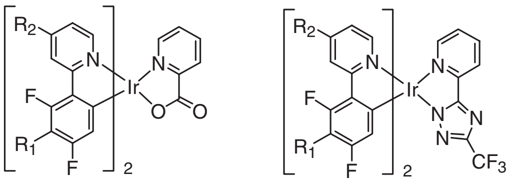
Finely-tuned Blue-phosphorescent Iridium Complexes Based on 2-Phenylpyridine Derivatives and Application to Polymer Organic Light-emitting Device

Shin-ya Takizawa,[1] Hidenori Echizen,[1] Jun-ichi Nishida,[1] Toshimitsu Tsuzuki,[2] Shizuo Tokito,[2] and Yoshiro Yamashita*[1]
[1]*Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,*
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502
[2]*NHK Science and Technical Research Laboratories, Kinuta, Setagaya-ku, Tokyo 157-8510*

(Received February 9, 2006; CL-060171; E-mail: yoshiro@echem.titech.ac.jp)

We have developed new blue-phosphorescent iridium complexes based on 2-phenylpyridine derivatives with pertinent substituents and an ancillary ligand to accomplish selective tuning of the HOMO and LUMO levels toward high energy gap: A polymer light-emitting device doped with the blue phosphor was fabricated to show blue emission.

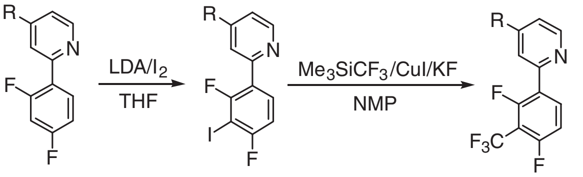
Recently, phosphorescent platinum or iridium complexes have become important emitting-materials for organic light-emitting diodes (OLEDs) because their efficient phosphorescence which originates from strong spin–orbit coupling leads to high internal quantum efficiencies in devices.[1–3] In particular, Ir(ppy)$_3$ (ppy: 2-phenylpyridine) and its derivatives have attracted much attention, and systematic control of the emission color has been carried out by introduction of substituents on the ligands or extension of π-conjugation.[3] Among them, blue-phosphorescent materials have been extensively investigated because these are strongly required for applications in full-color display.[2] The concept of molecular design for blue-phosphorescent complexes with 2-phenylpyridines is based on the fact that the HOMO locates on the phenyl-π and iridium-d orbitals, while the LUMO is localized on the pyridine ring.[4] In this regard, high-energy phosphorescence has been achieved by introducing electron-withdrawing groups on the phenyl ring to lower the HOMO level. For example, fluorine substitution at the meta position to Ir on the phenyl ring is effective to lower the HOMO level,[3a,3d,3f] and a trifluoromethyl (CF$_3$) group at the para position has the similar effect.[3a,3f] However, the color purities and quantum efficiencies of blue-phosphorescent materials are still unsatisfactory. In this context, we presumed that if both fluorine and CF$_3$ groups are introduced at the suitable positions on the phenyl ring, the HOMO energy level would be largely lowered to obtain the desired deep-blue color purity of phosphorescence. In this paper, we clearly demonstrated that the proposed method is greatly effective to blue-shift the emission compared to the respective introduction of these substituents on the ppy ligand. Furthermore, combination with the ancillary ligand of 2-pyridyltriazolate and a methyl substitution on the pyridine ring resulted in rare deep-blue phosphorescence at room temperature, whose emission maximum (447 nm) is remarkably shorter by 21 nm than that of well-known blue emissive iridium bis(4,6-difluorophenylpyridinato)picolate (FIrpic) (**1**).[2a,2b] We report here the synthesis and characterization of new blue-phosphorescent iridium complexes **2**–**5** (Scheme 1) along with the polymer light-emitting device (PLED) doped with the blue phosphor.



1: R$_1$ =H, R$_2$ = H
2: R$_1$ = CF$_3$, R$_2$ = H
3: R$_1$ = CF$_3$, R$_2$ = Me

4: R$_1$ =CF$_3$, R$_2$ = H
5: R$_1$ = CF$_3$, R$_2$ = Me

Scheme 1. Structures of the Ir complexes.



6a: R = H
6b: R = Me

7a: R = H (83%)
7b: R = Me (56%)

8a: R = H (32%)
8b: R = Me (33%)

Scheme 2. Synthesis of the ligands.

The new ligands **8a** and **8b** were readily prepared via iodination of difluorophenylpyridine derivatives **6** as shown in Scheme 2. The iodides **7a** and **7b** were obtained in 83 and 56% yields, respectively, by the reaction with iodine after treatment of **6** with LDA. The reaction of the iodides **7a** and **7b** with (trifluoromethyl)trimethylsilane in the presence of CuI and KF gave the CF$_3$-substituted ligands **8a** and **8b** in 32 and 33% yields, respectively. The biscyclometalated Ir complexes **2**–**5** were prepared by a conventional two-step reaction[3b] via dichloro-bridged dimer complexes in moderate total yields (20–58%).

Figure 1 shows the photoluminescence (PL) spectra of the complexes **1**–**5**, and the photophysical and electrochemical data are listed in Table 1. In the absorption spectrum of CF$_3$-substituted complex **2**,[5] the band, which can be assigned to the singlet metal to ligand charge-transfer (^{1}MLCT) transition, was ob-

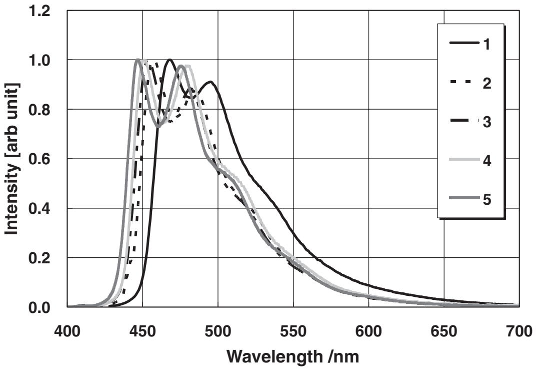


Figure 1. PL spectra of the Ir complexes in CH$_2$Cl$_2$.

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Table 1. Photophysical and electrochemical properties of **1–5**

Complex	λ_{em}/nm[a]	Φ[b]	$E_{1/2}{}^{ox}$/V[c]
1	468, 495	0.11	0.90
2	457, 485	0.27	1.14
3	454, 481	0.33	1.10
4	451, 480	0.28	1.31
5	447, 476	0.19	1.27

[a]In CH_2Cl_2. [b]In CH_2Cl_2 using 9,10-diphenylanthracene ($\Phi = 0.81$) as a reference. [c]In MeCN containing 0.1 mol dm^{-3} *n*-Bu_4NPF_6, vs Cp_2Fe/Cp_2Fe^+.

served at 374 nm. The shoulder at a longer wavelength around 400 nm can be attributed to a mixture of ^{3}MLCT and ligand centered triplet π–π^* transition. These bands were apparently blue-shifted compared to those of FIrpic (**1**), although the shape is similar to each other. Interestingly, complex **2** exhibited blue emission at room temperature and its emission maximum (457 nm) is shorter by 11 nm than that of **1**. This can be attributed to the lower HOMO level of **2** since the oxidation potential of **2** is much higher than that of **1** (see Table 1). This result indicates that the CF_3-substitution at that position greatly affects the HOMO energy level. On the other hand, complex **3** having a methyl group at the para position with respect to Ir on the pyridine ring showed a further 3 nm blue shift (454 nm). This may be explained by considering that the LUMO energy level, whose orbital is localized on the pyridine ring, is raised. This is supported by the fact that the oxidation potential is almost insensitive to the methyl substitution (**2**: 1.14 V; **3**: 1.10 V) even though the blue shift was observed. The similar blue shift by methyl-substitution on the pyridine ring has been also observed in $Ir(ppy)_3$.[3g]

Further blue shifts were achieved by replacement of the picolate ligand with 3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazolate.[2d] Thus, the emission maximum (451 nm) of complex **4** became shorter by 6 nm than that of complex **2**. This is ascribed to the lower HOMO energy level since complex **4** showed a higher oxidation potential (1.31 V) than **2** (1.14 V). In addition, methyl-substitution on the pyridine rings of complex **4**, leading to complex **5**, afforded the bluest emission (447 nm). This hypsochromic shift (4 nm) is consistent with the shift observed in complexes **2** and **3** (3 nm). The absorption spectrum provides an additional evidence for the largest HOMO–LUMO gap of complex **5**, where the absorption bands appear in shorter wavelength region compared with other complexes.[5] In addition, the emission lifetime of **5** (2.93 μs) suggests that its blue emission originates from triplet excited state. Such a deep-blue phosphorescence is rare to be observed at room temperature, although there are some iridium and platinum complexes exhibiting pure blue emission only at low temperatures.[1c,3d]

The PLED doped with complex **5** was fabricated by a wet process. PLEDs fabricated using wet processes have been important for the practical applications in large-area devices owing to their simple and low-cost fabrication processes.[6] Poly(*N*-vinylcarbazole) (PVK) was selected as a host material because it is known to have high triplet energy along with high hole mobility.[7] The simple device structure is as follows: indium tin oxide (ITO)/poly(ethylenedioxythiophene) doped with poly(stylenesulfonate) (PEDOT/PSS) as a hole-injecting layer (30 nm)/PVK and electron-transporting 1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) blend layer doped with 5 wt % **5** (100 nm)/Ba (3 nm)/Al (100 nm). The device showed clear electroluminescent characteristics.[5] It exhibited blue emission whose spectrum is similar to the PL spectrum of **5** in solution, and no emission from PVK was observed even at high current densities. The maximum external quantum efficiency and luminance efficiency were 1.2% and 2.3 cd/A, respectively. The Commission Internationale de l'Eclairage (CIE) coordinates at 100 cd/m^2 are in a blue region ($x = 0.20$, $y = 0.25$).

In conclusion, a series of new blue-phosphorescent iridium complexes based on ppy derivatives were prepared, and the systematic control of the HOMO and LUMO levels was carried out to achieve high energy gap by combining substituents and ancillary ligand effects. We succeeded in preparing complex **5** which shows deep-blue phosphorescence (447 nm) at room temperature. The introduction of both fluorine and CF_3 groups on the phenyl ring was found to be effective to lower the HOMO level. This methodology would provide a new approach to obtain high-energy phosphorescence, and be applicable to other systems containing metal–phenyl fragments. Our preliminary EL study demonstrated that complex **5** would be a potential candidate for deep-blue emitter in PLEDs, and the optimization of device structure is currently underway.

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