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Fluorine-free Blue Phosphorescent Emitters for Efficient Phosphorescent Organic Light Emitting Diodes

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Abstract

Two blue phosphorescent Ir(III) compounds with a main fluorine-free bipyridine ligand have been synthesized. These molecules have the general formula of $Ir(C^N)_2(L^X)$, where $C^N = 2', 6'$ -dimethoxy-4-methyl-2,3'-bipyridine [(MeO)₂pypy] and $L^X =$ ancillary ligand, such as acetylacetonate (acac) (1) or 2-picolinate (pic) (2). Thermal, photophysical, and electrochemical properties for 1 and 2 have also been investigated systematically. The two compounds show high thermal stability with decomposition temperatures at ~ 350 °C due to strong and varied intermolecular interactions. A sky-blue emission with moderate phosphorescence quantum efficiency (Φ_{PL} = 0.49~0.54) is observed in the spectral region of 460-470 nm for all compounds, which is attributed to both metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) transition. Compounds 1 and 2 show only ~ 10 nm redshifted emission in the fluid state, compared to similar fluorinated iridium counterparts. Multi-layered electroluminescent devices using compounds 1 and 2 as the dopant and 9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)diphenylphosphine oxide as a host material have been fabricated. The electroluminescent device of 2 at the doping level of 5 wt% shows the best performance with an external quantum efficiency of 15.3% and the color coordinate of (0.16, 0.28) at a brightness of 100 cd/m².

Introduction

Homoleptic and heteroleptic Ir(III) complexes bearing main C^N ligand have attracted much attention due to their unique photophysical properties, such as higher phosphorescence quantum efficiency and easy tuning emission energies from blue to red through substituent changes of the main ligand.¹ In particular, iridium compounds with green and red emission have been successful as triplet emitters in PHOLEDs(Phosphorescence Organic Light-Emitting Diodes).² However, the number of suitable blue iridium compounds for OLED applications is very limited compared to green and red iridium phosphors.³ To develop blue phosphorescent iridium compounds based on a phenylpyridine (ppy) chelating ligand, several approaches have been suggested.⁴ Among them, a representative example is the introduction of fluorine substituents to the phenyl ring of ppy.⁵ Such an approach lowers the HOMO energy in $Ir(ppy)_3$, leading to an increase in the energy between the HOMO and LUMO. From the view point of OLED device long-term stability, however, the fluorine substituents on ppy may impose severe problems.⁶ C-F bond cleavage occurs readily during device operation, as reported by Sivasubramaniam et al.⁷ Henceforth, to improve the long-term stability of the emitters in PHOLEDs(Phosphorescent Organic Light-Emitting Diodes), it is highly desirable to replace the fluoro group with other substituents while maintaining the blue phosphorescence.⁸

Recently, we have reported that deep blue Ir(III) complexes, $Ir(dfpypy)_3^9$ and $Ir(dfpypy)_2(L^X)$,¹⁰ were synthesized successfully using fluorinated-bipyridine, 2',6'-difluoro-2,3'-bipyridine (dfppy). $Ir(dfpypy)_2(L^X)$ especially showed pure blue color (CIE: x = 0.14, y = 0.18) and excellent external quantum efficiency (EQE: ~20%) in PHOLEDs.¹¹ In addition, an effective and one-pot alkoxylation using the intermediates (chlorine-bridged iridium dimer) was also established in the presence of a base and alcohol solvent.¹² Interestingly, alkoxy-functionalized bipyridine ligand-based iridium complexes do not significantly affect emission changes compared to their fluorinated congeners. This fact prompted us to further develop novel blue phosphorescent iridium compounds possessing a fluorine-free bipyridine chelating ligand as a main ligand. We report herein the efficient synthesis of fluorine-free heteroleptic Ir(III) compounds with two different O^O and N^O ancillary ligands, namely, acetylacetonate (acac) and picolinate (pic), and the systematic evaluation of the electroluminescence (EL) characteristics when they are employed as triplet emitters in phosphorescent organic light emitting diodes (PHOLEDs).

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Results and Discussion

Synthesis and X-ray Structure

The synthetic pathway and details for two $Ir[(MeO)_2pypy](O^O)$ and $Ir[(MeO)_2pypy](N^O)$ compounds, where (O^O) = acetylacetonate (1) and (N^O) = picolinate (2), are shown in Scheme 1. The chlorine bridged Ir(III) dimers and the corresponding 1 and 2 were synthesized according to our recent report in moderate to high yields.¹⁰ The structures of all compounds are confirmed by various spectroscopic analyses, such as NMR, elemental analysis and X-ray single crystallography.



Scheme 1. Synthetic pathway of 1 and 2.

The X-ray analysis reveals that the general features of **1** and **2** are very similar to those of our recent related structure with an *N*,*N*-*trans*-meridional configuration.^{10,12} As shown in Figure 1, the iridium center of all compounds is six-coordinated by two C^N main ligands and a N^O or O^O ancillary ligand, forming a distorted octahedral geometry due to narrow ligand bite angles ranging from 76.74(11) to 97.95(14)°. The average bond lengths of Ir-C are 1.981(4) Å for **1** and 1.991(4) Å for **2**, which are much shorter than that of the *fac*-Ir(dfpypy)₃ complex (Ir-C(av) = 2.001(5) Å).⁹ In addition, the Ir-N bond length, ranging from 2.026(3) to 2.047(3) Å, is also shorter than those of *fac*-Ir(dfpypy)₃ (2.116(4) - 2.135(4) Å). These results

are mainly attributed to the electron-donating nature of the methoxy and methyl groups in the main ligand. Within the ligands, the two pyridine rings of both compounds are approximately coplanar with maximum dihedral angle rings of $10.0(2)^{\circ}$ for **1** and $12.4(3)^{\circ}$ for **2**. However, the bond lengths of Ir–C, Ir–N, and Ir–O for all compounds are normally within the range reported for the related compounds (dfpypy)₂Ir(acac),¹⁰ iridium(III) (2'-methyl-6'-methoxy-2,3'-bipyridinato-*N*,*C*^{4'})(acac),¹² iridium(III) (2',6'-dimethoxy-2,3'-bipyridinato-*N*,*C*^{4'})(pico-linate), and iridium(III) (2',6'-bis(2-methoxyethoxy)-2,3'-bipyridinato-*N*,*C*^{4'})(picolinate).¹³ The selected bond lengths and angles for complexes **1** and **2** are listed in Tables S2-S3 in the Supporting Information.

The crystal packing structures of **1** and **2** are shown in Figure 2. In both crystal packing structures, weak intermolecular hydrogen bonds, such as the C-H···O hydrogen bonds [average H···O distance = 2.59 Å for **1** and 2.44 Å for **2**], and edge-to-face C-H··· π (py) interactions [average H···*Cg* distance = 3.28 Å for **1** and 3.07 Å for **2**; *Cg* denotes the centroid of the pyridine ring] are observed, resulting in the construction of three-dimensional supramolecular networks. Furthermore, these intermolecular interactions contribute to the stabilization of the crystal packing, in agreement with the result of the TGA experiment. The structural parameters for the intermolecular interactions are summarized in Tables S4-S5 in the Supporting Information.



Figure 1. Coordination environments of the Ir(III) ions in complexes (a) **1** and (b) **2**. The solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): for **1**, Ir1-C1 1.981(4), Ir1-N1 2.035(2), Ir1-O3 2.125(3); for **2**, Ir1-C10 1.978(4), Ir1-C23 1.989(4), Ir1-N1 2.036(3), Ir1-N3 2.040(3), Ir1-N5 2.142(3), Ir1-O5 2.148(3), Ir2-C42 2.001(4), Ir2-C55 1.995(4), Ir2-N6 2.047(3), Ir2-N8 2.026(3), Ir2-N10 2.139(3), Ir2-O11 2.159(3).



Figure 2. Crystal packing structure of the complexes 1(a) and 2(b) with weak intermolecular C-H···O (yellow) and C-H··· $\pi(py)$ (green) interactions shown as dashed lines. The solvent molecules and hydrogen atoms not involved in intermolecular interactions have been omitted for clarity.

Thermal and Photophysical Properties

To investigate the thermal stability of 1 and 2, thermogravimetric analysis (TGA) was conducted. In general, a suitable molecule for use in OLEDs should have a decomposition

temperature above than 300 °C.¹⁴ Such a temperature (>300 °C) is high enough to deposit molecules under reduced pressure without any degradation. As shown in Figure 3, the TGA curve of **2** exhibits thermal stability up to 320 °C. The weight loss of approximately 8~10% for **2** caused by the release of solvent molecules from the crystalline solid was observed at approximately 250 °C (see the description of the crystal structure). Subsequently, no loss of weight was observed up to 365 °C, while the decomposition temperature, which is defined as a 5% loss of weight, appeared at 384 °C. This value of compound **2** is comparable to that of its fluorinated analog, **FK306** (359 °C).¹⁵ However, it is slightly higher than that of compound **1** (344 °C) (see supporting information). This high thermal stability for **1** and **2** can be due to varied intermolecular interactions in the crystal lattice supported by their packing structures.¹⁶



Figure 3. TGA curve of 2 under a N₂ atmosphere.

The absorption and phosphorescent emission spectra of **1** and **2** in CH₂Cl₂ at ambient temperature are shown in Figure 4, and their photophysical data are summarized in Table 1. To compare the photophysical properties of **1** and **2**, a sky-blue emitter, iridium(III)bis(4,6-(difluorophenyl)pyridinato-N,C²)picolinate (**Firpic**), was used as a standard material. In addition, the absorption and emission spectra of **Firpic** are presented in Figure 4. Both **1** and **2** show similar spectral pattern in the absorption spectra. The intense absorption bands in the UV region of 260–300 nm ($\varepsilon \approx 35,000 \text{ M}^{-1} \text{ cm}^{-1}$) for **1** and **2** are mainly attributed to the spin-allowed ${}^{1}\pi$ - π * transition of the bipyridine ligand. However, the absorption bands at longer wavelengths (~370 nm) can be assigned to the combination of the ligand centered ${}^{1}\pi$ -

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 π^* and metal-to-ligand charge-transfer (¹MLCT) transitions. The next long tail extending to the visible region with a small extinction coefficient ($\varepsilon \approx 5,000 - 8,000 \text{ M}^{-1} \text{ cm}^{-1}$) originated from the ${}^{3}\pi$ - π * and ${}^{3}MLCT$ transitions that are enhanced by the strong spin-orbit coupling. This observation is typical based on the previously reported works.¹⁷ The distinct difference in the absorption spectra between the two compounds and fluorinated congeners, $(dfpypy)_2Ir(acac)$ and $(dfpypy)_2Ir(pic)$, is an extinction coefficient in the region of the ¹MLCT. The molar extinction coefficients of 1 and 2 at approximately 370 nm are larger than those (ε $> 5,000 \text{ M}^{-1} \text{ cm}^{-1}$) of (dfpypy)₂Ir(acac) and (dfpypy)₂Ir(pic), which implies that strong spinorbit coupling occurs in both 1 and 2. These absorption properties of 1 and 2 are also in good accordance with that of alkyl and alkoxo-functionalized iridium compound, EB343, which is recently reported by Baranoff et.al.¹² When irradiated by UV light (excitation at 352 nm), compounds 1 and 2 showed intense sky-blue emission at 468 nm for 1 and at 462 nm for 2, as shown in Figure 4. The emission energy of 1 and 2 is significantly blue shifted compared to that of the standard Firpic. It should be noted that 1 and 2 exhibit an ~ 10 nm blue shift despite the lack of fluorine substituents on the main C^N ligand fragment having a strong metal-carbon covalent interaction. This can be due to the replacement of a phenyl fragment in ppy with a pyridyl fragment in bipyridine. Based on previous reports, the phosphorescent emission of 1 and 2 originates dominantly from the ³MLCT lowest excited states rather than from the ligand-centered (LC) ${}^{3}\pi - \pi^{*}$ excited states because their emission profiles at room temperature are broad (fwhm: \sim 70 nm) and featureless. Both 1 and 2 do not show any obvious emission color change from the fluid to the solid state (10 wt%-PMMA film), indicating that there is little intermolecular interactions or aggregations in the solid state. The emission spectra of both compounds at 77 K display well resolved vibrational features along with an ~ 6 nm blue-shifted emission energy in contrast to the spectra at room temperature, as shown in Figure 5. The triplet energies of 1 and 2 were estimated to be 2.68 eV and 2.72 eV, respectively, using these emission spectra. These values are much higher than that of the standard Firpic ($E_T = 2.60$ eV). It is noteworthy that these values also imply that all compounds are suitable triplet emitters for blue phosphorescent organic light emitting diodes. Indeed, due to the electron donating alkoxy group, compounds 1 and 2 show an ~ 10 nm redshifted emission in the fluid and solid state compared to similar fluorinated iridium counterparts. The photoluminescence quantum yields (Φ_{PI}) of all compounds were estimated by using Firpic as a reference (Φ_{PL} = 0.6). The Φ_{PL} of 1 and 2 in the thin film are 0.40 and 0.44, respectively.

	Emission, 298 K,			ution/Solid ^b	Emission, 77 K ^d	
Compd	Absorption					
	$\lambda_{\max} [nm], \epsilon [10^{\circ}M^{\circ}cm^{-1}]^{a}$	$\lambda_{max} [nm]$	τ _p [μs]	$arPsi_{ m p}^{ m c}$	$\lambda_{max} [nm]$	τ _p [μs]
1	261 (3.5), 289 (3.4), 334(2.5), 379 (0.5)	468/466	2.5(3)	0.49 / 0.40	463	4.4(4)
2	268 (3.5), 291 (3.5), 333(2.7), 376 (0.7)	462/460	2.5(0)	0.54/ 0.44	456	4.3(2)

 Table 1. Photophysical and electrochemical data of 1-8.

^{*a*}The absorption spectra were measured in a degassed CH_2Cl_2 solution; $[M] = 2.0 \sim 3.0 \times 10^{-5}$. ^{*b*}Doped into PMMA at 10 wt%. ^{*c*}Phosphorescence quantum efficiency measured in CH_2Cl_2 , relative to Firpic ($\Phi = 0.6$). The solid state quantum efficiency was measured using an integration sphere. (Error range $\pm 10\%$) ^{*d*}In frozen CH_2Cl_2 or Me-THF glass.



Figure 4. Absorption and emission spectra of 1 and 2 in the fluid state at 298 K.



Figure 5. Emission spectra of 1 and 2 in frozen CH_2Cl_2 at 77 K.

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Electrochemical Properties

To investigate the electrochemical behavior of **1** and **2**, cyclic voltammetry experiments were carried out using ferrocene (Fc/Fc⁺) as the internal standard. All compounds showed quasi-reversible oxidations in CH₃CN, while irreversible reductions were observed under the same conditions (see ESI). Similar reversible oxidation and irreversible reduction have also been reported in (RO₂pypy)Ir(L^XX) derivatives. The oxidation potentials (E_{onset}) for **1** and **2** are 0.61 and 0.77 V (*vs* Fc/Fc⁺), respectively. Using an oxidation potential of ferrocene/ ferrocenium (4.8 eV below the vacuum level),¹⁸ the HOMO levels for **1** and **2** were deduced to be -5.41 and -5.57, respectively, which are significantly higher than that of Firpic (-5.7 eV). Consequently, the electrochemical and thermal stability, as well as moderate PL quantum efficiencies, make both **1** and **2** suitable candidates for use in blue phosphorescence OLEDs.

OLED Performance

To evaluate the performance of the new Ir(III) compounds in OLEDs, we prepared a series of devices using a multi-layered structure with mCPPO1 9-(3-(9H-carbazol-9-yl)phenyl)-9Hcarbazol-3-yl)diphenylphosphine oxide as the host. The typical structure of the multilayered devices is indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl) aniline] (TAPC, 20 nm)/mCP (10 nm)/host:dopant 1 or 2 (25 nm)/TSPO1(35 nm)/LiF (1 nm)/Al (200 nm), as shown in Figure 6. The device structure is mainly based on the consideration of our recent report.¹¹ The mCPPO1 host has high triplet energy (3.0 eV), and its HOMO energy is stronger than that of 1 and 2. In addition, the bipolar character of mCPPO1 can make holes and electrons in the emitting layer balance effectively. Therefore, we chose mCPPO1 as a host for dopant 1 and 2. Devices with Ir(III) compound doping levels from 3 wt% to 10 wt% were fabricated and examined. The best performance was observed at 10 wt% for 1 and 5 wt% for 2. Maximum external quantum efficiencies of the blue device with 1 and 2 blue emitters were 13.9% and 15.3%, respectively. High quantum efficiency was obtained in device 2 because of the relatively high PL quantum yield of 2 compared to that of 1. The high optimum doping concentration of device 1 is due to the strong hole trapping effect by 1. The shallow HOMO level of 1 induces a strong hole trapping effect, which reduces the hole current density in the emitting layer. The hole current density increased at the 10% doping concentration, as confirmed by the high current density of device 1 at the 10% 10% doping concentration, which balances the holes and electrons in the emitting layer, resulting in a high quantum efficiency at the 10% doping concentration. The hole trapping effect is not significant in device **2**, which optimizes the device performances at the 5% doping concentration, as shown in Figure 7. The reduced quantum efficiency at the 10% doping concentration is due to the concentration quenching effect. Overall, device **2** shows better quantum efficiency, current efficiency and power efficiency than device **1** because of the high PL quantum yield. The color coordinates (*x*, *y*) of device **1** and **2** were (0.18, 0.28) and (0.16, 0.28), respectively. The device performances of **1** and **2** are summarized in Table 2.



Figure 6. (a) Schematic energy level diagram of the compound 1/mCPPO1 (dopant/host) based device and the molecular structure in this study. (b) Current density *vs* voltage. (c) External quantum efficiency *vs* luminance at different doping levels.



Figure 7. (a) Current density vs voltage, (b) external quantum efficiency vs luminance and (c) EL spectra of the compound 2/mCPPO1 (dopant/ host) based device at different doping levels.

Table 2. OLED performances of 1 and 2.

	Von	L	$\eta_{ext}(\%)^{c}$			CIE
	$(V)^a$	$(cdm^{-2}, V)^{b}$	10 cd m ⁻²	100 cd m ⁻²	1000 cd m ⁻²	(x, y)
1- 10%	3.5	2921, 9	11.8	13.9	11.3	0.18, 0.28
2- 5%	3.5	1776, 8.5	15	15.3	12.1	0.16, 0.28

^aThe applied voltage (V_{on}) is defined as the brightness of 1 cd/m². ^b The luminance (L) is the maximum value. ^c External quantum efficiency (EQE, η_{ext}).

Conclusion

In summary, fluorine-free heteroleptic iridium compounds with blue phosphorescence have been developed. The ligand design is based on 2',6'-dimethoxy-4-methyl-2,3'-bipyridine as the main ligand and acetylacetonate/picolinate as the ancillary ligand. These compounds have high thermal stability and moderate photoluminescence quantum efficiencies in both the fluid and solid states. Although there are no fluorine substituents on the main C^N ligand, all compounds showed an ~10 nm blue-shifted emission compared to **Firpic**. This can be due to the replacement of a phenyl ring in ppy with one of the pyridine rings in bipyridine. Therefore, blue phosphorescent iridium(III) compounds can be developed by the combination of a bipyridine ligand and a proper ancillary ligand. Multi-layer EL devices using compounds **1** or **2** as the dopant and 9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)diphenylphosphine oxide as a host material have been fabricated successfully. EL devices based on compound **2** (5% doping level) have been found to give the best performance with a high external

quantum efficiency (15.3% at 100 cd/m², 12.1% at 1000 cd/m²) and a CIE coordinate of (x, y, = 0.16, 0.28). This result is one of the best performances using a blue phosphorescent iridium emitter with a fluorine-free bipyridine ligand.

Experimental Section

General Consideration

All experiments were performed under a dry N₂ atmosphere using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying reagents prior to use. All starting materials were purchased from either Aldrich or Strem and used without further purification. ¹H NMR spectra were recorded on a Bruker Avace 300 MHz spectrometer. UV-Vis spectra were obtained on a Varian Cary 50 UV/Visible spectrophotometer with all sample concentrations in the range of $10 \sim 50 \mu$ M. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster Model 2 spectrometer. Photoluminescent lifetimes were measured on a Photon Technology International Phosphorescent lifetime spectrometer, Timemaster C-631F, equipped with a xenon flash lamp and digital emission photon multiplier tube for both excitation and emission. All solutions for photophysical experiments were degassed with nitrogen. Cyclic voltammetry was performed using a BAS CV-50W voltammetric analyzer with scan rates of either 50 mV s⁻¹ or 100 mV/s⁻¹. The electrolytic cell used was a conventional three compartment cell with a Pt working electrode, Pt wire auxiliary electrode, and Ag/AgCl reference electrode. All experiments were performed at room temperature using 0.10 M NBu₄PF₆ as the supporting electrolyte in CH₃CN. All solutions for photophysical experiments were degassed for more than 30 min under N₂. The iridium dimer, $[{(OMe)(Me)pypy}Ir(\mu-Cl)]_2$, was synthesized according to previous reports.¹³

X-ray Crystallographic Analysis

Crystal data for **1** and **2** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation generated by a rotating anode and with a CCD detector. The cell parameters for the compounds were obtained from a least-squares refinement of the spots (from 36 collected frames). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.¹⁹ All of the calculations for the structure determination were carried out using the SHELXTL package.²⁰ In all cases, all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal collection data, refinement data for the crystal structures, the hydrogen bond geometries and the cif files of **1** and **2** can be found in the supporting information.

Syntheses of Compounds

2,6-dimethoxypyridine-3-boronic acid. A stirred solution of di-isopropylamine (5.5 mL, 39.2 mmol) in THF (10 mL) was cooled to -78 °C. The addition of *n*-BuLi (29.40 mL, 47 mmol, 1.6 M in hexane) over 20 min resulted in a pale yellow solution. After stirring for 1 h at this temperature, 2,6-dimethoxypyridine (5 mL, 39.2 mmol) in Et₂O (50 mL) was added. The solution was stirred for an additional hour, and then, trimethylborate (5.2 mL, 47 mmol) in Et₂O (100 mL) was added at -78 °C. The mixture was allowed to warm to room temperature and to react for 1 h. The mixture was quenched by the slow addition of 4% aqueous NaOH solution (150 mL). After 10 min, the mixture was acidified by the dropwise addition of 3 N HCl (pH 5~6). Extraction with ethyl acetate and evaporation of the organic layer furnished the pure title compound, which was obtained as a white solid in 40% yield. ¹H-NMR (300 MHz, CDCl₃) δ 8.00 (d, *J* = 7.9 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 1H), 5.74 (s, 2H), 4.02 (s, 3H), 3.94 (s, 3H).

2',6'-dimethoxy-4-methyl-2,3'-bipyridine. 2-Chloro-4-methyl-pyridine (1.08 mL, 9.8 mmol), 2,6-dimethoxypyridine-3-boronic acid (1.5 g, 8.2 mmol), and Pd(PPh₃)₄ (0.57 g, 0.49 mmol) were dissolved in THF (40 mL). A solution of 5% K₂CO₃ was added, and the mixture was refluxed with stirring for 12 h under a nitrogen atmosphere. After being cooled, the mixture was poured into water and extracted with ethyl acetate. The organic layer was dried over MgSO₄. The solvent was removed under reduced pressure to give a crude residue. The crude product was purified by column chromatography on silica gel (EtOAc/hexane, 1/3, v/v) to obtain a colorless solid (R_f = 0.5, 80%). ¹H-NMR (300 MHz, CDCl₃) δ 8.44 (d, *J* = 5.0 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.68 (t, J = 0.7 Hz, 1H), 6.93 (dd, *J* = 5.1, 0.8 Hz, 1H), 6.38 (d, *J* = 8.1 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 2.33 (s, 3H).

 $Bis(2',6'-dimethoxy-4-methyl-2,3'-bipyridinato-N,C^{4'})Ir(acac)$ (1). The iridium(III) dimer (0.2 g, 0.14 mmol) was dissolved in THF (15 mL). Li(acac) (0.04 g, 0.26 mmol) in methanol (5 mL) was added slowly to this solution. The reaction mixture was stirred for 12 h. The solvent was removed under reduced pressure. The mixture was poured into EtOAc (30 mL)

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and then washed with water (3 × 20 mL). An analytically pure compound was isolated by silica column chromatography (CH₂Cl₂/EtOAc: 1/1). A pale yellow powder was obtained in 73% yield based on the Ir(III) dimer. ¹H-NMR (300 MHz, CDCl₃) δ 8.18 (dd, *J* = 0.8, 0.4 Hz, 2H), 8.13 (d, *J* = 5.9 Hz, 2H), 6.78 (dd, *J* = 5.9, 1.5 Hz, 2H), 5.19 (s, 2H), 5.10 (s, 1H), 3.90 (s, 6H), 3.63 (s, 6H), 2.46 (s, 6H), 1.69 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃) 184.9, 165.8, 165.6, 161.4, 159.3, 148.7, 147.4, 123.1, 121.7, 121.2, 106.5, 100.7, 53.2, 53.1, 29.1, 22.0. Anal. Calcd for C₃₁H₃₃N₄O₆Ir; C, 49.66; H, 4.44; N, 7.47; found: C 49.59, H 4.39, N 7.51.

Bis(2',6'-dimethoxy-4-methyl-2,3'-bipyridinato-N,C^{d'})Ir(pic) (**2**). The iridium(III) dimer (0.5 g, 0.36 mmol), sodium carbonate (0.38 g, 3.6 mmol), and 2-picolinic acid (0.11 g, 0.9 mmol) were dissolved in THF/MeOH (5/5 mL). The reaction mixture was stirred overnight at ambient temperature. All volatile components were removed under reduced pressure. The mixture was poured into EtOAc (50 mL) and then extracted with water (3 × 50 mL) to remove excess sodium carbonate. Silica gel column purification with CH₂Cl₂/EtOAc(1/1) gave a yellow powder in 80% yield. ¹H-NMR (300 MHz, CDCl₃) δ 8.47 (d, *J* = 6.0 Hz, 1H), 8.29 (d, *J* = 10 Hz, 2H), 8.22 (t, *J* = 1.0 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.84 (dd, *J* = 5.0 Hz, 1H), 7.34 (td, *J* = 6.0, 1.0 Hz, 1H), 7.16 (d, *J* = 6.0 Hz, 1H), 5.42 (s, 1H), 5.29 (s, 2H), 5.20 (s, 1H), 4.07 (s, 3H), 4.02 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H) 2.48 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃) 173.1, 166.9, 166.2, 165.8, 164.7, 162.3, 161.8, 159.8, 159.7, 152.0, 149.4, 149.3, 148.5, 148.0, 147.2, 138.1, 128.6, 128.4, 123.9, 123.2, 122.1, 121.9, 121.2, 120.8, 105.9, 105.8, 53.8, 53.5, 53.4, 53.3, 22.0, 21.9. Anal. Calcd for C₃₂H₃₀N₅O₆Ir; C, 49.73; H, 3.91; N, 9.06; found: C 49.79, H 3.95, N 9.02.

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