

Phosphorescent Iridium Complexes Based on 2-Phenylimidazo[1,2-a]pyridine Ligands: Tuning of Emission Color toward the Blue Region and Application to Polymer Light-Emitting Devices

Shin-ya Takizawa,[†] Jun-ichi Nishida,[†] Toshimitsu Tsuzuki,[‡] Shizuo Tokito,^{†,‡} and Yoshiro Yamashita^{*†}

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan, and Science and Technical Research Laboratories, Japan Broadcasting Corporation (NHK), Kinuta, Setagaya-ku, Tokyo 157-8510, Japan

Received December 19, 2006

A series of new blue-phosphorescent iridium(III) complexes **1–14** with ligands of 2-phenylimidazo[1,2-a]pyridine (pip) derivatives were successfully prepared, and their electrochemical, photophysical, and electroluminescent (EL) properties were systematically investigated. It was found that the emission maxima are significantly dependent on the substituents on the phenyl ring in the range of 489–550 nm. For instance, electron-withdrawing groups such as F and CF₃ shift the emission maxima to shorter wavelengths by lowering the HOMO levels (complexes **4–8**), whereas the extended π -conjugation leads to bathochromic shifts (**2, 3**). To obtain further information about the frontier orbital, substitution effects on the imidazole part were also investigated here, and it was found that electron-withdrawing or -donating substituents on the imidazole ring affected the emission maxima (**9**, 557 nm; **10**, 525 nm). These results including their oxidation potentials suggest that the HOMO of the pip-based complex is a mixture of Ir-d, phenyl- π , and imidazole- π orbitals. From this viewpoint, combination of electron-withdrawing substituents on the phenyl ring with the use of another ancillary ligand enabled further blue shifts (**13**, 468, 499 nm; **14**, 464, 494 nm). This new system based on pip is one of the rare examples of iridium complexes whose emissions can be tuned to the blue region. Preliminary polymer light-emitting devices (PLEDs) employing the Ir complexes were fabricated, and the devices showed moderate EL efficiencies.

Introduction

Phosphorescent materials have been extensively studied during the past decade and continue to be the focus of intense interest in materials chemistry owing to their applications for organic light-emitting diodes (OLEDs) with high performances.^{1–3} In an emitting layer of OLEDs, singlet and triplet excitons are generated in 25 and 75%, respectively,

according to simple spin statistics of hole–electron recombination; this implies that utilization of phosphorescence can lead to an internal quantum efficiency approaching 100% which results in high external quantum efficiency of device. Therefore, many research groups have focused on the development of heavy metal complexes as phosphorescent materials since strong spin–orbit coupling induced by the heavy metal ion promotes intersystem crossing from the singlet to the triplet excited state and allows strong phosphorescence at room temperature.^{2–10}

* To whom correspondence should be addressed. E-mail: yoshiro@echem.titech.ac.jp. Phone: +81-45-924-5571. Fax: +81-45-924-5489.

[†] Tokyo Institute of Technology.

[‡] Japan Broadcasting Corp.

(1) Hoshino, S.; Suzuki, H. *Appl. Phys. Lett.* **1996**, *69*, 2, 224.
(2) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442. (c) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4. (d) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, *77*, 904.

(3) Reviews: (a) Hung, L. S.; Chen, C. H. *Mater. Sci. Eng., R* **2002**, *39*, 143. (b) Holder, E.; Langeveld, B. M. W.; Schubert, U. S. *Adv. Mater.* **2005**, *17*, 1109.

(4) (a) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055. (b) Che, C.-H.; Chan, S.-C.; Xiang, H.-F.; Chan, M. C. W.; Liu, Y.; Wang, Y. *Chem. Commun.* **2004**, 1484. (c) Sotoyama, W.; Satoh, T.; Sawatari, N.; Inoue, H. *Appl. Phys. Lett.* **2005**, *86*, 153505.

Through such studies, platinum (Pt)⁴ and iridium (Ir) complexes have been recognized as useful phosphors, and in particular, Ir complexes based on 2-phenylpyridine (ppy) ligands have been innumerable reported.^{5–8} In these complexes, emission color can be tuned by introducing various substituents at suitable positions of the ppy ligands.^{5,6} In addition, color tuning to blue has been achieved by introducing various ancillary ligands; for example, deep-blue emissive Ir complexes with ancillary ligands of pyrazolylborate, diphosphine, and isocyanide have been reported.^{9a} On the other hand, the extension of π -conjugation on the ligands tunes the color toward the red region.⁸ However, new color

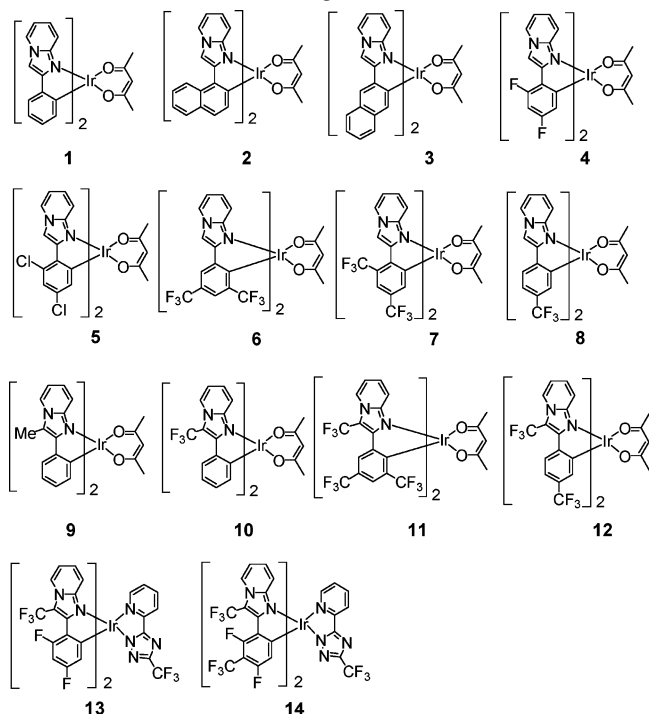
tunable Ir complexes based on new ligands^{9,10} have been less explored in contrast to the rapid progress of ppy-based complexes. Furthermore, pure-blue phosphorescent materials are in a great demand for the application to full-color display:^{6,9} the development of blue phosphors, regarding the improvement of quantum efficiency and color purity, has lagged behind that of green and red ones.

In this context, we believe that a breakthrough to solve the problem is the development of new phosphorescent materials along with better knowledge of structure–property relationship. In view of this point, Thompson and Forrest et al. recently reported near-UV phosphorescent Ir complexes with carbene ligands,^{9b,c} and subsequently, deep-blue phosphorescent phenyltriazole-based complexes were reported by Burn and Samuel et al.^{9d}

On the other hand, we have recently designed and prepared a series of Ir complexes with new ligands of 2-phenylimidazo[1,2-a]pyridines (pip)¹¹ and found that the emission maxima are significantly dependent on the substituents on the phenyl ring even though deep-blue emission could not be obtained. This new ligand has the following advantages: (1) The LUMO energy level of 2-phenylimidazo[1,2-a]pyridine is relatively high,^{11a} which is considered to be useful for making the emission blue-shifted. (2) Various derivatives can be easily prepared by a mild one-step reaction from the corresponding 2-aminopyridines and 2-bromoacetophenones.¹² (3) It is also possible to introduce various substituents to the imidazole ring.^{13a} A variety of derivatives brought about by these synthetic advantages are expected to facilitate the modification of physical and chemical properties such as emission color, morphology, carrier-transporting, and thermal stability of the complex. Moreover, although imidazo[1,2-a]pyridine derivatives have received considerable attention in the fields of organic chemistry and medicinal chemistry,^{13,14} there have been no reports concerning their applications to electronic devices, except for our recent attempt.^{11ab} In this paper, we have systematically synthesized

- (5) (a) Grushin, V. V.; Herron, N.; LeCloux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, 1494. (b) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304. (c) Ostrowski, J. C.; Robinson, M. R.; Heeger, A. J.; Bazan, G. C. *Chem. Commun.* **2002**, 784. (d) Tsuzuki, T.; Shirasawa, N.; Suzuki, T.; Tokito, S. *Adv. Mater.* **2003**, *15*, 1455. (e) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377. (f) Yang, C.-H.; Fang, K.-H.; Chen, C.-H.; Sun, I.-W. *Chem. Commun.* **2004**, 2232. (g) Nishida, J.; Echizen, H.; Iwata, T.; Yamashita, Y. *Chem. Lett.* **2005**, *34*, 1378. (h) Mak, C. S. K.; Hayer, A.; Pascu, S. I.; Watkins, S. E.; Holmes, A. B.; Köhler, A.; Friend, R. H. *Chem. Commun.* **2005**, 4708. (i) Bettington, S.; Tavasli, M.; Bryce, M. R.; Batsanov, A. S.; Thompson, A. L.; Attar, H. A. A.; Dias, F. B.; Monkman, A. P. *J. Mater. Chem.* **2006**, *16*, 1046.
- (6) (a) Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 2082. (b) Tokito, S.; Iijima, T.; Suzuri, Y.; Kita, H.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, *83*, 569. (c) Holmes, R. J.; D'Andrade, B. W.; Forrest, S. R.; Ren, X.; Li, J.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *83*, 3818. (d) Yeh, S.-J.; Wu, M.-F.; Chen, C.-T.; Song, Y.-H.; Chi, Y.; Ho, M.-H.; Hsu, S.-F.; Chen, C. H. *Adv. Mater.* **2005**, *17*, 285. (e) Coppo, P.; Plummer, E. A.; De Cola, L. *Chem. Commun.* **2004**, 1774. (f) Ragni, R.; Plummer, E. A.; Brunner, K.; Hofstra, J. W.; Babudri, F.; Farinola, G. M.; Naso, F.; De Cola, L. *J. Mater. Chem.* **2006**, *16*, 1161. (g) Takizawa, S.; Echizen, H.; Nishida, J.; Tsuzuki, T.; Tokito, S.; Yamashita, Y. *Chem. Lett.* **2006**, *35*, 748.
- (7) (a) Lo, S.-C.; Anthopoulos, T. D.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2005**, *17*, 1945. (b) Lo, S.-C.; Richards, G. J.; Markham, J. P. J.; Namdas, E. B.; Sharma, S.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2005**, *15*, 1451. (c) You, Y.; An, C.-G.; Lee, D.-S.; Kim, J.-J.; Park, S. Y. *J. Mater. Chem.* **2006**, *16*, 4706.
- (8) (a) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971. (b) Su, Y.-J.; Huang, H.-L.; Li, C.-L.; Chien, C.-H.; Tao, Y.-T.; Chou, P.-T.; Datta, S.; Liu, R.-S. *Adv. Mater.* **2003**, *15*, 884. (c) Zhu, W. G.; Ke, Y.; Wang, F.; Liu, C. Z.; Yuan, M.; Cao, Y. *Synth. Met.* **2003**, *137*, 1079. (d) Okada, S.; Okinaka, K.; Iwawaki, H.; Furugori, M.; Hashimoto, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Tsuboyama, A.; Takiguchi, T.; Ueno, K. *Dalton Trans.* **2005**, 1583. (e) Wu, F.-I.; Su, H.-J.; Shu, C.-F.; Luo, L.; Diao, W.-G.; Cheng, C.-H.; Duan, J.-P.; Lee, C.-H. *J. Mater. Chem.* **2005**, *15*, 1035. (f) Liang, B.; Jiang, C.; Chen, Z.; Zhang, X.; Shi, H.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 1281. (g) Chen, L.; You, H.; Yang, C.; Zhang, X.; Qin, J.; Ma, D. *J. Mater. Chem.* **2006**, *16*, 3332.
- (9) (a) Li, J.; Djurovich, P.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713. (b) Sajoto, T.; Djurovich, P.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. *Inorg. Chem.* **2005**, *44*, 7992. (c) Holmes, R. J.; Forrest, S. R.; Sajoto, T.; Tamayo, A.; Djurovich, P.; Thompson, M. E.; Brooks, J.; Tung, Y.-J.; D'Andrade, B. W.; Weaver, M. S.; Kwong, R. C.; Brown, J. J. *Appl. Phys. Lett.* **2005**, *87*, 243507. (d) Lo, S.-C.; Shipley, C. P.; Bera, R. N.; Harding, R. E.; Cowley, A. R.; Burn, P. L.; Samuel, I. D. W. *Chem. Mater.* **2006**, *18*, 5119.
- (10) (a) Huang, W.-S.; Lin, J. T.; Chien, C.-H.; Tao, Y.-T.; Sun, S.-S.; Wen, Y.-S. *Chem. Mater.* **2004**, *16*, 2480. (b) Paulose, B. M. J. S.; Rayabarapu, D. K.; Duan, J.-P.; Cheng, C.-H. *Adv. Mater.* **2004**, *16*, 2003. (c) Rayabarapu, D. K.; Paulose, B. M. J. S.; Duan, J.-P.; Cheng, C.-H. *Adv. Mater.* **2005**, *17*, 349. (d) Takizawa, S.; Sasaki, Y.; Akhtaruzzaman, M.; Echizen, H.; Nishida, J.; Iwata, T.; Tokito, S.; Yamashita, Y. *J. Mater. Chem.* **2007**, *17*, 841.
- (11) (a) Takizawa, S.; Nishida, J.; Tsuzuki, T.; Tokito, S.; Yamashita, Y. *Chem. Lett.* **2005**, *34*, 1222. (b) Takizawa, S.; Nishida, J.; Yamashita, Y.; Tsuzuki, T.; Tokito, S. *Mol. Cryst. Liq. Cryst.* **2006**, *455*, 381. (c) Lussier, B. B.; Deaton, J. C.; Giesen, D. J. U.S. Patent 7,147,937B2, Dec 12, 2006; 22 pp. (d) Deaton, J. C.; Huo, S.; Lussier, B. B.; Brown, C. T.; Garnett, J. C.; Blondell, D. B.; Landry, M. R. *Dig. Tech. Pap.— Soc. Inf. Display Int. Symp.* **2006**, *37* (Bk. 1), 939–941.
- (12) (a) Kaye, I. A.; Parris, C. L.; Burlant, W. J. *J. Am. Chem. Soc.* **1953**, *75*, 746. (b) Tomoda, H.; Hirano, T.; Saito, S.; Mutai, T.; Araki, K. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1327.
- (13) (a) Enguehard, C.; Renou, J.-L.; Collot, V.; Hervet, M.; Rault, S.; Gueffier, A. *J. Org. Chem.* **2000**, *65*, 6572. (b) Kazock, J.-Y.; Enguehard-Gueffier, C.; Thery, I.; Gueffier, A. *Bull. Chem. Soc. Jpn.* **2005**, *78*. (c) Kazock, J.-Y.; Thery, I.; Chezal, J.-M.; Chavignon, O.; Teulade, J.-C.; Gueffier, A.; Enguehard-Gueffier, C. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 775. (d) Kawano, T.; Kato, N.; *Chem. Lett.* **2006**, *35*, 270.
- (14) (a) Colletti, S. L.; Frie, J. L.; Dixon, E. C.; Singh, S. B.; Choi, B. K.; Scapin, G.; Fitzgerald, C. E.; Kumar, S.; Nichols, E. A.; O'Keefe, S. J.; O'Neill, E. A.; Porter, G.; Samuel, K.; Schmatz, D. M.; Schwartz, C. D.; Shoop, W. L.; Thompson, C. M.; Thompson, J. E.; Wang, R.; Woods, A.; Zaller, D. M.; Doherty, J. B. *J. Med. Chem.* **2003**, *46*, 349. (b) Zhuang, Z.-P.; Kung, M.-P.; Wilson, A.; Lee, C.-W.; Plössl, K.; Hou, C.; Holtzman, D. M.; Kung, H. F. *J. Med. Chem.* **2003**, *46*, 237. (c) Byth, K. F.; Culshaw, J. D.; Green, S.; Oakes, S. E.; Thomas, A. P. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2245. (d) Gudmundsson, K. S.; Williams, J. D.; Drach, J. C.; Townsend, L. B. *J. Med. Chem.* **2003**, *46*, 1449.

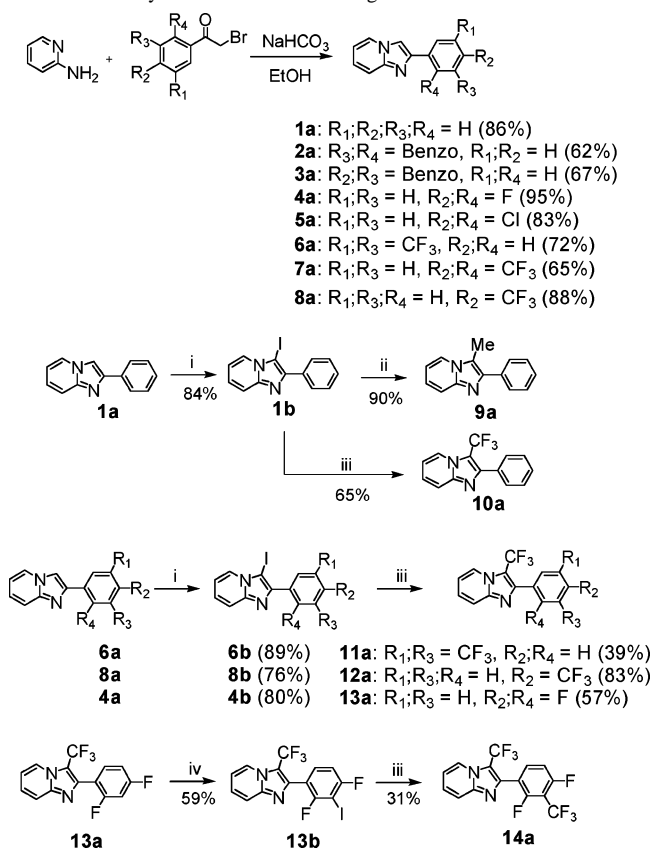
Chart 1. Structures of the Ir Complexes



and characterized a series of pip-based Ir complexes, which are illustrated in Chart 1. To gain an insight into the frontier orbitals of the complex, the substituent effects on the imidazole ring were also investigated. The phosphorescence color was successfully tuned to the blue region by the appropriate combination of electron-withdrawing substituents on both the phenyl and imidazole rings. In addition, we fabricated polymer light-emitting devices (PLEDs) based on some complexes to evaluate their applicability to devices.

Results and Discussion

Synthesis and Characterization. Synthetic routes for the ligands **1a–14a** are outlined in Scheme 1. 2-Phenylimidazo[1,2-*a*]pyridine (**1a**) and its derivatives **2a–8a** bearing substituents on the phenyl ring were readily prepared in good yields (62–95%) from 2-aminopyridine and the corresponding 2-bromoacetophenones. Ligands **9a** and **10a**, which have the substituent on the imidazole ring, were prepared via 3-iodo-2-phenylimidazo[1,2-*a*]pyridine (**1b**). For example, 3-methyl-2-phenylimidazo[1,2-*a*]pyridine (**9a**) was obtained in 90% yield by the Suzuki cross-coupling reaction of 3-iodo precursor **1b** and methylboronic acid.^{13a} On the other hand, 2-phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**10a**) was prepared in 65% yield by the reaction of **1b** with (trifluoromethyl)trimethylsilane ((TMS)CF₃) in the presence of CuI and KF.¹⁵ Furthermore, this method was applicable to the synthesis of other derivatives containing electron-withdrawing groups on the phenyl ring; the reactions of the corresponding iodo precursors, which were easily prepared from **4a**, **6a**, and **8a**, with (TMS)CF₃ proceeded well to give CF₃-substituted derivatives **11a–13a** (39–83% yields). For the

Scheme 1. Synthetic Routes of the Ligands^a

^a Key: (i) I₂/pyridine, 5 h, 50 °C; (ii) MeB(OH)₂, Pd(PPh₃)₄, DME, 40 h, 85 °C; (iii) TMSCF₃, CuI/KF, NMP, 24 h, RT; (iv) LDA/I₂, THF.

synthesis of multi-substituted ligand **14a**, the trifluoromethyl group could be additionally introduced to derivative **13a** by a method described in our recent paper.^{6g}

Bis-cyclometalated Ir complexes **1–14** containing acetylacetonate (acac) or pyridyltriazolate as an ancillary ligand were prepared by a two-step reaction via Ir(III)- μ -chloro-bridged dimer complexes according to a conventional procedure^{5b} in moderate overall yields (24–69%) except for **2** (18%) and **11** (12%). The complexes were purified by recrystallization from ethanol/dichloromethane after chromatography. Although single crystals were obtained for some complexes, complete X-ray structure analyses were unsuccessful probably due to the poor quality of crystals. All the complexes are thermally stable up to around 300 °C in air. These complexes were fully characterized by ¹H NMR, mass spectrometry, and elemental analysis. Some complexes could be finally purified by sublimation. Interestingly, the complexes containing fluorine atoms or trifluoromethyl groups, i.e., complexes **4**, **6–8**, and **10–14**, could be sublimed under high vacuum, while other derivatives including nonsubstituted complex **1** were not sublimable at all. These observations clearly suggest that fluorination of the C–H bonds makes sublimation of the complex easier because of reduced intermolecular interactions;¹⁶ this would be essential for purification of materials and the fabrication of thermally deposited OLEDs.

(15) Cottet, F.; Marull, M.; Lefebvre, O.; Schlosser, M. *Eur. J. Org. Chem.* **2003**, 8, 1559.

(16) Wang, Y.; Herron, N.; Grushin, V. V.; LeCloux, D.; Petrov, V. *Appl. Phys. Lett.* **2001**, 79, 449.

Table 1. Photophysical and Electrochemical Properties of the Ir Complexes

complex	λ_{abs} (log ϵ)/nm ^a	λ_{em} /nm (77 K) ^b	λ_{em} /nm (RT) ^d	Φ^c	$E_{1/2}^{\text{ox}}/V^d$
1	249 (4.72); 387 (3.93)	500; 538; 583 (sh)	521 (sh); 546	0.024	0.17
2	234 (4.75); 276 (4.66); 320 (4.42); 378 (3.98); 431 (3.95)	546; 591; 648	550; 597; 648 (sh)	0.019	0.18
3	258 (4.89); 417 (3.69)	514; 556; 608	522; 560; 602 (sh)	0.004	0.17
4	248 (4.72); 343 (4.04); 371 (4.00)	482; 520; 560	499; 531	0.035	0.50
5	259 (4.74); 355 (4.08); 386 (4.02)	486; 524; 565	500; 536	0.064	0.60
6	249 (4.70); 327 (4.18); 347 (4.15); 376 (4.07)	478; 514; 555	489; 523; 560 (sh)	0.032	0.68
7	247 (4.66); 373 (3.99); 401 (3.90)	499; 537; 583	505; 539	0.058	0.70
8	250 (4.73); 339 (4.03); 362 (4.01); 391 (3.93)	491; 531; 565	509; 540	0.045	0.45
9	259 (4.69); 366 (3.99); 393 (4.03)	509; 550; 596	535 (sh); 557	0.041	0.13
10	256 (4.77); 359 (3.84); 406 (3.81)	484; 517; 555 (sh)	525	0.045	0.34
11	250 (4.70); 350 (3.97); 378 (3.90)	457; 490; 527	473; 503; 541 (sh)	0.007	0.94
12	250 (4.77); 343 (3.95); 365 (3.88); 406 (3.80)	480; 515; 557 (sh)	490; 517 (sh)	0.064	0.56
13	247 (4.75); 317 (4.22); 337 (4.12); 362 (4.02)	457; 489; 526	468; 499; 535 (sh)	0.027	0.97
14	248 (4.64); 310 (4.18); 335 (4.10); 355 (3.99)	453; 485; 522	463; 493; 529 (sh)	0.033	

^a In CH₂Cl₂. ^b In 2-MeTHF. ^c In CH₂Cl₂ using *fac*-Ir(ppy)₃ ($\Phi = 0.40$) as a reference. ^d In DMF containing 0.1 M *n*-Bu₄NPF₆ vs Cp₂Fe/Cp₂Fe⁺.

Electrochemical Properties. To have an insight into the highest occupied molecular orbital (HOMO) energy levels of the complexes, oxidation potentials were measured in DMF solution versus SCE by cyclic voltammetry (CV). Their values are reported relative to a ferrocenium/ferrocene (Cp₂Fe⁺/Cp₂Fe) redox couple, as shown in Table 1. All the Ir complexes show reversible oxidation processes during the anodic scan with the rate of 100 mV/s. On the other hand, clear reduction peaks, which are associated with the lowest unoccupied molecular orbital (LUMO) levels, were not observable for the complexes. From the CV measurement, it was found that introducing the electron-withdrawing groups such as fluorine atom (F) and trifluoromethyl (CF₃) group on the phenyl rings leads to higher oxidation potentials for the complexes. For example, while nonsubstituted complex **1** has the oxidation potential of 0.17 V, complexes **4** and **6–8** with F or CF₃ groups on the phenyl ring have much higher potentials of 0.50, 0.68, 0.70, and 0.45 V, respectively. Additionally, chlorine atoms (Cl) affect the potential to give the value of 0.60 V. These results evidently indicate that electron-withdrawing groups effectively lower the HOMO energy level of pip-based complex. In contrast to the effects of electron-withdrawing groups, extended π -conjugation does not influence the HOMO level, as evidenced by the fact that complexes **2** and **3** with naphthyl groups have identical values (0.18, 0.17 V) with **1**.

Furthermore, it is important to note that substituents on the imidazole ring also affect the electrochemical behavior, in which complex **9** with a methyl group shows a slightly lower oxidation potential (0.13 V), compared to nonsubstituted **1**, whereas **10** containing a CF₃ group has a higher potential (0.34 V). This observation as well as the effects of substituents on the phenyl ring reveals that the HOMO of the complex is expanded over the imidazole ring, phenyl ring, and iridium center. This interpretation is also supported by the following electrochemical behavior: complexes **11** and **12** having CF₃ groups on both the phenyl and imidazole rings exhibited oxidation waves at further higher potentials (0.94, 0.56 V). In addition, replacement of the picolate ligand with 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazolate^{6d} for the ancillary ligand resulted in an additional positive shift of the potential (0.97 V for **13**), suggesting that the electron-accepting pyridyltriazole ligand interacts with the pip ligand

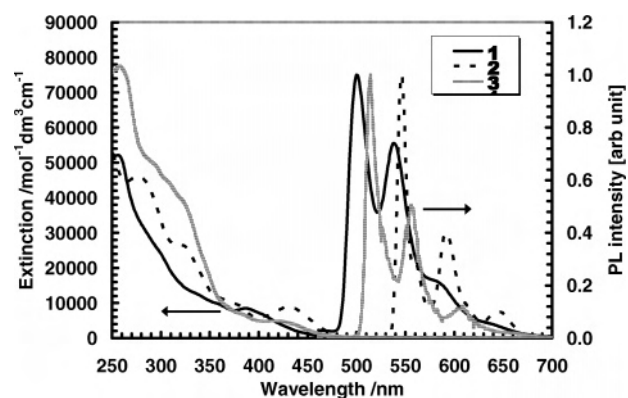


Figure 1. Absorption (in CH₂Cl₂ at RT) and PL (in 2-MeTHF at 77 K) spectra of complexes **1–3**.

in the HOMO including the metal orbital to further stabilize the energy level. In complex **14**, it is presumed that its further higher oxidation potential did not allow the detection of a peak in the potential window. It is noteworthy that these electrochemical properties discussed here are closely related to the photophysical properties of the Ir complexes (vide infra).

Photophysical Properties. Table 1 summarizes the photophysical data of the Ir complexes, and their absorption and photoluminescence (PL) spectra are shown in Figures 1–5. In the UV–visible absorption spectrum of complex **1** (Figure 1), a broad absorption at around 330 nm was observed. This is assigned to the π – π^* transition of the pip ligand since free ligand **1a** shows an absorption band at the similar wavelength (around 320 nm). On the other hand, the band at 387 nm, which is not observed in the spectrum of free ligand and is assignable to the singlet metal-to-ligand charge-transfer (¹MLCT) transition, appeared after cyclometalation with iridium. In addition, the longer wavelength band at around 440 nm was observed and can be attributed to a mixture of ³MLCT and ligand-centered (LC) triplet π – π^* transition.

Nonsubstituted complex **1** in solution exhibits broad green phosphorescence with an emission maximum at 546 nm at room temperature as shown in Figure 2. The maximum was blue-shifted at 77 K (500, 538 nm), and the spectrum became highly resolved as shown in comparison of Figures 1 and 2. The quantum efficiency in solution at ambient temperature

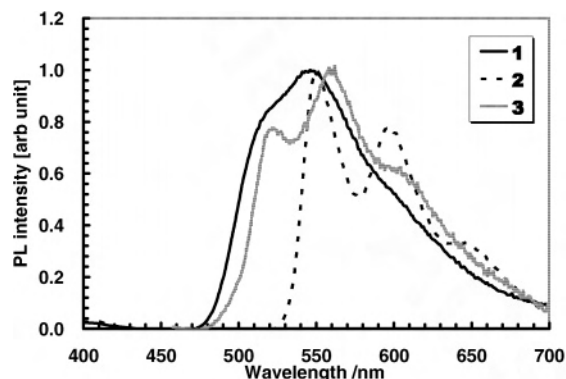


Figure 2. PL spectra of complexes **1–3** in CH_2Cl_2 at RT.

(0.024), however, is considerably low compared with those of ppy derivatives.⁴ Other derivatives have the same trend in quantum efficiency, which ranges from 0.004 to 0.064. Although the reason has not been clear at present, a plausible explanation for the low efficiencies involves the presence of thermally accessible nonradiative excited-state based on a metal-centered (MC) excited state.^{4a,9b,17} This is interpreted by the fact that these complexes exhibit strong emission at low temperature (77 K, in 2-MeTHF rigid matrix).

For complex **4** having fluorine atoms, the phosphorescence lifetime was measured in polycarbonate (PC) thin film at room temperature. The emission decayed double exponentially with relatively long lifetimes ($\tau_1 = 5.8 \mu\text{s}$, $\tau_2 = 15.5 \mu\text{s}$) compared with that of reported iridium (III) bis(2-phenylpyridinato-*N,C'*)acetylacetonate ($\text{Ir}(\text{ppy})_2(\text{acac})$) ($\tau = 1.6 \mu\text{s}$).^{5b} In addition, vibronic progressions clearly appear in the PL spectra of all complexes, and large Stokes shifts were observed. These findings suggest that the pip-based Ir complexes emit from the mixed ³LC and MLCT excited states. In particular, the phosphorescence of some Ir complexes originates from the excited state with large ³LC character.^{5b,8a}

1. Effect of Extended π -Conjugation. As shown in Figure 1, the emission maxima of the spectra for **2** and **3** at 77 K are red-shifted by 46 and 14 nm (energy difference: 0.21 and 0.07 eV), respectively, 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. However, these red-shifts are smaller than that of a ppy-based system (0.33 eV) of $\text{Ir}(\text{ppy})_2(\text{acac})$ ^{5b} and $\text{Ir}(\text{NaPy})_2(\text{acac})$ [$\text{NaPy} = 2$ -(1-naphthalenyl)pyridine].^{8c} This difference is rationalized by the assumption that the LUMO of pip is almost localized in the imidazo[1,2-*a*]pyridine side in contrast to a ppy-based complex whose LUMO is somewhat extended to the phenyl ring as revealed by the MO calculations.^{9a,18} Such a feature of the pip-based Ir complex seems favorable for a hypsochromic shift that results from the substitution of electron-withdrawing groups on the phenyl ring.

2. Effect of the Substituents Attached to the Phenyl Ring. For the achievement of phosphorescence color tuning

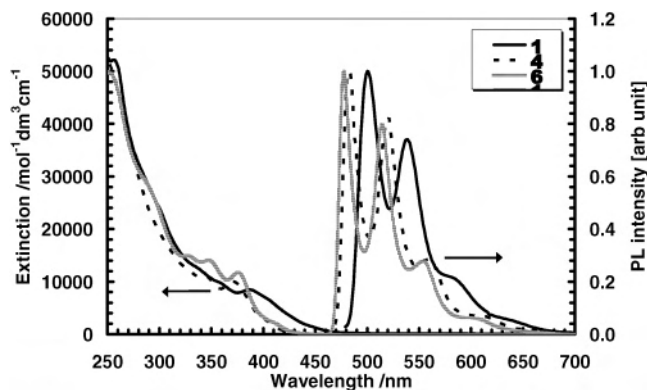


Figure 3. Absorption (in CH_2Cl_2 at RT) and PL (in 2-MeTHF at 77 K) spectra of complexes **1**, **4**, and **6**.

to the blue region, we investigated the effect of electron-withdrawing substituents attached to the phenyl ring (Figure 3). The emission maximum of the complex **4** containing two fluorine atoms at the *meta* position to Ir (482 nm at 77 K) was shorter by 18 nm than that of the unsubstituted complex **1** owing to stabilization of the HOMO energy level, indicating an increase of the HOMO–LUMO gap. This blue-shift is consistent with a shift of the end-absorption wavelength of complexes **1** and **4** (Figure 3). A similar effect has been observed in the study of ppy derivatives with regard to fluorine substitution; introducing fluorine atoms to the *meta* position to Ir is effective to lower the HOMO levels.^{5a,6a} In our study, chlorine atoms at the same positions similarly affected the emission, where the blue shift of 14 nm was observed for complex **5**. This is the first example of Ir complex utilizing a chlorine atom as an electron-withdrawing group to aim at developing blue phosphors.

In addition, in complex **6**, substitution of CF_3 groups at the *ortho* and *para* positions to Ir shifted the emission maximum to 478 nm, which is further shorter by 4 nm (10 nm at RT (room temperature)) than that of complex **4** with fluorines at the *meta* position. This shift is attributed to the fact that the HOMO level is lower than that of **4**, as judged from their electrochemical properties. However, this observation concerning the effect of the CF_3 substitution is contrastive to the results in the ppy system: 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, 499 nm) than a 2,4-F-substituted complex (461, 491 nm) although the HOMO level of the CF_3 substituted complex is lower than that of the F-substituted one.^{6c} A similar trend has been observed in the phosphorescent properties of iridium bis(4,6-difluorophenylpyridinato)picolate ($\text{Ir}(\text{pic})_2$)^{6a,b} and the corresponding CF_3 -substituted analogue [$(\text{CF}_3\text{ppy})_2\text{Ir}(\text{pic})$].¹⁹ These different results observed in pip-based complexes are rationalized by the difference in the degree of delocalization of the LUMOs, as mentioned before.

On the other hand, introduction of two CF_3 groups at the *meta* position in complex **7** also lowers the HOMO energy since **7** has an oxidation potential similar to that of complex **6**. Nevertheless, phosphorescence from complex **7** has an

(17) Nazeeruddin, Md. K.; Humphry-Baker, R.; Berner, D.; Rivier, S.; Zuppiroli, L.; Graetzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 8790.

(18) Hay, P. J. *J. Phys. Chem. A* **2002**, *106*, 1634.

(19) Tokito, S.; Iijima, T.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, *83*, 2459.

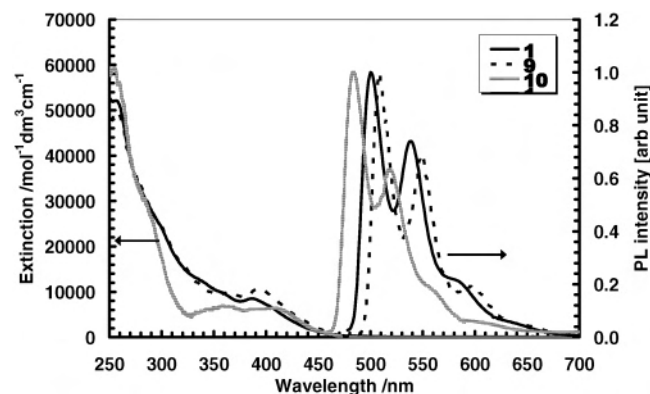


Figure 4. Absorption (in CH_2Cl_2 at RT) and PL (in 2-MeTHF at 77 K) spectra of complexes **1**, **9**, and **10**.

emission maximum similar to that of nonsubstituted **1** (499 nm for **7**, 500 nm for **1** at 77 K). Complex **8** with one CF_3 at the *meta* position shows a similar effect. These results are presumably due to lowering of the LUMO level, suggesting that the most effective substitution position of electron-withdrawing CF_3 group for the blue shift is *para* with regard to Ir on the phenyl ring.

Furthermore, the introduction of F, Cl, and CF_3 groups makes a slight change in quantum efficiencies of the complexes in solution at room temperature. Thus, quantum efficiencies of complexes **4–8** with these electron-withdrawing groups are higher than those of **1–3**. This may be due to a C–F bond with lower vibrational frequency compared with a C–H bond, reducing the degree of nonradiative deactivation.¹⁶ In addition, increased separation between radiative $^3\text{LC/MLCT}$ excited state and nonradiative MC excited state may be another reason because CF_3 groups lower the LUMO energy levels.

3. Effect of the Substituents Attached to the Imidazole Ring. The influence of the substituents linked to the imidazole ring upon the photophysical properties was investigated to obtain further information about the electronic states of the complexes. The emission maximum of complex **9**, which has an electron-donating methyl group on the imidazole ring, was red-shifted by 9 nm compared to that of **1**, while complex **10** with an electron-withdrawing CF_3 group exhibited a hypsochromic shift of 16 nm (Figure 4). This can be explained by considering that the methyl group destabilizes the HOMO level of the complex, whereas the CF_3 group stabilizes it, as evidenced by their oxidation potentials (0.17 V for **1**; 0.13 V for **9**; 0.34 V for **10**). These results imply that the HOMO mainly consists of the phenyl- π , imidazole- π , and Ir-d orbitals, while the LUMO is localized on the pyridine ring of the imidazo[1,2-*a*]pyridine part.

4. Tuning of Phosphorescence Color toward the Blue Region. From the viewpoint of the proposed HOMO distribution, it was expected that if electron-withdrawing substituents are introduced on both the phenyl and imidazole rings, the HOMO level would be largely lowered to give blue color phosphorescence. To investigate the effect of CF_3 substituents attached to the phenyl and imidazole rings, we synthesized complex **11** with three CF_3 groups, in which the

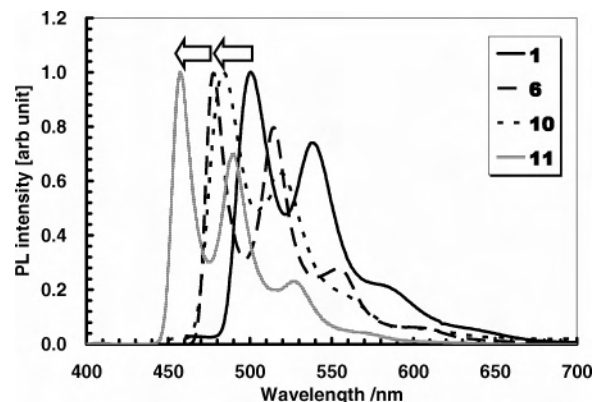


Figure 5. PL (in 2-MeTHF at 77 K) spectra of complexes **1**, **6**, **10**, and **11**.

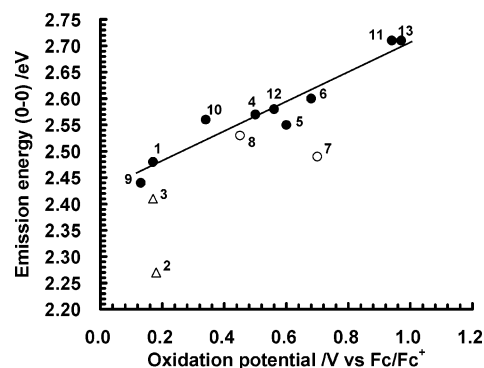
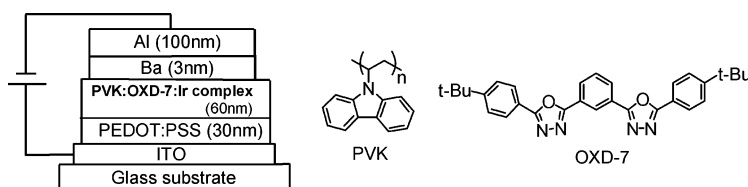


Figure 6. Plot of emission energy vs oxidation potential for the pip-based complexes.

introduction of CF_3 at the *para* position to Ir was expected to be favorable for the effective blue shift on the basis of the above discussion. As a result, complex **11** showed significant blue emission in 2-MeTHF at 77 K, and the emission maximum was found to be largely blue-shifted to 457 nm compared to those of **1** (500 nm), **6** (478 nm), and **10** (484 nm), as shown in Figure 5; complexes **6** and **10** contain CF_3 groups on the phenyl or imidazole ring, respectively. Figure 5 represents that the blue shift in emission increases with an increase of the number of CF_3 on the ligand. In addition, it should be also noted that the HOMO level of **11** is much lower since the oxidation potential is extremely high (0.94 V). On the other hand, complex **12**, which contains two CF_3 substituents on the phenyl and imidazole, shows a blue-shift in comparison with phosphorescent properties of **8** and **10**, although the PL color of **12** is not so blue. These results clearly demonstrate that the introduction of electron-withdrawing groups on both the phenyl and imidazole rings is effective for lowering the HOMO level to show a large blue shift in phosphorescence of pip-based Ir complexes.

However, it is not easy to synthesize blue phosphor **11**. Its overall yield of 15% is relatively low compared with those of other complexes. Therefore, other combination of the substituents as well as the use of 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazolate^{6d} as an alternative ancillary ligand was tested by preparing complexes **13** and **14**, whose overall yields were 60 and 58%, respectively. In complex **13**, the phenyl ring is substituted with fluorine atoms, while a CF_3

Scheme 2. Device Structure and the Materials Used for PLEDs

group is additionally introduced at the *para* position to Ir in complex **14**. Complex **13** exhibited blue emission (λ_{max} : 457 nm) that resembles luminescence of **11**. In addition, blue phosphorescence was observed at 468 nm at room temperature, which is similar to that of well-known blue phosphor, FIrpic,^{6a,b} even though the spectrum of **13** is significantly broader (see Supporting Information). On the other hand, the emission of complex **14** containing both F and CF₃ on the phenyl ring exhibited further 4 nm blue shift, resulting in 453 nm because of the lower HOMO level that originates from the additional CF₃ effect. Utility of this method using both F and CF₃ groups on the phenyl ring for color tuning has also been demonstrated by a ppy system in our recent paper.^{6g}

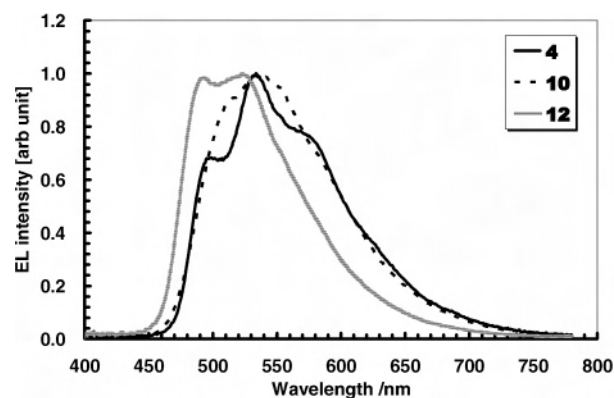
The relationship between the emission energy and the oxidation potentials of the complexes is illustrated in Figure 6, which clearly indicates that the HOMO level of an Ir complex is closely related to the emission energy. Complexes **2**, **3**, and **7** are considerably out of the relationship, which is probably due to their low LUMO levels. Although the PL efficiencies of the complexes at room temperature are still unsatisfactory compared to ppy derivatives, this class of complexes provides an excellent opportunity to tune phosphorescence color from green to blue by appropriate combination of the substituents on the pip ligand and the ancillary ligand. In particular, this new system based on pip is one of the rare examples of Ir complexes whose emission can be tuned to the blue region and, thereby, would provide important information for designing new phosphorescent materials.

Polymer Light-Emitting Devices Using the Pip-Based Complexes. We finally fabricated preliminary polymer light-emitting devices (PLEDs) doped with complexes **4**, **10**, and **12** to evaluate electroluminescent properties of our complexes. PLEDs fabricated using wet processes have been known to be advantageous for the practical applications in a large area display owing to their simple and low-cost fabrication processes.²⁰ In the present device, poly(*N*-vinylcarbazole) (PVK) was selected as a host material because it has a high triplet energy along with high hole mobility.²¹ The simple device structure is as follows (also depicted in Scheme 2): indium tin oxide (ITO)/poly-(ethylenedioxythiophene) doped with poly(stylenesulfonate) (PEDOT/PSS) as a hole-injecting layer (30 nm)/PVK and

Table 2. Performances of PLEDs^a

dopant	$\lambda_{\text{em}}/\text{nm}$	$L/\text{cd m}^{-2}$	$\eta_{\text{ext}}/\%$	$\eta_{\text{c}}/\text{cd A}^{-1}$	$\eta_{\text{p}}/\text{lm W}^{-1}$	CIE at 100 cd m ⁻²
4	499; 534	479	1.7 (1.5)	5.0 (4.5)	2.6 (0.9)	(0.37, 0.54)
10	537	639	2.9 (1.8)	8.8 (5.3)	4.9 (1.0)	(0.36, 0.55)
12	493; 523	1970	3.6 (3.6)	10.3 (10.3)	5.5 (4.5)	(0.28, 0.52)

^a The data for external quantum efficiency (η_{ext}), brightness (L), current efficiency (η_{c}), and power efficiency (η_{p}) are the maximum values. Values in parentheses are reported at 100 cd/m².

**Figure 7.** EL spectra of the PLEDs.

electron-transporting 1,3-bis([4-*tert*-butylphenyl]-1,3,4-oxadiazolyl]phenylene (OXD-7) blend layer doped with 5 wt % Ir complexes (60 nm)/Ba(3 nm)/Al(100 nm). PVK, OXD-7, and the Ir complex were of the ratio of 65:30:5 by weight.

Table 2 summarizes performances of the devices. Figures 8–10 show applied voltage–current density, current density–external quantum efficiency, and current density–luminous efficiency characteristics, respectively. Each of the devices shows clear electroluminescent characteristics. As shown in Figure 7, all the devices exhibited electroluminescence (EL), which originates from the doped Ir phosphors because of the similarity with the PL spectra of the complexes. It is noteworthy that the EL efficiencies seem to correlate with the PL efficiencies of the complexes in solution at room temperature. Among the PLEDs, the device using complex **12** shows the best external quantum efficiency of 3.6% and luminous efficiency of 10.3 cd/A, which are moderate compared to the efficiencies of some recent polymer LEDs doped with phosphors.^{5h,8e,22} The maximum brightness reached 1970 cd/m². Furthermore, the device based on **12** has the lowest turn-on voltage among the devices (see Figure 8). This is probably attributed to the different electrochemical property of complex **12**; that is, the LUMO level of **12** is

(20) (a) Lee, C.-L.; Lee, K. B.; Kim, J.-J. *Appl. Phys. Lett.* **2000**, *77*, 2280. (b) Gong, X.; Robinson, M. R.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 581. (c) Chen, F.-C.; Yang, Y.; Thompson, M. E.; Kido, J. *Appl. Phys. Lett.* **2002**, *80*, 2308. (21) (a) Yokoyama, M.; Tamamura, T.; Nakano, T.; Mikawa, H. *J. Chem. Phys.* **1976**, *65*, 272. (b) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1993**, *63*, 2627.

(22) (a) Zhang, X.; Jiang, C.; Mo, Y.; Xu, Y.; Shi, H.; Cao, Y. *Appl. Phys. Lett.* **2006**, *88*, 051116. (b) Shao, K.-F.; Xu, X.-J.; Yu, G.; Liu, Y.-Q.; Yang, L.-M. *Chem. Lett.* **2006**, *35*, 404. (c) Li, J.; Sano, T.; Hirayama, Y.; Tomita, T.; Fujii, H.; Wakisaka, K. *Jpn. J. Appl. Phys.* **2006**, *45*, 5232.

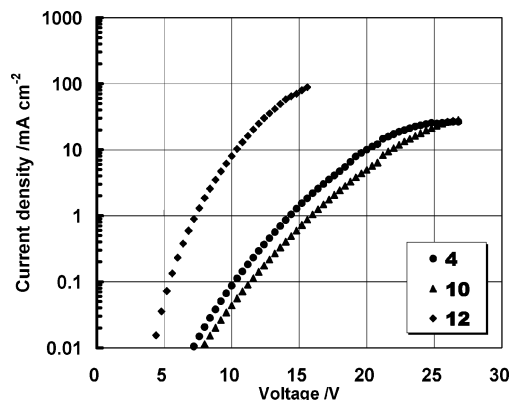


Figure 8. Applied voltage–current density characteristic.

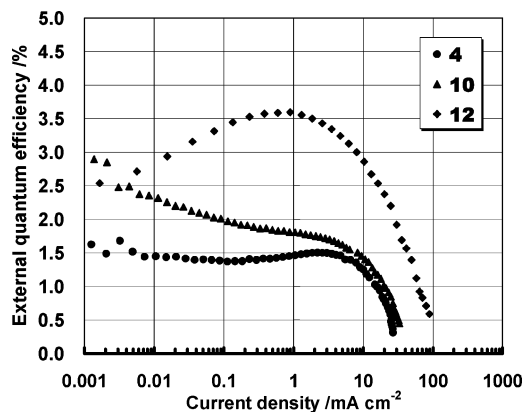


Figure 9. Current density–external quantum efficiency characteristic.

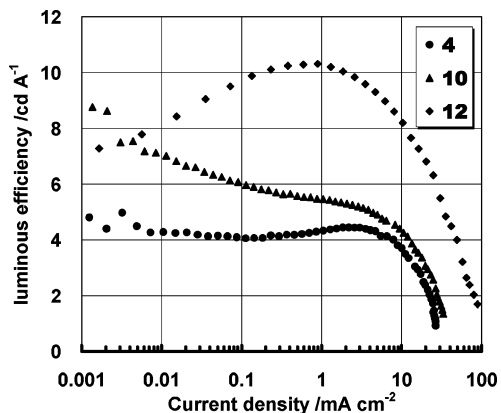


Figure 10. Current density–luminous efficiency characteristic.

lower than those of others, and direct injection of electron to the phosphor is considered to be more efficient.

Although the device structure is not fully optimized yet, these preliminary results suggest that the pip-based complexes act well as a color tunable emitter of PLED and would be candidates for new phosphorescent materials.

Conclusion

A series of new phosphorescent Ir complexes with 2-phenylimidazo[1,2-*a*]pyridine ligands have been prepared and examined for their electrochemical, photophysical, and EL properties. The electron-withdrawing substituents on the phenyl or imidazole rings of the pip ligands effectively lower the HOMO levels to afford emissions with shorter wave-

lengths, since the HOMO of the complex is a mixture of Ir-d, phenyl- π , and imidazole- π orbitals. In particular, the introduction of electron-withdrawing groups at the appropriate positions of both the phenyl and imidazole rings as well as the use of a proper ancillary ligand brought about further hypsochromic shifts to give blue phosphorescence. Additionally, the PLEDs using some complexes exhibited moderate EL efficiencies, suggesting that the pip-based Ir complexes would be candidates of new phosphorescent materials for OLEDs. This new ligand system, which can be finely modified, is also applicable to the cyclometalation with platinum and new functionalized metal complexes.

Various imidazo[1,2-*a*]pyridine derivatives with fluorinated substituents were prepared here, and the synthetic results would provide useful information on the synthesis of such compounds which are of interest in the fields of organic chemistry and medicinal chemistry.^{13,14}

Experimental Section

General Information. Melting and decomposition points were obtained on a Yanako MP-500D apparatus and uncorrected. ¹H NMR spectra were recorded on a JEOL JNM-ECP300 NMR spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). Elemental analyses were carried out with a LECO/CHNS-932 analyzer (Chemical Resources Laboratory at Tokyo Institute of Technology) and a YANAKO CHN corder MT-6 (Center for Advanced Materials Analysis at Tokyo Institute of Technology). EI mass spectra were collected on a SHIMAZU GCMA-QP5000 mass spectrometer. FAB-mass and HRMS spectra were collected on a JEOL JMS-700 mass spectrometer.

Cyclic voltammetry (CV) was carried out using a BAS 100B system. Anhydrous DMF (Kanto Chemical Co., Inc.) was used as the solvent under an argon atmosphere, and 0.1 M tetra-*n*-butylammonium hexafluorophosphate was used as the supporting electrolyte. A Pt disk, Pt wire, and SCE (Yanako MR-P2A) were used as the working, counter, and reference electrodes, respectively. Gel permeation chromatography (GPC) was performed using a JAI HPLC LC-918 with JAIGEL-2H column (eluent: chloroform).

UV–visible absorption and PL spectra were recorded on a Shimadzu MultiSpec-1500 and JASCO FP-6600 spectrometer, respectively. Luminescence quantum yield measurements were carried out at room temperature in an argon prepurged dichloromethane solution using an optically dilute method.²³ Before the measurements, argon was bubbled through the dichloromethane solutions of the complexes (10^{-6} M) for 1.5 min. A solution of *fac*-Ir(ppy)₃ in dichloromethane ($\Phi = 0.40$)²⁴ was used as a reference.

Fabrication of Polycarbonate Thin Film and Phosphorescence Lifetime Measurement. Polycarbonate (PC) thin film was fabricated by spin-coating from a chloroform solution containing 5 wt % complex **4** onto a cleaned quartz substrate (20×20 mm²; thickness, 0.5 mm) under nitrogen. After being dried at 100 °C for 1 h, the film was encapsulated with a glass cap under nitrogen using UV-epoxy adhesive. The sample was excited with the light at 355 nm with a diode-pumped passively Q-switched Nd:YAG laser (Crystal GmbH, FTSS355-Q). Then, the emission was detected using a photomultiplier tube and a streak camera (Hamamatsu

(23) DePriest, J.; Zheng, G. Y.; Goswami, N.; Eichhorn, D. M.; Woods, C.; Rillema, D. P. *Inorg. Chem.* **2000**, *39*, 1955.

(24) Kim, J., II; Shin, I.-S.; Kim, H.; Lee, J.-K. *J. Am. Chem. Soc.* **2005**, *127*, 1614.

Photonics, C4334). The lifetime was determined by fitting the decay curves to the double exponential function.

PLEDs Fabrication and Measurements. An ITO-coated glass substrate was rinsed and degreased by sonication in a detergent solution, pure water, acetone, and 2-propanol and cleaned in a UV-ozone chamber. Then, a nonemitting conducting polymer layer of poly(ethylenedioxythiophene) doped with poly(stylenesulfonate) (PEDOT/PSS) was spin-coated on a precleaned glass substrate and dried at 180 °C for 1 h. The 1 wt % 1,2-dichloroethane solution of poly(*N*-vinylcarbazole) (PVK), 1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7), and phosphorescent Ir complex was spin-coated on to the PEDOT/PSS layer and dried at 100 °C for 1 h. The remaining solvent was removed by drying the sample in vacuum at room temperature for ca. 16 h. The cathode electrode (Ba/Al) was deposited by high-vacuum (10^{-5} Pa) thermal evaporation onto the substrate. Finally, the device was encapsulated with a resin polymerized by UV irradiation under a nitrogen atmosphere. Current–voltage characteristics were measured with a Keithley 2400 source meter, while luminance was measured with a Minolta LS-110. External quantum efficiency was calculated from the luminance, current density, and electroluminescence (EL) spectrum under the assumption of Lambertian emission.

Materials. 2-Aminopyridine and 2-bromoacetophenone (phenacyl bromide) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd., and were used without further purification. The other 2-bromoacetophenone derivatives (i.e., 2-bromo-1'-acetanaphthone, 2-bromo-2'-acetanaphthone, 1-bromo-2',4'-difluoroacetophenone, 1-bromo-2',4'-dichloroacetophenone, 2-bromo-3',5'-bis(trifluoromethyl)acetophenone, 2-bromo-2',4'-bis(trifluoromethyl)acetophenone, 2-bromo-4'-trifluoromethylacetophenone) were prepared from the corresponding acetophenones by bromination using copper(II) bromide.^{12b} 3-(Trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazole for ancillary ligand was prepared according to the literature.²⁵ Iridium(III) chloride trihydrate ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$) was purchased from Acros Organics. 2-Methyltetrahydrofuran (2-MeTHF), which was purchased from TCI Co. Ltd. for PL measurements at low temperature, was distilled over lithium aluminum hydride. All other chemicals were purchased and used without further purification.

Synthesis of the Ligands. 2-Phenylimidazo[1,2-*a*]pyridine (1a)^{11,12} (General Procedure). A mixture of 2-aminopyridine (0.58 g, 6.2 mmol), phenacyl bromide (1.0 g, 5.0 mmol), and sodium hydrogen carbonate (0.65 g, 7.8 mmol) in ethanol (4 mL) was stirred for 12 h at room temperature. The solution was evaporated in vacuo, and water (50 mL) was added to the residue. This was extracted with chloroform twice (50 mL \times 2), and the chloroform solution was washed with water (50 mL) and brine (50 mL). The chloroform solution was dried over sodium sulfate, and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on alumina (solvent: dichloromethane) to obtain 2-phenylimidazo[1,2-*a*]pyridine (4.3 mmol; 86%). Other derivatives **2–8a** were also prepared from 2-aminopyridine and the corresponding 2-bromoacetophenones by the similar procedure except for the need of higher reaction temperature (80 °C).

2-Phenylimidazo[1,2-*a*]pyridine (1a): colorless solid, mp 135–136 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.12 (d, *J* = 5.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.87 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 6.0 Hz, 1H); MS/EI (70 eV) 194 [M]⁺.

2-(1-Naphthalenyl)imidazo[1,2-*a*]pyridine (2a):^{11a} yield: 62%, red oil; ¹H NMR (CDCl_3 , 300 MHz) 8.61 (d, *J* = 9.6 Hz, 1H), 8.20 (d, *J* = 6.9 Hz, 1H), 7.86–7.93 (m, 3H), 7.83 (d, *J* = 6.3 Hz, 1H), 7.72 (d, *J* = 9.3 Hz, 1H), 7.48–7.56 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 6.8 Hz, 1H); MS/EI (70 eV) 243 [M]⁺.

2-(2-Naphthalenyl)imidazo[1,2-*a*]pyridine (3a): yield 67%, colorless solid, mp 155–162 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.53 (s, 1H), 8.17 (d, *J* = 6.9 Hz, 1H), 7.83–8.04 (m, 5H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.46–7.50 (m, 2H), 7.18–7.26 (m, 1H), 6.81 (t, *J* = 7.1 Hz, 1H); MS/EI (70 eV) 244 [M]⁺.

2-(2,4-Difluorophenyl)imidazo[1,2-*a*]pyridine (4a):^{11a} yield 95%, colorless solid, mp 136–137 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.30–8.38 (m, 1H), 8.14 (d, *J* = 6.9 Hz, 1H), 8.00 (d, *J* = 4.2 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.17–7.23 (m, 1H), 6.98–7.04 (m, 1H), 6.88–6.95 (m, 1H), 6.80 (t, *J* = 6.8 Hz, 1H); MS/EI (70 eV) 230 [M]⁺.

2-(2,4-Dichlorophenyl)imidazo[1,2-*a*]pyridine (5a): yield 83%, colorless solid, mp 179–180 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.26–8.29 (m, 2H), 8.15 (d, *J* = 6.9 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.81 (t, *J* = 6.8 Hz, 1H).

2-[3,5-Bis(trifluoromethyl)phenyl]imidazo[1,2-*a*]pyridine (6a):^{11a} yield 72%, colorless solid, mp 130–132 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.41 (s, 2H), 8.17 (d, *J* = 6.6 Hz, 1H), 8.01 (s, 1H), 7.82 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 6.9 Hz, 1H); MS/EI (70 eV) 330 [M]⁺.

2-[2,4-Bis(trifluoromethyl)phenyl]imidazo[1,2-*a*]pyridine (7a): yield 65%, colorless solid, mp 83–85 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.15–8.24 (m, 2H), 8.03 (s, 1H), 7.88–7.90 (m, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.24 (t, *J* = 6.8 Hz, 1H), 6.85 (t, *J* = 6.5 Hz, 1H); MS/EI (70 eV) 330 [M]⁺.

2-(4-Trifluoromethylphenyl)imidazo[1,2-*a*]pyridine (8a): yield 88%, pale yellow solid, mp 197–200 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.15 (d, *J* = 6.6 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.94 (s, 1H), 7.64–7.70 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.82 (t, *J* = 6.8 Hz, 1H); MS/EI (70 eV) 262 [M]⁺.

3-Iodo-2-phenylimidazo[1,2-*a*]pyridine (1b)^{13a} (General Procedure for Iodination). To a solution of phenylimidazo[1,2-*a*]pyridine (0.50 g, 2.6 mmol) in pyridine (2 mL) was added iodine (0.98 g, 3.9 mmol). The reaction mixture was heated at 50 °C for 5 h and then poured into water (50 mL). The aqueous solution was extracted with dichloromethane (30 mL \times 3). The combined organic extracts were washed with water (50 mL), $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ (50 mL), and brine (50 mL). The dichloromethane solution was dried over sodium sulfate, and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on alumina (solvent: dichloromethane) to obtain **1b** (2.2 mmol; 84%). Other iodinated compounds **4b**, **6b**, and **8b** were prepared analogously from the corresponding pip ligands **4a**, **6a**, and **8a**.

3-Iodo-2-phenylimidazo[1,2-*a*]pyridine (1b): pale yellow solid, mp 169–171 °C (lit. mp:^{13a} 168 °C); ¹H NMR (CDCl_3 , 300 MHz) 8.24 (d, *J* = 6.9 Hz, 1H), 8.07 (d, *J* = 6.9 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.37–7.44 (m, 1H), 7.20–7.32 (m, 1H), 6.94 (t, *J* = 6.9 Hz, 1H); MS/EI (70 eV) 320 [M]⁺.

3-Iodo-2-[3,5-bis(trifluoromethyl)phenyl]imidazo[1,2-*a*]pyridine (6b): yield 89%, colorless solid, mp 176–180 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.62 (s, 2H), 8.27 (d, *J* = 6.9 Hz, 1H), 7.90 (s, 1H), 7.66 (d, *J* = 9.3 Hz, 1H), 7.26–7.38 (m, 1H), 7.01 (t, *J* = 6.9 Hz, 1H); MS/EI (70 eV) 456 [M]⁺.

3-Iodo-2-(4-trifluorophenyl)imidazo[1,2-*a*]pyridine (8b): yield 76%, colorless solid, mp 187–188 °C; ¹H NMR (CDCl_3 , 300 MHz) 8.17–8.32 (m, 3H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.31 (t, *J* = 6.6 Hz, 1H), 6.90–7.05 (m, 1H).

(25) (a) Medwid, J. B.; Paul, R.; Baker, J. S.; Brockman, J. A.; Du, M. T.; Hallett, W. A.; Hanifin, J. W.; Hardy, R. A., Jr.; Tarrant, M. E.; Torley, L. W.; Wrenn, S. *J. Med. Chem.* **1990**, *33*, 1230. (b) Funabiki, K.; Noma, N.; Kuzuya, G.; Matsui, M.; Shibata, K. *J. Chem. Res., Miniprint* **1999**, 1301.

2-(2,4-Difluorophenyl)-3-iodoimidazo[1,2-*a*]pyridine (4b): yield 80%, pale yellow solid, mp 179–180 °C; ¹H NMR (CDCl₃, 300 MHz) 8.21 (d, *J* = 6.6 Hz, 1H), 7.57–7.71 (m, 2H), 7.24–7.35 (m, 1H), 6.90–7.07 (m, 3H).

3-Methyl-2-phenylimidazo[1,2-*a*]pyridine (9a).^{13a} To a mixture of 3-iodo-2-phenylimidazo[1,2-*a*]pyridine (**1b**) (0.31 g, 1.0 mmol) and Pd(PPh₃)₄ (56 mg, 0.048 mmol) in 1,2-dimethoxyethane (16 mL) was added methylboronic acid (0.29 g, 4.8 mmol) followed by the addition of sodium hydroxide (0.18 g, 4.6 mmol) in water (8 mL). The reaction mixture was refluxed at 85 °C for 40 h under argon. Then the mixture was poured into water (40 mL). The aqueous solution was extracted with dichloromethane (30 mL × 3). The combined organic extracts were washed with water (50 mL) and brine (50 mL). The dichloromethane solution was dried over sodium sulfate, and the filtrate was evaporated in vacuo. The residue was subjected to column chromatography on alumina (solvent: dichloromethane) to obtain **9a** (0.87 mmol; 90%).

3-Methyl-2-phenylimidazo[1,2-*a*]pyridine (9a): pale yellow solid, mp 154–157 °C (lit. mp:^{13a} 157 °C); ¹H NMR (CDCl₃, 300 MHz) 7.92 (d, *J* = 6.9 Hz, 1H), 7.81 (d, *J* = 6.9 Hz, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.16–7.22 (m, 1H), 6.86 (t, *J* = 6.8 Hz, 1H), 2.66 (s, 3H); MS/EI (70 eV) 208 [M]⁺.

2-Phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (10a) (General Procedure for CF₃-Substitution on the Imidazole Ring^{6g,15}). A mixture of copper(I) iodide (0.22 g, 1.2 mmol) and spray-dried anhydrous potassium fluoride (68 mg, 1.2 mmol) was heated with a burner under reduced pressure while being gently shaken until the color changed into yellow. After the addition of iodo compound **1b** (0.25 g, 0.78 mmol), a vessel was Ar-purged, and *N*-methylpyrrolidinone (2 mL) and (trifluoromethyl)trimethylsilane (0.22 g, 1.6 mmol) were added to the mixture. Then, the suspension was vigorously stirred for 24 h at room temperature. The mixture was poured into 14% aqueous ammonia (30 mL) and extracted with dichloromethane (30 mL × 2). The organic layer was washed with water (30 mL × 2) and brine (30 mL) and dried over sodium sulfate. The filtrate was evaporated in vacuo. The residue was subjected to column chromatography on alumina (solvent: 1:4 EtOAc/*n*-hexane), followed by purification using gel permeation chromatography (GPC) (solvent: chloroform) to give pure **10a** (0.51 mmol, 65%). Other CF₃-substituted ligands **11–13a** were prepared analogously from the corresponding iodo compounds **6b**, **8b**, and **4b**.

2-Phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (10a): pale yellow solid, mp 80–81 °C; ¹H NMR (CDCl₃, 300 MHz) 8.32 (d, *J* = 6.3 Hz, 1H), 7.68–7.76 (m, 3H), 7.37–7.50 (m, 4H), 7.00 (t, *J* = 6.9 Hz, 1H); MS/EI (70 eV) 262 [M]⁺.

2-[3,5-Bis(trifluoromethyl)phenyl]-3-trifluoromethylimidazo[1,2-*a*]pyridine (11a): yield 39%, pale yellow solid, mp 59–60 °C; ¹H NMR (CDCl₃, 300 MHz) 8.35 (d, *J* = 6.9 Hz, 1H), 8.18 (s, 2H), 7.96 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.45–7.51 (m, 1H), 7.09 (t, *J* = 7.1 Hz, 1H); MS/EI (70 eV) 398 [M]⁺.

3-(Trifluoromethyl)-2-(4-trifluoromethylphenyl)imidazo[1,2-*a*]pyridine (12a): yield: 83%, colorless solid, mp 67–70 °C, ¹H NMR (CDCl₃, 300 MHz): 8.34 (d, *J* = 6.9 Hz, 1H); 7.83 (d, *J* = 8.4 Hz, 2H); 7.71–7.77 (m, 3H); 7.44 (t, *J* = 7.5 Hz, 1H); 7.05 (t, *J* = 7.4 Hz, 1H).

2-(2,4-Difluorophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (13a): yield 57%, colorless solid, mp 97–99 °C; ¹H NMR (CDCl₃, 300 MHz) 8.30 (d, *J* = 6.9 Hz, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.57–7.65 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 6.90–7.06 (m, 3H).

2-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-3-trifluoromethylimidazo[1,2-*a*]pyridine (14a). 2.0 M solution (3.1 mL) of lithium

diisopropylamide in heptane/THF/ethylbenzene was added dropwise to the THF (10 mL) solution of 2-(2,4-difluorophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**13a**) (0.74 g, 2.5 mmol) at –78 °C and stirred for 1 h. Then iodine (1.6 g, 6.3 mmol) dissolved in THF (10 mL) was added to the solution, and the mixture was stirred for 3 h at –78 °C and warmed to room temperature. Water (50 mL) was added, and the solution was extracted with diethyl ether (50 mL × 3). The ether solution was washed with Na₂S₂O₃(aq) (50 mL × 2) and brine (50 mL). The solution was dried over sodium sulfate, and the filtrate was evaporated in vacuo. The residue was subjected to column chromatography on alumina (solvent: dichloromethane), followed by purification using GPC (solvent: chloroform) to give 2-(2,4-difluoro-3-iodophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**13b**) (1.4 mmol, 59%). Iodide **13b** was then treated with (trifluoromethyl)trimethylsilane by the procedure similar to CF₃ substitution for **10a** to afford 2-(2,4-difluoro-3-(trifluoromethyl)phenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**14a**) (31%).

2-(2,4-Difluoro-3-iodophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (13b): pale yellow solid, mp 164–165 °C; ¹H NMR (CDCl₃, 300 MHz) 8.30 (d, *J* = 6.9 Hz, 1H), 7.74 (d, *J* = 9.3 Hz, 1H), 7.56–7.64 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 6.99–7.08 (m, 2H); MS/EI (70 eV) 424 [M]⁺.

2-(2,4-Difluoro-3-(trifluoromethyl)phenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (14a): colorless solid; ¹H NMR (CDCl₃, 300 MHz) 8.31 (d, *J* = 6.3 Hz, 1H), 7.73–7.84 (m, 2H), 7.45 (*J* = 8.0 Hz, 1H), 7.05–7.17 (m, 2H); MS/EI (70 eV) 366 [M]⁺.

Synthesis of the Ir Complexes. Iridium(III) bis(2-phenylimidazo[1,2-*a*]pyridinato-*N,C*²) acetylacetonate (1) (General Procedure). A mixture of iridium(III) chloride trihydrate (0.17 g, 0.48 mmol) and 2-phenylimidazo[1,2-*a*]pyridine (**1a**) (0.28 g, 1.5 mmol) in 2-ethoxyethanol/water (6.7 mL; 3:1) was refluxed under argon for 18 h at 125 °C. After cooling of the sample to room temperature, the precipitate was filtered off and washed with ethanol to give the Ir(III)– μ -chloro-bridged dimer complex. A mixture of the resulting dimer complex, acetylacetonate (0.11 g, 1.14 mmol), and sodium carbonate (0.17 g, 1.60 mmol) was heated at 125 °C in 2-ethoxyethanol (12 mL) for 8 h under argon. The solution was evaporated in vacuo, and the desired complex **1** was isolated by column chromatography on alumina (solvent: dichloromethane). The complex **1** was purified by recrystallization from dichloromethane/ethanol (0.17 mmol; overall yield 36%). Other complexes were also prepared from the corresponding ligands by a similar procedure.

Iridium(III) bis(2-phenylimidazo[1,2-*a*]pyridinato-*N,C*²) acetylacetonate (1):^{11a} ochreous solid, dec ca. 286 °C; ¹H NMR (CDCl₃, 300 MHz) 8.12 (d, *J* = 6.9 Hz, 2H), 7.74 (s, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.73 (t, *J* = 6.8 Hz, 2H), 6.53 (t, *J* = 6.6 Hz, 2H), 6.17 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 1H), 1.77 (s, 6H). Anal. Calcd for C₃₁H₂₅IrN₄O₂: C, 54.93; H, 3.72; N, 8.27. Found: C, 54.10; H, 3.68; N, 7.92. HRMS (FAB): calcd for C₃₁H₂₅IrN₄O₂, 678.16067; found, 678.1605 [M]⁺.

Iridium(III) bis[2-(1-naphthalenyl)imidazo[1,2-*a*]pyridinato-*N,C*²] acetylacetonate (2):^{11a} overall yield 18%, ochreous solid, dec ca. 285 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) 8.96 (s, 2H), 8.72 (d, *J* = 6.9 Hz, 2H), 8.28 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.1 Hz, 2H), 7.44 (d, *J* = 3.9 Hz, 4H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.12–7.17 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.23 (d, *J* = 8.1 Hz, 2H), 5.20 (s, 1H), 1.67 (s, 6H). Anal. Calcd for C₃₉H₂₉IrN₄O₂: C, 60.22; H, 3.76; N, 7.20. Found: C, 59.33; H, 3.85; N, 7.07. HRMS (EI): calcd for C₃₉H₂₉IrN₄O₂, 778.19197; found, 778.1921 [M]⁺.

Iridium(III) bis[2-(2-naphthalenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (3): overall yield 37%, yellow solid, dec ca. 272 °C; ¹H NMR (CDCl₃, 300 MHz) 8.11 (d, *J* = 6.9 Hz, 2H), 7.93 (s, 2H), 7.87 (s, 2H), 7.66 (d, *J* = 9.3 Hz, 2H), 7.53–7.56 (m, 2H), 7.12–7.18 (m, 4H), 7.02–7.05 (m, 4H), 6.84 (t, *J* = 6.6 Hz, 2H), 6.54 (s, 2H), 5.22 (s, 1H), 1.76 (s, 6H). Anal. Calcd for C₃₉H₂₉IrN₄O₂: C, 60.22; H, 3.76; N, 7.20. Found: C, 59.00; H, 3.65; N, 7.05. HRMS (FAB): calcd for C₃₉H₂₉IrN₄O₂, 778.19197; found, 778.1946 [M]⁺.

Iridium(III) bis[2-(4,6-difluorophenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (4):^{11a} overall yield 24%, yellow solid, dec ca. 320 °C; ¹H NMR (CDCl₃, 300 MHz) 8.17 (d, *J* = 6.9 Hz, 2H), 7.86 (s, 2H), 7.51 (d, *J* = 9.3 Hz, 2H), 7.21 (t, *J* = 8.1 Hz, 2H), 6.93 (t, *J* = 6.6 Hz, 2H), 6.29 (t, *J* = 9.9 Hz, 2H), 5.58 (d, *J* = 9.5 Hz, 2H), 5.21 (s, 1H), 1.78 (s, 6H). Anal. Calcd for C₃₁H₂₁F₄IrN₄O₂: C, 49.66; H, 2.82; N, 7.47. Found: C, 49.51; H, 2.77; N, 7.27. FAB-MS (*m/e*): found, 750 [M]⁺.

Iridium(III) bis[2-(4,6-dichlorophenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (5): overall yield 26%, yellow solid, dec ca. 330 °C; ¹H NMR (CDCl₃, 300 MHz) 8.26 (s, 2H), 8.19 (d, *J* = 6.6 Hz, 2H), 7.52 (d, *J* = 9.3 Hz, 2H), 7.19–2.26 (m, 2H), 6.94 (t, *J* = 6.8 Hz, 2H), 6.87 (s, 2H), 5.96 (s, 2H), 5.16 (s, 1H), 1.75 (s, 6H). Anal. Calcd for C₃₁H₂₁Cl₄IrN₄O₂: C, 45.65; H, 2.60; N, 6.87. Found: C, 45.78; H, 2.66; N, 6.91. HRMS (FAB): calcd for C₃₁H₂₁³⁵Cl₄IrN₄O₂, 814.00478; found, 814.0039 [M]⁺, 816.0027 [M + 2]⁺.

Iridium(III) bis[2-(3,5-bis(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (6):^{11a} The dimer complex is soluble in 2-ethoxyethanol. Therefore, the crude dimer complex was obtained by extraction with dichloromethane (30 mL × 3) after evaporation of 2-ethoxyethanol: overall yield 28%, yellow solid, dec ca. 280 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) 8.68 (s, 2H), 8.63 (d, *J* = 6.3 Hz, 2H), 8.26 (s, 2H), 7.23–7.31 (m, 4H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.03 (t, *J* = 6.8 Hz, 2H), 4.91 (s, 1H), 1.56 (s, 6H). Anal. Calcd for C₃₅H₂₁F₁₂IrN₄O₂: C, 44.26; H, 2.23; N, 5.90. Found: C, 44.02; H, 2.42; N, 5.73. FAB-MS: found, 950 [M]⁺.

Iridium(III) bis[2-(4,6-bis(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (7): overall yield 40%, yellow solid, dec ca. 277 °C; ¹H NMR (CDCl₃, 300 MHz) 8.18 (d, *J* = 7.2 Hz, 2H), 8.13 (s, 2H), 7.56 (d, *J* = 9.3 Hz, 2H), 7.37 (s, 2H), 7.22–7.27 (m, 2H), 6.99 (t, *J* = 6.9 Hz, 2H), 6.51 (s, 2H), 5.16 (s, 1H), 1.74 (s, 6H). Anal. Calcd for C₃₅H₂₁F₁₂IrN₄O₂: C, 44.26; H, 2.23; N, 5.90. Found: C, 44.20; H, 2.17; N, 5.50. FAB-MS (*m/e*): found, 950 [M]⁺.

Iridium(III) bis[2-(4-trifluoromethylphenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (8): overall yield 26%, yellow solid, dec ca. 270 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) 8.72 (d, *J* = 6.9 Hz, 2H), 8.55 (s, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 9.3 Hz, 2H), 7.14 (t, *J* = 6.7 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.13 (s, 2H), 5.22 (s, 1H), 1.71 (s, 6H). Anal. Calcd for C₃₃H₂₃F₆IrN₄O₂: C, 48.71; H, 2.85; N, 6.88. Found: C, 47.90; H, 3.17; N, 6.64. HRMS (FAB): calcd for C₃₃H₂₃F₆IrN₄O₂, 814.13544; found, 814.1342 [M]⁺.

Iridium(III) bis(3-methyl-2-phenylimidazo[1,2-*a*]pyridinato-*N,C*^{2'}) acetylacetonate (9): overall yield 55%, yellow solid, dec ca. 307 °C; ¹H NMR (CDCl₃, 300 MHz) 7.95 (d, *J* = 6.9 Hz, 2H), 7.56–7.63 (m, 4H), 7.12 (t, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 6.3 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 2H), 6.49 (t, *J* = 7.4 Hz, 2H), 6.13 (d, *J* = 6.9 Hz, 2H), 5.13 (s, 1H), 2.87 (s, 6H), 1.73 (s, 6H). Anal. Calcd for C₃₃H₂₉IrN₄O₂: C, 56.15; H, 4.14; N, 7.94. Found: C, 54.59; H, 4.16; N, 7.75. HRMS (FAB): calcd for C₃₃H₂₉IrN₄O₂, 706.19197; found, 706.1931 [M]⁺.

Iridium(III) bis(2-phenyl-3-(trifluoromethyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}) acetylacetonate (10): overall yield 69%, yellow solid, mp 324–326 °C; ¹H NMR (CDCl₃, 300 MHz) 8.43 (d, *J* = 6.9 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 9.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.82 (t, *J* = 6.9 Hz, 2H), 6.59 (t, *J* = 6.8 Hz, 2H), 6.23 (d, *J* = 6.9 Hz, 2H), 5.11 (s, 1H), 1.73 (s, 6H). Anal. Calcd for C₃₃H₂₃F₆IrN₄O₂: C, 48.71; H, 2.85; N, 6.88. Found: C, 48.53; H, 2.86; N, 6.74. FAB-MS: found, 814 [M]⁺.

Iridium(III) bis[2-[3,5-bis(trifluoromethyl)phenyl]-3-trifluoromethylimidazo[1,2-*a*]pyridinato-*N,C*^{2'}] acetylacetonate (11): The dimer complex is soluble in 2-ethoxyethanol. Therefore, the crude dimer complex was obtained by extraction with dichloromethane (30 mL × 3) after evaporation of 2-ethoxyethanol. In addition, GPC was needed for the isolation of **11** before recrystallization: overall yield 12%, yellow solid, mp ca. 340 °C; ¹H NMR (DMSO-*d*₆, 300 MHz) 8.81 (d, *J* = 6.9 Hz, 2H), 8.25 (s, 2H), 7.63 (t, *J* = 8.4 Hz, 2H), 7.46 (s, 2H), 7.32–7.38 (m, 4H), 4.88 (s, 1H), 1.56 (s, 6H). Anal. Calcd for C₃₇H₁₉F₁₈IrN₄O₂: C, 40.93; H, 1.76; N, 5.16. Found: C, 41.15; H, 1.88; N, 4.94. FAB-MS (*m/e*): found, 1086 [M]⁺.

Iridium(III) bis(3-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}) acetylacetonate (12): overall yield 60%, yellow solid, mp ca. 318 °C; ¹H NMR (CDCl₃, 300 MHz) 8.48 (d, *J* = 6.9 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 9.3 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.38 (s, 2H), 5.12 (s, 1H), 1.74 (s, 6H). Anal. Calcd for C₃₅H₂₁F₁₂IrN₄O₂: C, 44.26; H, 2.23; N, 5.90. Found: C, 44.10; H, 1.93; N, 5.75. FAB-MS (*m/e*): found, 950 [M]⁺.

Iridium(III) Bis[2-(2,4-difluorophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazolate (13) (General Procedure). A mixture of iridium(III) chloride trihydrate (0.046 g, 0.13 mmol) and 2-(2,4-difluorophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**13a**) (0.087 g, 0.29 mmol) in 2-ethoxyethanol/water (2.7 mL; 3:1) was refluxed under argon for 18 h at 125 °C. After cooling of the sample to room temperature, the precipitate was filtered off and washed with ethanol to give the Ir(III)-*μ*-chloro-bridged dimer complex. A mixture of the resulting dimer complex, 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazole (0.038 g, 0.18 mmol), and sodium carbonate (0.032 g, 0.30 mmol) was heated at 125 °C in 2-ethoxyethanol (3 mL) for 8 h under argon. After the reaction, water (40 mL) was added to the mixture. This was extracted with dichloromethane (30 mL × 3), and the combined dichloromethane solution was washed with water (40 mL × 2) and brine (40 mL). The dichloromethane solution was dried over sodium sulfate, and the filtrate was evaporated in vacuo. The crude product was subjected to column chromatography on alumina (solvent: dichloromethane). The obtained complex **13** was purified by recrystallization from dichloromethane/ethanol (0.078 mmol; overall yield 60%). Complex **14** was similarly prepared from ligand **14a**.

Iridium(III) bis[2-(2,4-difluorophenyl)-3-(trifluoromethyl)imidazo[1,2-*a*]pyridinato-*N,C*^{2'}] 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazolate (13): yellow solid, mp 375–378 °C; ¹H NMR (CDCl₃, 300 MHz) 8.40 (t, *J* = 6.6 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.84–7.92 (m, 2H), 7.28 (t, *J* = 6.3 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.94–7.03 (m, 3H), 6.41–6.58 (m, 2H), 6.29 (d, *J* = 9.0 Hz, 1H), 5.77–5.82 (m, 2H), 5.55 (d, *J* = 8.9 Hz, 1H). Anal. Calcd for C₃₆H₁₆F₁₃IrN₈: C, 43.25; H, 1.61; N, 11.21. Found: C, 42.94; H, 1.64; N, 10.39. HRMS (FAB): calcd for C₃₆H₁₆F₁₃IrN₈, 1000.09195; found, 1000.0932 [M]⁺, 1001.0998 [M + H]⁺.

Iridium(III) bis[2-(4,6-difluoro-5-(trifluoromethyl)phenyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridinate-*N,C*^{2'}] 3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazolate (14). The dimer complex is soluble in 2-ethoxyethanol. Therefore, the crude dimer complex was obtained by extraction with dichloromethane (30 mL × 3) after evaporation of 2-ethoxyethanol. In addition, GPC was needed for the isolation of **14** before recrystallization: overall yield 58%, yellow solid, mp ca. 343 °C; ¹H NMR (CDCl₃, 300 MHz) 8.43–8.51 (m, 2H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.95 (t, *J* = 7.4 Hz, 1H), 7.87 (d, *J* = 5.7 Hz, 1H), 7.36 (t, *J* = 6.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.03–7.11 (m, 3H), 6.27 (d, *J* = 9.0 Hz, 1H), 5.99 (d, *J* = 9.9 Hz, 1H), 5.78–5.83 (m, 1H), 5.70 (d, *J* = 11.4 Hz, 1H). Anal. Calcd for C₃₈H₁₄F₁₉IrN₈: C, 40.19; H, 1.24; N, 9.87. Found: C, 40.23; H, 1.40; N, 10.21. FAB-MS (*m/e*): found, 1137 [M + H]⁺.

Acknowledgment. This work was supported by the 21st Century COE program and Grant-in Aid for Scientific Research on Priority Areas (No. 15073212) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We thank Dr. Takanori Kiguchi and Mr. Yoshiaki Watanabe (Center for Advanced Materials Analysis, Tokyo Institute of Technology) for performing elemental analysis.

Supporting Information Available: Other absorption and PL spectra of the complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0624322