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Description	

TITLE

Design, synthesis, and properties of a series of charged iridium(III) complexes with a neutral bidentate ligand for deep-blue phosphorescent emitter

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ABSTRACT

We herein report a series of charged iridium(III) complexes with a neutral bidentate ligand for blue phosphorescent emitter. A molecular design bearing a 2-(3, 5-dimethyl-1*H*-pyrazol-1-yl)pyridine ligand proved suitable for efficient blue emission according to the comparison of photoluminescent properties of the complexes. Its Commission Internationale de L'Eclairage x,y-coordinates (CIEx,y) in solution was estimated to be (0.17, 0.18), indicating that the complex with the ligand is a promising candidate for a deep-blue emitter. We further demonstrated that this complex displays blue electroluminescence by successfully integrating it in a light-emitting device.

AUTHOR DECLARATION

1. Introduction

Phosphorescent transition-metal complexes have been extensively studied due to their potential application, particularly in light-emitting devices such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [1-3]. Phosphorescent iridium(III) complexes have attracted a great deal of attention because of their higher luminescence efficiency over fluorescent emitter, however, the blue-emitting phosphorescent complexes still have some drawbacks compared to their red and green counterparts. For instance, FIrpic, which is known as the standard blue emitter, has Commission Internationale de L'Eclairage x,y-coordinates (CIEx,y) of (0.16, 0.29) (Figure 1, left) [4]. These coordinates correspond to a sky-blue (typically CIEy >0.2) and cannot be considered sufficient as deep-blue emission (CIEy <0.2). Although various types of complexes besides FIrpic have been investigated, the number of studies reporting sufficient deep-blue emitting complexes is limited so far [5]. Among these studies, a major contribution is attributed to Lee et al. who have reported a new homoleptic iridium(III) complex, (dfpypy)$_3$Ir, bearing three 2',6'-difluoro-2,3'-bipyridine (dfpypy) ligands [6]. Unlike FIrpic and its related complexes based on 2-(2,4-difluorophenyl)pyridine (dfppy) surrogate, the resulting complex exhibited deep-blue emission. The work has introduced a new ligand design, thereby pioneering the intensive investigations on its analogous complexes (Figure 1, right) [7].
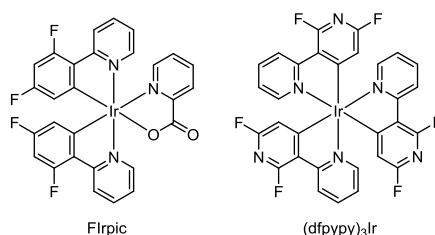

FIrpic   (dfpypy)$_3$Ir

Figure 1. FIrpic and (dfpypy)$_3$Ir

The neutral complexes such as FIrpic and (dfpypy)$_3$Ir can be used as emitting layers in light-emitting devices but require vacuum deposition process (dry process), which is typically standard in the current manufacturing process. Meanwhile, charged complexes are considered much more promising especially for large-area lighting and display applications due to some of their additional properties: (i) the presence of ionic species should facilitate electric charge injection from electrodes into the emission layers, and (ii) controllable solubility based on the structure of ligands as well as anion moiety enables solution process (wet process) fabrication of the devices. The processability from solution such as by inkjet printing has received broad attention due to its capability for large-area device manufacturing. During our initial studies focused on designing a structural motif for a deep-blue emitter, we isolated a charged complex bearing two acetonitrile molecules as ligands, exhibiting bright sky-blue emission under UV irradiation (Scheme 1) [8]. This finding led us to envision a key structural motif of a new series of iridum(III) complexes for efficient blue emission.
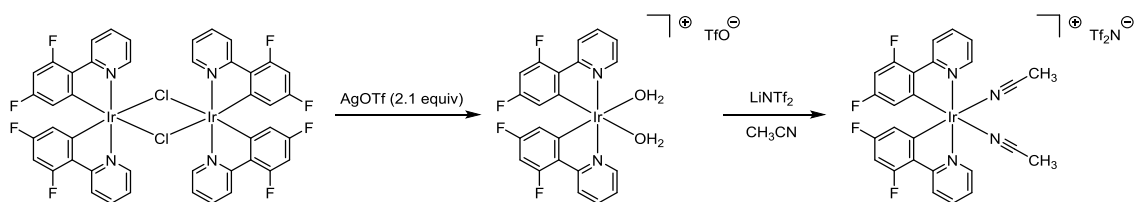
Scheme 1. Formation of a sky-blue emitting iridium(III) complex bearing two acetonitriles as ligands. Tf = trifluoromethanesulfonyl (triflyl).

We herein demonstrate the synthesis of a series of charged iridium(III) complexes which have potential as blue phosphorescent emitters. Among them, the complex bearing two dfpypy ligands and a N,N-bidentate ligand, that is 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine, efficiently emitted to give an excellent blue color in solution. Although the use of 2-(1*H*-pyrazol-1-yl)pyridine ancillary ligands is previously reported, the emission colors of the corresponding iridium(III) complexes are sky-blue to green [9,10]. Furthermore, we demonstrate that this complex can be successfully integrated into light-emitting devices and therefore, not only exhibit highly efficient photoluminescence but also electroluminescence.

2. Results and discussion

2.1 Design and synthesis of charged iridium(III) complexes

We employed a structural motif of a heteroleptic Ir(III) complex composed of two monoanionic C,N-bidentate (C^N) ligands and another neutral X,Y-bidentate (X^Y) ligand according to our finding described above (Figure 2).
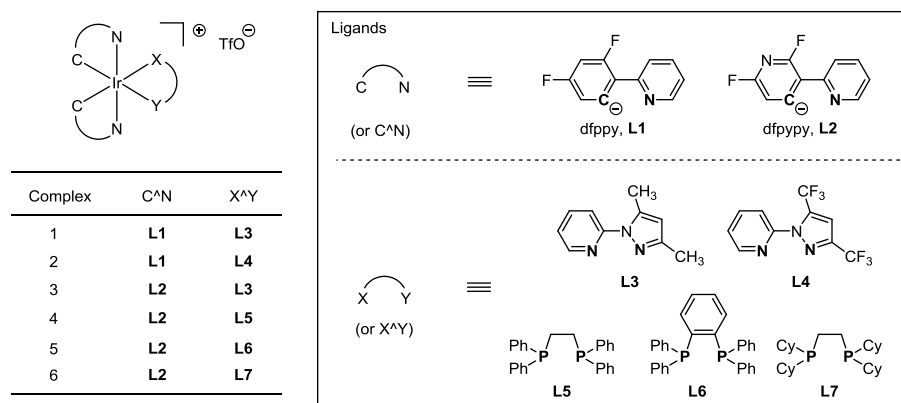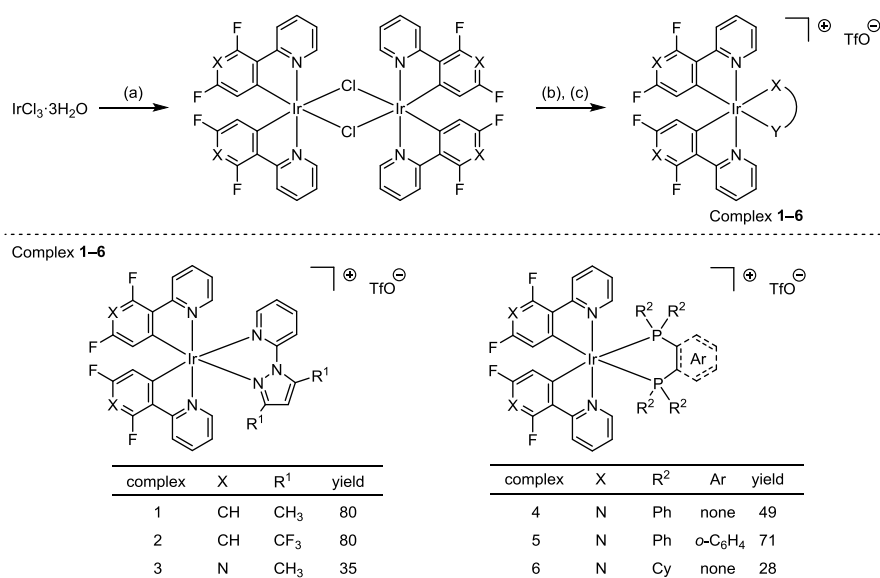

Figure 2. Structure of charged iridium(III) complexes. Cy = cyclohexyl, Ph = phenyl, TfO = trifluorometanesulfonate (triflate). Emboldened atoms in **L1−L7** would

coordinate the iridium center.

Six new complexes shown in Figure 2 were straightforwardly synthesized according to modified literature procedures (Scheme 2) [11,12]. Iridium(III) chloride trihydrate reacted with two equivalents of 2-(2,4-difluorophenyl)pyridine (dfppy, **L1**) or 2',6'-difluoro-2,3'-bipyridine (dfpypy, **L2**) to afford chloro-bridged cyclometallated iridium(III) dimer $[L_2Ir(\mu\text{-}Cl)]_2$ (L = **L1** or **L2**). Subsequent treatment with silver(I) trifluoromethanesulfonate followed by another X^Y ligand (**L3−L7**) yielded the charged complexes in moderate to good yields (28−80%) [13]. For complexes **3** and **6**, additional chromatographic procedures on their purification steps were needed to obtain spectroscopically pure sample and this might result in lower isolated yields (see Experimental Section for details). These synthetic procedures are scalable, and we thereby readily prepared complex **3** in multi-gram quantities for the following studies.

complex	X	R^1	yield
1	CH	CH$_3$	80
2	CH	CF$_3$	80
3	N	CH$_3$	35

complex	X	R^2	Ar	yield
4	N	Ph	none	49
5	N	Ph	o-C$_6$H$_4$	71
6	N	Cy	none	28

Scheme 2. Synthesis of charged complexes **1−6**. Reagents and conditions: (a) **L1** or **L2**,

2-ethoxyethanol/H$_2$O (3/1, v/v), 150 °C, 8−18 h; (b) AgOTf, CH$_3$OH/CH$_2$Cl$_2$, 1/1 (v/v), r.t., 2−5 h; (c) X^Y ligand (**L3**−**L7**), 1,2-dichloroethane, refl., 15−18 h. Yields are based on [L$_2$Ir(μ-Cl)]$_2$.

All complexes showed certain moisture, air, and sunlight tolerances, enabling the storage under ambient conditions without any detectable decomposition. Complex **3**, for example, was well soluble in the high boiling solvents such as *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, and 1,2-dichloroethane whereas toluene, xylene, cyclopentanone, and anisole have poor to moderate solubility. On the basis of HPLC/MS analysis, we have concluded that complex **3** used in this study contained no detectable impurities.

2.2 Properties of charged iridium(III) complexes

Studies on photoluminescent properties of N^N-coordinated complexes have revealed that **3** composed of two **L2** and one **L3** ligands is a promising candidate for deep-blue emitter. Comparison of complexes **1** and **2** bearing different X^Y ligands indicated that the emission wavelengths of **1** was much bluer than that of **2**, emphasizing that the electron-rich **L3** would contribute to bluer emission compared to the electron-deficient **L4** (Figure 3).
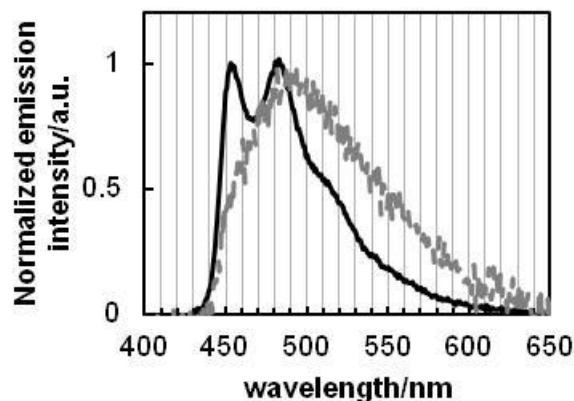
Figure 3. Normalized emission spectra of **1**- (solid line) and **2**-doped (dashed line) films (5 wt% in poly(methyl methacrylate), room temperature, excited at 337 nm)

Another study featuring the effect of C^N ligands highlighted the superior contribution of **L2** over **L1** in regard to both bluer color emission and enhanced photoluminescent quantum yield (PLQY). The emission maximum of **3** reached the deep-blue region (more than 15 nm-hypsochromic shift relative to **1**, see Figure 4), showing efficient contribution of **L2** over its counterpart **L1** Similarly to previous results presented by Lee et al. [6]. The PLQY value of **3** display a remarkable increase reaching up to 0.83, whereas that of **1** remains quite low (Table 1). Although complexes **1** and **3** gave high PLQY values in 5wt% poly(methyl methacrylate) (PMMA), we observed a drastic drop of the value of only complex **1** in fluid solution. The relevant reason for this peculiar observation still remains unclear. CIEx,y of **3** was notably better than that of the sky-blue emitter FIrpic, hence underlining its potential use as a deep-blue emitter.
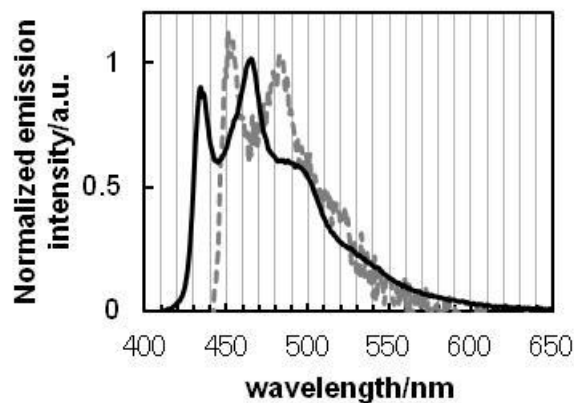
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Figure 4. Normalized emission spectra of **1** (dashed line) and **3** (solid line) (1.0×10^{-5} M in degassed 1,2-dichloroethane, room temperature, excited at 337 nm)

Table 1. Photoluminescent properties of **1** and **3** in solution (1.0×10^{-5} M in degassed 1,2-dichloroethane, room temperature, excited at 337 nm).

Complex	λ_{max}/nm	PLQY[a]	$CIE_{x,y}$
1	450, 482	0.04 (0.92)	(0.22, 0.25)
3	434, 464	0.83 (0.78)	(0.17, 0.18)
FIrpic[b]	−	−	(0.16, 0.29)

[a] Values in 5wt% PMMA film are given in the parentheses.

[b] See ref [4].

In order to consider the emission mechanism, we employed the molecular oxygen which is well-known to quench triplet-state excitons. As shown in Figure 5 where we described the drastic quenching of the emission from **3** by bubbling oxygen gas, it was

clearly indicated that the emission was attributed to phosphorescence. It should also be

noted that **3** was thermally stable over 300 °C without any decomposition [14].
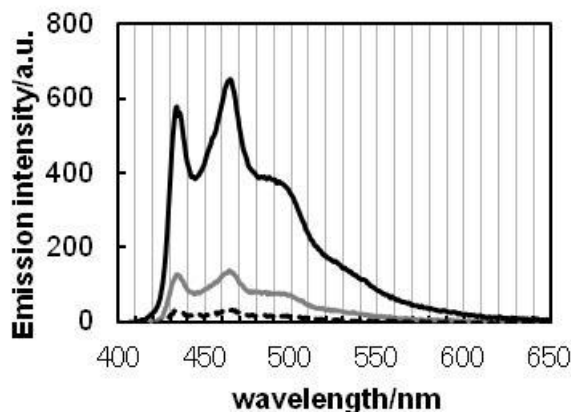

Figure 5. Emission spectra of **3** (1.0×10^{-5} M in 1,2-dichloroethane, room temperature,

excited at 337 nm. Nitrogen-bubbled (black line), without bubbling (gray line), and

oxygen-bubbled (dashed line) samples.

2.3 Device fabrication based on complex **3** as emitter

Several attempts for fabricating a thin film of **3** via thermal deposition were not

successful due to its thermal instability upon heating under the vacuum, probably

reflecting its charged nature. However, as the charged complexes are soluble in common

organic solvents, we fabricated light-emitting devices based on **3** through "wet process".

Our preliminary screening for obtaining a bright emission from **3**-embedded thin film

have successfully reached an optimal composition; a combination of **3**/

1,3-Bis(*N*-carbazolyl)benzene (mCP)/Poly(methyl methacrylate) (PMMA) as

emitter/host/matrix [15]. The device architecture of the light-emitting devices were as

follows (Figure 6): ITO (150 nm)/PEDOT:PSS (30 nm)/**3**:mCP:PMMA (30 nm)/BAlq$_3$ (60 nm)/LiF (1 nm)/Al(100 nm). Although the devices based on a blend active layer containing **3** exhibited a bright emission with a maximum EQE of approximately 0.54 %, a bathochromic-shifted sky-blue electroluminescence and its rapid emission decay within several minutes were also observed (Figure 7). A direct analysis of the emission layer in the decayed devices by laser desorption ionization/time-of-flight mass spectrometry (LDI-TOF MS) have suggested that no chemical structural changes of the emitter occurred [16]. The exact reasons for the rapid decay remained unclear, underscoring the necessary of further optimizations in both materials and device architectures.
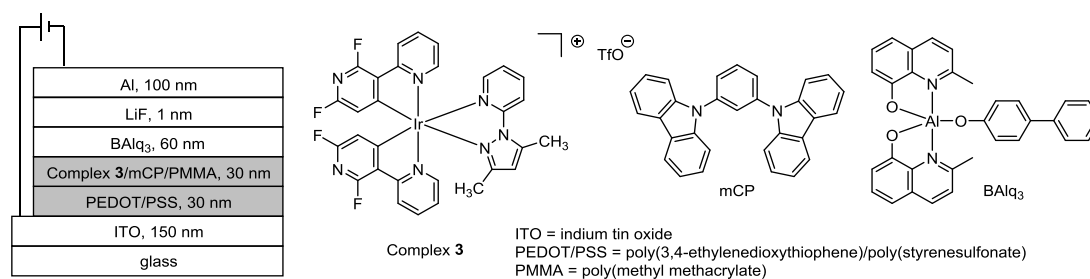

Figure 6. Schematic light-emitting device structure based on complex **3**. Bottom-side two layers (gray) and top-side three layers (white) were fabricated through wet and dry processes, respectively. The concentration of complex **3** is 15 wt% with respect to the amount of mCP.
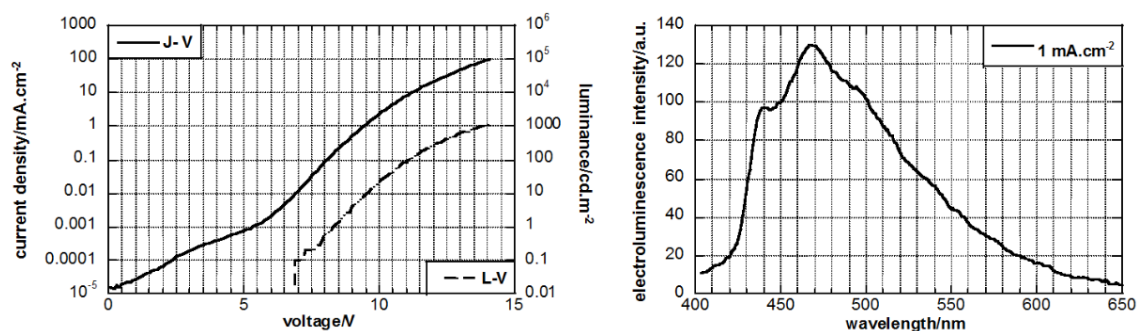
Figure 7. Current density and luminance-voltage curves (left) and electroluminescence spectra measured at the current density of 1 mA/cm^2 (right) of a light-emitting device based on **3**.

3. Conclusion

In conclusion, we have demonstrated a new, deep-blue emitting charged iridium(III) complex based on 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine ligand. Its CIEx,y of (0.17, 0.18) was notably superior to that of one of the standardemitter FIrpic, suggesting that this would be a good candidate as a deep-blue emitter for light-emitting devices.

4. Experimental

4.1 General

All reagents and dry solvents used for the experiments were purchased from Sigma-Aldrich, Kanto Chemical, Nacalai Tesque and Tokyo Chemical Industry (TCI) and used without further purification. ASAHIKLIN AK-225 was obtained from Asahi Glass. All solutions for photophysical experiments were degassed by gentle bubbling

with nitrogen or argon for more than 30 min prior to measurement. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. [1]H (300 MHz), [19]F (283 MHz) and [13]C (^{1}H decoupling, 75 MHz) NMR spectra were recorded on a JEOL JNM-AL300 FT-NMR spectrometer. [13]C (^{1}H and ^{19}F decoupling, 100 MHz) NMR spectra were recorded on a JEOL JNM-ECP400 FT-NMR spectrometer. Chemical shifts δ are reported in ppm units referenced to $(CH_3)_4Si$ (0.0 ppm in $CDCl_3$) or residual solvent peak (2.04 ppm in acetone-d_6) for ^{1}H; CCl_3F (0.0 ppm) for ^{19}F; residual solvent peak (77.0 ppm in $CDCl_3$, 29.7 ppm in acetone-d_6) for [13]C. NMR data were reported as follows: Chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, br = broad, m = multiplet), and coupling constants. Thermogravimetry-differential thermal analysis (TG-DTA) was undertaken using a MAC Science TG-DTA200SA thermal analyzer under a nitrogen atmosphere at a heating rate of 20 °C min^{-1} from 20 to 600 °C. Photoluminescence spectrum, quantum yield (PLQY) and CIEx,y coordinates were measured using a Hamamatsu C9920-02 absolute PL quantum yield measurement system (Excitation wavelength: 337 nm). LDI-TOF MS spectra were recorded on a JEOL JMS-S3000 SpiralTOF spectrometer.

4.2 Synthesis of complexes complexes **1**−**6**

In the first step, chloro-bridged cyclometallated iridium(III) dimers $[L_2Ir(\mu\text{-Cl})]_2$ (L = **L1** or **L2**) were synthesized from iridium(III) chloride hydrate according to the literature procedures. [11,12] In the second step, a mixture of $[L_2Ir(\mu\text{-Cl})]_2$ (0.1−0.2 mmol), silver(I) trifluoromethanesulfonate (2.1 equiv), methanol/dichloromethane = 1/1

(v/v, 12.5−25 mL) was stirred at ambient temperature for 2−5 h. Insoluble silver salts were removed by passing through a short pad of Celite, washed with dichloromethane, concentrated *in vacuo*. 1,2-Dichloroethane (2.5−5 mL) solution of the residue was added **L3−L7** (2.1 equiv, relative to $[L_2Ir(\mu\text{-}Cl)]_2$) was heated at reflux for 15−18 h. After cooling to 0 °C, insoluble materials were filtered off from the reaction mixture. Removal of the solvent gave the crude materials. The following purification procedures afforded the charged complexes **1−6**.

Complexes **1−4**: Sonication in solvent (using ethyl acetate for **1**; chloroform for **2**; chloroform/hexane for **3**; chloroform for **4**) yielded yellowish precipitate. The precipitate was collected by filtration to give desired charged complex (**1**, 80%; **2**, 80%; **3**, 35%; **4**, 49%). In the case of the isolation of **3**, additional silica gel and alumina column chromatography were required to obtain spectroscopically pure sample prior to the sonication.

Complexes **5** and **6**: Alumina column chromatography followed by sonication in chloroform/AK-225 gave yellowish precipitate. The precipitate was collected by filtration to give desired charged complex (**5**, 71%; **6**; 28%). For complex **6**, a repeated procedure, that is alumina column chromatography followed by sonication, is required to obtain spectroscopically pure sample.

4.3 Fabrication and characterization of light-emitting device based on **3**

For device fabrication, glass substrates coated with a 150 nm ITO layer having sheet resistance of 10 Ω/sq were cleaned using ultrasonication in acetone, followed by ultrasonication in detergent, pure water, and isopropanol. Then, the substrates were

placed in an ultraviolet (UV)-ozone treatment chamber for 30 min. The substrates were then coated with a 30nm PEDOT:PSS layer by spin-coating a suspension in water (Clevios AI4083) at a speed of 4000 rpm for 60 s. The 30 nm thick active layer was spin-coated from a blend solution of PMMA, mCP and **3** in 1,2-dichloroethane. The optimized PMMA:mCP ratio was 1:0.9 with a total concentration of 10 mg/ml to which 15 wt% **3** with respect to the amount of mCP was added. The samples were then placed in a vacuum chamber and the electron injecting layer and electrodes were deposited to finalize the devices. The finalized devices were encapsulated to avoid oxidation of the aluminum electrodes. The current density-voltage-external quantum efficiency characteristics of the devices were measured using a computer-controlled sourcemeter (2400, Keithley) and an integrating sphere installed with a calibrated silicon photodiode. The luminance and the power conversion efficiency of the OLEDs were measured using a computer-controlled luminance meter (BM-9, TOPCON). The EL spectra of the OLEDs were taken using a photonic multi-channel analyzer (C7473, Hamamatsu).

SUPPLEMENTARY DATA

Additional experimental procedures, TG curve of complex **3**, compound characterization data, and NMR spectra.

ACKNOWLEDGMENTS

REFERENCES

[1] H. Yersin, ed., Highly Efficient OLEDs with Phosphorescent Materials, Wiley-VCH, 2007.

[2] Y. Chi, P.-T. Chou, Chem. Soc. Rev. 39 (2010) 638-655.

[3] C. Ulbricht, B. Beyer, C. Friebe, A. Winter, U.S. Schubert, Adv. Mater. 21 (2009) 4418-4441.

[4] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 2082-2084.

[5] K.S. Yook, J.Y. Lee, Adv. Mater. 24 (2012) 3169-3190.

[6] S.J. Lee, K. Park, K. Yang, Y. Kang, Inorg. Chem. 48 (2009) 1030-1037.

[7] Selected examples, see:

(a) S.O. Yo, U.N. Ahn, Y. Ha, S.Y. Ahn, Mol. Cryst. Liq. Cryst. 530 (2010) 116/[272]-122/[278].

(b) N. Jung, E. Lee, J. Kim, H.H.-K. Park, K. Park, Y. Kang, Bull. Korean Chem. Soc. 33 (2012) 183-188.

(c) H.R. Park, D.H. Lim, Y.K. Kim, Y. Ha, J. Nanosci. Nanotechnol. 12 (2012) 668-673.

(d) C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich, L. De Cola, Chem. Mater. 24 (2012) 3684-3695.

(e) F. Kessler, R.D. Costa, D. Di Censo, R. Scopelliti, E. Ortí, H.J. Bolink, S. Meier, W. Sarfert, M. Grätzel, M.K. Nazeeruddin, E. Baranoff, Dalt. Trans. 41 (2012) 180-191.

(f) S.B. Meier, W. Sarfert, J.M. Junquera-Hernández, M. Delgado, D. Tordera, E. Ortí, H.J. Bolink, F. Kessler, R. Scopelliti, M. Grätzel, M.K. Nazeeruddin, E. Baranoff, J. Mater. Chem. C 1 (2013) 58-68.

(g) Y. Kang, Y.-L. Chang, J.-S. Lu, S.-B. Ko, Y. Rao, M. Varlan, Z.-H. Lu, S. Wang, J. Mater. Chem. C 1 (2013) 441-450.

(h) F. Kessler, Y. Watanabe, H. Sasabe, H. Katagiri, M.K. Nazeeruddin, M. Grätzel, J. Kido, J. Mater. Chem. C 1 (2013) 1070-1075.

(i) N. Darmawan, C.-H. Yang, M. Mauro, R. Fröhlich, L. De Cola, C.-H. Chang, Z.-J. Wu, C.-W. Tai, J. Mater. Chem. C 2 (2014) 2569- 2582.

[8] Schmid et al. have reported similar sovento complexes, see: B. Schmid, F.O. Garces, R.J. Watts, Inorg. Chem. 33 (1994) 9-14.

[9] 2-(1*H*-pyrazoly-1-yl)pyridine-based charged iridium(III) complexes, see:

(a) [1]   L. He, L. Duan, J. Qiao, R. Wang, P. Wei, L. Wang, et al., Blue-Emitting Cationic Iridium Complexes with 2-(1*H*-Pyrazol-1-yl)pyridine as the Ancillary Ligand for Efficient Light-Emitting Electrochemical Cells, Adv. Funct. Mater. 18 (2008) 2123–2131.

(b) N.M. Shavaleev, R. Scopelliti, M. Grätzel, M.K. Nazeeruddin, Inorganica Chimica Acta Steric hindrance at metal centre quenches green phosphorescence of cationic iridium (III) complexes with 1-(2-pyridyl)-pyrazoles, Inorganica Chim. Acta. 404 (2013) 210–214.

(c) V.A. Online, L. Duan, Y. Wei, L. He, L. Wang, Y. Qiu, Increased phosphorescent quantum yields of controlling the counter anions, Chem. Commun. (2014) 530–532.

(d) D. Ma, L. Duan, Y. Qiu, Tetraphenylborate versus tetraimidazolylborate as counterions for cationic iridium (III) complexes, Dalt. Trans. (2015) 8521–8528.

[10] Similar 2-(1*H*-pyrazoly-5-yl)pyridine-based neutral iridium(III) complexes were reported by Chi and Chou, see ref 2 and references therein.

[11] S. Sprouse, K. A. King, P. J. Spellane, R. J. Watts, J. Am. Chem. Soc., 106 (1984) 6647-6653.

[12] J. Li, P.I. Djurovich, B.D. Alleyne, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, Polyhedron 23 (2004) 419-428.

[13] See the experimental section for details.

[14] See the Supplementary Information.

[15] K. Fukuda, E. Murotani, Y. Takahira, V. Vohra, H. Murata, Poster presentation #P-27, International Conference on Fluorine Chemistry 2014 Tokyo, Yokohama, Japan, May 28-30, 2014.

[16] Y. Tachibana, Y. Nakajima, T. Isemura, K. Yamamoto, T. Satoh, J. Aoki, M. Toyoda, Oral presentation #S22-1040, 19th International Mass Spectrometry Conference, Kyoto, Japan, September 15-21, 2012.