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# Effect of the bipyridine ligand substituents on the emission properties of phosphorescent Ir(III) compounds



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## ABSTRACT

To investigate the effect of bipyridine ligand substituents on the emission properties of Ir(III) compounds, four homoleptic iridium(III) compounds, specifically, *mer*-Ir(**Mepypy**)<sub>3</sub> (**1**), *mer*-Ir(**Me\_2pypy**)<sub>3</sub> (**2**), *fac*-Ir(**OMe\_2pypy**)<sub>3</sub> (**3**) and Ir(**OMe\_2Bupypy**)<sub>3</sub> (**4**), where **Mepypy** = 2'-methyl-2,3'-bipyridine, **Me\_2pypy** = 2',6'-dimethyl-2,3'-bipyridine, **OMe\_2pypy** = 2',6'-dimethoxy-2,3'-bipyridine and **OMe\_2Bupypy** = 2',6'-dimethoxy-4-*tert*-butyl-2,3'-bipyridine, were prepared via a one-pot reaction of the corresponding methyl- or methoxy-substituted ligand with Ir[(COD)]BF<sub>4</sub> as the starting material. Under the same reaction conditions, the major isolated products differed depending on the substituent used. The methyl substituents resulted in Ir(III) compounds with a meridional geometry, while methoxy-substituted Ir(III) compounds with a draid geometry were isolated in high yields when the methoxy substituent was used. Compounds **1** and **2** emit a green phosphorescence ( $\Phi_{PL} = 0.3$ ) with a  $\lambda_{max} = 459$  –463 nm, while **3** and **4** show a bright, sky-blue emission ( $\Phi_{PL} = 0.5$ ). The dimethoxy-substituted bipyridine ligand was advantageous in terms of yield, thermal stability and quantum efficiency, and its iridium compound is a good candidate for triplet emitters in phosphorescence organic light-emitting diodes (PHOLEDs).

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# 1. Introduction

Bipyridine ligands, such as 2,3'-bipyridine, have C,N chelating modes with heavy transition metals, and they have recently attracted attention because of their high triplet energy (T<sub>1</sub>) [1–6]. In particular, iridium(III) compounds bearing the 2,3'-bipyridine ligand have been shown to be suitable blue emitting-phosphors in phosphorescence organic light-emitting diodes (PHOLEDs) due to their excellent external quantum efficiency (EQE ~20%) [7]. The phosphorescent emission for bipyridine(pypy)-based iridium compounds is thought to originate from both the ligand-centered triplet (<sup>3</sup>LC) transition and the metal-to-ligand charge transfer transition (MLCT) [8]. Moreover, the emission energy can be tuned via the introduction of substituents, such as electron-donating or withdrawing groups, into the main ligand [9]. Therefore, the judicious selection of both the C,N chelate ligand and the substituents

on the chelate ligand is necessary to control the phosphorescent emission of a compound. Although tuning the emission energy for bipyridine(pypy)-based iridium compounds can be achieved by incorporating an ancillary ligand into the ligand framework, the effect of the bipyridine ligand substituent in homoleptic iridium(III) has not been investigated thus far [10]. We recently developed blue triplet emitters, Ir(dfpypy)<sub>3</sub> [8] and Ir(OMe<sub>3</sub>pypy)<sub>3</sub> [11], using the fluorine- and methoxy-functionalized bipyridine ligands, 2',6'difluoro-2,3'-bipyridine (dfpypy) and 2',6',4-trimethoxy-2,3'bipyridine (OMe<sub>3</sub>pypy), respectively. Based on our observations, the triplet energies of the bipyridine derivatives with substituents appeared in the region of 2.70–2.82 eV, as shown in Fig. 1. The bipyridine ligand has a greater triplet energy than phenylpyridine (ppy), thus, it is a very promising ligand candidate for the development of blue phosphorescent iridium(III) compounds. However, because of the high reactivity and low selectivity of the pyridine ring, incorporating the proper substituents into a bipyridine ligand is usually problematic in regard to the yields and reaction conditions [10].

Therefore, we performed a systematic investigation on the effect of bipyridine ligand substituents on iridium(III) compounds. In our



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**Fig. 1.** Phosphorescence of dfpypy (black,  $T_1$ : 2.82 eV) and OMe<sub>2</sub>pypy (red,  $T_1$ : 2.70 eV). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ongoing investigation of homoleptic Ir(III) compounds using  $[Ir(COD)_2]BF_4$  as the starting material, we observed that homoleptic fac-Ir(C^N)\_3 derivatives were obtained with a high selectivity [11]. For example, fac-Ir(OMe\_3pypy)\_3, without the meridional isomer, was obtained via a one-pot reaction of  $[Ir(COD)_2]BF_4$  and 2',6',4-trimethoxy-2,3'-bipyridine (OMe\_3pypy) under mild conditions. This provides a potentially simple and selective synthetic pathway for blue phosphorescent fac-Ir(III) compounds with substituted bipyridine ligands. Herein, we report an efficient synthesis of homoleptic Ir(III) compounds possessing dimethyl- and dimethoxy-substituted bipyridine (pypy) ligands and their photophysical and electrochemical properties.

# 2. Result and discussion

The synthetic details for compounds (1-4) are shown in Scheme 1. The four different ligands were prepared via typical cross-coupling reactions using the corresponding boronic acid or tin reagent. The procedure to produce the  $Ir(C^N)_3$  compounds uses reactive Ir(I) and reacts it with the substituted bipyridine ligand in 1.2-propandiol at a high temperature (~180 °C) [11]. Based on our previous reports, the use of an Ir(I) compound as the starting material and this reaction condition usually result in iridium compounds with facial geometry. Compounds 3 and 4, bearing the dimethoxy and tert-butyl substituents on the bipyridine ligand, were obtained in the facial form in moderate yields. However, when using the dimethyl-substituted bipyridine ligand, the iridium compounds 1 and 2 were mainly isolated in the meridional form [12]. Moreover, the yields (<20%) for both 1 and 2 were much lower than those for 3 and 4. The molecular structures of 1-4 were confirmed using various spectroscopic methods, including X-ray analysis on 2. The molecular structure and crystal data of 2 are shown in Fig. 2 and Table 1, respectively. Based on the NMR and crystal structure data, both 1 and 2 have meridional geometries. The facial geometry was observed in **3** and **4**, as shown in Figure S8 and S10, respectively.

The normalized emission spectra of 1-4 in  $CH_2Cl_2$  at ambient temperature are shown in Fig. 3. The emission energy can be tuned from blue (462 nm) to green (511 nm) depending on the ligand substituents. Compounds **3** and **4** with the dimethoxy substituents have a shoulder peak (vibronic structure) in the emission spectra, indicating a mostly MLCT emission [13], whereas **1** and **2** exhibit broad emission bands without the vibronic structure. In addition, the emission maxima of **1** and **2** appear at 509 and 511 nm, respectively, which are remarkably redshifted compared to the emission maxima of **3** and **4**. These results indicate that the ligand



Scheme 1. Synthetic routes and structures of 1-4.

Table 1



**Fig. 2.** (a) Molecular structure of **2** with a meridional geometry. (b) Packing structure of 2 without solvent molecules for clarity. Selected bond lengths(Å) and bond angles(°): Ir1-C1 2.077(5), Ir1-C13 1973(5), Ir1-C25 2.056(5), Ir1-N1 2.140(4), Ir1-N3 2.040(4), Ir1-N5 2.049(4); C1-Ir1-N1 77.65(17), C1-Ir1-C13 96.84(18), C1-Ir1-N3 90.27(17), C1-Ir1-C25 171.06(18), C1-Ir1-N5 95.51(17), N1-Ir1-C13 173.68(16), N1-Ir1-N3 96.89(16), N1-Ir1-C25 94.85(16), N1-Ir1-N5 89.05(15), C13-Ir1-N3 79.89(19), C13-Ir1-N5 90.89(18), C13-Ir1-N5 94.63(19), N3-Ir1-C25 95.52(17), N3-Ir1-N5 172.49(14), C25-Ir1-N5 79.34(17).

Crystallographic data of <b>2</b> .							
Empirical formula	C <sub>38</sub> H <sub>41</sub> Ir N <sub>7</sub> O <sub>2.50</sub>						
	$[Ir(C_{12}H_{11}N_2)_3] \cdot CH_3CN \cdot 2.5H_2O$						
Formula weight	827.98						
Temperature (K)	173(2) K						
Crystal system	Monoclinic						
Space group	$P2_1/n$						
a (Å)	13.9880(10)						
b (Å)	14.1739(10)						
c (Å)	18.0320(14)						
α (°)	90						
β(°)	90.339(3)						
γ (°)	90						
Volume (Å <sup>3</sup> )	3575.0(5)						
Ζ	4						
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.538						
$\mu ({\rm mm}^{-1})$	3.780						
$2\theta_{\max}$ (deg)	54.00						
Reflections collected	31811						
Independent reflections	7791						
R <sub>int</sub>	0.0261						
Absorption correction	Semi-empirical from equivalents						
Max./min. transmission	0.7457 and 0.6086						
Goodness-of-fit on $F^2$	1.047						
$R_1, wR_2 [I > 2\sigma(I)]$	0.0333, 0.0838						
$R_1$ , $wR_2$ (all data)	0.0465, 0.0977						

substituents likely have significant contributions to the energy gap and phosphorescence of the compounds [14]. In particular, the dimethoxy substituents in one of the bipyridine rings, which is covalently bound to iridium, resulted in much wider energy gaps in the bipyridine-based iridium compounds than in the methyl or dimethyl substituents. The quantum efficiencies ( $\Phi_{PL}$ ) of **1–4** were estimated using FIrpic as a standard ( $\Phi_{PL} = 0.6$ ) [15], and the efficiencies were moderate to excellent. The quantum efficiency followed the order of 4 > 3 > 2 > 1. In general, as the number of substituents on a ligand in a triplet emitter increases, the vibronic modes in the excited state also increase, resulting in a quantum efficiency decrease. This fact is well-known based on previous reports [16]. However, the quantum efficiencies of 2 and 4 are better than those of their counterparts, 1 and 3, and even comparable to that of FIrpic. To understand this observation, further studies on the radiative/non-radiative decay processes and lifetime measurements are needed.



Fig. 3. Emission spectra of 1–4 in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature.





As shown in Fig. 4, the emission spectra of **1** and **2** at 77 K are similar to those of the corresponding compounds at ambient temperature, while the emission spectra of **3** and **4** at 77 K displayed a well-resolved vibronic structure along with a hypsochromic shift of a few nanometers. The structure and shift are mainly attributed to the ligand-centered triplet emission, which is typical of phosphorescent Ir(III) compounds [17]. The emission spectra at a low temperature also revealed the significant impact of the substituents on the emission energy. The photophysical data for **1–4** are summarized in Table 2.

The electrochemical behaviors of **1–4** were examined using cyclic voltammetry (CV), and their oxidations are shown in Fig. 5. The electrochemical characteristics and HOMO/LUMO levels of 1–4 are summarized in Table 2. The HOMO energy level was determined using the oxidation onsets ( $E_{ox}$ ) of **1–4**, and the LUMO energy was determined using the energy gap obtained from the emission spectra at 77 K [18]. The HOMO energy levels of **1** and **2** were –5.98 and –5.88 eV, respectively, and the HOMO energy levels of **3** and **4** with the alkoxy substituents were –5.48 and –5.45 eV, respectively. The much higher HOMO energies of compounds **3** and **4** than those of the methyl-substituted compounds **1** and **2** indicated that the electron-donating alkoxy groups significantly destabilize the HOMO level. Based on the electrochemical data, we concluded that the alkoxy groups cause shallower HOMO levels than the alkyl groups, as shown in Table 2. The electrochemical data also showed

Table 2Photophysical and electrochemical data of 1–4.

	Emission $\lambda_{max}$ , (nm)			${}^{\rm d}\Phi_{\rm (PL)}$	<sup>e</sup> Eox (onset)	<sup>f</sup> T <sub>1</sub>	<sup>g</sup> HOMO	LUMO
	<sup>a</sup> Solution	<sup>b</sup> Film	<sup>c</sup> 77 K		(V)	(eV)	(eV)	(eV)
1	509	489	520	0.29	1.18	2.38	-5.98	-3.60
2	511	497	500	0.41	1.08	2.48	-5.88	-3.40
3	464	462	461	0.53	0.68	2.69	-5.48	-2.79
4	462	459	457	0.57	0.65	2.71	-5.45	-2.74

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Doped into PMMA at 10 wt%.

<sup>c</sup> In frozen CH<sub>2</sub>Cl<sub>2</sub> or Me-THF glass

 $^d$  Phosphorescence quantum efficiency measured in CH\_2Cl\_2, relative FIrpic( $\Phi_{PL}=0.6).$ 

 $^e$  The redox potentials of all compounds were measured in CH<sub>3</sub>CN with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of either 50 mV s<sup>-1</sup> or 100 mV s<sup>-1</sup> (vs. Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup>).

 $^{\rm f}$  The triplet energy value (T1) was estimated by using the emission spectra at 77 K.

<sup>g</sup> Cp<sub>2</sub>Fe (4.8 eV) below the vacuum level.



Fig. 5. CV data of 3 and 4, showing quasi-reversible oxidation.

that the *tert*-butyl group in the dative pyridine ring causes a slight destabilization of the HOMO level compared with the HOMO level for a dative pyridine ring without substituents. In addition, the energy gap of **4** ( $T_1 = 2.71$  eV) is wider than that of **3** ( $T_1 = 2.69$  eV). The substituents in the bipyridine ring that are covalently bonded to the metal also have a notable effect on the energy levels, especially the HOMO level. This could be related to the donor strength of the substituents since the electron density of the HOMO level is dominated by the  $\pi$ -orbitals of the C,N chelate ligand and the *d*-orbital of Ir(III), according to our previous report [8].

The thermal stabilities of **1–4** were examined using TGA (thermal gravimetric analysis). In the first stage (up to  $250-300 \degree$ C), a small weight loss (*ca.* 10%) occurs in all the compounds, and the loss is likely due to the release of solvent molecules. Under a N<sub>2</sub> atmosphere and at a scan rate of 10 °C/min, a 5% weight loss (decomposition temperature, T<sub>d</sub>) appears at 247 °C for **1**, 310 °C for **2**, 370 °C for **3** and 365 °C for **4**, respectively(See Figure S12). Compound **1** has less thermal stability than the other compounds, further indicating that the substituents influence the thermal stability of the Ir(III) compounds. The introduction of methoxy substituents improved the thermal stability of the Ir(III) compounds relative to the methyl substituents.

# 3. Conclusions

In summary, a simple one-pot procedure for the synthesis of a

series of four alkoxo- or alkyl-functionalized homoleptic Ir(III) compounds with emissions from blue to green was successfully developed using [Ir(COD)<sub>2</sub>]BF<sub>4</sub> as the starting material and methylor methoxy-substituted C,N chelate ligands. Upon changing the substituents of bipyridine, the major isolated products were significantly different. Using a methyl-substituted bipyridine ligand resulted in the isolation of the meridional forms of the Ir(III) compounds as the major products. When a dimethoxy-substituted bipyridine ligand was used, the dimethoxy-functionalized Ir(III) compounds with a facial form were isolated in high yields. The Ir(pypy)<sub>3</sub> derivatives with alkoxy groups showed a bright blue emission color and enhanced quantum efficiency. The bipyridine methyl-substituent redshifted the emission to the green region. Regarding the thermal stability, the dimethoxy-functionalized Ir(III) compounds (3 and 4) have higher decomposition temperatures than 1 and 2. These results indicate that alkoxo substitution is a viable approach for achieving highly efficient and stable blue phosphorescent Ir(III) compounds. It is noteworthy that in spite of the same nature of electron donors(MeO-, CH<sub>3</sub>-) as ligand substituents, the difference of emission maximum exceeds 50 nm. The HOMO levels of **3** and **4** are much lower than those of **1** and **2** due to the introduction of the electron-donating methoxy unit on the main ligand. Compounds 3 and 4 in particular exhibit intense blue phosphorescent with a high quantum efficiency ( $\Phi_{PL} = 0.53$ ) and high thermal stability, making them good triplet emitter candidates for PHOLEDs; this application is being investigated in our laboratory.

# 4. Experimental section

General consideration: All experiments were performed under N<sub>2</sub> atmosphere using standard Schlenk technique. Solvents used were dried over suitable drying agents prior to use. All starting materials, 3-bromo-2,6-dimethylpyridine, 3-bromo-2-methylpyridine, 2,6-dimethoxypyridine and 2-bromo-pyridine were purchased from either Aldrich or TCI and used without further purification. The spectra of NMR were recorded on a 400 or 600 MHz Bruker avance FT-NMR spectrometer. The absorption and photoluminescence spectra were obtained using UV/Vis spectrometer Lambda 900 and Perkin Elmer Luminescence spectrometer LS 50B, respectively. All solvents were degassed with nitrogen before use. The cyclic voltammetry measurements were performed using BAS 100 series electrochemical analyzer under nitrogen with a scan rate of 100 mVs<sup>-1</sup> or 50 mVs<sup>-1</sup>. The measurements were carried out in three-electrode electrochemical cell using platinum wire as a counter electrode, Ag/AgCl as a reference electrode and 0.1 M solution of NBu<sub>4</sub>PF<sub>6</sub> in degassed CH<sub>3</sub>CN as electrolyte. Ferrocene and ferrocium redox couple was used as an internal reference. Two starting materials, (2,6-dimethoxypyridin-3-yl)boronic acid [19] and 2-chloro-4-tert-butylpyridine [20] were synthesized according to the literature procedure.

*X-ray analysis*: The X-ray data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with a graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation generated by a rotating anode and 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 semiempirical absorption correction (SADABS) [21] were carried out using the software package of APEX2 [22].

The structures were determined with direct methods using the SHELXS97 program [23], and refinement was performed against F2 using SHELXL2014 program [24].

In **2**, one water molecule (O1W) was located on general position but it was refined with the site occupancy factor of 0.5. Another water molecule was disordered over two positions (O3W and O4W) with equal site occupancy factors of 0.5. The DFIX restraint in the bond distance (N7-C37) in acetonitrile molecule was applied during the refinement processes due to the large variation of bond geometry. Displacement parameters of the lattice solvent molecules were restrained to be approximately isotropic (ISOR). The nonhydrogen atoms were refined anisotropically. All hydrogen atoms except the hydrogens of the lattice water molecules were placed in calculated positions and refined isotropically in a riding manner along with their respective parent atoms. All hydrogen atoms of the lattice water molecules were prepared using DIAMOND program [25]. Relevant crystal collection data, refinement data for the crystal structures, selected bond distances and angles, and inter- and intra-molecular C-H…O, C-H…N, and C-H… $\pi$  interactions are summarized in Tables S1-S3.

Synthesis of 2'-methyl-2,3'-bipyridine: Under nitrogen atmosphere, 3-bromo-2-methylpyridine (0.69 mL, 5.37 mmol), 2-(tributhylstannyl)pyridine(3.07 mL, 8.05 mmol), LiCl(1.14g, 26.85 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.19g, 0.27 mmol) were charged into a a Schlenk flask and then toluene(50 ml) was added to this reaction mixture. This mixture was refluxed at 120 °C for 3 days. After the reaction was completed, solvent was removed under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with. H<sub>2</sub>O. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated. The product was purified by column chromatography (ethylacetate/dichloromethane = 2/1,  $R_{\rm f}$  = 0.2) to give 60% yield of white solid. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ): 8.62 (m, 1H), 8.45 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.71 (td, *J* = 8, 1.6 Hz, 1H), 7.65(dd, *J* = 7.6, 1.6 Hz, 1H),7.34(d, J = 8 Hz, 1H), 7.21 (m, 1H), 7.14 (m, 2H) 2.52 (s, 3H).

Synthesis of 2',6'-dimethyl-2,3'-bipyridine: The product was prepared using the same procedure of 2'-methyl-2,3'-bipyridine except that 3-bromo-2,6-dimethylpyridine was used instead of 3-bromo-2-methylpyridine. Yield: 62% (ethylacetate/dichloromethane = 2/1,  $R_f = 0.2$ , white solid). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.67(m, 1H), 7.68 (td, J = 7.6, 1.9 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.33 (dt, J = 8, 0.8 Hz, 1H), 7.18 (m, 1H) 7.00(d, J = 8 Hz, 1H), 2.45(s. 3H) 2.44 (s, 3H).

Synthesis of 2',6'-dimethoxy-2,3'-bipyridine: Under nitrogen atmosphere, (2,6-dimethoxypyridin-3-yl)boronic acid (1.4 g, 7.65 mmol), 2-bromopyridine(0.62 mL, 6.38 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.44 g, 0.38 mmol) in THF (20 mL), and degassed 2 M K<sub>2</sub>CO<sub>3</sub> were subsequently added to a Schlenk flask. The solution was slowly heated to 80 °C and then refluxed for 12 h. The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and dried over MgSO<sub>4</sub>. All volatiles were removed *in vacuo*. The crude mixture was purified by column chromatography and yielding a product in 65% yields. Spectroscopic data was identical to that reported previously [10].

Synthesis of 2',6'-dimethoxy-4-tert-butyl-2,3'-bipyridine: The product was prepared using the same procedure of 2',6'-dimethoxy-2,3'-bipyridine except that 3-2-chloro-4-tert-butylpyridine was used instead of 2-bromopyridine. Yield: 65% (ethylacetate/hexane = 1/3,  $R_f = 0.5$ , white solid). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.49 (d, J = 5.4 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 1.8 Hz, 1H), 7.11 (dd, J = 5.3, 1.9 Hz, 1H), 6.38 (d, J = 8.3 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 1.28 (s, 9H).

Synthesis of Ir(III) (2'-methyl-2,3'-bipyridinato)-N, $C^4$ ) (1): [Ir(COD)<sub>2</sub>]BF<sub>4</sub>, and 2'-methyl-2,3'-bipyridine were charged into a Schlenk flask and then degassed 1,3-propandiol (5 ml) was added to this reaction mixture under nitrogen atmosphere. The solution was heated to 180 °C and then refluxed for 24 h. After the reaction was completed, 1,3-propandiol was removed under reduced pressure and the residue was washed with Et<sub>2</sub>O, then washed with hexane and dried under reduced pressure. The resulting solid was transferred to 150 mL of round bottom flask and was dissolved in THF(100 mL). The solution was recrystallized from ethylacetate/

ether to give 15% yield of solid product. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.16 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 1.2 Hz, 2H), 8.02 (d, *J* = 5.4 Hz, 1H), 7.83 (d, *J* = 5.4 Hz, 1H), 7.77–7.68 (m, 5H), 7.55 (t, *J* = 54.2 Hz, 2H), 6.99 (t, *J* = 4.0 Hz, 1H), 6.88 (m, 2H), 6.61 (d, *J* = 4.2 Hz, 1H), 6.25 (d, *J* = 4.2 Hz, 1H), 6.18 (d, *J* = 4.2 Hz, 1H), 2.94 (s, 3H). 2.89 (d, *J* = 3 Hz, 6H). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 168.0, 165.9, 165.1, 163.8, 153.8, 151.5, 148.7, 147.6, 145.5, 142.0, 141.6, 137.8, 137.7, 137.3, 136.2, 130.9, 126.3, 125.3, 124.2, 124.0, 123.7, 123.4, 123.4, 123.0, 29.7, 26.7, 26.1. Anal. calcd for C<sub>33</sub>H<sub>27</sub>N<sub>6</sub>Ir; C, 56.64; H, 3.89; N, 12.01; found: C 56.59, H 3.98, N 12.05.

Synthesis of Ir(III)  $(2',6'-dimethyl-2,3'-bipyridinato)-N,C^4)$  (2): [Ir(COD)<sub>2</sub>]BF<sub>4</sub>, 2'6'-dimethyl-2,3'-bipyridine and degassed 1,3propandiol were added to a Schlenk flask under nitrogen. The solution was heated to 180 °C and then refluxed for 24 h. After the reaction was complete, 1,3-propandiol was removed under reduced pressure and the residue was washed with Et<sub>2</sub>O, then washed with hexane and dried under reduced pressure. The resulting solid was transferred to 150 mL of round bottom flask and was dissolved in THF(100 mL). The solution was filtered through Celite, concentrated in vacuo. The crude product was recrystallized from EtOAc/Et<sub>2</sub>O to give over 20% yield of solid product. <sup>1</sup>H NMR (600 MHz,  $CD_2Cl_2$ ,  $\delta$ ): 8.06–7.98 (m, 4H), 7.84 (d, J = 4.8 Hz, 1H), 7.64 (td, J = 7.8, 1.2 Hz, 1H), 7.59–7.52 (m, 3H), 6.84 (t, J = 6.6 Hz, 1H), 6.71 (dt, *J* = 7.2, = 1.4 Hz, 2H), 6.46 (s, 1H), 6.05 (s, 1H), 5.90 (s, 1H), 2.76 (s, 3H), 2.74 (d, J = 1.2 Hz, 6H), 2.14 (s, 3H), 2.13 (s, 3H). 2.12 (s, 3H) <sup>13</sup>C {<sup>1</sup>H}-NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ): 189.2, 186.7, 168.9, 166.9, 166.5, 155.3, 154.9, 154.8, 153.7, 153.1, 153.0, 151.5, 148.4, 139.3, 136.8, 136.1, 134.9, 129.8, 125.3, 123.7, 123.5, 122.9, 122.5, 122.2, 122.1, 121.3, 53.8, 53.6. 53.4. 53.2. 53.1. 27.0. 26.7. 26.4. 23.7. 23.5. Anal. calcd for C<sub>36</sub>H<sub>33</sub>N<sub>6</sub>Ir; C, 58.28; H, 4.48; N, 11.33; found: C 58.25, H 4.51, N 11.28

Synthesis of Ir(III) (2',6'-dimethoxy-2,3'-bipyridinato)- $N,C^4$ ) (3): [Ir(COD)<sub>2</sub>]BF<sub>4</sub>, 2'6'-dimethoxy-2,3'-bipyridine and degassed 1,3propandiol were added to a Schlenk flask under nitrogen. The solution was refluxed for 24 h. After the reaction was complete, the solid product was produced by adding water(50 mL) in the Schlenk flask. The filtered solid was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> = 0.6) to give 45% yield of solid product. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.57(d*J* = 8.3 Hz, 1H), 7.63 (d, *J* = 4.3 Hz, 1H), 7.41 (d, *J* = 6.5 Hz, 1H), 6.81 (d, *J* = 6.2 Hz, 1H), 5.84 (s, 1H), 4.04(s, 3H), 3.77(s, 3H). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 178.8, 164.2, 162.9, 160.6, 147.2, 137.0, 123.3, 120.9, 120.7, 108.6, 52.4. Anal. calcd for C<sub>36</sub>H<sub>33</sub>N<sub>6</sub>O<sub>6</sub>Ir; C, 51.60; H, 3.97; N, 10.03; found: C 56.65, H 3.98, N 10.08.

*Synthesis* of Ir (III) (2',6'-dimethoxy-4-*tert*-butyl-2,3'-bipyridinato)-*N*,*C*<sup>4</sup>) (**4**): Synthetic procedure of **4** is almost the same as that of **3**. Yield: 40%. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.64(d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 45.9 Hz, 1H), 6.84 (dd, *J* = 6.5, 7.1 Hz, 1H), 5.86 (s, 1H), 4.04 (s, 3H), 3.77(s, 3H), 1.33(s, 9H). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 178.8, 163.1, 162.0, 160.4, 159.6, 145.9, 120.5, 119.5, 117.8, 108.7, 52.6, 52.5, 34.8, 30.6, 30.2, 29.6. Anal. calcd for C<sub>48</sub>H<sub>57</sub>N<sub>6</sub>O<sub>6</sub>Ir; C, 57.29; H, 5.71; N, 8.35; found: C 57.26, H 5.75, N 8.41.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.07.034.

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