Preparation and Electroluminescent Characteristics of a Series of Cyclometalated Ir(III) Complexes Based on Phenylpyridines with a Diphenylamino Group

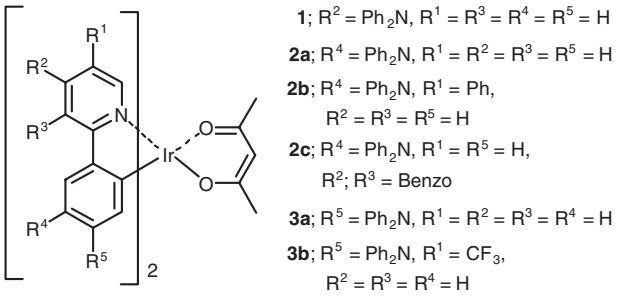
Jun-ichi Nishida, Hidenori Echizen, Takeshi Iwata,† and Yoshiro Yamashita*
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
†*Central Reserch Labolatory, Takasago International Corporation, Nishiyawata, Hiratsuka 254-0073*

(Received August 5, 2005; CL-051011)

A series of cyclometalated iridium complexes with a strong electron-donating and bulky diphenylamino group was prepared and the phosphorescence wavelengths were found to be greatly dependent on the substituent positions: some of them afforded high performance electroluminescence (EL) devices.

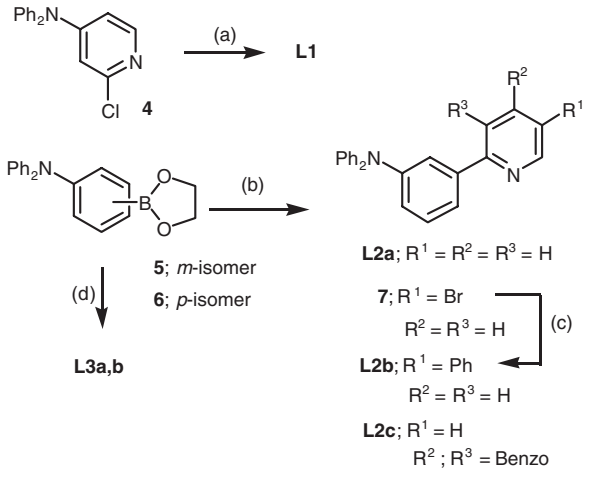
Phosphorescent materials incorporating heavy transition metals have attracted considerable attention for applications as highly efficient EL emitters.[1] Cyclometalated iridium complexes such as $Ir(ppy)_3$ (ppy; 2-phenylpyridine) and $(ppy)_2Ir(acac)$ (acac; acetylacetonate) are excellent phosphorescent materials whose EL devices have nearly quantitative internal quantum efficiencies.[2,3] Color tuning is important for fabricating EL devices and has been accomplished by introducing substituents in the ppy ligand. For example, the substituent effects of electron-withdrawing fluoro, trifluoromethyl, and pentafluorophenyl groups have been systematically investigated[4,5] and these groups were found to be effective for shifting the emission maxima to shorter wavelengths. On the other hand, electron-donating diphenylamino groups have often been used as units of hole transporting materials.[6] When this group is introduced in the ppy ligand of Ir complexes, it would strongly affect the energy levels of the Ir complexes leading to significant phosphorescence color changes. Introduction of the diphenylamino group is also expected to enhance the EL efficiency owing to the good hole-transporting property as well as the bulky size suppressing a self-quenching process.[7] We report here the synthesis of a series of $(ppy)_2Ir(acac)$ complexes **1**–**3** bearing a diphenylamino group at the different positions and their physical properties involving the EL behavior (Scheme 1).

The syntheses of new ppy ligands **L1**–**L3** are shown in Scheme 2. Thus, the ppy ligand **L1** having a diphenylamino group as R^2 was prepared by the Suzuki coupling reaction of phenylboronic acid with (2-chloro-4-pyridyl)diphenylamine (**4**), which was prepared by the Cu(I)-catalyzed substitution reaction of 2-chloro-4-iodopyridine with diphenylamine. Ligands **L2a** and **L2c** with a diphenylamino group as R^4 were prepared using the Suzuki coupling reaction of *meta*-diphenylaminophenylboronic ester **5**, which was obtained from 3-bromophenyldiphenylamine by a conventional method. Ligand **L2b** was obtained by the Suzuki coupling reaction of a ppy derivative **7** with a bromo substituent. Ligands **L3a** and **L3b** with a diphenylamino group as R^5 were prepared by the coupling reaction of *para*-diphenylaminophenylboronic ester **6** with the corresponding bromopyridines. Ir complexes **1**–**3** with these and acac ligands were prepared via the dichloro-bridged dimers according to the method reported by Nonoyama.[8] Purification was performed via chromatography, as described in the Supporting Information.



Scheme 1.

Remarkable differences in the absorption spectra of the Ir complexes **1**–**3** were observed.[9] Complex **3a** with a diphenylamino group as R^5 exhibits a strong absorption at 350–400 nm ascribed to the π–π^* transition of the ligand. The absorption maximum is red-shifted to 418 nm in the complex **3b** with an electron-withdrawing trifluoromethyl group as R^1. On the other hand, the complex **2a** with a diphenylamino group as R^4 shows the absorption around 300 nm with a weak absorption at 482 nm. Other derivatives of **2** show the similar weak absorptions (**2b**; 501 nm, **2c**; 580 nm). In contrast, complex **1** having a diphenylamino group on the pyridine ring exhibits a broad absorption at



Scheme 2. Preparation of ligands **L1**–**L3** by the Suzuki coupling reactions ($NaOH_{aq}$, $Pd(PPh_3)_4$, toluene). (a) **L1**: phenylboronic acid, 69%; (b) **L2a**: **5**, 2-bromopyridine, 55%; **7**: **5**, 2,5-dibromopyridine, 74%; **L2c**: **5**, 1-chloroisoquinoline, 61%; (c) **L2c**: phenylboronic acid, 50% (d) **L3a**: **6**, 2-bromopyridine, 95%; **L3b**: **6**, 2-bromo-5-trifluoromethylpyridine, 84%.

Table 1. Emission maxima[a] and redox potentials[b] of complexes **1**–**3** and $(ppy)_2Ir(acac)$

Complex	λ_{max}^{em}/nm	E_1^{pa}	E_1^{pc}
$(ppy)_2Ir(acac)$	516	+0.85	−2.10
1	518	+0.70	−2.24
2a	585	+0.58	−2.00
2b	611	+0.58	−1.84
2c	671	+0.55	−1.58
3a	530	+0.78	−2.12
3b	555	+0.96	−1.70

[a]In CH_2Cl_2. [b]nBu_4NPF_6 in DMF, V vs SCE, scan rate 100 mV/s, Pt electrode. The oxidation waves of **1**–**3** were reversible in their CVs.

350–380 nm with no clear red-shift of end-absorption.

Photoluminescence spectra[9] of these derivatives were measured and the emission maxima are summarized in Table 1. A comparison of **1**, **2a**, and **3a** containing only a diphenylamino group at the different positions demonstrates a clear positional effect. Thus, complex **1** shows almost the same emission maximum as $(ppy)_2Ir(acac)$. In contrast, red-shifts are observed in **2a** (69 nm) and **3a** (14 nm). It is noteworthy that the difference depending on the substitution position reaches to 67 nm. Furthermore, extention of π-conjugation in **2** induces remarkable red-shifts to afford red-color emission in **2b** (611 nm) and **2c** (671 nm). Introduction of an electron-withdrawing trifluoromethyl group on the pyridyl ring also brings about a red-shift as observed in **3b**.

These substituent effects are considered to be closely related to the HOMO and LUMO energy levels of the complexes. In order to investigate the energy levels, the redox potentials were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox peaks measured by DPV are listed in Table 1. The complexes **1**–**3** except **3b** show lower oxdation potentials than $(ppy)_2Ir(acac)$ owing to the electron-donating diphenylamino group. Complexes **2a**–**2c** show lower oxidation potentials (0.55–0.58 V) than **1** and **3**. This fact indicates that the diphenylamino group para to Ir in **2** more efficiently interacts with the d orbital of the Ir to raise the HOMO level. Large red-shifts of emission maxima of **2b** and **2c** compared with **2a** are related to the large positive shift of reduction potentials of **2b** and **2c**. On the other hand, the reduction potential of **1** is the lowest among them, indicating that the substituent on the pyridyl ring raises the LUMO level.

Preliminary organic light emitting devices of complexes **2a**, **3a**, and $(ppy)_2Ir(acac)$ were prepared by a thermal deposition method onto a clean glass substrate with an indium-tin-oxide (ITO). A 40-nm-thick film of *N*,*N*′-di(naphthalen-1-yl)-*N*,*N*′-diphenylbenzidine (NPD) as hole transporting layer, a 35-nm-thick layer of 4,4′-di(carbazol-9-yl)biphenyl (CBP) consisting of 6% the Ir complex, a 10-nm-thick layer of 2,9-dimethy-4,7-diphenylphenanthroline (BCP) as hole block layer and a 35-nm-thick of tris(8-hydroxyquinoline)aluminium (Alq_3) as electron transporting layer, and 0.5-nm-thick LiF and 100-nm-thick Al layers as cathode electrode were successively deposited. The EL peak maxima of **2a** and **3a** (**2a**, 595 nm; **3a**, 531 nm) are similar to the PL maxima in solution. The Commission Internationale de l'Eclairage (CIE) coordinates of **2a** ($x = 0.559$, $y = 0.436$) and **3a** ($x = 0.379$, $y = 0.609$) mean dark orange and yellow color, respectively. The external quantum efficiency (η_{ext}) and power efficiency of the device using **3a** were 11.8% and 23.7 lm W^{-1} at 100 cd m^{-2}, respectively, which are higher than those of $(ppy)_2Ir(acac)$ (11.4% and 22.4 lm W^{-1}) fabricated under the same conditions. The device using complex **2a** also showed a high performance (η_{ext}: 7.6%, 7.4 lm W^{-1}) at 100 cd m^{-2}.

In conclusion, we have prepared a series of cyclometalated iridium complexes with an electron-donating diphenylamino group and fabricated high performance EL devices. They showed remarkable color changes of phosphorescence depending on the substitution positions. Since the diphenylamino group has been used as a unit of dendrimers,[10] the present systems would be possibly developed to dendrimers.

This work was supported by the 21st Century COE program and a Grant-in-Aid for Scientific Research on Priority Areas (No. 15073212) of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature*, **395**, 151 (1998). b) D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.*, **74**, 442 (1999).

2 a) M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Nature*, **403**, 750 (2000). b) C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Appl. Phys. Lett.*, **77**, 904 (2000). c) D. Kolosov, V. Adamovich, P. Djurovich, M. E. Thompson, and C. Adachi, *J. Am. Chem. Soc.*, **124**, 9945 (2002).

3 a) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, *J. Am. Chem. Soc.*, **123**, 4304 (2001). b) C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, and R. C. Kwong, *Appl. Phys. Lett.*, **78**, 1622 (2001).

4 a) V. V. Grushin, N. Herron, D. D. LeCloux, W. J. Marshall, V. A. Petrov, and Y. Wang, *Chem. Commun.*, **2001**, 1494. b) S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.*, **83**, 569 (2003). c) P. Coppo, E. A. Plummer, and L. D. Cola, *Chem. Commun.*, **2004**, 1774.

5 T. Tsuzuki, N. Shirasawa, T. Suzuki, and S. Tokito, *Adv. Mater.*, **15**, 1455 (2003).

6 a) C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **55**, 1489 (1989). b) M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.*, **88**, 4707 (1984).

7 a) J. C. Ostrowski, M. R. Robinson, A. J. Heeger, and G. C. Bazan, *Chem. Commun.*, **2002**, 784. b) H. Z. Xie, M. W. Liu, O. Y. Wang, X. H. Zhang, C. S. Lee, L. S. Hung, S. T. Lee, P. F. Teng, H. L. Kwong, H. Zheng, and C. M. Che, *Adv. Mater.*, **13**, 1245 (2001).

8 M. Nonoyama, *Bull. Chem. Soc. Jpn.*, **47**, 767 (1974).

9 Absorption and phosphorescence spectra are depicted in Supporting Information.

10 a) E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo, and P. L. Burn, *J. Phys. Chem. B*, **108**, 1570 (2004). b) M. J. Frampton, E. B. Namdas, S.-C. Lo, P. L. Burn, and I. D. W. Samuel, *J. Mater. Chem.*, **14**, 2881 (2004).

Published on the web (Advance View) September 10, 2005; DOI 10.1246/cl.2005.1378