	μ_h[a]	μ_e[a]	I_p[b]	E_g[c]	E_a[d]	E_T[e]	T_g[f]
1	1.2 × 10^{-4}	7.5 × 10^{-4}	5.84	3.13	2.71	2.05	74
2	4.1 × 10^{-4}	2.3 × 10^{-3}	6.01	3.29	2.72	2.84	71
2-Ph	7.9 × 10^{-5}	3.2 × 10^{-3}	5.81	3.21	2.60	2.70	99
2-Ph$_2$	1.7 × 10^{-4}	3.2 × 1010^{-4}	5.64	3.15	2.49	2.69	124
CBP	1 × 10^{-3}	1 × 10^{-3}	6.02	3.45	2.57	2.64	85

[a] Hole and electron mobility (cm^2 V^{-1}s^{-1}) of the vacuum-deposited thin films were determined by the time-of-flight (TOF) method. See ref 15b for CBP. [b] Ionization potentials (eV) were determined by photoelectron spectroscopy in air (PESA). [c] Optical band gaps (eV) were estimated from onset wavelengths of the UV/vis absorption spectra of the vacuum-deposited thin films. [d] Electron affinities (eV) were calculated from I_p and E_g. [e] Triplet energies (eV) were estimated from the emission maxima of the phosphorescence spectra of saturated EtOH solutions at 77 K. [f] Glass-transition temperatures (°C) were determined by differential scanning calorimetry (DSC).

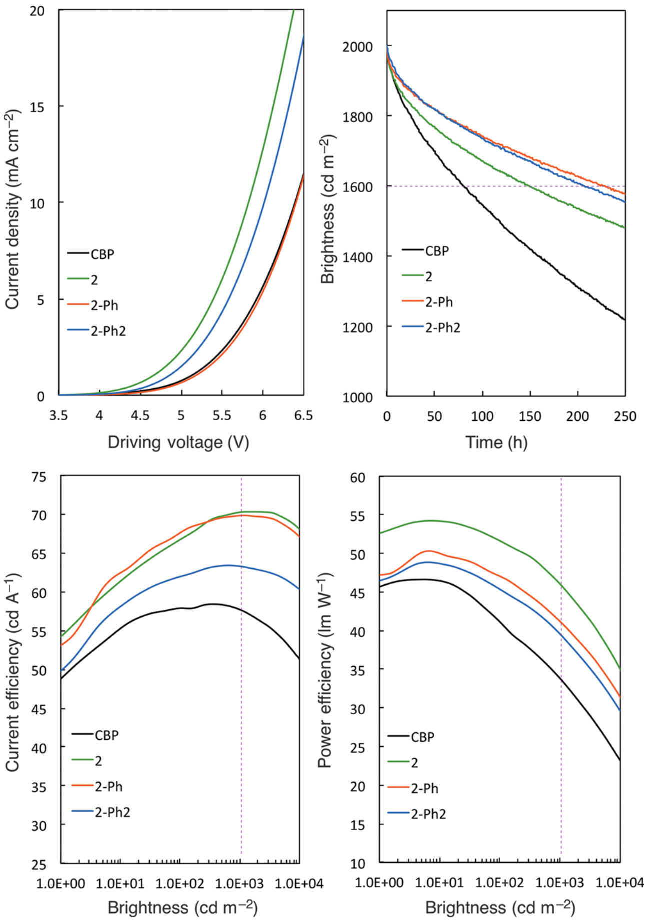


Figure 6. Characteristics of PHOLED using CBP (black line), **2** (green line), **2-Ph** (red line), and **2-Ph$_2$** (blue line) as an ambipolar host material.

Table 2). While the device containing the carbon analog **1** exhibited a very poor performance, those containing **2**, **2-Ph**, and **2-Ph$_2$** exhibited a superior performance over the CBP device in terms of the driving voltage (V_{1000}), current efficiency ($\eta_{c,1000}$), power efficiency ($\eta_{p,1000}$), and the external quantum efficiency (EQE$_{1000}$). Such a small driving voltage can be attributed to the lower I_p or to the higher E_a of the BN compounds, which can reduce the contact resistance between the carrier transport and the emissive layers. The better performance of the BN compounds in terms of EQE may also be explained considering their large E_T values, which can prevent back-energy transfer from the dopant. In addition, the lifetime of OLEDs was also measured at the initial brightness of 2000 cd/m^2. The devices obtained from **2** showed longer lifetimes than CBP (148 and 80 h, respectively), probably owing to its redox stability. The introduction of one or two phenyl groups significantly improved the lifetime (226 and 206 h, respectively). This is possibly caused by their large T_g, 99 and 124 °C, respectively. Thus, these measurements suggested that the compounds containing BN may be suitable as a new class of ambipolar host materials for PHOLEDs.

Table 2. Properties of the 10 wt % Ir(ppy)$_3$-Doped PHOLEDs

host	V_{1000}[a]	$\eta_{c,1000}$[a]	$\eta_{p,1000}$[a]	EQE$_{1000}$[a]	LT80[b]
1	(7.5)[c]	(0.014)[c]	(0.006)[c]	(0.008)[c]	
2	4.8	70.2	46.1	19.5	148
2-Ph	5.3	69.8	41.3	19.3	226
2-Ph$_2$	5.0	63.3	39.6	17.4	206
CBP	5.4	57.7	33.9	16.0	80

[a] Driving voltage (V), current efficiency (cd A^{-1}), power efficiency (lm W^{-1}), and external quantum efficiency (%) at 1000 cd m^{-2}. [b] Time (h) when brightness (L0 = 2000 cd m^{-2}) decreases to 80% (1600 cd^{-2}). [c] Data at 10 cd m^{-2}.

■ CONCLUSIONS

In this work, we have successfully synthesized 4b-aza-12b-boradibenzo[*g*,*p*]chrysene derivatives; by means of time-of-flight and phosphorescent measurements, we confirmed their ambipolar carrier-transport abilities and their high singlet−triplet excitation energy. Notably, phosphorescent organic light-emitting diodes that employed the synthesized 4b-aza-12b-boradibenzo[*g*,*p*]chrysene derivatives as host materials showed higher efficiencies and longer device lifetimes than those with CBP, a representative host material. Density functional theory calculations suggested that the replacement of the central CC unit of boradibenzo[*g*,*p*]chrysene with a BN unit causes the localization of singly occupied molecular orbitals in the triplet state and reduces the exchange interaction between SOMOs, thereby increasing the singlet−triplet excitation energy dramatically. We believe that our results clearly indicated a new strategy to achieve the triplet-energy control of aromatic compounds, a crucial outcome that can provide not only a new class of ambipolar host materials but also thermally activated delayed fluorescence materials.

■ EXPERIMENTAL SECTION

General Procedure. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Organic solutions were concentrated by rotary evaporation at ca. 30−400 mm Hg. Gel permeation chromatography was performed on a JAIGEL-1H and 2H (20 mm i.d.) with an LC-9204 (Japan Analytical Industry Co., Ltd.). Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on JEOL ECS400 (400 MHz) NMR spectrometers. Proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the tetramethylsilane (δ 0) or *o*-dichlorobenzene-d_4 (δ 7.20). ^{13}C NMR spectra were recorded at 101 MHz. Carbon chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of CDCl$_3$ (δ 77.0). ^{11}B NMR spectra were recorded at 128 MHz. Boron chemical shift values are reported in parts per million (ppm, δ scale) and are referenced to the external standard boron signal of BF$_3$·Et$_2$O (δ 0). Data are presented as chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, and br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (italic). IR spectra were recorded on an ATR-FTIR spectrometer (FT/IR-Spectrum One, Perkin-Elmer). Characteristic IR absorptions are reported in cm^{-1}. Melting points were recorded on a Yanaco MP-500 V. High-resolution mass spectra (HRMS) were obtained using the electron impact (EI) method with a JEOL JMS-700, JMS-SX102A. UV−visible absorption spectra were measured with a JASCO V-560 and V-570. Fluorescence spectra were collected with a HORIBA Scientific FluoroMax-4 and a Hitachi High-Tech F-7000. The purity of isolated compounds was determined by GC analysis on a Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, InertCap 1MS (GL Sciences Inc., 30 m × 0.25 mm i.d., 0.25 μm film thickness) and/or ^{1}H NMR analyses. High glass-transition temperatures were measured with a Perkin-Elmer Diamond DSC.

4b-Aza-12b-boradibenzo[*g*,*p*]chrysene (2). A solution of butyllithium in hexane (29.3 mL, 1.60 M, 46.9 mmol) was added slowly to a solution of **3** (15.0 g, 46.9 mmol) in toluene (250 mL) at −75 °C under nitrogen. After the reaction mixture was stirred at 0 °C for 1 h, a solution of boron trichloride in heptane (46.9 mL, 1.0 M, 46.9 mmol) was added at −75 °C. After being stirred at room temperature for 8 h, the solvent was removed in vacuo, and the reaction mixture was added to a solution of aluminum trichloride (25.0 g, 188 mmol) and 2,2,6,6-tetramethylpiperidine (13.8 g, 98.5 mmol) in *o*-dichlorobenzene (300 mL) at room temperature. After stirring at 160 °C for 12 h, 1,4-diazabicyclo[2.2.2]octane (21.0 g, 188 mmol) was added. The reaction mixture was filtered with a pad of Celite. After the solvent was removed in vacuo, the crude product was purified by alumina column chromatography [eluent: toluene/AcOEt/Et_3N = 90/10/1 (volume ratio)] and reprecipitation from mixture of ethyl acetate and heptane to obtain the title compound (10.9 g, 71% yield) as a white-yellow powder. IR (neat): cm^{-1} 3056 (Ar−H), 1598, 1575, 1485, 1445, 1430, 1319, 1300, 1286, 1259, 1238, 1166, 1134, 1049, 935, 744, 723, 624, 587, 558. mp 226.5−227.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (td, *J* = 1.2, 7.6 Hz, 2H, NCCCHC*H*), 7.36 (td, *J* = 1.6, 7.6 Hz, 2H, NCCHC*H*), 7.60 (td, *J* = 0.8, 7.6 Hz, 2H, BCCHC*H*), 7.77 (td, *J* = 1.6, 7.6 Hz, 2H, BCCCHC*H*), 8.10 (dd, *J* = 1.2, 7.6 Hz, 2H, NCC*H*), 8.36 (dd, *J* = 1.6, 7.6 Hz, 2H, NCCC*H*), 8.41 (d, *J* = 7.6 Hz, 2H, BCCC*H*), 8.68 (d, *J* = 7.6 Hz, 2H, BCC*H*). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.4 (2C), 123.0 (4C), 125.5 (2C), 126.8 (2C), 127.5 (4C), 131.1 (2C), 132.5 (br, 2C, CBC), 135.6 (2C), 137.1 (2C), 138.8 (2C). ^{11}B NMR ($CDCl_3$, 128 MHz): δ 35.6. HRMS(EI) *m*/*z* $[M]^+$ calcd for $C_{24}H_{16}NB$, 329.1376; observed, 329.1380. Anal. Calcd for $C_{24}H_{16}NB$: C, 87.56; H, 4.90; N, 4.25. Found: C, 87.79; H, 5.14; N, 4.31.

2-Phenyl-4b-aza-12b-boradibenzo[*g*,*p*]chrysene (2-Ph). A solution of butyllithium in hexane (29.3 mL, 1.60 M, 46.9 mmol) was added slowly to a solution of *N*-([1,1′-biphenyl]-2-yl)-[1,1′:3′,1″-terphenyl]-4-amine **4** (18.6 g, 46.8 mmol) in toluene (250 mL) at −70 °C under argon. After 1 h, the reaction mixture was stirred at 0 °C for 1 h. A solution of boron trichloride in heptane (46.9 mL, 1.0 M, 46.9 mmol) was added at −60 °C. After being stirred at room temperature, the solvent was removed in vacuo, and the reaction mixture was added to a solution of aluminum trichloride (25.0 g, 188 mmol) and 2,2,6,6-tetramethylpiperidine (13.9 g, 98.4 mmol) in *o*-dichlorobenzene (300 mL). After the solution was stirred at 170 °C for 20 h, a suspension of sodium carbonate (10.0 g) and sodium acetate (31.0 g) in ice water was poured. The extracted organic layer was filtered with a pad of Celite. After the solvent was removed in vacuo, the crude product was purified by alumina column chromatography (eluent: toluene/Et_3N = 100/1) and trituration with reprecipitation from a mixture of ethyl acetate and heptane to obtain the title compound (14.0 g, 74% yield). IR (neat): cm^{-1} 3055 (Ar−H), 1599, 1483, 1442, 1320, 1256, 1125, 1049, 941, 881, 832, 781, 747, 724, 692, 649, 620. mp: 214.8−216.4 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (td, *J* = 1.2 Hz, 7.6 Hz, 1H, NCCCHC*H*), 7.37−7.41 (m, 2H, NCCHC*H*CH, $(CHCH)_2CH$), 7.50 (t, *J* = 8.0 Hz, 2H, $(CHCH)_2CH$), 7.59 (dd, *J* = 2.0 Hz, 8.8 Hz, 1H, NCCHC*H*CPh), 7.60−7.63 (m, 2H, BCCHC*H*), 7.73 (dd, *J* = 1.2 Hz, 8.0 Hz, 2H, $(CHCH)_2CH$), 7.78 (td, *J* = 1.6 Hz, 8.0 Hz, 1H, BCCCHC*H*), 7.79 (td, *J* = 1.2 Hz, 8.0 Hz, 1H, BCCCHC*H*(Ph-side)), 8.13 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, NCC*H*CHCH), 8.16 (d, *J* = 8.8 Hz, 1H, NCC*H*CHCPh), 8.37 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H, NCCC*H*CH), 8.42 (d, *J* = 8.0 Hz, 1H, BCCC*H*), 8.48 (d, *J* = 8.0 Hz, 1H, BCCC*H*(Ph-side)), 8.56 (d, *J* = 2.0 Hz, 1H, NCCC*H*CPh), 8.69 (br, d, *J* = 7.2 Hz, 2H, BCC*H*). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.4, 121.8, 123.0 (2C), 123.1, 124.0, 125.5, 125.7, 126.8 (2C), 126.9, 127.1 (2C), 127.2, 127.5, 127.7, 128.9 (2C), 131.1 (2C), 132.5 (br, 2C, CBC), 135.6, 135.6, 135.8, 136.4, 137.0, 138.8 (2C), 140.9. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 35.2. Anal. Calcd for $C_{30}H_{20}NB$: C, 88.90; H, 4.97; N, 3.46. Found: C, 89.20; H, 5.12; N, 3.48.

2,7-Dibromo-4b-aza-12b-boradibenzo[*g*,*p*]chrysene (5). *N*-Bromosuccinimide (0.178 g, 1.00 mmol) was added to a solution of **2** (0.165 g, 0.50 mmol) in dichloromethane (6.0 mL) and acetonitrile (2.0 mL). After the mixture was stirred at room temperature for 1 h, the solvent was removed in vacuo. The residue was triturated with acetonitrile to afford the title compound (0.228 g, 94% yield) as a colorless powder. IR (neat): cm^{-1} 3046 (Ar−H), 1598, 1570, 1554, 1542, 1482, 1436, 1392, 1325, 1297, 1281, 1260, 1236, 1194, 1162, 1097, 1047, 1013, 937, 886, 876, 862, 833, 811, 781, 756, 744, 720, 669, 643, 630, 620, 605. mp: 244−245 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (dd, *J* = 2.3, 9.0 Hz, 2H, NCCHC*H*), 7.62 (td, *J* = 0.8, 7.4 Hz, 2H, BCCHC*H*), 7.78 (td, *J* = 1.2, 7.6 Hz, 2H, BCCHCHC*H*), 7.82 (d, *J* = 9.0 Hz, 2H, NCC*H*), 8.30 (d, *J* = 7.4 Hz, 2H, BCCC*H*), 8.42 (d, *J* = 2.3 Hz, 2H, NCCC*H*), 8.63 (dd, *J* = 1.2, 7.4 Hz, 2H, BCC*H*). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 116.2 (2C), 122.8 (2C), 123.1 (2C), 127.5 (2C), 128.3 (2C), 129.5 (2C), 129.6 (2C), 131.4 (2C), 132.4 (br, 2C, CBC), 135.6 (2C), 135.7 (2C), 137.5 (2C). ^{11}B NMR ($CDCl_3$, 128 MHz): δ 35.5. Anal. Calcd for $C_{24}H_{14}NBBr_2$: C, 59.19; H, 2.90; N, 2.88. Found: C, 59.13; H, 3.08; N, 2.93.

2,7-Diphenyl-4b-aza-12b-boradibenzo[*g*,*p*]chrysene (2-Ph$_2$). Pd-132 (20.0 mg, 0.028 mmol) was added to a solution of **5** (0.700 g, 1.4 mmol), phenylboronic acid (0.430 g, 3.5 mmol), and tripotassium phosphate (1.49 g, 7.0 mmol) in toluene (15 mL). After the mixture was stirred at 70 °C for 1 h, the resulting solution was cooled to room temperature and water added to quench the reaction. The organic materials were extracted with toluene, and the solvent was removed in vacuo. The crude product was purified by Al_2O_3 column chromatography (eluent: toluene/Et_3N = 99/1) and washed by heptane and ethyl acetate. The residue was purified by recrystallization (heptane/chlorobenzene) to obtain the title compound (0.510 g, 74%). IR (neat): cm^{-1} 3053 (Ar−H), 3026 (Ar−H), 1599, 1566, 1543, 1504, 1482, 1440, 1396, 1335, 1321, 1283, 1254, 1238, 1200, 1178, 1151, 1125, 1103, 1074, 1052, 1028, 1008, 978, 941, 910, 885, 837, 826, 753, 730, 707, 669, 637, 628, 617, 609. mp: 269−271 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (tt, *J* = 1.6, 7.4 Hz, 2H, CHCHC*H*CHCH), 7.50 (t, *J* = 7.4 Hz, 4H, CHC*H*CHC*H*CH), 7.59−7.64 (m, 4H), 7.73 (d, *J* = 7.4 Hz, 4H, C*H*CHCHCHC*H*), 7.79 (td, *J* = 0.8, 7.8 Hz, 2H, BCCHCHC*H*), 8.18 (d, *J* = 8.2 Hz, 2H, NCC*H*), 8.49 (d, *J* =

7.8 Hz, 2H, BCCC*H*), 8.57 (d, *J* = 2.0 Hz, 2H, NCCC*H*), 8.70 (d, *J* = 7.4 Hz, 2H, BCC*H*). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.8 (2C), 123.1 (2C), 124.0 (2C), 125.7 (2C), 127.0 (2C), 127.1 (4C), 127.2 (2C), 127.8 (2C), 128.9 (4C), 131.1 (2C), 132.6 (br, 2C, CBC), 135.7 (2C), 135.9 (2C), 136.4 (2C), 138.8 (2C), 140.9 (2C). ^{11}B NMR ($CDCl_3$, 128 MHz): δ 36.0. Anal. Calcd for $C_{36}H_{24}NB$: C, 89.82; H, 5.03; N, 2.91. Found: C, 90.04; H, 5.14; N, 2.89.

Fabrication of PHOLEDs and Their Characteristics. PHOLEDs were fabricated on glass substrates coated with a patterned transparent indium tin oxide (ITO) conductive layer. Substrates were cleaned in a detergent solution for 5 min and then in distilled water for 10 min with an ultrasonic bath. They were predried with a jet spin washer, then dried for 5 min in an oven at 150 °C, and finally treated with ozone plasma. The PHOLED structures of ITO (50 nm)/HIL (10 nm)/HTL (60 nm)/EBL (10 nm)/EML (30 nm)/ETL (50 nm)/LiF (1 nm)/Al (100 nm) were prepared by vacuum evaporation. Dipyrazino[2,3-f:2′,3′-h]quinoxaline- 2,3,6,7,10,11-hexacarbonitrile (HAT-CN), N^4,N^4,$N^{4\prime}$,$N^{4\prime}$-tetra([1,1′-biphenyl]-4-yl)-[1,1′-biphenyl]-4,4′-diamine (TBBD), tris(4-carbazoyl-9-ylphenyl) amine (TCTA), and 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]-imidazol-2-yl)benzene (TPBi) were used as HIL, HTL, EBL, and ETL, respectively. The EML consists of 10 wt % of Ir(ppy)$_3$ and 90 wt % of one of the five host materials. The pressure of the vacuum evaporation was 5.0×10^{-4} Pa, and the film thickness was controlled with a calibrated quartz crystal microbalance during deposition. After the deposition of all layers, the PHOLED test modules were encapsulated with capping glass in the evaporation chamber filled with nitrogen. The OLED characteristics of all the fabricated devices were evaluated at room temperature in air atmosphere using a voltage−current−luminance measuring system, which consisted of a source meter (Keithley 2400) and a spectral-radiance meter (Topcon SR-3AR). Assuming a perfect diffusion surface light emitting surface, the external quantum efficiency was calculated with EL spectrum. The operational stability (or lifetime) was tested at a constant current corresponding to an initial luminance of 2000 cd/m^{-2} for each device at room temperature. The elapsed time, luminance, and voltage during the lifetime tests were recorded in situ by a computer until the end of the testing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details, charge mobility measurements, spectroscopy, and NMR spectra. 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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■ ABBREVIATIONS

PAHs, polycyclic aromatic hydrocarbons; CC, carbon−carbon; BN, boron−nitogen; OLEDs, organic light-emitting diodes; PHOLEDs, phosphorescent organic light-emitting diodes; SOMO, singly occupied molecular orbitals; TD-DFT, time-dependent density functional theory; CBP, 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl; TOF, time of flight; EQE, external quantum efficiency; ITO, indium tin oxide; HIL, hole injection layer; HTL, hole transport layer; EBL, electron blocking layer; EML, emissive layer; ETL, electron transport layer

■ REFERENCES

(1) (a) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (c) Würthner, F.; Schmidt, R. *ChemPhysChem* **2006**, *7*, 793. (d) Klauk, H. *Organic Electronics*; Wiley-VCH: Weinheim, 2006. (e) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (f) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (g) Zhang, L.; Fonari, A.; Zhang, Y.; Zhao, G.; Coropceanu, V.; Hu, W.; Parkin, S.; Brédas, J.-L.; Briseno, A. L. *Chem.—Eur. J.* **2013**, *19*, 18028. (h) Gao, X.; Hu, Y. *J. Mater. Chem. C* **2014**, *2*, 3099.

(2) (a) Fabian, J.; Nakazumi, H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197. (b) Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809. (c) Zhang, Y.; Galoppini, E. *ChemSusChem* **2010**, *3*, 410. (d) Sun, Z.; Ye, Q.; Chi, C.; Wu, J. *Chem. Soc. Rev.* **2012**, *41*, 7857.

(3) (a) Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207. (b) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novák, P. *Adv. Mater.* **1998**, *10*, 725. (c) Baker, T. A.; Head-Gordon, M. *J. Phys. Chem. A* **2010**, *114*, 10326. (d) Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato, K.; Takui, T. *Nat. Mater.* **2011**, *10*, 947.

(4) (a) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902. (b) Kaafarani, B. R. *Chem. Mater.* **2011**, *23*, 378. (c) O'Neill, M.; Kelly, S. M. *Adv. Mater.* **2011**, *23*, 566.

(5) (a) Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817. (b) Dong, H.; Zhu, H.; Meng, Q.; Gong, X.; Hu, W. *Chem. Soc. Rev.* **2012**, *41*, 1754. (c) Yan, Q.; Luo, Z.; Cai, K.; Ma, Y.; Zhao, D. *Chem. Soc. Rev.* **2014**, *43*, 4199.

(6) (a) Braga, D.; Horowitz, G. *Adv. Mater.* **2009**, *21*, 1473. (b) Klauk, H. *Chem. Soc. Rev.* **2010**, *39*, 2643. (c) Meng, Q.; Hu, W. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14152.

(7) (a) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Gather, M. C.; Köhnen, A.; Meerholz, K. *Adv. Mater.* **2011**, *23*, 233. (c) Hofmann, S.; Thomschke, M.; Lüssem, B.; Leo, K. *Opt. Express* **2011**, *19*, A1250. (d) Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y. *Adv. Mater.* **2011**, *23*, 1137. (e) Huang, J.; Su, J.-H.; Tian, H. *J. Mater. Chem.* **2012**, *22*, 10977. (f) Chen, Y.; Ma, D. *J. Mater. Chem.* **2012**, *22*, 18718.

(8) Ho, M.-H.; Balaganesan, B.; Chen, C. H. *Isr. J. Chem.* **2012**, *52*, 484.

(9) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. *Adv. Mater.* **2011**, *23*, 926. (c) Chaskar, A.; Chen, H.-F.; Wong, K.-T. *Adv. Mater.* **2011**, *23*, 3876. (d) Sasabe, H.; Kido, J. *J. Mater. Chem. C* **2013**, *1*, 1699. (e) Murawski, C.; Leo, K.; Gather, M. C. *Adv. Mater.* **2013**, *25*, 6801. (f) Minaev, B.; Baryshnikov, G.; Agren, H. *Phys. Chem. Chem. Phys.* **2014**, *16*, 1719.

(10) (a) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 242. (b) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2009**, *87*, 8. (c) Ashe, A. J., III *Organometallics* **2009**, *28*, 4236. (d) Campbell, P. G.; Marwitz,

A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074. OLEDs using BN embedded heteroacenes as blue emitting materials: (e) Wang, X.; Zhang, F.; Liu, J.; Tang, R.; Fu, Y.; Wu, D.; Xu, Q.; Zhuang, X.; He, G.; Feng, X. *Org. Lett.* **2013**, *15*, 5714.

(11) The BN replacement also localizes LUMO and HOMO in the ground state (S0). Since the singlet−triplet transitions correspond to HOMO−LUMO transitions, marked similarities were found between LUMO and SOMO1, HOMO and SOMO2, respectively. See Supporting Information for further details.

(12) The most conventional way to localize molecular orbitals is combining electron-deficient and electron-rich units. See ref 9d and references cited therein.

(13) TD-DFT calculations were performed for the optimized grand-state structures (S0) with Gaussian09 packages at the B3LYP/6-31G(d) level of theory. See Supporting Information for further details.

(14) (a) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 18614. (b) Hatakeyama, T.; Hashimoto, S.; Oba, T.; Nakamura, M. *J. Am. Chem. Soc.* **2012**, *134*, 19600.

(15) Charge mobilities are comparable to those of representative organic semiconductors (measured with the TOF method), such as α-naphthylphenylbiphenyl diamine (α-NPD, $\mu_h = 7 \times 10^{-4}$ cm^2 V^{-1} s^{-1}) and 1,3,5-tris(1-phenyl-1*H*-benzo[d]imidazol-2-yl)benzene (TPBi, $\mu_e = 9 \times 10^{-5}$ cm^2 V^{-1} s^{-1}). (a) Hung, W.-Y.; Ke, T.-H.; Lin, Y.-T.; Wu, C.-C.; Hung, T.-H.; Chao, T.-C.; Wong, K.-T.; Wu, C.-I. *Appl. Phys. Lett.* **2006**, *88*, 064102. (b) Li, C.; Duan, L.; Sun, Y.; Li, H.; Qiu, Y. *J. Phys. Chem. C* **2012**, *116*, 19748.