

Highly Efficient Green Phosphorescent OLED Based on Pyridine-containing Starburst Electron-transporting Materials

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Starburst materials, 1,3,5-tris[3,5-bis(pyrid-4-yl)phenyl]benzene (**1a**) and 1,3,5-tris[3,5-bis(pyrid-3-yl)phenyl]benzene (**1b**) were designed and synthesized. By using *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)₃] as a green emitter and **1** as an electron-transporting material, a green OLED was fabricated. The OLED exhibited a maximum power efficiency (PE) of 96 lm W⁻¹ with an external quantum efficiency (EQE) of 23% at 2.1 cd m⁻², and a PE of 75 lm W⁻¹ with an EQE of 23% at 100 cd m⁻².

It is well known that phosphorescent emitters, such as Ir(ppy)₃ enable the internal quantum efficiency of OLED to be as high as 100%, because phosphorescent emitters can convert not only singlet state but also triplet excitation energy into photons.^{1,2} To develop highly efficient OLED using phosphorescent emitters, wide energy gap materials are indispensable to confine the triplet exciton on the emitter.^{3–5} Recently our group demonstrated highly efficient blue and green phosphorescent devices using wide energy gap electron-transporting materials (ETMs) containing phenylpyridine moieties, bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine,⁶ 3,3'',5,5''-tetra(3-pyridyl)-1,1',3',1''-terphenyl,⁷ 1,3,5-tris(3-pyrid-3-ylphenyl)benzene.⁸ The OLEDs showed extremely high efficiency and low operating voltage compared with OLEDs using conventional ETMs, such as 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ)⁵ and 2,9-dimethyl-4,7-diphenylphenanthroline (BCP).^{2c} Here we introduce novel starburst ETMs, 1,3,5-tris[3,5-bis(pyridyl)phenyl]benzene derivatives **1a** and **1b** and the application to Ir(ppy)₃-based green OLED. These ETMs showed much higher thermal stability and solubility than those of previously reported materials^{6–8} maintaining high electron-transporting properties, hole-blocking ability and triplet energy (*E*_{T1}) level over 2.77 eV.

Novel wide energy gap 1,3,5-tris[3,5-bis(pyrid-4-yl)phenyl]benzene derivatives containing three 3,5-dipyridylphenyl moieties were designed. The synthetic route is shown in Figure 1. The precursor 1,3,5-tris(3,5-dibromophenyl)benzene (**4**) was prepared by modified literature procedure.⁹ The target materials **1a** and **1b** were obtained via the Suzuki–Miyaura coupling reaction¹⁰ of hexabromide **4** with corresponding pyridine boronic acid esters in 40% yield for **1a** and 66% yield for **1b**, respectively.¹¹ The products were purified by repeated temperature gradient vacuum sublimation before device fabrication.

The thermal properties of **1** were estimated by differential scanning calorimetry (DSC). For **1a**, it was crystallized during a cooling cycle, thus the glass transition temperature (*T*_g) was not observed. On the other hand, *T*_g of **1b** was observed to be 161 °C, which indicated high morphological stability of thin film. The electrochemical properties were determined by UV–vis, PL, and atmospheric photoelectron yield spectroscopy

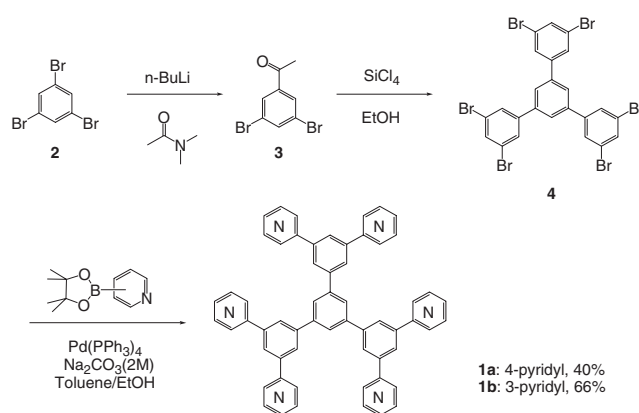


Figure 1. Synthetic routes of **1a** and **1b**.

Table 1. Thermal and electrochemical properties of **1**

Comp.	<i>T</i> _g /°C ^a	<i>T</i> _m /°C ^a	<i>T</i> _d /°C ^b	<i>I</i> _p /eV ^c	<i>E</i> _g /eV ^d	<i>E</i> _a /eV ^e
1a	n.d. ^f	387	558	6.71	3.90	2.81
1b	161	388	561	6.68	3.85	2.83

^aDetermined by DSC measurement. ^bObtained from TGA analysis. ^cMeasured by AC-3 UV photoelectron yield spectrometer. ^dTaken as the point of intersection of the normalized absorption spectra. ^eCalculated using *I*_p and *E*_g values. ^fn.d.: not detected.

(AC-3, Riken Keiki Co.). The ionization potentials (*I*_p) were observed around 6.70 eV, suggesting high hole-blocking ability. The electron affinity (*E*_a) was calculated by subtraction of the HOMO–LUMO energy gap (*E*_g). The physical properties are summarized in Table 1.

The *E*_{T1} levels were determined by the solid-state phosphorescent spectra at 4.2 K (Figure 2). The onset of phosphorescence was observed at 437 nm for **1a**, and 447 nm for **1b**, respectively. Those are equivalent to the excited triplet energy level of 2.84 eV for **1a** and 2.77 eV for **1b**, respectively. Therefore, these novel ETMs are considered to be applicable for blue and green phosphorescent OLEDs.

To examine the electron-transporting properties of **1a**, an OLED with a structure of [ITO (110 nm)/poly(arylene ether sulfone)-containing tetraphenylbenzidine (TPDPES) doped with 10 wt % tris(4-bromophenyl)aminium hexachloroantimonate (TBPAH)¹² (20 nm)/4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl (α-NPD) (30 nm)/CBP: 8 wt % Ir(ppy)₃ (20 nm)/**1a** (40 nm)/LiF (0.5 nm)/Al (100 nm)] was fabricated. The current density–voltage and luminance–voltage characteristics were measured with a Keithley source meter 2400 and a Konica Minolta CS-200, respectively. The EQE was calculated by using current density, luminance, EL spectrum, and the relative

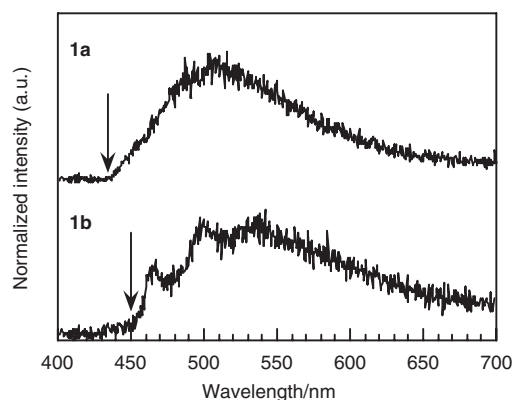


Figure 2. Photoluminescent spectra of vacuum-deposited films of **1a** and **1b** excited by a nitrogen laser ($\lambda = 337$ nm) at 4.2 K.

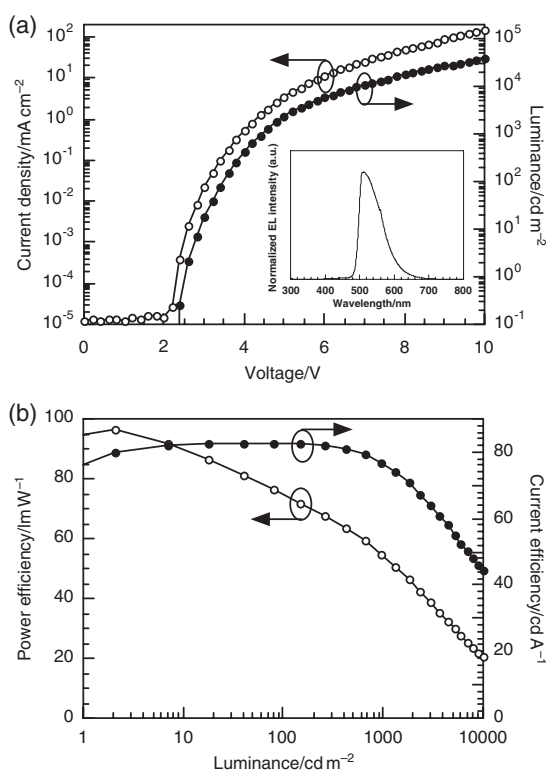


Figure 3. (a) J - V - L characteristics and (b) PE - L - CE characteristics of green PHOLED using **1a** as an ETM. Inset: EL spectrum of the device.

luminous efficiency curve. The current density–luminance–voltage (J - V - L) and power efficiency–luminance–current efficiency (PE - L - CE) of the device using **1a** are shown in Figure 3. The turn-on voltage at 1.0 cd m^{-2} was 2.5 V, and the applied voltages at 100 cd m^{-2} and $1,000 \text{ cd m}^{-2}$ were 3.4 and 4.4 V respectively. The device exhibited a maximum PE of 96 lm W^{-1} and a maximum EQE of 23% at 2.1 cd m^{-2} , and a power efficiency of 75.2 lm W^{-1} and an EQE of 23% at 100 cd m^{-2} . Even though this device has no n-doping layer, such as Cs-doped 4,7-diphenyl-1,10-phenanthroline (BPhen), these device performances are comparable with n-doped PHOLEDs.¹³

In summary, we designed and synthesized novel ETMs **1** with three 3,5-dipyridylphenyl moieties. By using **1** and Ir(ppy)_3 , the green OLED showed a maximum PE of 96 lm W^{-1} with an EQE of 23% at 2.1 cd m^{-2} , and a PE of 75 lm W^{-1} with an EQE of 23% at 100 cd m^{-2} .

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References and Notes

- 1 H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, **2008**.
- 2 a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151. b) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4. c) C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **2000**, *77*, 904.
- 3 K. Goushi, R. Kwong, J. J. Brown, H. Sasabe, C. Adachi, *J. Appl. Phys.* **2004**, *95*, 7798.
- 4 S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, F. Sato, *Appl. Phys. Lett.* **2003**, *83*, 569.
- 5 Y. Agata, H. Shimizu, J. Kido, *Chem. Lett.* **2007**, *36*, 316.
- 6 a) D. Tanaka, H. Sasabe, Y.-J. Li, S.-J. Su, T. Takeda, J. Kido, *Jpn. J. Appl. Phys.* **2007**, *46*, L10. b) H. Sasabe, T. Chiba, S.-J. Su, Y.-J. Pu, K. Nakayama, J. Kido, *Chem. Commun.* **2008**, 5821.
- 7 a) H. Sasabe, E. Gonmori, T. Chiba, Y.-J. Li, D. Tanaka, S.-J. Su, T. Takeda, Y.-J. Pu, K. Nakayama, J. Kido, *Chem. Mater.* **2008**, *20*, 5951. b) S.-J. Su, E. Gonmori, H. Sasabe, J. Kido, *Adv. Mater.* **2008**, *20*, 4189. c) H. Sasabe, Y.-J. Pu, K. Nakayama, J. Kido, *Chem. Commun.* **2009**, 6655.
- 8 a) S.-J. Su, T. Chiba, T. Takeda, J. Kido, *Adv. Mater.* **2008**, *20*, 2125. b) S.-J. Su, Y. Takahashi, T. Chiba, T. Takeda, J. Kido, *Adv. Funct. Mater.* **2009**, *19*, 1260.
- 9 a) S. S. Elmorsy, A. Pelter, K. Smith, *Tetrahedron Lett.* **1991**, *32*, 4175. b) V. S. Iyer, M. Wehmeier, J. D. Brand, M. A. Keegstra, K. Müllen, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604.
- 10 A. Suzuki, H. C. Brown, *Organic Synthesis via Boranes, vol. 3, Suzuki coupling*, Aldrich Chemical Company, Milwaukee, **2003**.
- 11 **1a** was synthesized by the Suzuki cross-coupling reaction between 1,3,5-tris(3,5-dibromophenyl)benzene (**4**) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine using tetrakis(triphenylphosphine)palladium(0) and 2 M aqueous sodium carbonate in toluene and ethanol. Data for **1a**: $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.61 (dd, $J = 2.8, 1.6$ Hz, 12H), 7.91 (t, $J = 1.6$ Hz, 3H), 7.97 (s, 3H), 7.99 (d, $J = 1.6$ Hz, 6H), 8.73 (dd, $J = 2.8, 1.6$ Hz, 12H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 109.74, 120.25, 121.50, 121.89, 126.78, 140.41, 147.63, 148.72, 150.58, 150.67. UV-vis (film): $\lambda_{\text{max}} = 264$ nm. PL (film): $\lambda_{\text{max}} = 368$ nm. MS(EI): m/z 769 $[\text{M}]^+$. For **1b**: $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.41 (dd, $J = 4.8, 3.2$ Hz, 6H), 7.81 (t, $J = 1.6$ Hz, 3H), 7.93 (d, $J = 1.6$ Hz, 6H), 7.99–8.02 (m, 9H), 8.65 (dd, $J = 3.2, 1.6$ Hz, 6H), 8.97 (d, $J = 2.4$ Hz, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 109.80, 115.90, 124.46, 126.39, 126.83, 135.78, 136.83, 140.49, 143.07, 143.40, 148.18, 149.84. UV-vis (film): $\lambda_{\text{max}} = 262$ nm. PL (film): $\lambda_{\text{max}} = 365$ nm. MS(EI): m/z 769 $[\text{M}]^+$.
- 12 a) Y. Sato, T. Ogata, J. Kido, *Proc. SPIE* **2001**, *4105*, 134. b) T. Ogata, Y. Sato, T. Suzuki, J. Kido, *Abstr. Int. Conf. Science and Technologies of Advanced Polymers*, **1999**, p. 166.
- 13 a) G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, J. Salbeck, *Appl. Phys. Lett.* **2004**, *85*, 3911. b) S. Watanabe, N. Ide, J. Kido, *Jpn. J. Appl. Phys.* **2007**, *46*, 1186.