

# Wide-Energy-Gap Electron-Transport Materials Containing 3,5-Dipyridylphenyl Moieties for an Ultra High Efficiency Blue Organic Light-Emitting Device

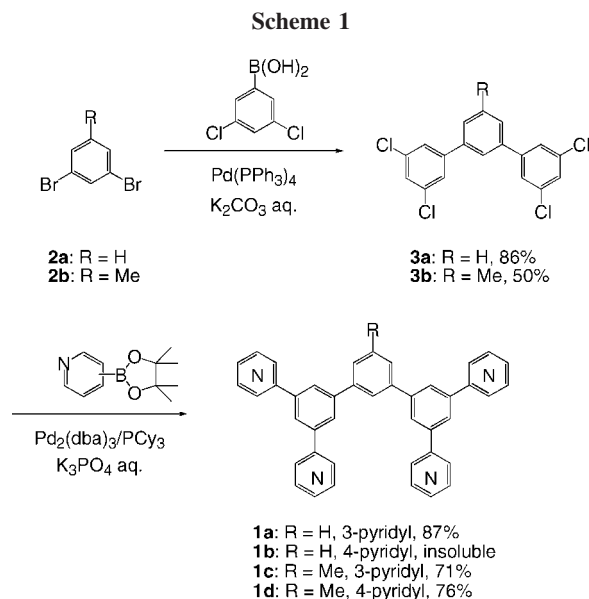
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Received July 3, 2008

Revised Manuscript Received August 5, 2008

One of the most promising candidates for the next-generation lighting and flat display panel systems is a high efficiency organic light-emitting device (OLED).<sup>1</sup> An imperative methodology realizing high efficiency OLEDs is use of phosphorescent materials.<sup>2</sup> Phosphorescent dyes, such as *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)<sub>3</sub>] and iridium(II)-bis(4,6-(difluorophenyl)pyridinato-N,C<sup>2'</sup>)picolinate (FIrpic) enable the internal efficiency to be as high up to 100% converting both singlet and triplet excitons into photons.<sup>3</sup> Therefore, the devices with these dyes as an emitter achieve extremely high electron to photon conversion. Recently, ultra high efficiency green phosphorescent OLEDs (PHOLEDs) using Ir(ppy)<sub>3</sub> as an emitter, which realized high power efficiencies (PEs) and external quantum efficiencies (EQEs) of 133 lm/W and 29% at 100 cd/m<sup>2</sup> respectively, were developed.<sup>4</sup> These results clearly indicate that the devices using Ir(ppy)<sub>3</sub> or FIrpic as an emitter can be essentially improved with the EQEs up to 30%. However, in general, efficiencies of the FIrpic-based blue PHOLEDs are not high compared with that expected from their potential abilities.<sup>5,6</sup> This low efficiency is mainly attributed to two reasons: (i)



the materials neighboring FIrpic-doped emissive layer (EML) have lower triplet energy ( $E_{T1}$ ) than that of FIrpic ( $E_{T1} = 2.77$  eV)<sup>6c</sup> to consume the triplet excitons by nonradiative decay, (ii) the carrier balance in the EML is not enough presumably because of the lack of electrons compared with holes. The former issue can be solved using appropriate materials with high  $E_{T1}$  over 2.77 eV. The latter one can be improved by using the electron-transport materials (ETMs) with high electron mobility and injection property to enhance the carrier recombination ratio in the EML. Therefore, the multifunctional ETMs with both the high triplet energy and electron-transport property are highly desirable. Here, we wish to report design, synthesis, physical properties, and OLED performances of the novel ETMs **1** with two 3,5-dipyridylphenyl moieties.

For the molecular design of novel ETMs **1**, we focused on the phenylpyridine moiety to realize the high electron-transport ability.<sup>6c,e,f</sup> Because the LUMO level of the pyridine ring is deeper than that of C=N double-bond-containing 5-membered heteroaromatic compounds, such as oxadiazole, triazole, and imidazole, the 3,5-dipyridylphenyl moiety containing ETMs **1** are expected to enhance the electron injection process.<sup>7</sup> To possess a high  $E_{T1}$  level, all the aromatic rings of **1** were connected with *meta*-conjugation.<sup>8</sup>

The synthetic route of ETMs **1a–1d** is shown in Scheme 1. The precursors **3** were prepared *via* the standard Pd-catalyzed Suzuki–Miyaura coupling reaction of dibromoarene **2** with 3,5-dichlorophenylboronic acid in 86 and

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**Table 1. Physical Properties of Compounds 1a–1d**

compd	$T_g$ (°C) <sup>a</sup>	$T_m$ (°C) <sup>a</sup>	$T_d$ (°C) <sup>b</sup>	$I_p$ (eV) <sup>c</sup>	$E_g$ (eV) <sup>d</sup>	$E_a$ (eV) <sup>e</sup>
<b>1a</b>	106	264	439	6.67	4.05	2.62
<b>1c</b>	116	232	436	6.52	3.97	2.55
<b>1d</b>	n.d.	359	441	6.60	4.00	2.60

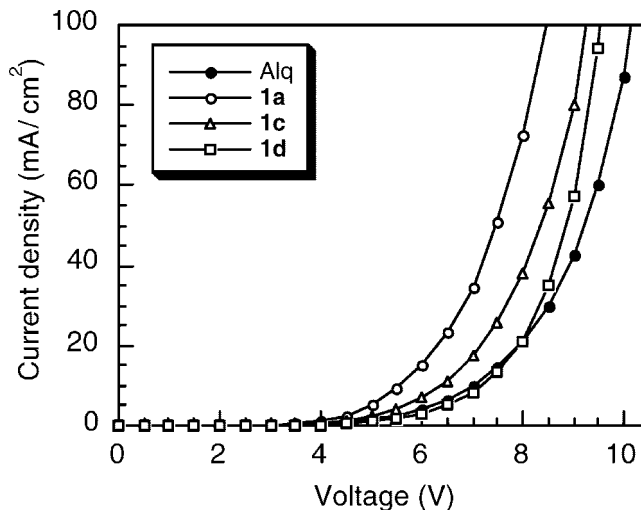
<sup>a</sup> Determined by DSC measurement. <sup>b</sup> Obtained from TGA analysis. <sup>c</sup> Measured by AC-3 UV photoelectron spectrometer. <sup>d</sup> Taken as the point of intersection of the normalized absorption spectra. <sup>e</sup> Calculated using  $I_p$  and  $E_g$  values.

50% yields, respectively. The resulting tetrachlorides **3** were coupled with pyridine boronic acid esters using Pd<sub>2</sub>(dba)<sub>3</sub>/PCy<sub>3</sub>/K<sub>3</sub>PO<sub>4</sub> catalyst system<sup>9</sup> to afford **1** in 71–86% yields. All the compounds were purified by silica gel column chromatography except **1b** because of its low solubility in ordinary organic solvents. It led us to introduce a methyl group into **1c** and **1d** to increase the solubility in organic solvents. The compounds were characterized by mass spectrometry, <sup>1</sup>H NMR, and elemental analyses and purified by train sublimation before device fabrication.

The thermal properties of **1** were estimated by differential scanning calorimetry (DSC). The glass transition temperatures ( $T_g$ ) of **1a** and **1c** were over 106 °C, which indicated high morphological stability of thin films. The compounds **1a** and **1c** exhibited the crystallization exotherms ( $T_c$ ), as well as  $T_g$ , at 193 and 189 °C, respectively. The compound **1d** was crystallized during the cooling cycle, and thus the  $T_g$  was not detected. The electrochemical properties were determined by UV–vis, PL and atmospheric photoelectron spectroscopy (AC-3, Riken Keiki Co.). The ionization potentials ( $I_p$ ) of these materials are observed at deeper than 6.50 eV, suggesting the high hole blocking ability. The electron affinity ( $E_a$ ) was calculated by subtraction of the HOMO–LUMO energy gap ( $E_g$ ). The physical properties were summarized in Table 1.

The triplet energy level ( $E_{T1}$ ) of **1a** was determined by phosphorescence spectrum at 4.2 K. The highest triplet energy of **1a** was obtained at 2.77 eV (448 nm), which is equal to that of FIrpic ( $E_{T1} = 2.77$  eV). The transient photoluminescence decay of 3 wt % FIrpic-doped **1a** was measured at room temperature. The decay curve was not a monoexponential, but its second exponential part (2%) was much smaller than its first one (98%). This is very similar to the case of FIrpic-doped TmPyPB thin film.<sup>6f</sup> Even though **1a** has a triplet energy equal to FIrpic, this result indicates that the energy transfer of the FIrpic excitons to **1a** is not favorable. Therefore, FIrpic-based PHOLEDs with **1a** as an electron-transport layer (ETL) are expected to suppress the FIrpic exciton quenching at the EML/ETL interface. To evaluate the electron mobility, we carried out the time-of-flight measurements of **1a** (thickness: 10.9 μm). Compound **1a** has a high electron mobility of  $\mu_e = 1.0 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at an electric field of  $3.3 \times 10^{-5}$  V cm<sup>-1</sup>, which is 100 times higher than that of conventional ETMs, such as Alq<sub>3</sub> and 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (*t*-Bu TAZ).<sup>10</sup>

To investigate the electron-transport property of **1**, we fabricated OLEDs with a structure of [ITO/4,4'-bis[*N*-(1-



**Figure 1.** Current density–voltage ( $J$ – $V$ ) characteristics of  $\alpha$ -NPD/Alq<sub>3</sub> type devices using **1** or Alq<sub>3</sub> as an ETL.

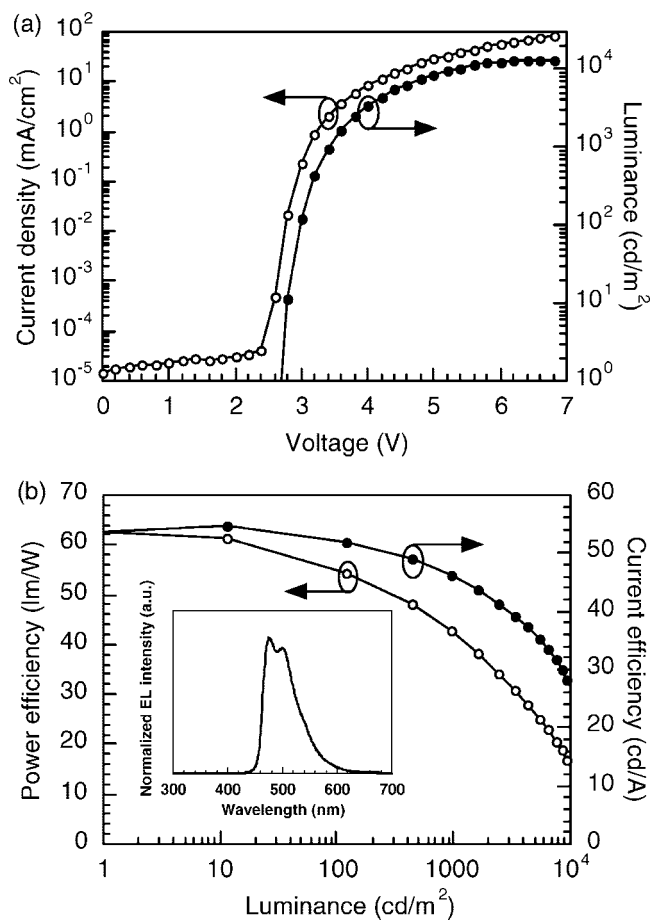
naphthyl)-*N*-phenylamino]biphenyl ( $\alpha$ -NPD) (50 nm)/tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) (40 nm)/**1** or Alq<sub>3</sub> (30 nm)/LiF (0.5 nm)/Al (100 nm)]. The current density–voltage ( $J$ – $V$ ) characteristics are shown in Figure 1.

Although the estimated LUMO levels of **1** (ca. 2.6 eV) were much higher than Alq<sub>3</sub> (3.2 eV), the current density of the devices was greater than that with Alq<sub>3</sub>. Thus, it was deduced that the favorable electron injection property of **1** was presumably derived from the coordination effect of the nitrogen atom on the pyridine ring toward a lithium cation. The high current density of 100 mA/cm<sup>2</sup> was achieved for **1a** at an applied voltage of 8.2 V, for **1c** at 9.2 V, for **1d** at 9.5 V, and for Alq<sub>3</sub> at 10.1 V, respectively. The introduction of a methyl group reduced the electron-transport property of **1**, probably because of the low intermolecular packing. Therefore, we chose **1a** as an ETL for FIrpic-based blue PHOLED.

A FIrpic-based PHOLED with a structure of [ITO/MCC-PC1020<sup>11</sup> (20 nm)/1,1-bis[4-[*N,N*-di(4-tolyl)amino]phenyl]cyclohexane (TAPC) (20 nm)/7 wt% FIrpic-doped 4,4',4''-tris(*N*-carbazolyl)triphenylamine (TCTA) (5 nm)/20 wt% FIrpic-doped TCTA (5 nm)/**1a** (50 nm)/LiF (0.5 nm)/Al (100 nm)] was fabricated. The current density–voltage and luminance–voltage characteristics are shown in Figure 2a. The applied voltages at 100 and 1000 cd/m<sup>2</sup> were 2.96 and 3.41 V, respectively, which are much lower than the other reported FIrpic-based blue PHOLEDs. These reduced driving voltages mainly result from two factors: (i) high carrier mobility of TAPC ( $1 \times 10^{-3}$  cm<sup>2</sup>/V s order) and **1a** ( $1 \times 10^{-4}$  cm<sup>2</sup>/V s order), and (ii) a high electron injection property of **1a**. The EL spectrum at 100 cd/m<sup>2</sup> is illustrated as the inset in Figure 2b. The emission chromaticity of the device was characterized by Commission Internationale de l'Éclairage of ( $x = 0.16$ ,  $y = 0.40$ ) which is attributed to the emission of FIrpic.

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**Figure 2.** (a) Current density–voltage and luminance–voltage characteristics of blue PHOLED using **1a** as an ETL. (b) Power efficiency–luminance and current efficiency–luminance characteristics. Inset: EL spectrum of the device.

The emission is only from FIrpic with no emission from neighboring materials, TAPC, TCTA and **1a**. 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 PE–luminance and current efficiency–luminance characteristics are shown in Figure 2(b). Extremely high PE of 56 lm/W and EQE of 23% (53 cd/A) were observed at 100 cd/m<sup>2</sup> without light outcoupling enhancement. Moreover, at 1000 cd/m<sup>2</sup>, high PE of 42 lm/W and EQE of 21% (46 cd/A) were also observed.<sup>12</sup> These are the highest performances so far reported for FIrpic-based blue devices.<sup>5,6</sup>

In summary, we synthesized novel wide-energy-gap electron-transport materials **1** containing 3,5-dipyridylphenyl moieties and developed an ultra high efficiency FIrpic-based blue PHOLED. The optimized device showed low driving voltages, which were 2.96 V at 100 cd/m<sup>2</sup> and 3.41 V at 1000 cd/m<sup>2</sup>, respectively. The extremely high PEs of 56 lm/W (53 cd/A) at 100 cd/m<sup>2</sup> and 42 lm/W (46 cd/A) at 1000 cd/m<sup>2</sup> were also observed.

**Acknowledgment.** The authors greatly acknowledge the financial support in part by the New Energy and Industrial Technology Development Organization (NEDO) through the “Advanced Organic Device Project”.

**Supporting Information Available:** Spectroscopic and analytical data, UV–vis and PL spectra of vacuum deposited film (Figures S1, S2), phosphorescent spectrum of vacuum deposited film (Figure S3), transient photoluminescent decay of 3 wt% FIrpic-doped thin film (Figure S4), transient photocurrent profile (Figure S5), electron mobility of **1a**, Alq<sub>3</sub>, and TAZ by TOF measurement (Figure S6) (PDF). This materials is available free of charge via Internet at <http://pubs.acs.org>.

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