Electronic Supplementary Information

Amidinate-Ligated Iridium(III) Bis(2-pyridyl)phenyl Complex as an Excellent Phosphorescent Material for Electroluminescence Devices

Yu Liu,[a,b] Kaiqi Ye,[b] Yan Fan,[b] Weifeng Song,[b] Yue Wang,[b] and Zhaomin Hou*,[a]
Organometallic Chemistry Laboratory, RIKEN Advanced Science Institute, 2-1
Hirosawa, Wako, Saitama 351-0198, Japan, and State Key Laboratory 0f
Supramolecular Structure and Materials,
Jilin University, Changchun 130012, People's Republic of China
E-mail: houz@riken.jp

Contents

Synthesis: Materials obtained from commercial suppliers were used without further purification. Anhydrous Hexane was distilled with sodium benzophenone ketyl under a nitrogen atmosphere, degassed by the freeze-pump-thaw method. All glass wares, syringes, magnetic stirring bars and needles were dried in the convection oven at least 4 hours. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were developed and the spots were seen under UV light at 254 and 365 nm. Silica column chromatography was done with silica gel 60 G (particle size 5~40 µm, Merck Co.). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANVE 300 MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer.

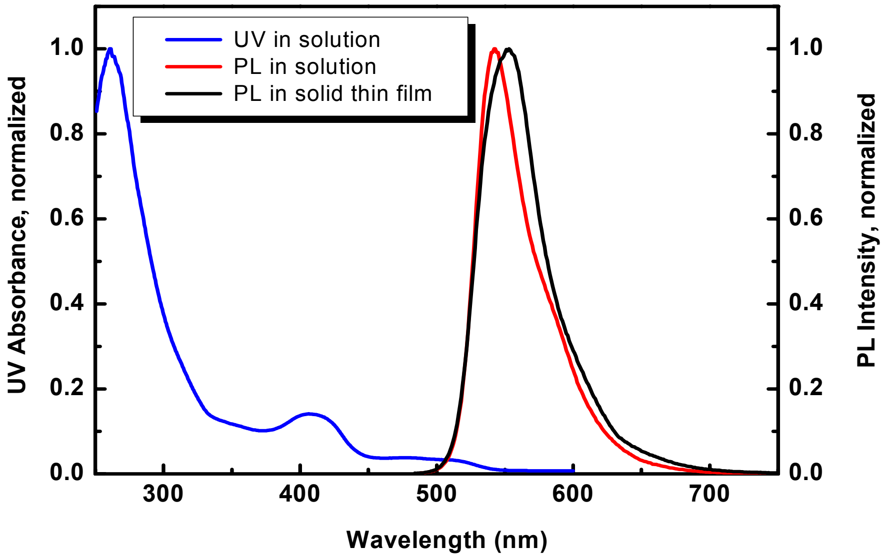
[(ppy)$_2$Ir(μ-Cl)]$_2$ was synthesized according to a modified version of the Nonoyama procedure, by refluxing $IrCl_3.nH_2O$ (7 mmol, 2.5 g) with 2.5 equiv of the ligands (2.8 g of phenylpyridine) in a 3:1 mixture of 2-methoxyethanol and water for 6-7 h. The reaction mixture was cooled to room temperature, and more water was added to precipitate the product. The resulting mixture was subsequently filtered through a Buchner funnel and then washed with hexane and ethyl ether several times to provide the crude product, $[(ppy)_2Ir(\mu\text{-}Cl)]_2$: 85% yield.[S1]

(ppy)$_2$Ir(dipba). In a 50-mL flask, a hexane solution of n-BuLi (0.15 mL x 2.6 M) was added to 1-bromobenzene (65 mg, 0.4 mmol) in hexane (10 mL) under argon. The reaction mixture was stirred at room temperature for 1 hour, and was then added dropwise to *N*,*N'*-diisopropylcarbodiimide (50 mg, 0.4 mmol). The colorless solution was stirred rapidly for 30 min, and then added dropwise to $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ (0.2 mmol, 220 mg) in hexane solvent (15 mL). After being stirred at 80℃ for 8 hours, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum, and the product was washed with Et_2O (20 mL) three times, giving rise to $(ppy)_2Ir(dipba)$ (74%).

***(ppy)$_2$Ir(dipba)*:** MS: *m/z* 704 (M^+). Anal. Calcd for $C_{35}H_{35}IrN_4$: C, 59.72; H, 5.01; N, 7.96. Found: C, 59.76; H, 5.09; N, 7.88. ^1H NMR (300 MHz, $CDCl_3$) δ 9.36 (d, J = 5.70, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.72 (t, J = 7.2 Hz, 2H), 7.56 (d, J = 8.1, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.26-7.20 (m, 5H), 6.77 (t, J = 7.2 Hz, 2H), 6.66 (t, J = 7.2 Hz, 2H), 6.36 (d, J = 7.8 Hz, 2H), 3.24-3.16 (m, 2H), 0.67 (d, J = 6.3, 6H), -0.09 (d, J = 6.3, 6H); ^{13}C NMR ($CDCl_3$) δ 24.39, 24.66, 47.94, 117.83, 119.29, 121.13, 123.51, 127.90, 128.16, 128.86, 131.98, 135.24, 137.07, 144.11, 150.92, 156.05, 169.75, 174.63.

Absorption, PL, Electrochemical Measurements and DFT Calculations: Absorption spectra were obtained using a Shimadzu UV-2550 UV-vis spectrometer. PL spectra were recorded by a Perkin-Elmer LS-55 fluorescence spectrometer with a Xe arc lamp excitation source. All solvents were degassed via three freeze-pump-thaw cycles. The PL quantum yields were measured by using quinine sulfate in 1 M sulfuric acid as the standard (Φ= 0.546).[S2] Emission lifetime of the different samples were measured on the microsecond time scale by a quanta ray DCR-3 pulsed Nd: YAG laser system (pulse output 355 nm, 6 ns). The lifetimes and the quantum yields have errors bars of ±10 %. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/Ag^+ as reference electrode, standardized against ferrocene/ferrocenium couple, scan rate 100 mV/s.

The absorption and PL spectra of the iridium complex $(ppy)_2Ir(dipba)$ in degassed dichloromethane and solid thin film are shown in S-Figure 1. The strong absorption bands below 360 nm can be assigned to spin-allowed $^1\pi\text{-}\pi^*$ transitions on the cyclometalated ligands. The broad absorption bands at lower energies are typical for (metal-ligand charge transfer) ^{1}MLCT and ^{3}MLCT.



S-Figure 1. UV-Vis absorption and PL spectra of $(ppy)_2Ir(dipba)$.

The electrochemical behavior of the iridium complex $(ppy)_2Ir(dipba)$ was studied by cyclic voltammetry using ferrocene as an internal standard and the results are listed in S-Table 1. Due to the limitation[S4] in measuring reduction potential in the range of -2.7 V to -3.5 V in CH_2Cl_2, we obtained only the oxidation potential for $(ppy)_2Ir(dipba)$. The potential for oxidation was observed to be 0.23, it is noteworthy that this complex showed lower oxidative potential than that of the complex having acetylacetonate (acac) as an ancillary ligand such as $(ppy)_2Ir(acac)$ or those of the analogous $Ir(C{\wedge}N)_3$ complex $Ir(ppy)_3$.[S3,S4,S5]

S-Table 1. Electrochemical data for the $(ppy)_2Ir(dipba)$ and some materials used in this work.

	HOMO [eV]	LUMO [eV]	E_g [eV]	E^{ox} [V]
NPB	-5.4	-2.4	3.0	--
CBP	-6.1	-3.0	3.1	--
$(ppy)_2Ir(dipba)$ [a]	-4.78	-2.49	2.29	0.23
BCP	-6.7	-3.2	3.5	--
AlQ	-6.0	-3.3	2.7	--

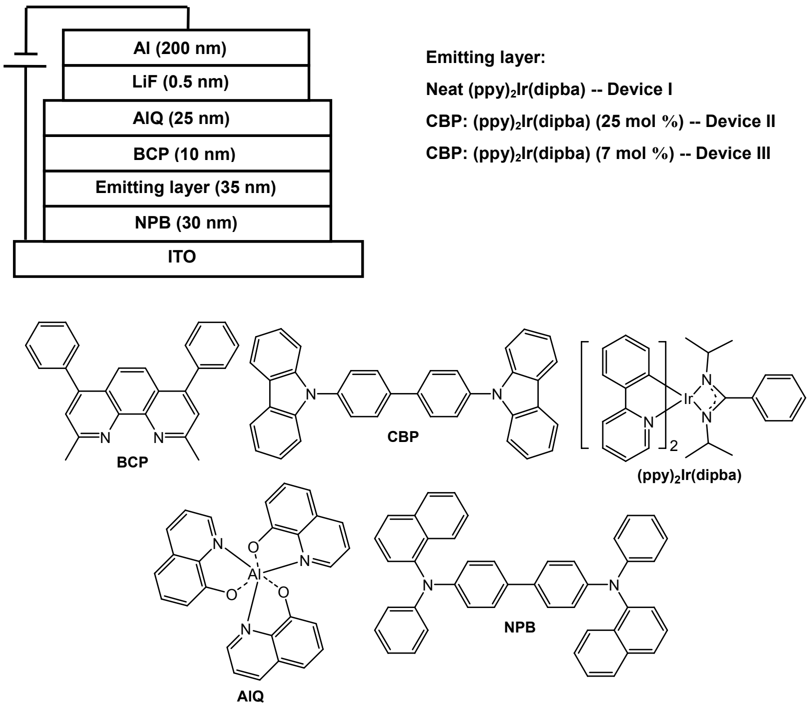
[a] 0.1 M $[Bu_4N]PF_6$ in CH_2Cl_2, scan rate 100 mV s^{-1}, versus Fc/Fc $^+$ couple. LUMO = HOMO + E_g. E_g are estimated from the onset wavelength of the optical absorption. The values for NPB, CBP, BCP and AlQ are taken from literature.[S6, S7]

S-Table 2. Molecular Orbital Compositions (Percent) in the Ground State for $(ppy)_2Ir(dipba)$ at the B3LYP

	Orb.	Ir		Part I			Part II			Part III			
	Energy				py			py					
Orb.	(eV)	sp	d	ben	total	N	ben	total	N	total	N1	N2	ben
155	1.20	2.2	22.1	17.7	17.3	3.4	17.7	17.3	3.4	5.7	0.6	0.6	1.5
154	1.15	5.7	5.3	10.8	6.1	0.0	10.8	6.0	0.0	55.4	8.6	8.6	8.3
153	0.85	1.2	6.2	43.8	1.7	0.4	43.9	1.7	0.4	1.6	0.4	0.4	0.0
152	0.67	3.4	5.1	40.9	2.1	0.4	40.9	2.1	0.4	5.5	1.2	1.2	0.9
151	-0.11	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	99.7	0.1	0.1	97.9
150	-0.29	0.7	1.0	0.5	0.7	0.1	0.5	0.7	0.1	96.0	2.6	2.6	84.9
149	-0.66	1.1	0.7	5.5	43.3	2.6	5.5	43.3	2.6	0.5	0.0	0.0	0.3
148	-0.76	1.4	1.1	6.7	41.5	3.2	6.8	41.6	3.2	1.0	0.0	0.0	0.4
147	-1.14	0.3	4.6	11.3	35.7	8.9	11.3	35.7	8.9	1.1	0.3	0.3	0.0
146(LUMO)	-1.29	1.4	2.6	13.0	34.0	7.9	13.0	34.0	7.9	1.9	0.4	0.4	0.6
145(HOMO)	-4.62	0.7	29.6	8.6	1.7	0.5	8.6	1.7	0.5	49.1	20.4	20.4	0.2
144	-4.89	0.6	29.9	15.7	3.2	0.4	15.7	3.2	0.4	31.7	12.8	12.8	0.1
143	-5.56	0.2	57.4	9.6	8.1	1.9	9.7	8.1	1.9	6.8	0.7	0.7	1.5
142	-5.70	0.0	9.9	34.6	6.8	0.6	34.6	6.8	0.6	7.5	2.2	2.2	0.9
141	-5.75	0.7	36.7	14.2	7.9	2.0	14.2	7.9	2.0	18.4	6.9	6.9	0.8
140	-6.06	0.2	18.5	27.4	10.4	0.2	27.4	10.4	0.2	5.8	2.1	2.1	0.2
139	-6.09	0.0	6.5	37.5	7.2	0.4	37.5	7.2	0.4	4.0	1.0	1.0	0.2
138	-6.61	4.1	10.5	16.0	0.5	0.0	15.9	0.5	0.0	52.5	15.5	15.4	10.2
137	-6.66	1.7	4.3	20.6	0.8	0.3	20.7	0.8	0.4	51.1	13.4	13.5	14.5
136	-6.77	0.1	1.4	2.8	0.8	0.2	2.8	0.8	0.2	91.4	3.1	3.1	73.7

The ground-state was fully optimized by the DFT[S8] method with Becke's three-parameter functional and the Lee-Yang-Parr functional[S9] (B3LYP). In the calculations, "Double-ζ" quality and polarization basis sets were employed for the ligands (6-31G(d)) and the Ir (LANL2DZ). A relativistic effective core potential (ECP) on Ir[S10] replaced the inner core electrons leaving the outer core $[(5s)^2(5p)^6]$ electrons and the $(5d)^6$ valence electrons of Ir(III). On the basis of the optimized ground-state, the absorption property in dichloromethane (CH_2Cl_2) media was calculated by time-dependent DFT (TDDFT)[S11] associated with the polarized continuum model (PCM).[S12] This kind of theoretical approach has been proven to be reliable for transition-metal complex systems.[S13] All of the calculations were accomplished by using the Gaussian 03 software package.[S14]

<u>Fabrication of the OLEDs and EL Measurements</u>: The general architecture of the complex multilayer diodes used in this study is as follows: The ITO (indium-tin oxide) coated glass substrates (20Ω/square) were first cleaned in ethanol, acetone, and soap ultrasonic bathes. All organics were purified by gradient sublimation and thermally evaporated at a rate of 1.0 Å/s at a base pressure of around $3.5*10^{-4}$ Pa. A LiF layer (0.5 nm) was deposited at a rate of 0.2 Å/s. The finishing Al electrode (cathode) was deposited at a rate of 10 Å/s in another chamber. The active area of the diode segments was $2*3$ mm^2. EL spectra and brightness-current density-voltage characteristics of the devices were measured by combining a Spectrascan PR-650 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient condition at room temperature.



Emitting layer:
Neat (ppy)$_2$Ir(dipba) -- Device I
CBP: (ppy)$_2$Ir(dipba) (25 mol %) -- Device II
CBP: (ppy)$_2$Ir(dipba) (7 mol %) -- Device III

S-Figure 2. Electrophosphorescent devices structure. Also shown are the structures of the materials used in this work.

***S-reference*:**

S1 M. Nonoyama, *Bull. Chem. Soc. Jpn.* 1974, **47**, 767.

S2 Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991-1024.

S3 S.Jung, Y. J. Kang, H. S. Kim, Y. H. Kim, C. L. Lee, J. J. Kim, S. K. Lee, S. K. Kwon, *Eur. J. Inorg. Chem.* 2004, **17**, 3415.

S4 S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, **40**, 1704.

S5 A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* 2003, **125**, 7377.

S6 T. Tsuzuki, S. Tokito, *Adv. Mater.* 2007, **19**, 276.

S7 C. Adachi, M. E. Thompson, S. R. Forrest, *IEEE J. Select. Top. Quantum Electron.* 2002, **8**, 372.

S8 E.Runge, E. K. U. Gross, *Phys. Rev. Lett.* 1984, **52**, 997.

S9 A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

S10 (a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270. (b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299.

S11 (a) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* 1998, **108**, 4439. (b) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* 1998, **109**, 8218. (c) N. N. Matsuzawa,; A. Ishitani, D. A. Dixon, T. Uda, *J. Phys. Chem. A* 2001, **105**, 4953.

S12 (a)Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* 1997, **107**, 3210. (b)Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* 2002, **117**, 43.

S13 (a) J. E. Monat, J. H. Rodriguez, J. K. McCusker, *J. Phys. Chem. A* 2002, **106**, 7399. (b) X. Zhou, H. X. Zhang, Q. J. Pan, B. H. Xia, A. C. Tang, *J. Phys. Chem. A* 2005, **109**, 8809. (c) T. Liu, B. H. Xia, X. Zhou, H. X. Zhang, Q. J. Pan, J. S. Gao, *Organometallics* 2007, **26**, 143. (d) T. Liu, H. X. Zhang, B. H. Xia, *J. Phys. Chem. A* 2007, **111**, 8724.

S14 M. J. Frisch,; G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery , T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02. Gaussian, Inc.: Pittsburgh, PA* 2003.