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HEXAARYL-BENZODIPYRROLES: PROPERTIES AND APPLICATION AS AMORPHOUS CARRIER-TRANSPORTING MATERIALS

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This paper is dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday.

Abstract – We have newly synthesized 1,2,3,5,6,7-hexaarylbenzo[1,2-*b*:4,5-*b'*]dipyrroles (HABDPs) and studied their properties. The HABDPs showed UV absorption maxima at 377–390 nm, indicating their extended π -conjugation system. They were also found to serve as efficient amorphous materials, featuring high electrochemical and thermal stability with high carrier mobility of up to 10^{-3} cm²/Vs using the time-of-flight technique. Application of the HABDPs to organic light-emitting diodes resulted in significantly improved performance in driving voltage and efficiency compared with α -NPD, a commonly used hole-transporting material.

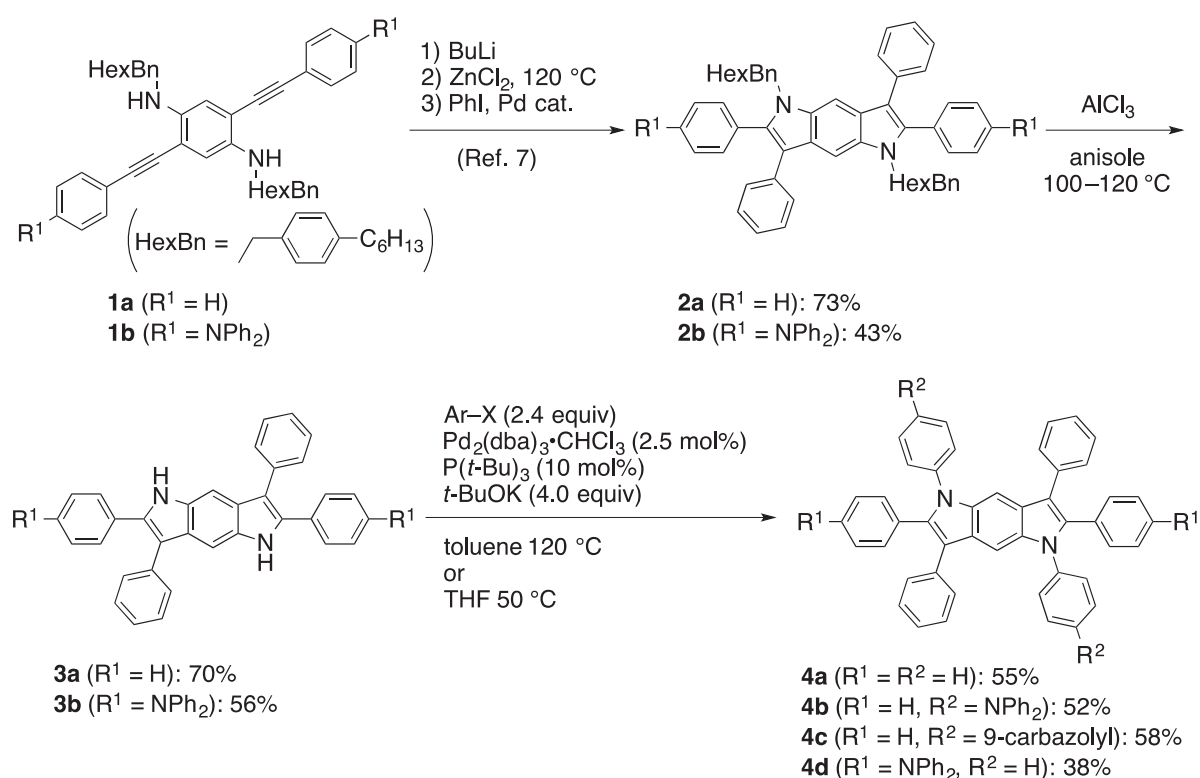
INTRODUCTION

Pyrrole derivatives are acknowledged as an important class of compounds in a broad range of fields, such as natural products and bioactive molecular chemistry,^{1,2} supramolecular and coordination chemistry,³ and materials science.⁴ We have so far developed novel fused polycyclic heteroaromatic compounds,^{5–11} including *N,N'*-HexBn-protected (HexBn = (4-hexylphenyl)methyl) benzo[1,2-*b*:4,5-*b'*]dipyrroles (HexBn-BDPs), and found that the HexBn-BDPs serve as solution-processable hole injection materials in organic light-emitting diodes (OLEDs) and afforded mechanistic insights for the hole injection. In this manuscript, we report newly synthesized *N,N'*-diaryl-BDPs, that is, 1,2,3,5,6,7-hexaarylbenzo[1,2-*b*:4,5-*b'*]dipyrroles (HABDPs), which show intriguing properties, such as high stability and high carrier mobility, and are suitable to serve as a novel class of hole-transporting materials

in OLEDs to achieve significant improvement in driving voltage and efficiency.

RESULTS AND DISCUSSION

Synthesis of the HABDPs is shown in Scheme 1. Using our previously developed zinc-mediated cyclization reaction, *N,N'*-HexBn-protected BDPs **2** were prepared, which was followed by deprotection using AlCl_3 in anisole¹² to obtain *N,N'*-protonated BDPs **3** in moderate yield. A palladium-catalyzed *N*-arylation reaction¹³ afforded the new class of compounds HABDPs **4a–d** in 55%, 52%, 58%, and 38% yields, respectively.



Scheme 1

Photophysical and electrochemical property measurements of the HABDPs **4** in solution demonstrated their extended π -conjugation character (Table 1). The UV absorption spectra of **4a–c** ($R^1 = \text{H}$) showed similar longest absorption maxima and onset wavelengths at 377–382 nm and 424–430 nm, respectively (Figure 1), while that of **4d** ($R^1 = \text{NPh}_2$) is somewhat redshifted with shoulder-like transition around 390 nm and onset at 449 nm, indicating the extension of π -conjugation because of the additional diphenylamino group at the 2,6-positions. These absorption maximum wavelengths are similar to those of the benzo[1,2-*b*:4,5-*b'*]difurans (BDFs), which we have previously reported,⁵ showing a small difference in the absorption nature from the oxygen counterparts. The cyclic voltammogram of these BDPs in CH_2Cl_2 showed a reversible first oxidation wave with potentials of 0.23, 0.18, 0.25, and 0.12 V (vs

Fc/Fc⁺) for **4a–d**, respectively, indicating electrochemical stability toward oxidation. No reduction wave was observed within the solvent window. The HOMO energy levels were estimated to be -5.03 , -4.98 , -5.05 , and -4.92 eV, respectively. The LUMO energy levels, calculated from the HOMO energy and the optical gap (E_g), were -2.15 , -2.10 , -2.13 , and -2.16 eV, respectively. These HOMO and LUMO energy levels are somewhat higher than those of the corresponding BDFs (e.g., HOMO: -5.49 eV; LUMO: -2.54 eV for 2,3,6,7-tetraphenylbenzo[1,2-*b*:4,5-*b'*]difuran), representing the increased electron-donating nature of the incorporated nitrogen atoms compared with oxygen.

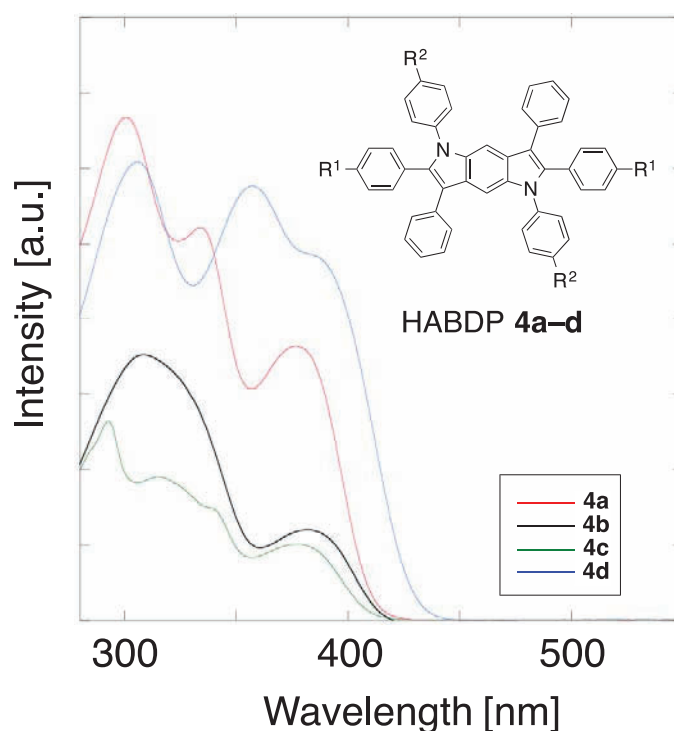


Figure 1. UV Absorption spectra of HABDPs **4a–d** in CH₂Cl₂ at room temperature

Table 1. Summary of photophysical and electrochemical properties of HABDPs **4a–d**.

Cmpd	R ¹	R ²	λ_{\max} /nm ^a	λ_{onset} /nm ^a	E_g /eV ^b	HOMO/eV ^c	LUMO/eV ^d
4a	H	H	301, 335, 377	430	2.88	-5.03	-2.15
4b	H	NPh ₂	308, 382	430	2.88	-4.98	-2.10
4c	H	9-carbazolyl	293, 315, 377	424	2.92	-5.05	-2.13
4d	NPh ₂	H	306, 357, 390(sh) ^e	449	2.76	-4.92	-2.16

^aIn CH₂Cl₂ at room temperature. ^bDeduced from the equation: E_g [eV] = $1240/\lambda_{\text{onset}}$ [nm]. ^cHOMO energy level deduced from the equation: HOMO [eV] = $-(4.8 + E_{\text{ox}} [\text{V}])$, where E_{ox} refers to oxidation potential (vs Fc/Fc⁺) in CH₂Cl₂. ^dDeduced from the equation: LUMO [eV] = HOMO [eV] – E_g . ^eShoulder.

The thermal stabilities of the BDPs are high: thermogravimetric analysis (TGA) showed 5% weight loss (T_d) at 424 °C for **4a** because of sublimation and 489, >500, and 486 °C for **4b–d**, respectively. The BDP **4d** exhibited a glass transition temperature (T_g) at 121 °C seen by differential scanning calorimetry (DSC). The observed T_g values are substantially higher than those for a commonly used p-type material α -NPD (95 °C. Structure is shown in Figure 3),¹⁴ indicating that the compounds show high stability in their amorphous state. The BDP **4b** did not show perceivable T_g , but the amorphous state was secured by the X-ray diffraction measurement of the powder sample, whereas amorphous samples of BDPs **4a** and **4c** were not successfully prepared.

The carrier mobilities of the BDPs **4a–c** were very high for their amorphous state (Figure 2). Time-of-flight (TOF) technique was applied for the vacuum deposited μm -thick amorphous film of BDPs. The BDPs **4a** and **4b** showed nondispersive transient currents for hole and no current for electron, indicating p-type noncarrier trap transportation. The hole mobility at room temperature of these compounds was $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for both compounds at an electric field of $2.5 \times 10^5 \text{ V/cm}$ with little electric field dependence (Figure 2a). Interestingly, the carbazole-substituted BDP **4c** displayed transient currents for both hole and electron, i.e., ambipolar character,¹⁵ similar to the carbazole-substituted BDF (CZBDF) that we previously reported⁵ or commonly known 1,1'-di(*N*-carbazolyl)-4,4'-biphenyl (CBP).¹⁶ The hole and electron mobilities were 6×10^{-4} and $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively, at an electric field of $2.5 \times 10^5 \text{ V/cm}$.¹⁷

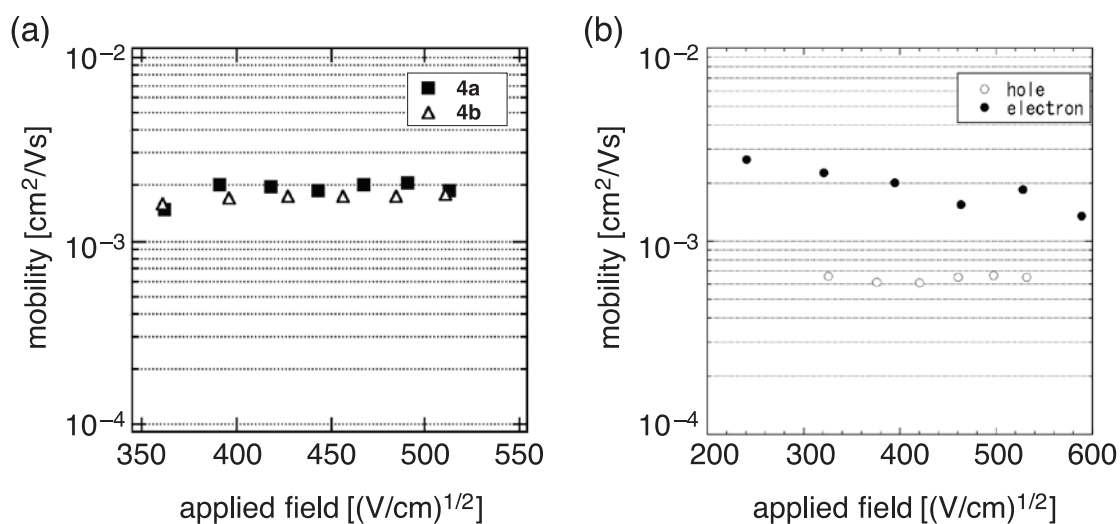


Figure 2. Carrier mobility of HABDPs **4a–c** plotted against the square root of the applied electric field. (a) Hole mobility of the p-type BDPs **4a** and **4b**. (b) Hole and electron mobilities of the ambipolar BDP **4c**.

Based on the measurements above, we have revealed the advantageous character of BDPs for their application to OLEDs: transparency in the visible region, appropriate orbital energy (HOMO level for

carrier injection from an indium–tin oxide (ITO) anode, and LUMO for electron-blocking ability), high electrochemical and thermal stability, and high carrier mobility. Taking advantage of these features, we applied the p-type BDPs **4a** and **4b** as a hole transport layer (HTL) in OLEDs. The application of ambipolar BDP **4c** is under investigation and will be reported elsewhere. OLEDs have found practical uses as flexible, lightweight, and power-saving display and illumination devices.^{18,19} For further improvement of device performance in driving voltage and efficiency, development of new materials for various parts of these devices has been extensively explored.²⁰

The OLEDs have a standard configuration (Figure 3a): ITO (anode)/PEDOT:PSS (hole injection layer)/HTL (45 nm)/Alq₃ (emitting and electron transport layer; 60 nm)/lithium fluoride (LiF) (electron injection layer; 1 nm)/Al, where the PEDOT:PSS²¹ layer was fabricated by spin-coating, and the following layers by vacuum deposition. We fabricated OLEDs using α -NPD as a HTL as a reference. The OLED performance was evaluated for three standard criteria at a luminance of 1,000 cd/m²: driving voltage (V_{1000}), luminance efficiency (η_{1000}), and current efficiency (L/J_{1000}). The data are summarized in Table 2. These devices showed green electroluminescence from Alq₃, indicating that the carriers are effectively confined within the Alq₃ layer. The driving voltage of the device using **4a** was 7.0 V, which is 1.5 V lower than that of the reference device (i.e., 8.5 V for the α -NPD-based device), while that of the **4b**-based device was the same as for the reference (8.5 V). The luminance and the current efficiencies were also significantly improved: $\eta_{1000} = 0.81, 0.84,$ and 0.59 lm/W; $L/J_{1000} = 1.80, 2.29,$ and 1.60 cd/A for **4a**, **4b**, and α -NPD, respectively. We attribute the improved performance of the BDP-based devices to their HOMO energy levels, which are suitable for carrier injection processes both from the anode and to Alq₃, and for facile carrier transport because of their high carrier mobility.

Table 2. Summary of OLED performance using either BDPs **4a** and **4b** or α -NPD as a hole transport layer^a

Material	V_{1000} [V] ^b	η_{1000} [lm/W] ^c	L/J_{1000} [cd/A] ^d
4a	7.0	0.81	1.80
4b	8.5	0.84	2.29
α -NPD	8.5	0.59	1.60

^aAll OLED performance data were collected at a luminance of 1,000 cd/m². ^bDriving voltage. ^cLuminance efficiency. ^dCurrent efficiency.

In summary, we found that HABDPs serve as excellent amorphous materials with high stability. The carrier mobility measurement and application to OLEDs unambiguously demonstrated that BDP itself has

hole-transporting ability. Incorporation of substituents would synergistically improve the device performance by tuning the material properties.

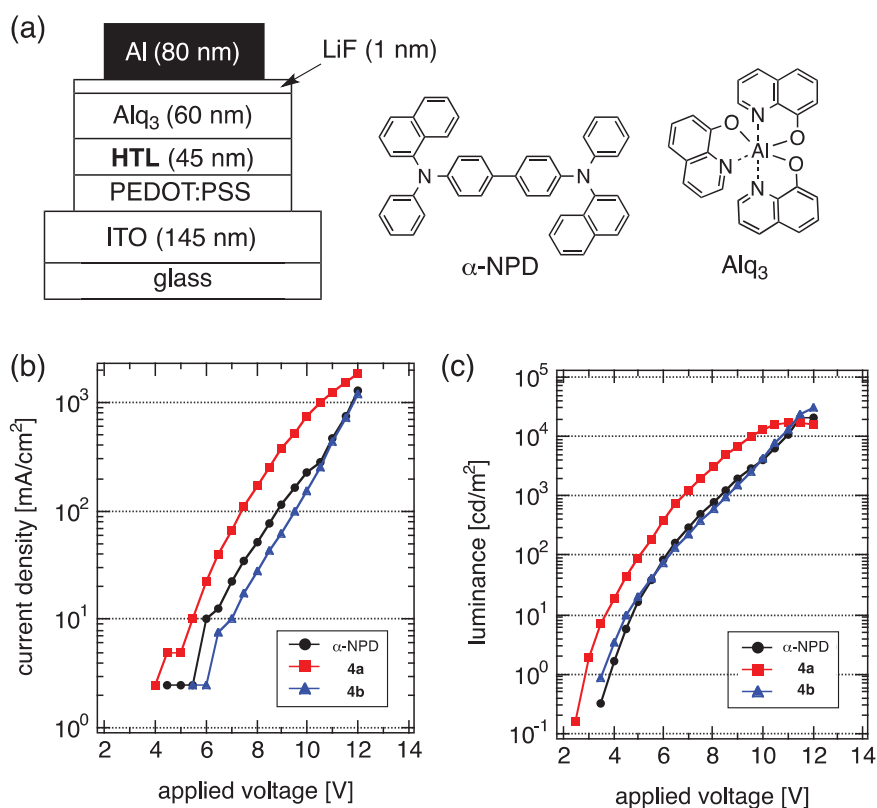


Figure 3. Evaluation of the performance of OLEDs composed of BDPs **4a** and **4b** for a hole-transporting material, together with that of α -NPD as a reference: (a) device configuration, where HTL stands for hole transport layer, (b) J - V characteristics, and (c) L - V characteristics.

EXPERIMENTAL

Synthesis.

General. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded using a JEOL ECA-500 (500 MHz) NMR spectrometer. High-vacuum train sublimation (pressure below 30 mTorr) was performed using a P-100HT instrument (ALS Technology Company). Melting points of solid materials were determined using a Mel-Temp II capillary melting-point apparatus and are uncorrected. Mass spectra were obtained on a JEOL Accu TOF JMS-T100LC spectrometer. *N,N'*-HexBn-protected BDPs **2** were prepared according to our previously reported method.⁷

2,3,6,7-Tetraphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (3a). To a suspension of 1,5-bis[(4-hexylphenyl)methyl]-2,3,6,7-tetraphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (167 mg, 0.206 mmol) in anisole (1 mL) was added AlCl₃ (440 mg, 3.30 mmol) at 0 °C. The mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction was quenched with H₂O. The organic layer was separated and

the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were concentrated in vacuo. After dissolving in toluene, 2-propanol was added to precipitate. The precipitate was collected by filtration and washed with 2-propanol to afford the title compound as a yellow solid (66.7 mg, 0.145 mmol, 70%). Mp 340–341 °C. ^1H NMR (500 MHz, $\text{THF-}d_8$) δ 7.19–7.29 (m, 8H, ArH), 7.36 (t, $J = 7.6$ Hz, 4H, ArH), 7.48–7.50 (m, 8H, ArH), 7.55 (s, 2H, ArH). ^{13}C NMR (125 MHz, $\text{THF-}d_8$) δ 99.2, 114.0, 126.4, 127.7, 128.6, 129.04, 129.06, 129.13, 131.0, 134.7, 135.4, 135.9, 137.8. MS (APCI+): 461 (M+1). Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_2$: C, 88.67; H, 5.25; N, 6.08. Found: C, 88.43; H, 5.29; N, 5.90.

2,6-Bis(4-*N,N*-diphenylaminophenyl)-3,7-diphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (3b). The reaction was conducted at 100 °C. Mp 344–345 °C. ^1H NMR (500 MHz, $\text{THF-}d_8$) δ 7.00–7.03 (m, 8H, ArH), 7.07 (d, $J = 8.3$ Hz, 4H, ArH), 7.14–7.18 (m, 116H, ArH), 7.23–7.28 (m, 12H, ArH), 7.35 (d, $J = 7.5$ Hz, 4H, ArH), 7.63 (s, 2H, ArH). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane- d_2) δ 98.88, 113.62, 123.66, 123.85, 125.42, 126.35, 128.61, 128.80, 129.13, 129.49, 130.06, 131.10, 135.24, 135.41, 138.07, 147.67, 148.64. MS (APCI+): 795 (M+1). Anal. Calcd for $\text{C}_{58}\text{H}_{42}\text{N}_4$: C, 87.63; H, 5.33; N, 7.05. Found: C, 87.33; H, 5.56; N, 6.86.

Typical procedure for palladium-catalyzed *N*-arylation: 1,2,3,5,6,7-Hexaphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (4a). To a suspension of 2,3,6,7-hexaphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (1.38 g, 3.00 mmol) in toluene (15 mL) were added $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (124 mg, 0.120 mmol), $\text{P}(t\text{-Bu})_3$ in toluene (0.24 mL, 1.0 M, 0.24 mmol), sodium *tert*-butoxide (1.15 g, 12.0 mmol), and iodobenzene (1.01 mL, 14.4 mmol). The mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction was quenched with H_2O . The mixture was filtered and the precipitate was washed several times with toluene and EtOAc. The resulting crude solid was purified by high vacuum (pressure under 20 mTorr) train sublimation at 300–320 °C to afford the title compound as a yellowish white solid (1.01 g, 1.65 mmol, 55%). Mp: sublimation. ^1H NMR (500 MHz, 1,1,2,2-tetrachloroethane- d_2) δ 7.08–7.09 (m, 10H, ArH), 7.15 (t, $J = 7.2$ Hz, 2H, ArH), 7.23–7.26 (m, 10H, ArH), 7.30–7.35 (m, 8H, ArH), 7.59 (s, 2H, ArH). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane- d_2) δ 99.0, 116.5, 125.7, 126.4, 126.8, 127.1, 127.7, 128.2, 128.5, 129.0, 130.3, 131.3, 132.3, 135.6, 136.4, 138.6, 139. MS (APCI+): 613 (M+1). Anal. Calcd for $\text{C}_{46}\text{H}_{32}\text{N}_2$: C, 90.16; H, 5.26; N, 4.57. Found: C, 90.13; H, 5.39; N, 4.62.

1,5-Bis(4-*N,N*-diphenylaminophenyl)-2,3,6,7-tetraphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (4b). Yield: 52%. Mp 360–361 °C. ^1H NMR (500 MHz, $\text{THF-}d_8$) δ 7.00–7.03 (m, 8H, ArH), 7.07 (d, $J = 8.3$ Hz, 4H, ArH), 7.14–7.18 (m, 116H, ArH), 7.23–7.28 (m, 12H, ArH), 7.35 (d, $J = 7.5$ Hz, 4H, ArH), 7.63 (s, 2H, ArH). MS (APCI+): 947 (M+1). Anal. Calcd for $\text{C}_{70}\text{H}_{50}\text{N}_4$: C, 88.76; H, 5.32; N, 5.92. Found: C, 88.69; H, 5.60; N, 5.82.

1,5-Bis(carbazolyl)-2,3,6,7-tetraphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (4c). Yield: 58%. Mp 410–411 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.22–7.25 (m, 10H, ArH), 7.29–7.33 (m, 4H, ArH), 7.35–7.38 (m, 4H,

ArH), 7.42–7.44 (m, 6H, ArH), 7.46–7.48 (m, 6H, ArH), 7.50–7.52 (m, 4H, ArH), 7.58–7.59 (m, 4H, ArH), 7.85 (s, 2H, ArH), 8.15–8.17 (m, 4H, ArH). MS (APCI+): 943 (M+1). Anal. Calcd for C₇₀H₄₆N₄: C, 89.14; H, 4.92; N, 5.94. Found: C, 88.86; H, 5.03; N, 5.77.

2,6-Bis(4-*N,N*-diphenylaminophenyl)-1,3,5,7-tetraphenylbenzo[1,2-*b*:4,5-*b'*]dipyrrole (4d). Yield: 38%. Mp 363–364 °C. ¹H NMR (500 MHz, THF-*d*₈) δ 6.77 (d, *J* = 8.9 Hz, 4H, ArH), 6.94–7.00 (m, 16H, ArH), 7.14 (t, *J* = 7.5 Hz, 2H, ArH), 7.19–7.22 (m, 8H, ArH), 7.25–7.31 (m, 10H, ArH), 7.37–7.42 (m, 8H, ArH), 7.61 (s, 2H, ArH). ¹³C NMR (125 MHz, 1,1,2,2-tetrachloroethane-*d*₂) δ 99.12, 116.68, 122.79, 123.91, 125.47, 126.39, 126.78, 127.23, 127.51, 128.94, 129.30, 129.80, 130.01, 130.93, 132.87, 136.80, 137.14, 138.53, 140.25, 147.73, 148.46. MS (APCI+): 947 (M+1). Anal. Calcd for C₇₀H₅₀N₄: C, 88.76; H, 5.32; N, 5.92. Found: C, 88.80; H, 5.57; N, 5.91.

Property measurements. UV–visible absorption spectra were recorded using a JASCO V-570 spectrophotometer at a resolution of 0.5 nm. Spectroscopy-grade CH₂Cl₂ was used as a solvent. Ca. 10⁻⁵ M sample solutions in a 1-cm square quartz cell were used for the measurements. All measurements were conducted at room temperature.

Cyclic voltammetry (CV) measurements were conducted using a Hokuto Denko HZ-5000 voltammetric analyzer. All measurements were conducted at room temperature in a one-compartment cell under N₂ gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag⁺ reference electrode (10 mM AgClO₄ in 0.1 M Bu₄NPF₆).

Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 204/F1 thermal analyzer. The glassy state sample was heated at a rate of 5 K min⁻¹ under N₂ gas, at a flow rate of 18 mL min⁻¹.

Thermogravimetry-differential thermal analysis (TG-DTA) was performed using a Rigaku TG8120 analyzer. Temperature was raised at 10 K min⁻¹ under N₂ using Al₂O₃ as a reference.

Carrier mobility measurement using time-of-flight (TOF) technique. Films were prepared on ITO-coated (145 nm) glass substrates by vacuum sublimation under heating (3–4 × 10⁻⁴ Pa and 2–4 × 10⁻⁴ Pa for **4a** and **4b**, respectively), with an average deposition rate of 4.0 nm/s. An ITO-coated glass substrate was spaced at 100 mm from the sample crucible, and it was maintained at 25 °C. The thickness of the film obtained was 4.57 and 3.83 μm for **4a** and **4b**, respectively. After Al cathode deposition (80 nm), the device was encapsulated under nitrogen atmosphere. The vacuum deposition was performed using a Ulvac Kiko VPC-260 system. The TOF measurement was conducted using a Sumitomo TOF-401 instrument.

Device fabrication and evaluation. Compounds of analytical purity were further purified by train sublimation. All the other materials were commercially available and were used as purchased. The typical fabrication procedure for a phosphorescent green OLED is described for the device using either compound **4a** or **4b** as a hole-transporting material. An ITO-coated glass substrate treated by O₃-plasma

was used as the anode. A PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) water dispersion was spin-coated into this substrate, it was dried at 120 °C, then it was annealed at 180 °C under nitrogen. Next, a HTL with the thickness of 45 nm was fabricated by vacuum deposition. An emitting layer was subsequently fabricated by vacuum deposition of Alq₃ with the thickness of 60 nm. An ultrathin layer (1 nm) of LiF was deposited at the cathode interface to enhance electron injection. After Al cathode deposition (80 nm), the device was sealed by encapsulation with a fresh desiccant under nitrogen. The emissive area of the device was 2 × 2 mm².

Electroluminescence spectra and luminance-voltage characteristics of the OLED devices were measured using a Precise Gauges EL 1003 instrument. All measurements were conducted under ambient atmosphere.

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