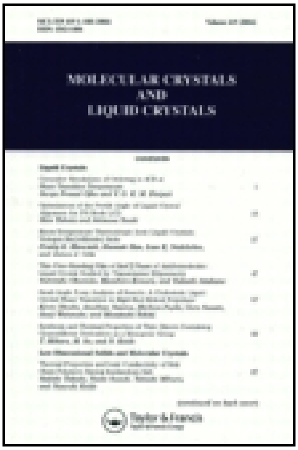

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Phosphorescence Color Tunable Iridium Complexes with Ligands of 2-Phenylimidazo[1,2-a]Pyridine Derivatives

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New iridium complexes with ligands of 2-phenylimidazo[1,2-a]pyridines were prepared, and their emission maxima were found to be greatly dependent on the substituents. A trifluoromethyl group on the imidazole part made the emission maximum blue-shifted, and combination with the same groups on the phenyl ring resulted in the bluest phosphorescence among the derivatives.

Keywords: 2-phenylimidazo[1,2-*a*] pyridine; blue phosphorescence; iridium complex; organic light-emitting diodes

INTRODUCTION

Iridium (Ir) and platinum (Pt) complexes as phosphors have attracted considerable interest because of their applications to organic light-emitting diodes (OLEDs) with high performances [1–4]. In particular,

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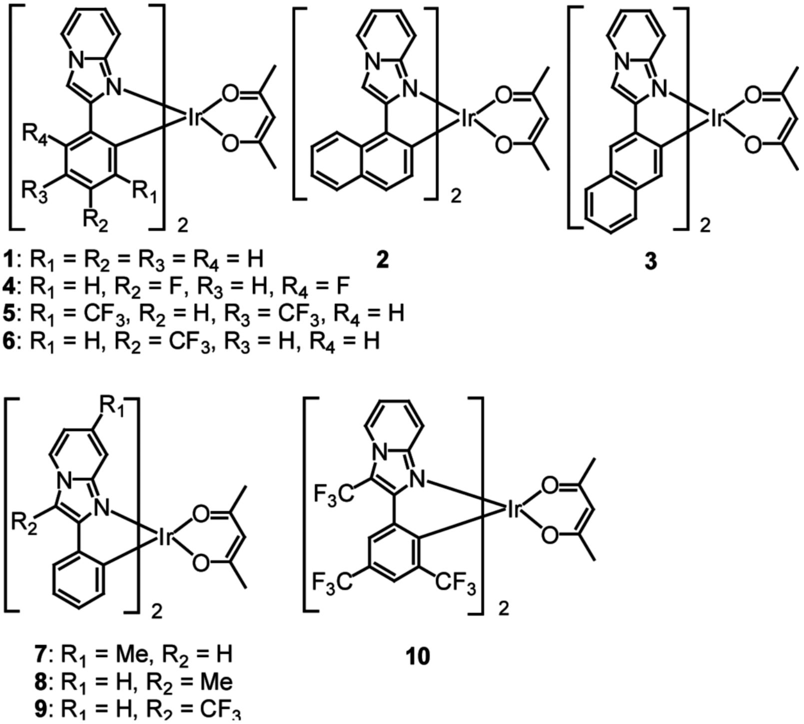
$Ir(ppy)_3$ (ppy: 2-phenylpyridine) and its derivatives have been extensively investigated. However, Ir complexes based on new ligands, as well as the relationship between structures and photophysical properties, have not been fully explored. Therefore, we have focused our study on 2-phenylimidazo[1,2-*a*]pyridine as a new ligand because of its following advantages: various derivatives can be easily prepared by a mild one-step reaction, leading to easy tuning of the emission color. In addition, the LUMO energy level is relatively high, which would be useful for the development of desired new blue phosphors. We have recently reported new Ir complexes **1**, **2**, **4**, and **5** with ligands of 2-phenylimidazo[1,2-*a*]pyridines (Fig. 1), and found that their emission maxima unusually depend on the substituents on the phenyl ring [5]. We have now extended the work by investigating other derivatives and found that the HOMOs are extended to the imidazole part, and the substitution of trifluoromethyl groups at the 3-position on the imidazole and at the para position to Ir on the phenyl ring leads to the bluest phosphorescence among the derivatives.



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

2

3

7: $R_1 = Me, R_2 = H$
8: $R_1 = H, R_2 = Me$
9: $R_1 = H, R_2 = CF_3$

10

FIGURE 1 Structure of Ir complexes.

RESULTS AND DISCUSSION

The ligands of complexes **3**, **6**, and **7** were prepared in 67, 88, and 86% yields, respectively, from the corresponding 2-aminopyridines and bromoacetophenones according to the similar method reported in the previous paper [5]. 3-Substituted ligands of complexes **8**, **9**, and **10** were prepared *via* 3-iodo-2-phenylimidazo[1,2-*a*]pyridines [6]. For example, 3-methyl-2-phenylimidazo[1,2-*a*]pyridine was obtained in 90% yield by the Suzuki cross coupling reaction of an 3-iodo precursor and methylboronic acid. On the other hand, 2-phenyl-3-trifluoromethylimidazo[1,2-*a*]pyridine was prepared in 65% yield by the reaction of the corresponding iodide with (trifluoromethyl)trimethylsilane in the presence of CuI and KF. The ligand of **10** was obtained by the similar method. 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 [2] in moderate total yields (37–69%) except for **10** (15%).

Complex **1** exhibited green phosphorescence with two main emission maxima at 516 and 537 nm (Table 1). In the absorption spectrum of complex **1**, 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 maximum of **2** is red-shifted by 31 nm due to the effect of extended π-conjugation. However, this bathochromic shift is smaller by 53 nm than that observed in the complexes with known ppy [2] and 2-(1-naphthyl) pyridine ligands [4]. Notably, the emission maximum of **3** is scarcely

TABLE 1 Emission Maxima and Oxidation Potentials of Ir Complexes

Complex	λ_{em}/nm^a	$E^{ox}_{1/2}$/V^b
1 [5]	516; 537	0.17
2 [5]	547; 587	0.18
3	517; 551	0.17
4 [5]	497; 518	0.50
5 [5]	487; 517	0.68
6	504	0.45
7	517; 542	0.16
8	522; 546	0.13
9	509	0.34
10	471; 499	0.94

^{a}In CH_2Cl_2 at room temperature.

^{b}In DMF containing 0.1 mol dm^{-3} n-Bu_4NPF_6, vs. Fc/Fc$^+$.

shifted compared to **1** despite the presence of naphthyl groups (517 nm). These results may be explained by the fact that the LUMO of the complex is almost localized on the imidazopyridine part.

Hence, the effects of substituents on the imidazopyridine side have now been investigated to obtain further information about the electronic state of the complexes. For instance, 3-trifluoromethyl substituted complex **9** showed a blue shift by 7 nm compared to **1**. This fact can be explained by considering that only the HOMO level is lowered since the oxidation potential of **9** is higher than that of **1** (Table 1). Interestingly, the shape of the emission spectrum for **9** with one main emission maximum is different from that of **1** with two main emission maxima (Fig. 2). On the other hand, the emission maximum of complex **8**, having an electron-donating methyl group on the imidazole ring, was 6 nm red-shifted compared with **1**, while the emission maximum of complex **7** with a methyl group at the 7-position was similar to that of **1**. These results suggest that the HOMO of the complexes is extended to the imidazole part, whereas it had been found that the HOMO locates on the phenyl ring according to the previous investigation of substitution effects [5]. On the other hand, the LUMO is almost localized on the pyridine part of imidazopyridine. From this viewpoint, we have next prepared new complex **10** with three trifluoromethyl groups on both the imidazole and phenyl rings to develop new blue phosphors by lowering only the HOMO level as much as possible. Complex **10** exhibited the bluest phosphorescence (471 nm) which is

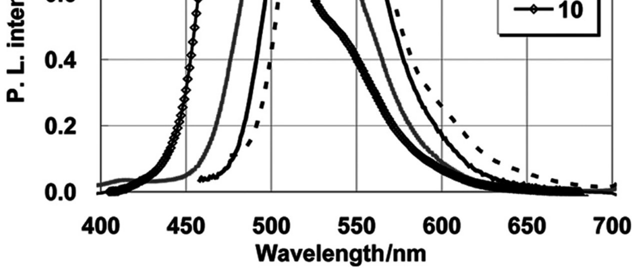


FIGURE 2 Phosphorescence spectra of Ir complexes.

comparable to that of known FIrpic [3]. This is consistent with the fact that the HOMO level is the lowest in the derivatives, supported by the highest oxidation potential (0.94 V). In this case, the substitution of the trifluoromethyl group at the 3-position on the imidazole and at the para position to Ir on the phenyl ring is considered to be the most effective to lower only the HOMO level.

In summary, 2-phenylimidazo[1,2-*a*]pyridine ligands afford promising Ir phosphors because substituents easily introduced at the 3-position on the imidazole part besides the phenyl ring can effectively tune the HOMO levels. The complexes with these ligands would be modified to afford other new blue phosphors by introduction of other ancillary ligands such as picolinic acid [3]. The fabrication of OLEDs using these complexes as well as optimization is currently underway.

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