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Pyridine-Modified Acridine-Based Bipolar Host Material for Green Phosphorescent Organic Light-Emitting Diodes

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In phosphorescent organic light-emitting diodes (PHOLEDs) it is important to balance holes and electrons in the light-emitting layer to obtain a high external quantum efficiency. In general, the charge balance in the emitting layer depends on the charge transport properties of the host materials and charge injection from charge transport layers to the emitting layer. Therefore, bipolar host materials with balanced hole and electron transport properties have been typically used as the host materials to improve the external quantum efficiency of PHOLEDs.[1–10]

Bipolar host materials generally contain both hole and electron transport units in their molecular structure. Carbazole and aromatic amine moieties have been used as hole transport units,[1–10] while triazine,[1] pyridine,[2,3] phosphine oxide,[4–7] imidazole[8,9], and oxadiazole[10] units have been introduced as electron transport units. Various host materials have been synthesized by combining hole transport units and electron transport units, and yielded high external quantum efficiencies in PHOLEDs. However, further design and synthesis of new hole transport moieties are required to develop improved bipolar host materials for PHOLEDs.

In this work, a phenyl-modified acridine-based hole transport core structure was synthesized, and a bipolar host material with the acridine core and a pyridine unit was developed. We demonstrate that the phenyl-modified acridine-type host material shows a balanced charge transport and a high quantum efficiency of 13.5 %.

The phenyl-modified acridine was designed as the hole transport-type high triplet energy core structure. All phenyl groups in the acridine core were connected to the amine unit, and two phenyl groups were linked through sp^3 carbon linkage. Therefore, the conjugation of the triphenylamine group is not extended and the acridine can have the high triplet energy of triphenylamine. In addition, the rotation of the two phenyl units is limited by the sp^3 carbon linkage, thus increasing the glass transition temperature of the acridine-based materials. As the acridine is a hole transport-type core, an electron transport-type pyridine was attached to the phenyl-modified acridine core to develop a bipolar host material.

The phenyl-modified acridine core was synthesized by the reaction of 1,2-dibromobenzene with diphenylamine followed by lithiation using *n*-butyllithium and a ring-closing reaction with 4,4′-dibromobenzophenone.[11] The resulting brominated acridine intermediate was modified with pyridine. The route for the synthesis of 10-phenyl-9,9-bis(4-(pyridin-3-yl)phenyl)-9,10-dihydroacridine (PBPPA) is shown in Scheme 1.

The photophysical properties of PBPPA were analyzed using UV/Vis and photoluminescence (PL) spectroscopy. UV/Vis absorption, solution PL, and low-temperature PL spectra of PBPPA are presented in Figure 1. PBPPA showed absorption of the acridine core and phenylpyridine between 250 nm and 340 nm. As the conjugation length of the acridine was the same as that of triphenylamine, PBPPA exhibited a similar π–π* absorption peak to that of triphenylamine.[12] The band gap of PBPPA was calculated as 3.58 eV from the absorption edge of the UV/Vis absorption peak. The PL emission of PBPPA was centered at 400 nm. Low-temperature PL measurement was carried out to obtain the triplet energy of PBPPA; the obtained value from the first emission peak was 2.76 eV. The high triplet energy of the PBPPA is due to the limited conjugation in the phenyl-modified acridine structure by the sp^3 carbon linkage. PBPPA also showed a high glass transition temperature of 125 °C due to the rigidity of the phenyl-modified acridine core.

The highest occupied molecular orbital (HOMO) of PBPPA was measured using cyclic voltammetry, and the lowest unoccupied molecular orbital (LUMO) was calculated from the HOMO and the band gap. The HOMO of PBPPA was 5.97 eV and the LUMO was 2.39 eV.

Molecular simulation of PBPPA was carried out to study the HOMO and LUMO distribution. Density functional theory calculations of the compounds were carried out using Gaussian 03 and the nonlocal density functional of Becke's 3-parameters employing Lee–Yang–Parr functional (B3LYP) with 6-31G* basis sets.[13] Figure 2 shows the HOMO and LUMO distribution of PBPPA. The HOMO of PBPPA was localized on the acridine core, while the LUMO of PBPPA was dispersed over the pyridine unit. As the HOMO and LUMO were distributed on the hole transport acridine and electron transport pyridine, respectively, bipolar charge transport properties were expected from PBPPA.

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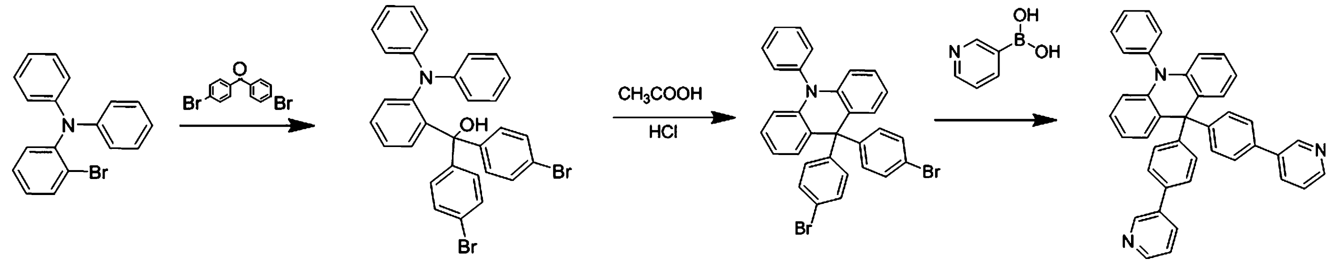

Scheme 1. Synthesis of PBPPA.

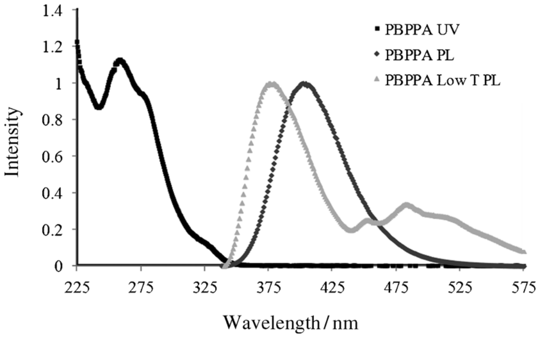

Figure 1. UV/Vis absorption, solution PL, and low-temperature PL spectra of PBPPA.

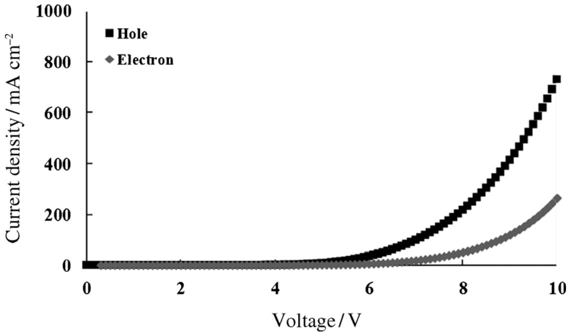

Figure 3. Current density–voltage curves of hole-only and electron-only devices.

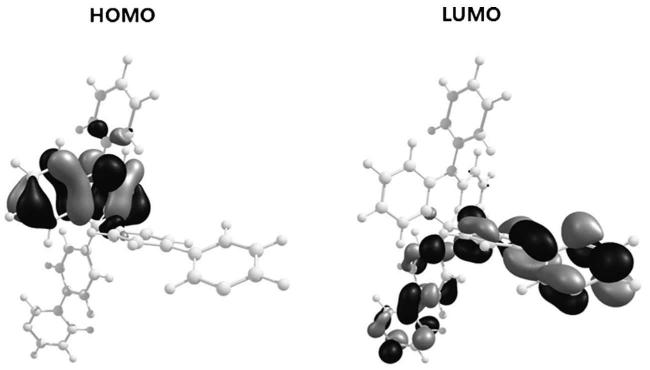

Figure 2. Calculated HOMO and LUMO of PBPPA.

To confirm the bipolar charge transport properties of PBPPA, hole-only and electron-only devices were fabricated. The structure of the hole-only device was indium tin oxide (ITO)/*N*,*N*′-diphenyl-*N*,*N*′-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4, 4′-diamine (DNTPD, 60 nm)/ *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB, 5 nm)/ PBPPA (30 nm)/DNTPD (5 nm)/Al, and the device structure of the electron-only device was ITO/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 5 nm)/PBPPA (30 nm)/TSPO1 (25 nm)/LiF/Al. Figure 3 shows the device data of hole-only and electron-only devices. The current density of the hole-only device was higher than that of the electron-only device over the entire voltage range. However, the difference in current density was less than an order of magnitude, thus indicating a bipolar charge transport property of PBPPA. As explained in the molecular simulation results, the bipolar charge transport property of PBPPA was induced by the hole transport-type acridine core and electron transport-type pyridine unit. The hole mobility of PBPPA was $8.1\times10^{-6}\,\mathrm{cm^2V^{-1}s^{-1}}$.

As PBPPA showed high triplet energy for use as the host for green PHOLEDs, green PHOLEDs with the PBPPA host were fabricated. The doping concentration of PBPPA was changed to optimize the performance of PBPPA devices. Figure 4 shows current density–voltage and luminance–voltage curves of PBPPA devices at different doping concentrations of green-emitting iridium(III) tris(2-phenylpyridine) ($\mathrm{Ir(ppy)_3}$). The doping concentration of $\mathrm{Ir(ppy)_3}$ was changed from 3 % to 20 %. The current density of green PHOLEDs was increased with an increase in the doping concentration. The high current density at high doping con-

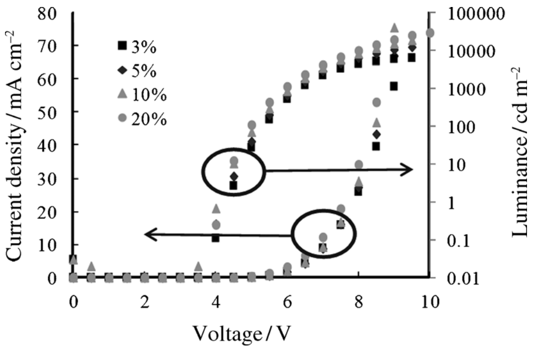

Figure 4. Current density–voltage–luminance curves of PBPPA devices at different $\mathrm{Ir(ppy)_3}$ doping concentrations.

centrations is due to a reduced hopping distance. Holes and electrons are transported through both host and dopant materials. The hopping distance between dopant materials is shortened at high doping concentrations, resulting in better charge transport at high doping concentrations. The luminance was also high at high doping concentrations due to a high current density.

Quantum efficiency–luminance curves of PBPPA devices are shown in Figure 5. The quantum efficiency gradually increased with an increase in the doping concentration up to 10 % and then decreased at a 20 % doping concentration. Thus, the optimum doping concentration of PBPPA PHOLEDs was 10 %. The maximum quantum efficiency of green PHOLED with 10 % doping concentration was 13.5 %, and the quantum efficiency at 1000 cd m^{-2} was 13.2 %. As both holes and electrons are transported by host and dopant materials, the charge balance in the emitting layer was greatly dependent on the doping concentration. Although the quantum efficiency was optimal at 10 % doping concentration, the efficiency roll-off of PHOLEDs was minimized at 20 % doping concentration. The quantum efficiency of PBPPA device was higher than that of the common 4,4′-di(9H-carbazol-9-yl)biphenyl (CBP) device.

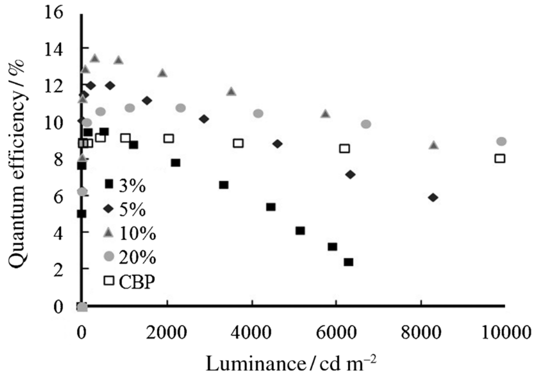

Figure 5. Quantum efficiency–luminance curves of PBPPA devices at different Ir(ppy)$_3$ doping concentrations.

EL spectra of PBPPA devices are shown in Figure 6. Green emission of Ir(ppy)$_3$ was observed over all doping concentrations without any host emission, indicating complete energy transfer from host to dopant materials, even at the low doping concentration of 3 %.

In conclusion, a bipolar host material with an acridine core and a pyridine unit was effectively synthesized as the high triplet energy bipolar host material by the ring-closing reaction of a brominated aromatic amine unit. The PBPPA host showed bipolar charge transport properties and a high quantum efficiency of 13.5 % in green PHOLEDs. Our study demonstrates that the acridine core can be useful for future development of host materials.

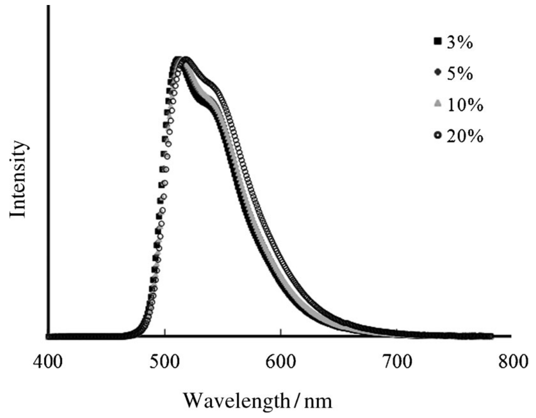

Figure 6. Electroluminescence spectra of PBPPA devices at different Ir(ppy)$_3$ doping concentrations.

Experimental Section

The synthetic procedure and characterization of PBPPA as well as the device fabrication process are described in the Supporting Information.

Keywords: acridine · bipolar host · electron transport

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