2-Phenylpyrimidine skeleton-based electron-transport materials for extremely efficient green organic light-emitting devices†

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2-Phenylpyrimidine skeleton-based multifunctional electron-transport materials are designed and synthesized. By using these materials and green phosphorescent emitter, *fac-tris*(2-phenylpyridine)iridium [Ir(ppy)$_3$], extremely efficient green organic light-emitting devices are developed. The devices show the efficiencies of 128 lm W^{-1} (105 cd A^{-1}) at 100 cd m^{-2} and 96 lm W^{-1} (99 cd A^{-1}) at 1000 cd m^{-2}.

High-efficiency organic light-emitting devices (OLEDs) are expected to be the key technology for energy-saving lighting and environmentally-friendly flat-display panels.[1] Among them, phosphorescent OLEDs (PHOLEDs) have gained considerable attention because phosphorescent emitters, such as Ir(ppy)$_3$, enable an internal efficiency four times higher than that of fluorescent ones converting both singlet and triplet excitons into photons.[2] Additionally, Kawamura and co-workers reported that Ir(ppy)$_3$-doped 4,4′-N,N′-dicarbazolylbiphenyl (CBP) solid thin film exhibited the high photoluminescent quantum efficiency (PLQE) of nearly 100%.[3] Therefore, extremely high efficiency PHOLEDs can be realized by using CBP/Ir(ppy)$_3$ as an emissive layer (EML).

To maximize CBP/Ir(ppy)$_3$-based PHOLEDs efficiency, the neighboring hole- and electron-transport materials (HTMs and ETMs) require: (a) the higher triplet energy (E_{T1}) than that of Ir(ppy)$_3$ to suppress the triplet exciton quenching of the emitter, (b) the carrier blocking ability to confine the carriers within EML and (c) the high carrier injection property to reduce the driving voltage of devices.[4] Among PHOLED materials, only a few ETMs can fulfil the above-mentioned requirements.[5–7] Thus, the development of multifunctional ETMs, which possess exciton/hole-blocking and high electron injection properties, is strongly desirable.

We have already revealed that the pyridine-containing wide-energy-gap ETMs showed high electron-transport properties.[7] Through our continuous material improvements, we found that 2-phenylpyrimidine skeleton-based ETMs, 2-phenyl-4,6-bis(3,5-dipyridylphenyl)primidine (BPyPPM) **1** possessed excellent electron injection properties. In this communication, we report the design, synthesis, physical properties and green PHOLED performances of **1**.

All the aromatic rings of **1** are connected with *meta*-conjugation to possess high E_{T1} level.[8] To enhance the electron injection process, the pyridine rings are introduced on the outer sphere of the molecule. Oyamada and co-workers have already pointed out that the coordination effect of the nitrogen atom with a metallic compound efficiently promoted the carrier injection.[9] Thus, the favorable electron injection property of **1** can be realized by the coordination effect of nitrogen atoms toward a cathode metal.[7] Additionally, in order to estimate the effect of 2-phenylpyrimidine skeleton, we conducted the density functional theory (DFT) calculations of four molecules, B3PyPPM (**1a**), B3PyMPM,[7b] 3,3″,5,5″-tetra(3-pyridyl)-1,1′;3′,1″-terphenyl (B3PyPB)[7f] and 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) as a reference. Calculated highest occupied molecular orbital (HOMO) energies, lowest unoccupied molecular orbital (LUMO) energies and HOMO–LUMO energy gaps (E_g) are summarized in Table 1. All the materials have deep HOMO energies compared with BCP. The pyrimidine derivatives B3PyPPM (**1a**) and B3PyMPM have much lower-lying LUMO energies than that of B3PyPB and BCP due to their deeper HOMO and narrower E_g. Thus, the expected features of **1** are the hole-blocking and enhanced electron injection from the calculations.

The synthetic route of BPyPPM derivatives **1** is shown in Scheme 1. The precursor **3** was prepared *via* Suzuki–Miyaura coupling reaction of 4,6-dichloro-2-phenylpyrimidine **2**[10] with 3,5-dichlorophenyboronic acids in 70% yield using PdCl$_2$(PPh$_3$)$_2$/Na$_2$CO$_3$/CH$_3$CN catalyst system.[11] The resulting tetrachloride **3** was coupled with an excess amount of 3- and 4-pyridine boronate ester **3** to afford B3PyPPM **1a** in 83% yield and B4PyPPM **1b** in 68% yield, respectively.[12] The characterization of compounds was established on the basis of mass spectrometry, NMR, and elemental analyses (see ESI† for details). Compounds **1** were purified by train sublimation before device fabrication.

Table 1 Calculated HOMO, LUMO and E_g values

Compound	HOMO/eV^a	LUMO/eV^a	E_g/eV^a
B3PyPPM (**1a**)	6.67	2.34	4.33
B3PyMPM	6.80	2.42	4.38
B3PyPB	6.61	1.82	4.79
BCP	6.07	1.71	4.36

^{a} Optimized structures and single-point energies were calculated at the RB3LYP 6-31G(d) and 6-311 + G(d,p) levels, respectively.

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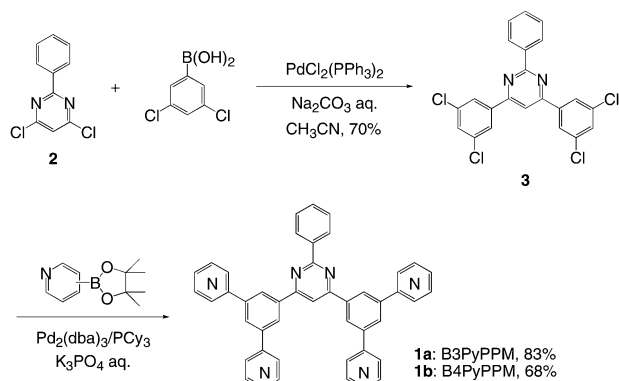
Scheme 1 Synthetic route of BPyPPM derivatives 1.

The thermal properties of 1 were estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperatures (T_g) of 1 were not detected, and the weight loss of 5% (T_{d5}) of 1 was found over 450 °C, indicating the thermal stability of 1. The melting point (T_m) of 1b was observed ca. 40 °C higher than that of 1a. This result may come from the weak intermolecular CH–N hydrogen bonding interactions in the solid state,[13] because the difference between 1a and 1b is the position of the substituted pyridine rings (3-pyridine for 1a, 4-pyridine for 1b). Compound 1b is supposed to form a denser vacuum-deposited film than 1a. The electrochemical properties were determined by UV-Vis, PL and photoelectron yield spectroscopy (PYS). The HOMO levels of 1 were observed at the same value of 7.15 eV. While the LUMO levels were estimated at 3.74 and 3.71 eV by subtraction of the optical energy gaps (E_g) from the HOMO levels. As expected from the DFT calculations, 1 has deep HOMO to block holes as well as low-lying LUMO to inject electrons. The E_{T1} level of 1 was determined from the highest energy of the phosphorescent spectra at 4.2 K, and was estimated at 2.81 eV (440 nm), which is enough high to confine the triplet emitter of Ir(ppy)₃ (E_{T1} = 2.53 eV) (see also ESI, Fig. S1 and S2†).[4d]

To evaluate the electron mobility, we carried out the time-of-flight (TOF) measurements of 1. Fig. 1 shows representative
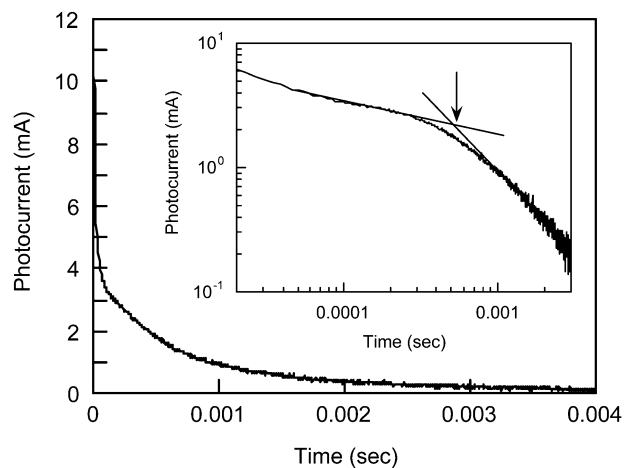
Table 2 Physical properties of BPyPPM derivatives 1

Compound	T_g^a/ °C	T_m^a/ °C	T_{d5}^b/ °C	HOMO^c/ eV	LUMO^d/ eV	E_g^e/ eV	Mobility^f/ cm² V⁻¹ s⁻¹
1a	N.d.	318	451	7.15	3.41	3.74	10^{-7}
1b	N.d.	356	467	7.15	3.44	3.71	10^{-6}

^{a} Determined by DSC measurement. ^{b} Obtained from TGA analysis. ^{c} Measured by photoelectron yield spectroscopy (PYS). ^{d} Calculated using HOMO and E_g values. ^{e} Taken as the point of intersection of the normalized absorption spectra. ^{f} Determined by TOF measurement.

TOF transient of electrons for 1b measured at room temperature (see also ESI, Fig. S3 and S4†). The electron mobilities (μ_E) were 10^{-7} cm² V⁻¹ s⁻¹ order for 1a and 10^{-6} cm² V⁻¹ s⁻¹ order for 1b, respectively. These values were almost same as that of conventional ETMs, Alq₃ and 3-(4-biphenylyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (t-BuTAZ), and 1/100 of that of BPyMPM derivatives.[5,7b,e] Further, it is important to note that the deposited film of 1 did not crystallize over 6 months in the air. All the physical properties of 1 are summarized in Table 2.

OLEDs with a structure of [ITO (110 nm)/poly(arylene ether sulfone)-containing tetraphenylbenzidine (TPDPES) doped with 10 wt% tris(4-bromophenyl)aminium hexachloroantimonate (TBPAH) layer[14] (20 nm)/TAPC (30 nm)/Ir(ppy)₃ 8 wt% doped
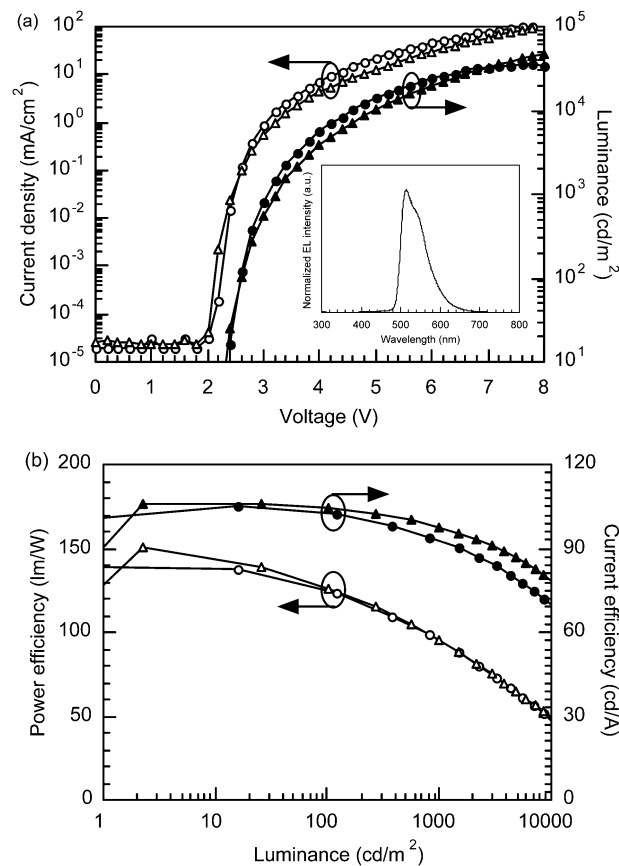

Fig. 1 Transient photocurrent profile for 1b measured at room temperature. Electric field ($E^{1/2}$) was 754 [V cm⁻¹]¹/². Sample thickness was 8.6 μm. Inset: Double logarithmic plot.

Fig. 2 (a) Current density–voltage and luminance–voltage characteristics for 1a (circles) and for 1b (triangles). Inset: EL spectrum of the device. (b) Power efficiency–luminance and current efficiency–luminance characteristics for 1a (circles) and for 1b (triangles).

CBP (10 nm)/BPyPPM **1** (50 nm)/LiF (0.5 nm)/Al (100 nm)] were fabricated.

The current density–voltage and luminance–voltage characteristics are shown in Fig. 2(a). The applied voltages at 100 cd m^{-2} and 1000 cd m^{-2} are 2.62 and 3.26 V for **1b**, respectively. The reduced driving voltages are presumably derived from the excellent electron injection properties of **1**. The EL spectrum is illustrated as the inset in Fig. 2(a). The emission is only from Ir(ppy)$_3$ with no emission from neighboring materials. This result indicates that holes and electrons are completely confined within the EML and recombination of the charge carriers takes place only in the EML. The power efficiency (PE)-luminance and current efficiency–luminance characteristics are shown in Fig. 2(b).

Extremely high PE of 128 lm W^{-1} was achieved for **1b** at 100 cd m^{-2} without light outcoupling enhancement, and at 1000 cd m^{-2}, high PE of 96 lm W^{-1} was observed. Almost the same performances were obtained for use of **1a** (126 lm W^{-1}, 103 cd A^{-1} at 100 cd m^{-2}). These results clearly indicate that the appropriately-designed ETMs enable the driving voltage of OLEDs extremely low without using *n*-doping.[15] The smaller current efficiency roll-off was observed in the device with **1b** than that with **1a**. This indicates that balanced carrier transport was achieved even at high brightness of 10 000 cd m^{-2}. Considering that the electron mobility of **1b** is higher than that of **1a**, an ETM with the higher electron mobility can realize the more balanced carrier transport in the EML.

In summary, we designed and synthesized 2-phenylpyrimidine skeleton-based multifunctional ETMs **1**. By using **1** and green phosphorescent emitter, Ir(ppy)$_3$, extremely high efficiency green OLEDs were developed.

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