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ARTICLE TYPE

Efficient bipolar host materials based on carbazole and 2-methyl pyridine for green phosphorescent organic light-emitting diodes.

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Two host materials based on carbazole/pyridine end-capping group were designed and synthesized for green phosphorescent organic light-emitting diodes (PHOLEDs). One of those, 9-[9,9-diethyl-2-(6-methylpyridin-2-yl)-9H-fluoren-7-yl]-9H-carbazole (2) exhibited excellent properties for efficient green

¹⁰ PHOLEDs as host material. A device using compound **2** as host material with the green phosphorescence dopant bis[2-(1,1',2',1"-terphen-3-yl)pyridinato-*C*,*N*]iridium(III)(acetylacetonate), (tphpy)₂Ir(acac), showed the external quantum efficiency (EQE) of 10.7 %, a power efficiency (PE) of 17.27 lm/W and luminous efficiency (LE) of 39.72 cd/A at 20 mA/cm², respectively, with the Commission International de L'Eclairage (CIE) chromaticity coordinates of (0.34, 0.62) at 8.0 V.

15 Introduction

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In the display industry, PHOLEDs have attracted much attention due to their theoretically higher internal quantum efficiency than fluorescent OLEDs. It is because PHOLEDs can use not only singlet excitons but also triplet excitons to generate emission by 20 originated from spin-orbital coupling caused by heavy transition

metal such as Ir and Pt.¹ However, it has problems that must be solved which derived from numerically increased triplet excitons such as triplet-triplet annihilation and triplet-polaron annihilation in neat film state. To prevent those efficiency decrement

- ²⁵ problems, PHOLEDs usually adopt a host-dopant system. ^{2,3} To obtain high efficiency from host-dopant system PHOLEDs, the choice of host materials has great effects for efficiencies of device and host materials should satisfy the following conditions. (i) the triplet energy (E_T) of the host material must be higher than
- ³⁰ that of the dopant to prevent of flow back the energy from dopant to host,^{4,5} (ii) the host material needs to well-matched highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels with the neighboring layers such as hole transporting layer and electron transporting
- ³⁵ layer to get hole and electron easily, and (iii) good and balanced carrier mobility to make the broad electron-hole recombination zone within the emitting layer (EML) and reduce the efficiency roll-off. In these aspects, bipolar materials having high triplet energy is suitable for host materials with their good dual mobility ⁴⁰ of hole and electron to lead to the high efficiency of device.⁶⁻¹²
- In this paper, we report two bipolar host materials 9-[4-(6-methylpyridin-2-yl)phenyl]-9*H*-carbazole (1) and 9-[9,9-diethyl-2-(6-methylpyridin-2-yl)-9*H*-fluoren-7-yl]-9*H*-carbazole (2) bearing carbazole, which have sufficiently large triplet energy
- ⁴⁵ and good hole transporting ability¹³⁻¹⁵ and 2-methylpyridine having good electron accepting ability with high electron affinity

and high triplet energy.^{16,17}

Results and Discussion

Synthesis of bipolar materials

⁵⁰ Bipolar host materials were synthesized with a yield of 93% and 78%. As described in Scheme 1, product 1 and 2 were synthesized by Suzuki coupling from the corresponding boronic esters and 2-bromo-6-methylpyridine in the presence of palladium catalyst Pd(PPh₃)₄ and base K₂CO₃. These products ⁵⁵ were characterized by ¹H and ¹³C NMR, mass spectrometry, and element analysis.



Scheme 1. a) Pd(PPh₃)₄, 2M K₂CO₃, aliquat 336, toluene, ethanol, 90 $^{\circ}\text{C}$ reflux for 2 hours.

60 Physical and Photo-physical Properties of compounds

Thermogravimetric analysis (TGA) were performed to determine the thermal stability of compounds **1** and **2**, respectively. The decomposition temperature (T_d), corresponding to 5% weight loss, were detected at 266 °C and 305 °C, respectively. Increased T_d ⁶⁵ value about 40 °C implies that the introduction of the fluorene moiety bring thermal stability of compound due to its stable structure. Published on 13 May 2015. Downloaded by Freie Universitaet Berlin on 14/05/2015 08:47:47.

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 Table 1. Physical and photo-physical properties of host materials 1 and 2.

Compounds	$\lambda_{\max}^{abs, a}$ (nm)	$\lambda_{\max}^{em, a}$ (nm)	E_g^b (eV)	HOMO ^c /LUMO ^d (eV)	E_T^e (eV)
1	283	394	3.55	5.77/2.22	2.71
2	344	402	3.37	5.89/2.52	3.05

 ${}^{a}\lambda_{max}^{abs}$ and λ_{max}^{em} measured in CH₂Cl₂ solution (ca.1×10⁻⁵M).^bThe energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. ^cThe HOMO energy levels of the compounds ⁵ were measured using a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). ^dThe LUMO energy levels were estimated by subtracting the energy band gap from the HOMO energy levels. ^eE_T determined by the absorption energy from the absorption spectra of the materials in 2-MeTHF solution at 77K.



Fig.1. (a) UV-Vis absorption and PL emission spectra host materials 1, 2 and (b) PL emission spectra of host materials 1, 2, and CBP and UV/Vis absorption spectra of dopant materials, (tphph)₂Ir(acac).

- ¹⁵ Photo-physical properties of compounds 1 and 2 were analyzed by using UV-vis and photoluminescence (PL) spectrometers in Table 1. Fig. 1 shows UV-Vis spectra compounds 1 and 2, and PL spectra of compounds 1, 2, and CBP as well as UV/Vis absorption spectra of dopant materials, (tphph)₂Ir(acac). In Fig. ²⁰ 1(a), compound 2 is exhibiting red-shifted absorption and
- emission spectra due to longer π -conjugation length than that of compound 1 by replacing phenyl by fluorene moiety. Also, compound 2 shows smaller Stokes shift than compound 1 about 53 nm. It implies that the replacement phenyl by fluorene brings
- ²⁵ structural rigidity for molecule. Triplet energy of compounds 1 and 2, which were determined from the first phosphorescent emission peaks in 77 K, were 2.71eV and 3.05eV, respectively. These values are higher than the 2.43 eV triplet energy of (typhpy)₂Ir(acac) dopant and 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl
- ³⁰ (CBP, $E_T = 2.56$ eV), which commonly used material as host material for green and red PHOLEDs.^{18,19} Sufficiently higher triplet energy of compound **1** and **2** than dopant material meets the condition for good host materials for PHOLEDs.

Performance of electroluminescence devices

³⁵ Green electroluminescence (EL) devices **A-C** were fabricated by using (tphpy)₂Ir(acac) as the dopant in emitting layer (EML) and compounds **1**, **2** and CBP as the host materials. The energy levels of the materials used in each layer of the devices are displayed in Fig 2.



Fig. 2. Energy-level diagram of devices A-C.

Devices A and B consist of the following layer structure : Indium tin oxide (ITO)/ N,N-bis(naphthalen-1-yl)-N,N-bis(phenyl)benzidine (NPB)(50nm)/ tris(4-carbazoyl-9-ylphenyl)amine 45 (TcTa)(10nm)/ (tphpy)2Ir(acac)(8%):Host(30nm)/ bathophenanthroline (Bphen)(30nm)/ 8-hydroxyquinoline lithium (Liq)(2nm)/ Al(100nm). NPB and TcTa are selected as hole transport layers (HTL). Compounds 1 and 2 are used for host materials. Bphen is used for the electron transport layer (ETL), and Al is the cathode. 50 The reference device C consists of the same structure except using CBP instead of compound 1 and 2 as host. EL spectra of (tphpy)₂Ir(acac) doped devices A-C are plotted in Fig. 3 and EL data of devices A-C are listed in Table 2. In all devices, quite similar green emission peaks were exhibited at 526 nm, 527 nm 55 and 529 nm, respectively. It means that the emissions from device A-C are not originated from host material but triplet excitons of dopant, (tphpy)₂Ir(acac) and the energy transfer from hosts to dopant occured perfectly.



Fig. 4 shows (a) current density- and luminance-voltage, (b) luminous efficiency- and power efficiency-current density, and (c) the external quantum efficiencies-current density plots of devices **A-C**. In particular, device **B** shows higher external quantum efficiencies than those of device **A** and **C**. Device **B** exhibited an external quantum efficiency of 10.7 %, a power efficiency of 17.27 lm/W, and a luminous efficiency of 39.72 cd/A at 20 mA/cm², respectively, with the Commission International de L'Eclairage chromaticity coordinates of (0.34, 0.62) at 8.0 V.

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Table 2. EL performance characteristics of devices A-C.

Devices	Luminance	LE ^{a/b}	PE ^{a/b}	EQE ^{a/b}	CIE ^c	$\lambda_{\max}^{EL, c}$ (nm)
(host)	(cd/m ²)	(cd/A)	(lm/W)	(%)	(x, y)	
A (1)	7207 (10V)	30.9/ 19.11	18.69/ 6.67	7.87/ 5.19	(0.34, 0.62)	526
B (2)	18680 (9.5V)	57.25/ 39.72	45.05/ 17.27	15.42/ 10.7	(0.34, 0.62)	527
C	40520	45.6/	31.84/	12.44/	(0.35,	529
(CBP)	(11V)	36.2	13.10	9.74	0.60)	

^a Maximum values. ^bAt 20 mA/cm². ^c At 8V.

The significant improvement of whole efficiencies of device **B** in comparison with device **A** and **C** could be explained based on (i) ⁵ the efficient energy transfer from host to dopant through the Förster energy transfer pathway and (ii) the appropriate HOMO and LUMO energy levels with adjacent layers such as HTL, ETL, and (iii) the well-balanced carrier mobility derived from bipolar structure.

¹⁰ In Fig. 1(b), PL emission peaks of compound 1 and 2 are observed at 394 nm, 402 nm and that of CBP are exhibited at 350 nm. Also, a singlet metal-to-ligand transfer (¹MLCT) absorption band of dopant material is located at range of 400-450 nm, broadly. It implies that the Förster energy transfer from 1s compound 1 and 2 to dopant would be more efficiently occured than that of CBP. The resulting singlet excitons of dopants are transformed to triplet excitons by strong spin-orbital coupling originated from Ir. It would be an important part for improving EL efficiencies of device A and B equally, compared to device

- ²⁰ C.^{20,21} However, the much smaller energy gap between the LUMOs energy levels of compound 2 and ETL than those of compound 1 and ETL makes electron transfer easily from ETL to EML in device B. This effective electron injection of device B would contribute the improved EL efficiencies of device B in a comparison with device A. In an expect of comparison between the second seco
- ²⁵ comparison with device A. In an aspect of energy gaps between EML and neighboring layers, CBP in device C is more effectively positioned to get higher efficiencies than compound 2 in device B. Nevertheless, device B shows more high efficiencies than device C. The pyridine moiety in compound 2 of device B
- ³⁰ provides a good electron-accepting ability (or electronwithdrawing ability) to compound **2**, and it improves the electron mobility of compound **2**. CBP is end-capped with two carbazole unit and thus has hole transfer unit only. This difference brings a well-balanced charge carrier mobility to compound **2**, compared
- ³⁵ to CBP. The resulting well-balanced carrier population in the emitting layer of device **B** using compound **2** as host would contribute the improve EL efficiencies of device **B** in comparison with device **C**. However, in high current-density region, the larger energy gap between LUMOs of ETL and EML in device **B**
- ⁴⁰ than those in device **C** brings higher efficiency roll-off of device **B** than that of device **C**. This larger energy gap of device **B** than device **C** would make the electron injection in device **B** more difficult than device **C**, and thus induce the narrower exciton recombination zone near the ETL in the EML of device **B** in
- ⁴⁵ comparison with device **C**. Particularly, in high current density, the populated triplet-excitons in narrow recombination zone of device **B** would become to interact with each other. The resulting triplet-triplet annihilation in the EML of device **B** would contribute to the reduced EL efficiency, and thus high efficiency roll affect device **B** in the balance pair of the balance
- ⁵⁰ roll-off of device **B** in the high current-density region.²²

Conclusions

In summary, we have synthesized new bipolar green host materials based on carbazole and 2-methylpyridine. Green phosphorescent devices using these compounds as hosts were 55 fabricated and their electroluminescence (EL) properties were investigated. Especially, a device using 9-[9,9-diethyl-7-(6methylpyridin-2-yl)-9H-fluoren-2-yl]-9H-carbazole (2) as the host and bis[2-(1,1',2',1"-terphen-3-yl)pyridinatoC,N]iridium(III) (acetylacetonate), (tphpy)₂Ir(acac), as the dopant exhibited the 60 improved EL efficiencies (an external quantum efficiency of 10.7 %, a power efficiency of 17.27 lm/W and luminous efficiency of 39.72 cd/A at 20 mA/cm², respectively), in comparison with a device using CBP as host (an external quantum efficiency of 9.74 %, a power efficiency of 13.10 lm/W and luminous efficiency of 65 36.2 cd/A at 20 mA/cm², respectively). The effective energy transfer, charge injection and the well-matched electronaccepting/ electron-donating capabilities of compound 2 would play important roles in improving the EL efficiencies of OLED device using compound 2 as host.



Fig. 4. (a) The external quantum efficiencies-current density, (b) luminance efficiency- and power efficiency-current density, and (c) current density- and luminance-voltage plots of devices A-C.

Experimental Details

General information

The ¹H- and ¹³C- nuclear magnetic resonance (NMR) spectra

were recorded on a Varian Unity Inova 300Nb spectrometer. Elemental analysis (EA) was measured using an EA 1108 spectrometer. The low resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in EI and APCI mode 5 and a JMS-T100TD (AccuTOF-TLC) in positive ion mode. The UV-Vis absorption and photoluminescence spectra of the newly designed host materials were measured in a CH₂Cl₂ solution (10⁻⁵ M) using a Shimadzu UV-1650PC and AMINCO-Bowman Series 2 Luminescence Spectrometer. The ionization potentials 10 (or HOMO energy levels) of the compounds were measured using a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. The LUMO energy levels were estimated by subtracting the 15 energy band gap from the HOMO energy levels. The thermal properties were measured by thermogravimetric analysis (TGA) (DTA-TGA, TA-4000) and differential scanning calorimetry (DSC) (Mettler Toledo; DSC 822) under N2 at a heating rate of 10 °C/min. A heat-cold-heat method was used with an initial

²⁰ heating rate of 10 °C/min, rapidly quenched-cooled in liquid nitrogen, and finally heated at rate of 10 °C/min.

General Procedure for the Suzuki Cross-Coupling Reaction

2-Bromo-6-methylpyridine (1.0 mol) and the corresponding boronic ester derivatives (1.2 mol), Pd(PPh₃)₄ (0.04 mol),
²⁵ aqueous 2.0 M K₂CO₃ (10.0 mol), Aliquat 336 (0.1 mol), and toluene were mixed in a flask, and heated under reflux for 2 h. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous MgSO₄ and filtered with silica
³⁰ gel. The solution was then evaporated. The crude product was recrystallized from CH₂Cl₂/EtOH.

9-[4-(6-Methylpyridin-2-yl)phenyl]-9*H***-carbazole (1)** : Yield = 93%. ¹H NMR (300 MHz, CDCl3): δ ppm 8.19 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H), 7.67-7.62 (m, 3H), 7.56 (d, *J* = 7.6

³⁵ Hz, 1H), 7.47-7.45 (m, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.11 (d, J = 7.3 Hz, 1H), 2.65 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 158.9, 156.3, 141.0, 139.1, 138.4, 137.3, 128.8, 127.4, 126.3, 123.7, 122.2, 120.6, 120.3, 117.9, 110.1, 25.1; MS (EI+, m/z): 334 [M+]; Anal. calcd for C₂₄H₁₈N₂ : C ⁴⁰ 86.20, H 5.43, N 8.38. Found C 85.83, H 5.37, N 8.31.

9-[9,9-Diethyl-7-(6-methylpyridin-2-yl)-9H-fluoren-2-yl]-9Hcarbazole (2) : Yield = 78%. ¹H NMR (300 MHz, CDCl3): δ ppm 8.19 (d, J = 7.8 Hz, 2H), 8.09-8.06 (dd, J = 1.5, 6.6 Hz, 1H), 8.02 (s, 1H), 7.96 (d, J = 3.6 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H),

- ⁴⁵ 7.69-7.60 (m, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.1 Hz, 4H), 7.35-7.29 (m, 2H), 7.12 (d, J = 6.9 Hz, 1H), 2.67(s, 3H), 2.24-2.03(m, 4H), 0.49(t, J = 7.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 158.8, 157.4, 152.7, 151.0, 141.7, 141.4, 140.8, 139.4, 137.2, 136.9, 126.7, 126.3, 123.7, 122.2, 121.8, 121.7, ⁵⁰ 121.4, 120.7, 120.4, 120.2, 118.0, 110.1, 56.9, 33.1, 25.2, 9.1;
- MS (APCI+, m/z): 479 [M+]; Anal. calcd for $C_{35}H_{30}N_2$: C 87.83, H 6.32, N 5.85. Found C 87.22, H 6.25, N 5.81.

Device fabrication and characterization

OLEDs using green-light-emitting molecules were fabricated by vacuum (5×10^{-7} torr) thermal evaporation onto precleaned ITO coated glass substrates. The Structure was as follows: ITO/ *N*,*N*'diphenyl-*N*,*N*'-(1-napthyl)-(1,1'-phenyl)-4,4'-diamine (NPB)(50 nm)/ 4,4',4''-tris(*N*-carbazole)triphenylamine (TcTa)(10nm)/ Phosphorescent host materials: Green dopant material 60 (tphpy)₂Ir(acac) (30nm, 8%)/ 4,7-diphenyl-1,10- phenanthroline (Bphen)(30nm)/ lithium quinolate (Liq)(2nm)/ Al (100nm). The current density (*J*), luminance(*L*), LE, PE, and CIE chromaticity coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. EL was measured using a Roper 65 Scientific Pro 300i.

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70 Notes and references

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