Synthesis and Characterization of Novel Iridium Complexes with Ligands of 2-Phenylimidazo[1,2-*a*]pyridine Derivatives and Application to Organic Light-emitting Diode

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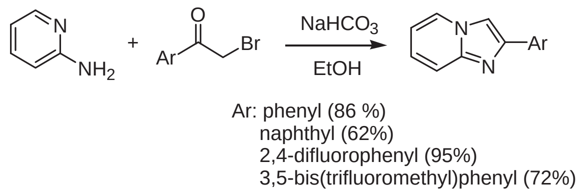
Novel iridium complexes with ligands of 2-phenylimidazo[1,2-*a*]pyridines were prepared, and the emission maxima were found to be unusually dependent on the substituents on the phenyl ring. An OLED using the derivative was fabricated to show white emission.

Recently, phosphorescent materials such as iridium (Ir) and platinum (Pt) complexes have attracted great attention because of their applications to organic light-emitting diodes (OLEDs).[1,2] Particularly, the devices using Ir complexes show high external quantum efficiencies and the emission wavelengths greatly depend on the organic ligands.[3,4] For instance, the effects of substituents on the ppy (2-phenylpyridine) ligand have been extensively studied to afford blue or red phosphors so far.[4] However, Ir complexes based on new ligands besides ppy, as well as the relationship between ligand structures and photophysical properties, have not been well explored. For the development of new phosphors, 2-phenylimidazo[1,2-*a*]pyridine seems to be a promising ligand because of the following advantages. First, the LUMO energy level of 2-phenylimidazo[1,2-*a*]pyridine is relatively high,[5] so it is considered to be useful for making the emission blue-shifted. Second, various derivatives can be easily prepared by a mild one-step reaction from the corresponding 2-aminopyridines and 2-bromoacetophenones,[6] leading to easy functionalization and tuning of the emission color. In this context, we have now prepared and characterized a series of Ir complexes with these ligands. In addition, an OLED using one of the complexes as a dopant emitter was fabricated here.

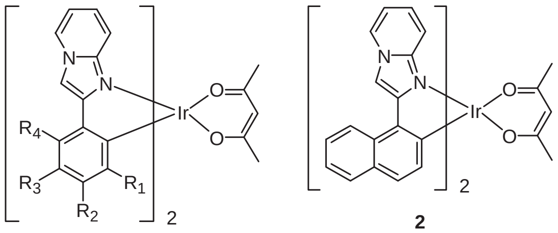
2-Phenylimidazo[1,2-*a*]pyridine and its derivatives were prepared in good yields (62–95%) from the corresponding 2-aminopyridines and 2-bromoacetophenones (Scheme 1). The Ir complexes containing acetylacetonate as an ancillary ligand were prepared by two-step reactions via Ir(III)-μ-chloro-bridged dimer complexes according to a conventional procedure.[4b] The dimer complexes could be obtained from iridium(III) chloride trihydrate and the free ligands in moderate yields. The final Ir complexes **1**–**4** were prepared in 20–29% yields by treatment of the dimer complexes with acetylacetone in the presence of sodium carbonate.



Scheme 1. Synthesis of 2-phenylimidazo[1,2-*a*]pyridines.

In the absorption spectrum of the complex **1**,[7] the band, which can be assigned to the singlet metal to ligand charge-transfer (^{1}MLCT) transition, was observed at 387 nm. The band at around 440 nm can be attributed to a mixture of ^{3}MLCT and ligand-centered triplet π–π^* transition.

The emission maxima and oxidation potentials are summarized in Table 1. Figure 1 depicts the emission spectra of complexes. The complex **1** exhibits two main peaks at 516 and 537 nm. On the other hand, the emission maximum of **2** is red-shifted by 31 nm compared to that of **1** owing to the effect of extended π conjugation without a remarkable change of the HOMO level, as supported by the electrochemical data (see Table 1). This red shift is smaller than that observed in bis(2-phenylpyridinato-$N,C^{2'}$)acetylacetonate ($Ir(ppy)_2(acac)$)[4b] and $Ir(NaPy)_2(acac)$ [NaPy: 2-(1-naphthalenyl)pyridine][4e] (84 nm). This difference may be explained by the fact that the LUMO of the 2-phenylimidazopyridine is almost localized in the imidazopyridine side in contrast to ppy whose LUMO is extended to the phenyl group as revealed by the MO caluculations.[8] This fact is supported by the following investigation of the electron-withdrawing substituent effects in the complexes **3** and **4**. In the corresponding Ir complexes with ppy ligands, fluorine substitution at the meta position to Ir on the phenyl ring is the most effective to lower the HOMO level based on a mixture of phenyl–π and Ir–d orbitals, whereas trifluoromethyl and perfluorophenyl groups at the ortho or para position make the HOMO level lower.[4a,4c] The similar effect was observed in our study with regard to fluorine substitution: the emission maximum of the complex **3** (497 nm) was shorter by 19 nm than that of the non-substituted complex **1**. This can be explained by considering that the HOMO level is lowered since the oxidation potential of **3** is much higher than that of **1** (Table 1). In addition, these shifts of



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1: $R_1 = R_2 = R_3 = R_4 = H$
3: $R_1 = H, R_2 = F, R_3 = H, R_4 = F$
4: $R_1 = CF_3, R_2 = H, R_3 = CF_3, R_4 = H$

Scheme 2. Structures of iridium complexes.

Table 1. Photophysical and electrochemical properties of **1**–**4**

Complex	λ_{em}/nm[a]	Φ[b]	$E_{1/2}{}^{ox}$/V[c]
1	516; 537	0.024	0.17
2	547; 587	0.019	0.18
3	497; 518	0.035	0.50
4	487; 517	0.032	0.68

[a] In CH_2Cl_2 at room temperature. [b] In CH_2Cl_2 using *fac*-Ir(ppy)$_3$ ($\Phi = 0.40$)[9] as the reference. [c] In DMF containing 0.1 mol dm^{-3} *n*-Bu_4NPF_6, vs Cp_2Fe/Cp_2Fe^+.

emission maxima for the complex **1**, **2**, and **3** are consistent with shifts of end-absorption wavelengths in their absorption spectra.[7] On the other hand, a recent research by Coppo et al. reveals that an Ir complex with a 3,5-CF_3-substituted ppy ligand exhibits longer emission maxima (466 and 499 nm) than a 2,4-F-substituted complex (461 and 491 nm), even though the HOMO level of the CF_3-substituted complex is lower than that of the F-substituted complex.[4f] This can be attributed to a simultaneous lowering of the LUMO level due to a stronger electron-inductive nature of CF_3 than F. In contrast, our 3,5-CF_3-substituted complex **4** exhibits a further blue shift (487 nm) by 10 nm compared to the 2,4-F-substituted complex **3**. The electrochemical data shows that the HOMO level of **4** is lower than that of **3**. Thus, introduction of CF_3 groups to the phenyl ring makes the HOMO–LUMO gap slightly large without a notable change of the LUMO level. This is a unique characteristic which is different from that of ppy derivatives.

The phosphorescence life time of **3** was also measured in polycarbonate thin film. The emission decayed double exponentially with long life times ($\tau_1 = 5.8\,\mu s$, $\tau_2 = 15.5\,\mu s$). In addition, a vibronic fine structure clearly appeared in the emission spectra of all complexes, and large Stokes shifts were observed. These results may be interpreted by considering that this kind of complexes emits primarily from the ligand-based $^3(\pi$–$\pi)$ exited states.[4b,4d]

A preliminary OLED using complex **3** as a dopant emitter was fabricated by a high-vacuum thermal deposition method onto a clean glass substrate. The device structure is as follows: indium tin oxide (ITO)/4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl (α-NPD) (40 nm)/3% complex **3** doped in 4,4′-*N*,*N*′-dicarbazolylbiphenyl (CBP) (35 nm)/2,9-dimethyl-4,7-diphenylphenanthroline (BCP) (10 nm)/tris(8-hydroxyquinoline)aluminium (Alq_3) (35 nm)/LiF (0.5 nm)/Al (100 nm). The resulting EL spectra were found to be dependent on the luminance.[7] Interestingly, the Commission Internationale de l'Eclairage (CIE) coordinate at 2862 cd/m^2 is near a white region ($x = 0.28$, $y = 0.41$) owing to the broad emission from **3** and a slight mixing of the blue emission from α-NPD. The emission maximum of **3** is not so changed from that in the PL spectrum. The external quantum efficiency η_{ext} is 1.2% at 146 cd/m^2, $J = 4.6$ mA/cm^2, where the luminance efficiency and power efficiency are 3.2 cd/A and 1.4 lm/W.

In conclusion, we prepared novel Ir complexes with ligands of 2-phenylimidazo[1,2-*a*]pyridine derivatives, and succeeded in fabrication of the OLED using **3**. The complex **1** was found to exhibit green phosphorescence, whose emission maximum could be changed to shorter wavelengths by introduction of strong electron-withdrawing groups into the phenyl rings: the behavior is different from that of known ppy derivatives because of the difference in distribution of their frontier orbitals. These Ir complexes would be modified to give new blue phosphorescent materials by combination with electron-donating substituents on the imidazopyridine side as well as use of other ancillary ligands such as picolinic acid.[2]

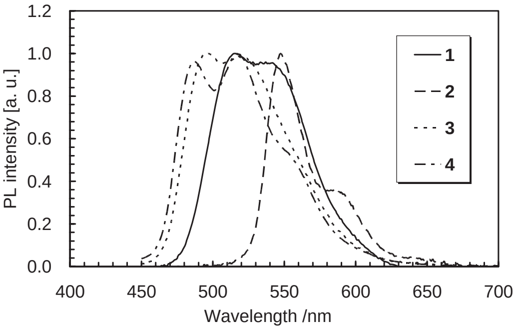

Figure 1. Emission spectra of Ir complexes in CH_2Cl_2.

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5 This fact is confirmed by the reduction potentials of 2-phenylimidazo-[1,2-*a*]pyridine ($E_p{}^{red} = -3.28$ V and -3.10 V vs Cp_2Fe/Cp_2Fe^+) and ppy ($E_p{}^{red} = -3.13$ V). In addition, the LUMO of free 2-phenylimidazo[1,2-*a*]pyridine ligand was found to be almost localized in the imidazopyridine side by the PM3 calculations.

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