Contents lists available at SciVerse ScienceDirect

Organic Electronics



journal homepage: www.elsevier.com/locate/orgel

fac-Tris(2-phenylpyridine)iridium (III)s, covalently surrounded by six bulky host dendrons, for a highly efficient solution-processed organic light emitting device

Yong-Jin Pu*, Noriaki Iguchi, Naoya Aizawa, Hisahiro Sasabe, Ken-ichi Nakayama, Junji Kido*

Department of Organic Device Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

ARTICLE INFO

Article history: Received 3 May 2011 Received in revised form 29 July 2011 Accepted 24 August 2011 Available online 12 September 2011

Keywords: Organic light emitting device Phosphorescence Iridium complex Dendrimer

ABSTRACT

The fully surrounded complexes by six host dendrons showed high photoluminescence quantum efficiency in a neat film, comparable to in a dilute solution. The surrounding host dendrons efficiently suppressed intermolecular interaction between central Ir complexes and prevented concentration quenching. The complex, (**mCP**)₆**Ir**, fully surrounded by six carbazole type hosts showed much better performance, compared with the complex, (**DAP**)₆**Ir**, surrounded by arylamine type hosts, because of well balanced charge injection and transporting in the devices.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Organic light-emitting devices (OLEDs) have attracted a great deal of attention because of their potentials for next generation of flat panel displays and general lighting [1-4]. Solution processes such as ink-jet printing are considered to have an advantage of low cost over the vacuum process for manufacturing of large area displays or lighting. On the other hand, the device using phosphorescent heavy metal complexes such as *fac*-tris(2-phenylpyridine)iridium (III) as an emitter shows much higher efficiency than the device using a fluorescent emitter, because the phosphorescent complex can utilize all of singlet and triplet excitons for the emission [5,6]. That is why the combination of the solution-process and the phosphorescent compounds can be an ideal choice to achieve low cost and high efficiency in OLEDs in the future. For the solution-process, substitution of functional dendrons on the complex is one of approaches to solubilize it, and P.L. Burn group has been done a lot of pioneering work on the dendrimer OLEDs [7–9]. The dendron is bulky in volume, so that it can prevent intermolecular interaction between the emitting complexes, resulting in reduction of concentration quenching and high photoluminescence quantum efficiency (PLQE) [9-11]. From the OLED application point of view, those dendrons have to have enough high charge-transporting ability for low driving voltage [12-20] and have a larger triplet energy level (T_1) than that of the core complex not to quench the triplet exciton of the complex [21,22]. In phosphorescent OLEDs. *m*-carbazolylbenzene (mCP) is one of wellknown and widely-used host materials, because its triplet energy level is enough high (3.0 eV) to confine the phosphorescent emission of the iridium complex, and has bipolar charge-transporting ability [23,24]. We previously reported the phosphorescent iridium complex, (mCP)₃Ir, attached three mCP dendrons having alkyl groups, and high efficiencies of the OLEDs using that complex [25,26]. In (mCP)₃Ir, mCP dendrons are attached on each phenyl ring of Ir(ppy)₃, and (mCP)₃Ir is a facial isomer, so that the three mCP dendrons are attached spacially same side in the complex, and surround only half side of Ir(ppy)₃. In this study, we designed two type of fully surrounded $Ir(ppy)_3$ by six



^{*} Corresponding author.

E-mail addresses: pu@yz.yamagata-u.ac.jp (Y.-J. Pu), kid@yz.yamaga-ta-u.ac.jp (J. Kido).

^{1566-1199/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.orgel.2011.08.015



Scheme 1. Chemical structure of the iridium complexes.

bulky dendrons, (**mCP**)₆**Ir** and (**DAP**)₆**Ir** (Scheme 1). Both of the complexes showed higher PLQE in a neat film than that of half-surrounded (**mCP**)₃**Ir** and (**DAP**)₃**Ir**, well-supporting the results reported in the literature [9]. Solution-processed OLED with (**mCP**)₆**Ir** showed high efficiencies, 19 lm/W, 32 cd/A, and 12% of external quantum efficiency at 100 cd/m², and 11 lm/W, 25 cd/A, 9.1% at 1000 cd/m². The energy levels of the surrounding dendrons intensely affected the charge injection into the emitting layer and the device performance.

2. Results and discussion

Scheme 2 shows synthesis route of (**mCP**)₆**Ir**, (**DAP**)₆**Ir**, and (**DAP**)₃**Ir**. The ligands of the complexes, **2**, **5**, and **6**, were synthesized via several steps of palladium catalyzed coupling reactions. The complexes were prepared from the two steps of complexation. First, a mixture of iridium chloride trihydrate and excess of the ligands afforded dichloro bridged dimer complexes, **7**, **8**, and **9**. Second, the dimers were reacted by the ligands with silver trifluorom-



Scheme 2. Synthetic procedure of (DAP)₃Ir, (DAP)₆Ir and (mCP)₆Ir: (i) 3,5-dichlorophenylboronic acid, Pd(PPh₃)₄, K₂CO₃ aq., THF, N₂, reflux, (ii) di(4-(*n*-butyl)phenyl)amine, Pd₂(dba)₃, PCy₃, NaOt-Bu, toluene, N₂, reflux, (iii) 2,4-dibromopyridine, Pd₂(dba)₃, dppf, K₂CO₃ aq., toluene, N₂, reflux, (iv) di(4-(*n*-butyl)phenyl)amine, Pd₂(dba)₃, P(Cy)₃, NaOt-Bu, toluene, N₂, reflux, (v) 3,6-di(*n*-butyl)carbazole, Pd(OAc)₂, P(*t*-Bu)₃, NaOt-Bu, o-xylene, N₂, 120 °C, (vi) IrCl₃·3H₂O, H₂O, 2-ethoxyethanol, N₂, 130 °C, (vii) 2, CF₃SO₃Ag, diglyme, N₂, 130 °C, (viii) 5, CF₃SO₃Ag, diglyme, N₂, 130 °C, (ix) 6, CF₃SO₃Ag, ethyldiglyme, N₂, 150 °C.



Fig. 1. Photoluminecence spectra of (mCP)₃Ir (solid line), (mCP)₆Ir (circle), (DAP)₃Ir (triangle), and (DAP)₆Ir (square) in a neat film.

ethane sulfonate to give homoleptic functionalized complexes. The complexes were fully characterized by ¹H-NMR, matrix-assisted laser desorption/ionization time-offlight (MALDI) mass spectrometry (MS), and elemental analysis.

Photoluminescence of the neat film of the complexes fully-surrounded by the six bulky dendrons showed the peaks around 580 nm for (mCP)₆Ir and 577 nm for (DA-P)₆Ir, and the spectra were red-shifted compared with the emission of the less-surrounded complexes around 514 nm for (mCP)₃Ir and 528 nm for (DAP)₃Ir (Fig. 1). These results indicated that substitution on 3-position of phenyl ring did not change emission color of $Ir(ppy)_3$, but substitution on 4-position of pyridine ring made the emission red-shifted. The emission of Ir(ppy)₃ is mainly ascribed to triplet metal-to-ligand charge transfer (³MLCT) transition. Its highest occupied molecular orbital (HOMO) corresponds to *d* orbital of Ir and lowest unoccupied molecular orbital (LUMO) correspond to π^* orbital of ppy ligand, especially pyridine part of the ligand. That is why electron-donating group on pyridine ring decrease the energy gap of π - π ^{*} and LUMO level, on the other hand the same electron-donating group on 3-position of phenyl ring does not affect the pyridine ring because of less π -conjugation via meta-linkage [27,28].

PLQEs of the complexes in the neat film are important parameter to estimate the shielding effect of the surrounding dendrons to Ir(ppy)₃. PLQEs of the toluene solution and the films were measured by using an integrating sphere system under 331 nm excitation (Fig. 2). In a diluted solution, all complexes showed higher PLQE than 70%, which are comparable to 85% of unsubstituted Ir(ppy)₃. This result demonstrated that these surrounding dendrons are optically inert and does not affect the emission efficiency of Ir(ppy)₃ core. The fully-surrounded complexes, (**mCP)**₆**Ir** and (**DAP)**₆**Ir**, showed high PLQE even in a neat film, which is comparable to PLQE in a dilute solution. On the other hand, the half-surrounded complexes, (**mCP)**₃**Ir** and



Fig. 2. Photoluminescent quantum efficiencies (PLQEs) of the compounds in a neat film or a toluene solution ($2 \times 10^{-6} \text{ mol } L^{-1}$).

(DAP)₃Ir, showed much lower PLQE in a neat film than that in a dilute solution. These complexes are facial isomers, therefore, in (mCP)₃Ir and (DAP)₃Ir, a some space around pyridyl groups of $Ir(ppy)_3$ core are opened and their three dimensional structure is like a hemisphere, shown in Fig. 3, resulting in only partial suppression of concentration-quenching in a neat film of an iridium complex. However, in (mCP)₆Ir and (DAP)₆Ir, the bulky host dendrons fully surrounded Ir(ppy)₃ and effectively prevented the intermolecular interaction between Ir(ppy)₃s. There are still small amount of reduction of PLQEs from a solution to a neat film, due to the concentration-quenching even in the fully-substituted complexes. The substituted host dendrons are not enough large to completely suppress the interaction between the core complexes. Adachi et al. reported that an average distance between iridium complexes in a doped film critically influenced on PLQE [29]. Förster type energy transfer between Ir(ppy)₃ cores through an overlap of the emission and the absorption causes a decrease of neat film PLQY. If the average distance between iridium complexes is shorter than Förster radius, a strong quenching occurs. The stronger quenching of (mCP)₃Ir in the neat film than that of (mCP)₆Ir is due to the shorter average distance between the cores derived from a less number of bulky host dendrons of (mCP)₃Ir than that of (mCP)₆Ir. Substitution of more branched and larger dendrons to the core complexes are desirable to achieve the complete suppression of concentrationquenching.

HOMO level of the complexes and the surrounding host dendrons themselves, 3,5-(3,6-di(*n*-butyl)carbazol-9-yl)benzene **DAP** and 3,5-(*N*,*N*-di(4-(*n*-butyl)phenyl)amine) benzene **mCP**, were estimated from ionization potentials measured by photoelectron yield spectroscopy (Fig. 4). LUMO levels of **DAP** and **mCP** were estimated from the difference of optically obtained energy gap and ionization potential. LUMO level of the dendrimer complexes are still unknown because the optically obtained energy gap dose



Fig. 3. The optimized structures of: (a) **(mCP)**₃**Ir** and (b) **(mCP)**₆**Ir** by PM6 calculation. The butyl groups were replaced to hydrogen in calculation.

not correspond to HOMO–LUMO gap in the case of $Ir(ppy)_3$ derivatives. HOMO levels of the dendrimer complexes were close to that of $Ir(ppy)_3$, rather than that of the surrounding host dendrons. This result suggest that HOMO are mainly located on the central $Ir(ppy)_3$ group.

Single layer devices with the configuration of ITO/ poly(3,4-ethylenedioxythiophene) (PEDOT): poly(styrene sulfonic acid) (PSS) (40 nm)/(DAP)₃Ir, (DAP)₆Ir, or (mCP)₆Ir (120 nm)/LiF (1 nm)/Al (100 nm) and double layer devices with the configuration of ITO/PEDOT:PSS (40 nm)/(DAP)₃Ir, (DAP)₆Ir, or (mCP)₆Ir (60 nm)/bis-4,6-(3,5-di-4-pyridylphenyl)-2-methylpyrimidine (B4PyMPm) (60 nm)/LiF (1 nm)/Al (100 nm) were fabricated. In single layer devices, (DAP)₃Ir and (DAP)₆Ir exhibited higher current density than (mCP)₆Ir, probably because HOMO level of (DAP)₃Ir and (DAP)₆Ir are shallower than (mCP)₆Ir to enhance hole injection from PEDOT:PSS (Fig. 5). Therefore, hole current should be dominant in single layer devices. However, in contrast to the result of the current density-voltage plots, (mCP)₆Ir showed higher luminance than the others. As well as the luminance, current efficiencies of the single layer device with (mCP)6Ir were much higher than those of the other two complexes. This improvement showed that the surrounding **mCP** dendron has better electron injection and/or electron transport



Fig. 4. HOMO and LUMO levels of the surrounding host groups, **DAP** (fine solid line) and **mCP** (fine solid line), and Ir(ppy)₃ (dotted line), and HOMO levels of the complexes (thick solid line). Chemical structure of **DAP** and **mCP**.

property than **DAP** dendron to improve charge balance. The double layer devices were fabricated using B4PyMPm as an electron transporting and hole-blocking material on the emitting layer. DAP-surrounding complex, (DAP)₃Ir and (DAP)₆Ir, showed higher current density, as well as single layer device. This results suggest that hole current is still excess even in the device with electron transporting layer. High luminance was obtained at much lower voltage, and the efficiency were drastically improved. In the device with (mCP)₆Ir, thickness of the emitting layer was reduced from 60 to 40 nm to improve charge balance, resulting in increasing efficiencies (Table 1). Current efficiency of the device with (mCP)₆Ir was 32 cd/A, 19 lm/ W, 12% at 100 cd/m², and 25 cd/A, 11 lm/W, 9.1% at 1000 cd/m². There have been several reports on solution-processed phosphorescence OLED with dendrimer iridium complexes, and their high efficiencies, as mentioned in Section 1. However the most of papers emphasized peak efficiencies at a low current density and luminance, and did not revealed the efficiencies at practically high luminance, e.g. for lighting application. The efficiencies with our fully-surrounded Ir(ppy)₃ are one of high values among the solution-processed OLED ever reported.



Fig. 5. Current density-voltage, luminance-voltage, and current efficiency-voltage characteristics of the single layer device (a) and the double layer device (b).

Table 1Efficiencies of the solution-processed OLEDs.

Device structure	Compound	100 cd/m ²				1000 cd/m ²			
		Voltage (V)	$\eta_{ m P}$ (lm W $^{-1}$	$\eta_{\rm C}~({\rm cd}~{\rm A}^{-1})$	η_{EXT} (%)	Voltage (V)	$\eta_{ m P}({ m lm}{ m W}^{-1})$	$\eta_{\rm C}~({ m cd}~{ m A}^{-1})$	η_{EXT} (%)
Single layer	(DAP)₃Ir	-	-	-	-	-	-	-	-
	(DAP) ₆ Ir	13.9	0.016	0.071	0.028	-	-	-	-
	(mCP) ₆ Ir	10.3	0.23	0.75	0.29	13.6	0.23	1.0	0.39
Double layer	(DAP)₃Ir	4.0	2.6	3.2	1.0	6.3	1.9	3.8	1.1
	(DAP)6Ir	10.5	0.057	0.19	0.075	14.3	0.065	0.30	0.11
	(mCP) ₆ Ir	6.5	12	25	9.4	8.4	7.8	21	7.8
	(mCP) ₆ Ir ^a	5.2	19	32	12	7.3	11	25	9.1

^a Thickness of emitting layer is 40 nm.

3. Conclusion

We synthesized the solution processable iridium complexes for OLEDs, surrounded by diphenylamine derivatives or carbazole derivatives. The fully surrounded complexes, **(DAP)**₆**Ir** and **(mCP)**₆**Ir**, by six host dendrons showed high PLQE in a neat film, comparable to their PLQE in a dilute solution, demonstrating that the surrounding host dendrons efficiently suppressed intermolecular interaction between central Ir complexes and prevented concentration quenching. Not only PLQE of the complex but also energy levels and charge transporting property of the surrounding host dendron are important to achieve high efficiencies in a device. The complex, (**mCP**)₆**Ir**, fully surrounded by six carbazole type hosts showed much better performance, compared with the complexes surrounded by arylamine type hosts, because of well balanced charge injection and transporting in the devices.

4. Experimental

4.1. Measurements

¹H-NMR spectra were measured in deuterated solvents on a JEOL ECX 400 MHz spectrometer. Mass spectra were recorded on a IEOL IMS-K9 for electron impact-ionization (EI) or an Applied Biosystems Voyager DE-PRO for matrix-assisted laser desorption/ionization-time-of-flight (MALDI-TOF) from dithranol (DITH) in linear or reflection mode. Elemental analyses were carried out by the Elemental Analysis Service, Yamagata University, Japan. Thermal gravimetric analysis (TGA) was performed on Seiko SII EX-STAR 6000 and TGA/DTA 6200 analyzers. Differential Scanning Calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC calorimeter. Ionization potentials were measured with a photoelectron spectrometer surface analyzer (RIKEN KEIKI AC-3). UV-visible absorption spectra were recorded of solutions in chloroform or films on quartz with a Shimadzu UV-3150 spectrometer. PL spectra were recorded on a Jobin Yvon Fluoromax-4 fluorometer. PL quantum efficiencies were measured on a Hamamatsu C9920-01 calibrated integrating sphere system under nitrogen. Light emitting devices were fabricated on indium tin oxide (ITO) coated glass substrates, which were prepared by ultrasonication sequentially in detergent, methanol, 2-propanol and acetone, then exposed to UV-ozone under ambient conditions for 15 min. PEDOT:PSS was spin-coated as an anode buffer layer on pre-cleaned ITO substrate. On the top of PEDOT:PSS layer, dendrimers were spin-coated from 1,2-dichloroethane or toluene solution. The electron transporting material B4PyMPm was deposited by thermal evaporation at less than 1×10^{-4} Pa. The aluminum cathode was deposited through a shadow mask at less than 1×10^{-4} Pa. The active area of each device is $2 \text{ mm} \times 2 \text{ mm}$. Layer thickness calibration was performed using a Dektak 3 surface profilometer. The EL spectra were measured on a Hamamatsu PMA-11 photonic multichannel analyzer. The current-voltage (I-V) characteristics and luminance of the devices were measured using a Keithley 2400 Source Meter and Konica Minolta CS-200 chromameter, respectively. External guantum efficiencies were calculated assuming a Lambertian emission pattern and considering all spectral features in the visible region.

5. Materials

2-(3-(3,5-Dichlorophenyl)phenyl)pyridine **1**: a mixture of 2-(3-bromophenyl)pyridine (1.20 g, 5.13 mmol), 3,5dichlorophenylboronic acid (1.97 g, 10.3 mmol), K₂CO₃ (1.42 g, 10.3 mmol), and THF (100 ml) was deoxygenated by bubbling N₂ for 30 min. After that, Pd(PPh₃)₄ (0.240 g, 0.208 mmol) and degassed deionized water (5.2 ml) were added in the mixture, and then the mixture was refluxed under N₂ for 24 h. The mixture was allowed to cool to room temperature, and then diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the residue was purified by column chromatog-raphy over silica using a chloroform–ethyl acetate mixture (30:1) as eluent to give the compound **1** (1.26 g, 82%). $\delta_{\rm H}(400 \text{ MHz}, \text{CD}_2\text{Cl}_2)$ 8.67 (1H, d, *J* = 4.1 Hz), 8.23 (1H, s), 8.02 (1H, d, *J* = 7.3 Hz), 7.82–7.76 (2H, m), 7.61–7.53 (4H, m), 7.37 (1H, t, *J* = 1.8 Hz), 7.27 (1H, td, *J* = 5.7, 1.8 Hz). *m*/*z* [EI] 299: (M⁺). Found: C, 67.74; H, 3.60; N, 4.45. C₁₇H₁₁C₁₂N requires C, 68.02; H, 3.69; N, 4.67%.

2-(3-(3,5-Bis(di-(4-n-butylphenyl)amino))phenyl)phen yl)pyridine 2: the compound 1 (0.500 g, 1.67 mmol), di(4-(n-butyl)phenyl)amine (1.41 g, 5.00 mmol), sodium tertbutoxide (0.721 g, 7.50 mmol), Pd₂(dba)₃ (0.114 g, 0.125 mmol), and $P(Cy)_3$ (0.0701 g, 0.250 mmol) in a sealed tube was degassed in vacuo and filled with N2. After that, degassed toluene (5.0 ml) was added into the mixture, and then the mixture was refluxed for 24 h. After the mixture was allowed to cool to room temperature, diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography over silica using chloroform and a hexane-chloroform mixture (from 1:0 to 0:1) as eluent to give the compound **2** (0.929 g, 71%). $\delta_{\rm H}$ (400 MHz, CD₂Cl₂) 8.62 (1H, d, J = 5.0 Hz), 7.97 (1H, s), 7.88 (1H, d, *I* = 6.4 Hz), 7.74–7.67 (2H, m), 7.41–7.38 (2H, m), 7.22 (1H, td, J = 5.7, 1.4 Hz), 7.04–6.97 (16H, m), 6.81 (2H, d, *J* = 2.3 Hz), 6.67 (1H, t, *J* = 1.8 Hz), 2.52 (8H, t, *J* = 7.8 Hz, -CH₂CH₂CH₂CH₃), 1.58–1.50 (8H, m, -CH₂CH₂CH₂CH₃), 1.38-1.29 (8H, m, -CH₂CH₂CH₂CH₃), 0.90 (12H, t, I = 7.4 Hz, -CH₂CH₂CH₂CH₃). m/z [EI] 791: (M⁺). Found: C, 86.49; H, 7.75; N, 5.24. C₅₇H₆₃N₃ requires C, 86.65; H, 8.04; N, 5.32%.

4-Bromo-(2-(3-bromophenyl))pyridine 3: the mixture of 3-bromophenylboronic acid (2.81 g, 14.0 mmol), 2,4dibromopyridine (3.31 g, 14.0 mmol), K₂CO₃ (3.87 g, 28.0 mmol), deionized water (14 ml), and toluene (60 ml) was deoxygenated by bubbling N₂ for 30 min. After that, $Pd_2(dba)_3$ (0.385 g, 0.420 mmol) was added, and then the mixture was refluxed for 36 h. After the mixture was allowed to cool to room temperature, diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography over silica using a hexane-dichloromethane mixture (from 1:0 to 0:1) as eluent to give the compound **3** (1.76 g, 40%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.50 (1H, d, J = 5.0 Hz), 8.14 (1H, t, J = 1.8 Hz), 7.89–7.87 (2H, m, ArH), 7.56 (1H, d, J = 7.8 Hz), 7.43 (1H, dd, J = 5.3, 1.4 Hz), 7.34 (1H, t, J = 8.0 Hz). m/z [EI] 313: (M⁺), Found: C, 42.41; H, 2.02; N, 4.45. C₁₁H₇Br₂N requires C, 42.21; H, 2.25: N. 4.48%.

2-(3-(3,5-Dichlorophenyl)phenyl)-4-(4-(3,5-dichloroph enyl)phenyl)pyridine **4**: the compound **3** (1.75 g, 5.59 mmol), 3,5-dichlorophenylboronic acid (4.26 g, 22.3 mmol), K₂CO₃ (1.55 g, 11.2 mmol), deionized water (5.6 ml), and toluene (95 ml) was deoxygenated by bubbling N₂ for 30 min. After that, Pd(PPh₃)₄ (0.224 g, 0.194 mmol) was added, and then the mixture was refluxed for 24 h. After the mixture was allowed to cool to room temperature, diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography over silica using a hexane–chloroform mixture (from 1:0 to 0:1) as eluent to give the compound **4** (2.01 g) as a crude. The crude product was directly used for next step without further purification. $\delta_{\rm H}(400 \text{ MHz}, \text{CDCl}_3) 8.73 (1\text{H}, \text{s}), 8.18 (1\text{H}, \text{s}), 7.99 (1\text{H}, dt,$ *J*= 7.1, 1.8 Hz), 7.84 (1H, s), 7.58–7.50 (6H, m), 7.40 (1H, t,*J*= 1.8 Hz), 7.37 (1H, dd,*J*= 5.0, 1.8 Hz), 7.30 (1H, t,*I*= 1.8 Hz).

2-(3-(3,5-Bis(di(4-n-butylphenyl)amino))phenyl)phenyl)-4-(3-(3,5-bis(di(4-n-butylphenyl)amino))phenyl)pyridine 5: the mixture of di(4-*n*-butylphenyl)amine (18.0 g, 64.0 mmol), crude **4** (3.56 g), sodium *tert*-butoxide (8.85 g, 96.0 mmol), and toluene (80 ml) was deoxygenated by bubbling N_2 for 30 min. After that, $Pd_2(dba)_3$ (1.47 g, 1.60 mmol), PCy₃ (1.79 g, 6.40 mmol) was added, and then the mixture was refluxed for 24 h. After the mixture was allowed to cool to room temperature, diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography over silica using a hexane-chloroform mixture (from 1:0 to 0:1) and a hexane-chloroform mixture (from 1:0 to 1:3) as eluent, respectively, to give the compound **5** (7.30 g, 57%). $\delta_{\rm H}(400 \text{ MHz}, \text{CD}_2\text{Cl}_2) 8.52 (1\text{H}, \text{d}, I = 5.0 \text{ Hz}), 7.99 (1\text{H}, \text{s}),$ 7.74 (1H, s), 7.65 (1H, s), 7.36 (2H, d, J = 4.6 Hz), 7.16 (1H, s), 7.04–6.96 (32H, m), 6.78 (4H, t, J = 2.1 Hz), 6.72 (1H, t, *J* = 1.8 Hz), 6.66 (1H, t, *J* = 1.8 Hz) 2.51 (16H, t, *J* = 7.6 Hz, -CH₂CH₂CH₂CH₃), 1.57-1.50 (16H, m, -CH₂CH₂CH₂CH₃), 1.37-1.28 (16H, m, -CH₂CH₂CH₂CH₃), 0.90 (24H, t, I = 7.3 Hz, -CH₂CH₂CH₂CH₃). [MALDI:DITH] (m/z) 1424.9: (MH⁺). Found: C, 86.55; H, 8.48; N, 4.84. C₁₀₃H₁₁₇N₅ requires C, 86.81; H, 8.28; N, 4.91%.

2-(3-(3,5-Bis(3,6-di(n-butyl)carbazol-9-yl)phenyl)phenyl-4-(3,5-bis(3,6-di(n-butyl)carbazol-9-yl)phenyl))pyridi ne 6: the mixture of 3,6-di-n-butylcarbazole (7.21 g, 25.8 mmol), crude **4** (1.91 g), palladium(II) acetate (0.231 g, 1.03 mmol), K₂CO₃ (10.7 g, 77.4 mmol), and o-xylene (40 ml) was deoxygenated by bubbling N_2 for 30 min. After that, $P(t-Bu)_3$ (0.75 ml, 3.10 mmol) was added, and then the mixture was refluxed for 24 h. After the mixture was allowed to cool to room temperature, diethylether was added. The organic layer was washed by deionized water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography over silica using a hexanechloroform mixture (from 1:0 to 1:1) as eluent to give the compound **6** (3.84 g, 51%). $\delta_{\rm H}$ (400 MHz, CD₂Cl₂) 8.75 (1H, d, J = 5.0 Hz), 8.45 (1H, s), 8.06 (1H, s), 8.04 (1H, d, *J* = 1.8 Hz), 7.98 (2H, d, *J* = 1.8 Hz), 7.95 (2H, d, *J* = 1.8 Hz), 7.91 (8H, s), 7.88 (1H, t, J = 1.8 Hz), 7.78–7.76 (2H, m), 7.61–7.56 (2H, m), 7.49 (8H, dd, J = 8.2, 5.0 Hz), 7.22 (8H, dt, J = 8.2, 2.0 Hz), 2.77 (16H, t, J = 7.8 Hz, -CH₂CH₂CH₂CH₃), 1.70-1.63 (16H, m, -CH₂CH₂CH₂CH₃), 1.43-1.34 (16H, m, -CH₂CH₂CH₂CH₃), 0.93 (24H, t, J = 7.3 Hz, -CH₂CH₂CH₂CH₂), [MALDI:DITH] (*m*/*z*) 1417.17: (MH⁺), Found: C, 87.14; H, 8.02; N, 4.88. C₁₀₃H₁₀₉N₅ requires C, 87.30; H, 7.75; N, 4.94%.

7: the mixture of **2** (1.00 g, 1.27 mmol), iridium chloride trihydrate (0.186 g, 0.527 mmol), deionized water (8.5 ml), and 2-ethoxyethanol (36 ml) was heated at 130 °C for 24 h under N_2 . After the solvent was removed in vacuo, the res-

idue was washed with K_2CO_3 aq. (0.33 M, 6.0 ml) and deionized water to give crude compound **7**. The crude product was directly used for next step without further purification.

5.1. (DPA)₃Ir

The mixture of 7 (0.933 g), 5 (1.25 g, 1.58 mmol), silver trifluoromethanesulfonate (0.162 g, 0.632 mmol), and diglyme (31 ml) was heated at 130 °C under N₂ for 114 h. After the mixture was allowed to cool to room temperature, insoluble part was removed by column chromatography over silica using dichloromethane as eluent. The solvent was removed in vacuo, and then the residue was purified by chromatography over silica using a dichloromethane-hexane mixture (2:3) as eluent. Further purification by preparative TLC using a dichloromethane-hexane mixture (15:8) as eluent gave the complex (DPA)₃Ir (0.415 g, 31%). δ_H(400 MHz, CD₂Cl₂) 7.81-7.78 (3H), 7.60-7.55 (6H), 7.48-7.45 (3H), 7.03-6.94 (48H, m), 6.88-6.84 (3H), 6.78-6.72 (8H), 6.66-6.59 (6H), 2.54 (24H, t, J = 7.5 Hz, -<u>CH₂CH₂CH₂CH₂CH₃), 1.52–1.72 (24H, m, -CH₂CH₂</u> CH₂CH₃), 1.32–1.52 (24H, m, -CH₂CH₂CH₂CH₃), 0.94 (36H, t, J = 7.3 Hz, $-CH_2CH_2CH_2CH_3$). $\delta_C(100 \text{ MHz}, CD_2Cl_2)$ 14.1, 22.7, 34.0, 35.3, 115.2, 116.1, 119.2, 122.4, 122.6, 124.4, 128.6, 129.2, 132.9, 136.5, 137.2, 137.5, 143.9, 144.4, 145.6, 147.4, 149.4, 160.8, 166.2. [MALDI:DITH] (m/z) 2559.68: (MH⁺). Found: C, 80.40; H, 7.17; N, 4.88. C₁₇₁H₁₈₆IrN₉ requires C, 80.24; H, 7.32; N, 4.93%.

8: the mixture of **5** (2.50 g, 1.75 mmol), iridium chloride trihydrate (0.258 g, 0.731 mmol), deionized water (12 ml), and 2-ethoxyethanol (49 ml) was heated at 130 °C for 24 h under N₂. After the solvent was removed in vacuo, the residue was washed with K_2CO_3 aq. (0.33 M, 38 ml) and deionized water to give crude compound **8** (2.41 g). The crude product was directly used for next step without further purification.

5.2. (DAP)₆Ir

The mixture of 8 (2.41 g), 5 (4.80 g, 3.37 mmol), silver trifluoromethanesulfonate (0.225 g, 0.877 mmol), and diglyme (15 ml) was heated at 130 °C under N₂ for 192 h. The mixture was allowed to cool to room temperature, and then purified by column chromatography over silica using a dichloromethane-hexane mixture (1:2 and 1:3, respectively) as eluent. Further purification by preparative TLC using a dichloromethane-hexane mixture (1:3) as eluent gave the complex (**DPA**)₆Ir (0.526 g, 16%). $\delta_{\rm H}$ (400 MHz, CD₂Cl₂) 7.72 (3H, s), 7.52 (3H, s), 7.31 (3H, d, J = 5.9 Hz), 7.00-6.94 (96H, m), 6.70-6.63 (21H, m), 6.59-6.55 (6H, m), 2.51 (48H, t, I = 7.7 Hz, $-CH_2CH_2CH_2CH_3$), 1.57–1.50 (48H, m, -CH₂CH₂CH₂CH₃), 1.37-1.28 (48H, m, -CH₂CH₂ <u>CH₂</u>CH₃), 0.89 (72H, t, J = 7.3 Hz, -CH₂CH₂CH₂CH₂CH₃). $\delta_{\rm C}(100 \text{ MHz}, \text{ CD}_2\text{Cl}_2)$ 166.1, 161.1, 149.6, 149.3, 149.2, 147.1, 145.6, 145.1, 144.2, 140.0, 138.1, 137.4, 137.1, 133.0, 129.3, 129.2, 128.8, 124.7, 124.3, 122.3, 120.9, 116.9, 116.8, 115.98, 115.95, 115.3, 114.4, 35.2, 33.97, 33.95, 22.7, 14.0. [MALDI:DITH] (*m/z*) 4462.45: (MH⁺), Found: C, 83.30; H, 7.83; N, 4.64. C₃₀₉H₃₄₈IrN₁₅ requires C, 83.13; H, 7.86; N, 4.71%.

9: the mixture of **6** (1.70 g, 1.19 mmol), iridium chloride trihydrate (0.175 g, 0.496 mmol), deionized water (8.0 ml), and 2-ethoxyethanol (33 ml) was heated at 130 °C for 24 h under N₂. After the solvent was removed in vacuo, the residue was washed with K_2CO_3 aq. (0.33 M, 24 ml) and deionized water to give crude compound **9** (1.79 g). The crude product was directly used for next step without further purification.

5.3. (mCP)₆Ir

The mixture of 9 (1.46 g), 6 (2.89 g, 2.03 mmol), silver trifluoromethanesulfonate (0.498 g, 1.94 mmol), and ethyldiglyme (10 ml) was heated at 150 °C under N₂ for 133 h. The mixture was allowed to cool to room temperature, and then purified by column chromatography over silica using a dichloromethane-hexane mixture (1:3) as eluent, twice, to give the complex (mCP)₆Ir (0.316 g, 16%). δ_H(400 MHz, CD₂Cl₂) 8.28 (3H, s), 8.09 (3H, s), 7.93–7.89 (15H, m), 7.86 (24H, dd, J=4.6, 1.4 Hz), 7.82 (3H, t, *I* = 1.8 Hz), 7.61 (3H, t, *I* = 1.8 Hz), 7.44 (12H, d, *I* = 8.7 Hz), 7.40 (12H, d, J=8.2 Hz), 7.34-7.29 (6H, m), 7.15-7.11 (27H, m), 2.72 (48H, t, J = 7.6 Hz, -<u>CH₂CH₂CH₂CH₂CH₃), 1.67-</u> 1.59 (48H, m, -CH₂CH₂CH₂CH₃), 1.41-1.31 (48H, m, -CH₂CH₂CH₂CH₃), 0.92 (72H, t, *J* = 7.3 Hz, -CH₂CH₂CH₂CH₃). $\delta_{\rm C}(100 \text{ MHz}, \text{ CD}_2\text{Cl}_2)$ 166.5, 162.2, 148.0, 147.9, 145.4, 144.6, 141.3, 140.5, 139.9, 139.2, 139.0, 137.8, 135.1, 134.7, 132.0, 129.3, 126.7, 126.6, 124.8, 123.7, 123.6, 123.5, 122.9, 122.7, 121.9, 121.6, 119.6, 119.4, 117.4, 109.5, 109.3, 35.5, 34.42, 34.40, 29.7, 22.4, 13.8. [MALDI:-DITH] (*m*/*z*) 4439.73: (MH⁺), Found: C, 83.58; H, 7.10; N, 4.78. C₃₀₉H₃₂₄N₁₅ requires C, 83.58; H, 7.35; N, 4.73%.

Acknowledgment

This work was supported by Grant-in-Aid for Young Scientists (A) No. 21685014 from MEXT, Japan.

References

- [1] R.F. Service, Science 310 (2005) 1762.
- [2] F. So, J. Kido, P. Burrows, MRS Bull. 33 (2008) 663.

- [3] S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, K. Leo, Nature 459 (2009) 234.
- [4] C.-W. Han, S.-H. Pieh, H.-S. Pang, J.-M. Lee, H.-S. Choi, S.-K. Hong, B.-S. Kim, Y.-H. Tak, N.-Y. Lee, B.-C. Ahn, SID Int. Symp. Dig. Tech. 41 (2010) 136.
- [5] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
- [6] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 75 (1999) 4.
- [7] J.M. Lupton, I.D.W. Samuel, M.J. Frampton, R. Beavington, P.L. Burn, Adv. Funct. Mater. 11 (2001) 287.
- [8] J.P.J. Markham, S.C. Lo, S.W. Magennis, P.L. Burn, I.D.W. Samuel, Appl. Phys. Lett. 80 (2002) 2645.
- [9] S.-C. Lo, T.D. Anthopoulos, E.B. Namdas, P.L. Burn, I.D.W. Samuel, Adv. Mater. 17 (2005) 1945.
- [10] T. Sato, D.-L. Jiang, T. Aida, J. Am. Chem. Soc. 121 (1999) 10658.
- [11] A.W. Freeman, S.C. Koene, P.R.L. Malenfant, M.E. Thompson, J.M.J. Fréchet, J. Am. Chem. Soc. 122 (2000) 12385.
- [12] S. Bettington, M. Tavasli, M.R. Bryce, A. Beeby, H. Al-Attar, A.P. Monkman, Chem. Eur. J. 13 (2007) 1423.
- [13] T.-H. Kwon, M.K. Kim, J. Kwon, D.-Y. Shin, S.J. Park, C.-L. Lee, J.-J. Kim, J.-I. Hong, Chem. Mater. 19 (2007) 3673.
- [14] G. Zhou, W.-Y. Wong, B. Yao, Z. Xie, L. Wang, Angew. Chem. Int. Edit. 46 (2007) 1149.
- [15] B. Liang, L. Wang, Y. Xu, H. Shi, Y. Cao, Adv. Funct. Mater. 17 (2007) 3580.
- [16] J. Ding, J. Lü, Y. Cheng, Z. Xie, L. Wang, X. Jing, F. Wang, Adv. Funct. Mater. 18 (2008) 2754.
- [17] G.-J. Zhou, W.-Y. Wong, B. Yao, Z. Xie, L. Wang, J. Mater. Chem. 18 (2008) 1799.
- [18] J. Ding, B. Wang, Z. Yue, B. Yao, Z. Xie, Y. Cheng, L. Wang, X. Jing, F. Wang, Angew. Chem. Int. Edit. 48 (2009) 6664.
- [19] R. Guan, Y. Xu, L. Ying, W. Yang, H. Wu, Q. Chen, Y. Cao, J. Mater. Chem. 19 (2009) 531.
- [20] S. Gambino, S.G. Stevenson, K.A. Knights, P.L. Burn, I.D.W. Samuel, Adv. Funct. Mater. 19 (2009) 317.
- [21] S.-C. Lo, R.E. Harding, C.P. Shipley, S.G. Stevenson, P.L. Burn, I.D.W. Samuel, J. Am. Chem. Soc. 131 (2009) 16681.
- [22] J.J. Kim, Y. You, Y.-S. Park, J.-J. Kim, S.Y. Park, J. Mater. Chem. 19 (2009) 8347.
- [23] V. Adamovich, J. Brooks, A. Tamayo, A.M. Alexander, P.I. Djurovich, B.W. D'Andrade, C. Adachi, S.R. Forrest, M.E. Thompson, New J. Chem. 26 (2002) 1171.
- [24] B.W. D'andrade, S.R. Forrest, J. Appl. Phys. 94 (2003) 3101.
- [25] N. Iguchi, Y.-J. Pu, K. Nakayama, J. Kido, J. Photopolym. Sci. Technol. 20 (2007) 73.
- [26] N. Iguchi, Y.-J. Pu, K. Nakayama, M. Yokoyama, J. Kido, Org. Electron. 10 (2009) 465.
- [27] P.J. Hay, J. Phys. Chem. A 106 (2002) 1634.
- [28] F.-M. Hwang, H.-Y. Chen, P.-S. Chen, C.-S. Liu, Y. Chi, C.-F. Shu, F.-I. Wu, P.-T. Chou, S.-M. Peng, G.-H. Lee, Inorg. Chem. 44 (2005) 1344.
- [29] Y. Kawamura, J. Brooks, J.J. Brown, H. Sasabe, C. Adachi, Phys. Rev. Lett. 96 (2006) 17404.