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PAPER

Synthesis and characterization of new blue light emitting iridium complexes containing a trimethylsilyl group[†]

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New blue iridium complexes with a trimethylsilyl group as a bulky electron donating group, Ir(F₂-*p*-trimethylsilyl)₂(fptp) and Ir(F₂-*m*-trimethylsilyl)₂(fptp), were synthesized *via* μ -chloro-bridged dimer and perfluoropropylated triazole-based ancillary ligands and then characterized using various spectroscopic studies. Both Ir(F₂-*p*-trimethylsilyl)₂(fptp) and Ir(F₂-*m*-trimethylsilyl)₂(fptp) exhibited high photoluminescence quantum efficiencies of 75 ± 5% and 76 ± 5% in films, respectively. The DFT calculation demonstrated that the new blue iridium complexes have a wide bandgap compared with FIrpic and the Ir(F₂-*p*-trimethylsilyl)₂(fptp) with a trimethylsilyl group in the para position has a slightly deeper HOMO level than that of the Ir(F₂-*p*-trimethylsilyl)₂(fptp) with a trimethylsilyl group in the meta position. The UV-vis absorption and photoluminescent (PL) spectra of the complexes were blue shifted compared with those of FIrpic. The device using the Ir(F₂-*p*-trimethylsilyl)₂(fptp) exhibited a maximum external quantum efficiency of 19.3% (at 0.00152 mA cm⁻²) and commission Internationale de l'Eclairage (CIE) coordinates of (0.145, 0.247).

Organic light emitting diodes (OLEDs) have been successfully employed as small size displays, and have been actively researched for applications in large size, flexible displays and solid state lighting. The efficiency of the OLEDs has been improved significantly by adopting phosphorescent emitters that can harvest triplet excitons as well as singlet excitons for light, enabling nearly 100% internal quantum efficiencies.²⁻⁴ In particular, iridium complexes have been very successful as phosphorescent emitters, especially for green and red emissions, due to their high photoluminescent (PL) efficiency and relatively short excited state lifetime.¹

However, iridium complexes with blue emissions are rare, compared with those of the phosphorescent green and red.⁵ Deep blue emitters have a low PL quantum efficiency due to their high band gap. Furthermore, the $T_1 \rightarrow S_0$ transition probability is reduced as the band gap increases due to decreases in the admixture of the ligand-centered $\pi \rightarrow \pi^*$ and

metal-to-ligand charge-transfer (MLCT) transition.⁶ The general approach toward the synthesis of an efficient deep blue emitting complex has been to control the electronic structure of the iridium complex to shift the emission from green to blue. Examples of this method include the addition of fluorine atoms to phenyl rings, and the introduction of electron-donating groups to the ortho and para positions of the pyridine.⁷

Recently, our group reported that a trimethylsilyl group could be easily incorporated as a substituent in the pyridine ring of the phenylpyridine ligand. Since the trimethylsilyl group is a minor electron-donating group, the incorporation modifies the HOMO and/or the LUMO level, as well as the 3MLCT state of the complex.⁸ Moreover, the incorporation improves the solubility, thermal stability, and steric bulk through having higher volumes that can inhibit the triplet–triplet annihilation.^{8–18}

In this research, we designed a new iridium complex using the dippy ligand combined with a trimethylsilyl group as a bulky electron donating group for OLEDs. The ancillary ligand is extended to include the perfluoropropyl-substituted triazole. We recognized that the C-linked 2-pyridyl-azoles were capable of using two adjacent nitrogen atoms to form a stable chelate interaction. Moreover, perfluoropropyl-substituted triazole has strong acidity, which is also reinforced further with the electron withdrawing $CF_2CF_2CF_3$ substituent. The perfluoropropylated triazole-based ancillary ligand has an added advantage of easy purification through sublimation when compared with picolinic acid and acetylacetone.^{18–25}

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This report provides the syntheses and characterization of two new blue Ir(III) complexes that contain the perfluoropropylatedtriazole ancillary ligand and trimethylsilyl substituted dippy ligand. Furthermore, the substituent effect of trimethylsilyl group on the para and meta orientations of the phenyl ring was also studied.

The Ir(F₂-*m*-trimethylsilyl)₂(fptp) and Ir(F₂-*p*-trimethylsilyl)₂(fptp) depicted in Scheme 1 were obtained in high yields. The ancillary ligand, 2-(3-(perfluoropropyl)-1H-1,2,4-triazole-5-yl) pyridine, was obtained *via* cyclization of the acetamidine hydrochloride and adduct of the ethyl pentafluoropanoate and hydrazine monohydrate. The μ -chloro-bridged dimer was formed through the reaction of the cyclometalated ligand precursor with IrCl₃·H₂O in a mixture of 2-ethoxyethanol and water. The new Ir complexes were obtained in the presence of sodium carbonate *via* the reaction of the μ -chloro-bridged dimer and ancillary ligand. The resulting complexes were air-stable, sublimable and sufficiently soluble for photophysical and electrochemical measurements. The Ir(F₂-*m*-trimethylsilyl)₂(fptp) and Ir(F₂-*p*-trimethylsilyl)₂(fptp) were characterized by NMR, mass spectra and elemental analysis.

A density function theory (DFT) calculation of the Ir(F₂-mtrimethylsilyl)₂(fptp), Ir(F₂-*p*-trimethylsilyl)₂(fptp) and bis(4,6difluorophenylpyridinato-N,C2)picolinatoiridium (FIrpic) was carried out in order to estimate the energy level and electron density distribution of the orbitals. The Dmol3 module installed within Materials Studio 4.2 was used for the simulation. The double numerical plus polarization (DNP) basis set and Perdew-Burke-Ernzerhof (PBE) function were chosen.²⁶ The optimized structures and the highest occupied molecular orbital/ lowest unoccupied molecular orbital (HOMO/LUMO) for the Ir(F2-mtrimethylsilyl)₂(fptp), Ir(F₂-*p*-trimethylsilyl)₂(fptp) and FIrpic are shown in Fig. 1. The HOMO orbitals of the Ir(F2-m-trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp) were mostly distributed over the main ligand, but those of the FIrpic were observed at the ancillary ligand as well as the main ligand. The HOMO levels of Ir(F₂-*m*-trimethylsilyl)₂(fptp) and Ir(F₂-*p*-trimethylsilyl)₂(fptp) were -5.33 and -5.34 eV, respectively, which are lower than that of -5.17 eV for the FIrpic. However, the LUMO orbitals of the molecules were almost identical. These



Scheme 1 Synthetic scheme of $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp).



Fig. 1 Electronic density distributions of the HOMO and LUMO orbitals of (a) $Ir(F_2-p$ -trimethylsilyl)₂(fptp), (b) $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and (c) FIrpic.

results imply that the perfluoropropyl triazole unit affects the lower HOMO level of the $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp), and it leads to a larger bandgap. Moreover, the $Ir(F_2-p$ -trimethylsilyl)₂(fptp) with the trime-thylsilyl group in the para position of the pyridine exhibited slightly lower HOMO levels than that of the $Ir(F_2-m$ -trimethylsilyl)₂(fptp) with the trimethylsilyl)₂(fptp) with the trimethylsilyl)₂(fptp) with the trimethylsilyl group in the meta position of the pyridine.

The thermal stabilities of the $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp) were studied using thermo gravimetry analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. (Fig. 2) The degradation temperature (T_d) was 350 °C for $Ir(F_2-p$ -trimethylsilyl)₂(fptp) and 333 °C for $Ir(F_2-m$ -trimethylsilyl)₂(fptp). The glass transition temperatures of the $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp) were 140 °C and 136 °C, respectively.

Fig. 3 shows the UV-vis absorption and PL spectra of the complexes in the CH₂Cl₂ solution at room temperature. The two complexes exhibited very similar absorption spectra, which suggest that the position of the trimethylsilyl group does not contribute to the absorption process. The high energy bands around 256 nm were assigned to the intraligand π - π * transition



Fig. 2 TGA and DSC thermograms of (a) Ir(F₂-*m*-trimethylsilyl)₂(fptp), (b) Ir(F₂-*p*-trimethylsilyl)₂(fptp).



Fig. 3 UV-vis absorption and PL spectra of complexes in CH_2Cl_2 solution.

of the ligand. The spin allowed ligand-centered absorptions to appear at approximately 306 nm and the spin enabled the metalto-ligand charge transfer (¹MLCT) absorptions to be clearly distinguished at approximately 365 nm. In addition, the spinforbidden triplet ³LC and/or ³MLCT transitions appeared as low-energy absorption shoulders at approximately 450 nm. Apparently, the absorption spectra of the new complexes were overall blue shifted compared with that of the FIrpic. The emission spectra of the complexes in the solution at room temperature were dominated by phosphorescence in the region of 450-500 nm with maximum values of 464 and 495 nm for the Ir(F₂-*m*-trimethylsilyl)₂(fptp), and 464 and 492 nm for the Ir(F₂p-trimethylsilyl)₂(fptp). The optical bandgaps of the Ir(F₂-mtrimethylsilyl)₂(fptp) and Ir(F₂-p-trimethylsilyl)₂(fptp) deduced from the absorption edges, were the same at 3.0 eV, which is larger than that of the FIrpic (2.9 eV). The triplet energy levels were 2.69 eV for the new iridium complexes, and 2.65 eV for FIrpic. The PL efficiencies of the iridium complexes were measured using the TCTA : 3TPYMB (1 : 1) films doped with the iridium complexes using an integrating sphere. Both the $Ir(F_2-p-trimethylsilyl)_2(fptp)$ and $Ir(F_2-m-trimethylsilyl)_2(fptp)$ exhibited very high PL quantum efficiencies of 75 \pm 5% and 76 \pm 5%, respectively, which were lower than that of the FIrpic (87 \pm 3%). The lifetimes of the excited states were determined to be 1.8 µs for Ir(F₂-*p*-trimethylsilyl)₂(fptp) and 2.1 µs for the Ir(F₂*m*-trimethylsilyl)₂(fptp), which are a little longer than FIrpic (1.4 µs) (Fig. 4).

Fig. 4 Transient PL of $Ir(F_2-m$ -trimethylsilyl)₂(fptp) and $Ir(F_2-p$ -trimethylsilyl)₂(fptp).

The HOMO levels of the complexes were measured using cyclic voltammetry (CV). Pt was used as the working and counter electrode, and an Ag/AgCl electrode was used as the reference electrode. NPB was used for the potential calibration (HOMO level of -5.4 eV) (Fig. 5).²⁴ The LUMO energy levels of the materials were estimated using the HOMO level and the UV-Vis absorption spectra. The HOMO levels of the Ir(F2-m-trimethylsilyl)₂(fptp) and Ir(F₂-*p*-trimethylsilyl)₂(fptp) were identical at -6.1 eV. This value was slightly lower than that of the FIrpic (-6.0 eV). The trend is consistent with the prediction of the DFT calculation. This result can be explained by the electron withdrawing ability of the perfluorinated triazole ancillary ligand of $Ir(F_2-m-trimethylsilyl)_2(fptp)$ and $Ir(F_2-p-trimethylsi-trimethylsilyl)_2(fptp)$ the lyl)₂(fptp). The LUMO levels of the Ir(F₂-*p*-trimethylsilyl)₂(fptp) and $Ir(F_2-m-trimethylsilyl)_2(fptp)$ were -3.1 eV, which is the same as FIrpic. In Table 1 we summarise the physical properties of $Ir(F_2-m-trimethylsilyl)_2(fptp)$, $Ir(F_2-p-trimethylsilyl)_2(fptp)$ and FIrpic.

OLEDs were fabricated using the iridium complexes as the phosphorescent emitter. The structure of the OLEDs was as follows: ITO (150 nm)/2TNATA (30 nm)/TAPC (40 nm)/TCTA : 3TPYMB (3 : 1), and iridium complex 10% (20 nm)/TCTA : 3TPYMB (1 : 3), and iridium complex 10% (20 nm)/3TPYMB (30 nm)/LiF (1 nm)/Al (100 nm) (Fig. 6). 4,4',4''-Tris(*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine (2TNATA) was used as the hole injection material. 1,1-Bis[(di-4tolylamino)phenyl]

Fig. 5 CV of (a) $Ir(F_2-m-trimethylsilyl)_2(fptp)$ and (b) $Ir(F_2-p-trimethylsilyl)_2(fptp)$.

Table 1 Basic properties of the three dopants

	PL peak (nm)	PL efficiency (%)	Exciton lifetime (µs)	T1 level (eV)	Band gap (eV)	HOMO (eV)	LUMO (eV)	HOMO ^{<i>a</i>} (eV)	LUMO ^{<i>a</i>} (eV)	<i>T</i> ^{<i>b</i>} (°C)	T_{d}^{c} (°C)
Ir(F_2 - <i>p</i> - trimethylsilyl) ₂ (fptp) Ir(F_2 - <i>m</i> - trimethylsilyl) ₂ (fptp) FIrpic	462, 491	75	1.8	2.69	3.0	-6.1	-3.1	-5.34	-2.94	140	350
	461, 493	76	2.1	2.69	3.0	-6.1	-3.1	-5.33	-2.92	136	333
	468, 494	87	1.4	2.65	2.9	-6.0	-3.1	-5.17	-2.91	192	377
^a Obtained from DFT calculation. ^b Glass transition temperature. ^c Decomposition temperature.											

Fig. 6 Structure of the device and the molecular structures of the compounds used in the device.

cyclohexane (TAPC) as the hole transport material, and tris[3-(3-pyridyl)-mesityl]borane (3TPYMB) as the electron transport material, respectively. 4,4',4''-Tris(*N*-carbazolyl)triphenylamine

Fig. 7 J-V-L characteristics and external quantum efficiency of devices.

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(TCTA) and 3TPYMB were used as a co-host of the emission layer to remove the energy barrier for charge injection from the charge transporting layers to the emission layer. TAPC, TCTA, and 3TPYMB have higher triplet and singlet levels than the iridium complexes.

Fig. 7 shows the current density-voltage-luminance (J-V-L)characteristics and external quantum efficiency of OLEDs. The device using the Ir(F₂-p-trimethylsilyl)₂(fptp) as a dopant, exhibited the maximum external quantum efficiency of 19.3%, which is slightly lower than the FIrpic based device (EQE = 23%) with the same structure. However, the emission color is much deeper blue than the FIrpic based device. The commission Internationale de l'Eclairage (CIE) coordinate of the EL was (0.145, 0.247) compared to the FIrpic based device of (0.16, (0.38)²⁷ The device using the Ir(F₂-*m*-trimethylsilyl)₂(fptp) as a dopant showed lower maximum EQE (14.2%) with a CIE coordinate of (0.151, 0.256) and it had a higher turn on voltage. Since the emitting material was the only one difference between the two devices and both emitters had the same energy level and high PL efficiency we surmised that the position of the trimethylsilyl unit affected the charge trapping and transport. The bulky trimethylsilyl unit might hinder the charge transport from the host material to the iridium complexes, and the particular position of the unit obstructs the charge flow more effectively. The devices showed high roll-off of efficiency at high current density due to instability of the devices, which is frequently observed in blue phosphorescent OLEDs (Fig. 8).

In conclusion, new blue iridium complexes with trimethylsilyl groups and perfluoropropylated triazole-based ancillary ligands were synthesized. The new Ir complexes have high photo-luminescence quantum efficiencies over 75% and blue-shifted

emission compared with FIrpic, and the OLEDs fabricated using the new Ir complexes exhibited deeper blue emission than FIrpic. In particular, $Ir(F_2-p$ -trimethylsilyl)₂(fptp) with the trimethylsilyl group in the para position exhibited the maximum EQE of 19.3% with color coordinates of (0.145, 0.247) while the $Ir(F_2-m$ -trimethylsilyl)₂(fptp) with the trimethylsilyl group in the meta position exhibited and a maximum EQE of 14.2% with a CIE index of (0.151, 0.256).

Experimental

All syntheses were performed under a dry N_2 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 of TCI and used without further purification.

Synthesis of Ir(F₂-*m*-trimethylsilyl)₂(fptp)

 $(F_2-5-Trimethylsilyl)_2Ir(\mu-Cl)Ir(F_2-5-trimethylsilyl)_2$ (0.5 g, 0.33) mmol), ancillary ligand (fptp) (0.27 g, 0.86 mmol) and Na₂CO₃ (0.35 g, 3.32 mmol) were dissolved in 2-ethoxyethanol (30 mL) and the mixture was stirred under N2 at 135 °C overnight. After it cooled to room temperature, the solvent was removed under reduced pressure to give a dark yellow oil. The crude product was purified by chromatography on silica gel (MC/hexane, 5/1, v/v) to obtain a yellow solid. Yield (0.41 g, 61%). $T_{\rm m} = 292$ °C. IR (KBr): 3021, 1609, 1112, 721. ¹H NMR (300 MHz, CDCl₃, δ): 8.38 (d, 1H), 8.23 (t, 2H), 7.93 (t, 1H), 7.80 (m, 4H), 7.33 (s, 1H), 7.28 (m, 1H), 6.52 (m, 2H), 5.77 (d, 1H), 5.68 (d, 1H), 0.14 (s, 9H), 0.05 (s, 9H) ppm. ¹³C NMR (85 MHz, CDCl₃, δ): -1.5, -1.4, 97.7, 97.9, 98.1, 98.2, 98.4, 98.6, 104.5, 114.0, 114.2, 114.0,114.2, 114.4, 114.5, 119.9, 122.3, 122.5, 122.7, 122.8, 122.9, 128.9, 133.8, 135.6, 138.5, 142.5, 142.9, 149.8, 150.4, 151.7, 154.3, 154.8, 154.9, 155.8, 160.1, 163.0, 164.8 HRMS (FAB+) m/z calcd for $C_{38}H_{32}F_{11}IrN_6Si_2$ (M⁺) 1030.07, found 1030.3.

Synthesis of Ir(F₂-*p*-trimethylsilyl)₂(fptp)

The procedure used is the same as that for the preparation of compound Ir(F₂-*m*-trimethylsilyl)₂(fptp). Yield (0.49 g, 73%). T_m = 295 °C. (KBr): 3022, 1610, 1113, 722. ¹H NMR (300 MHz, CDCl₃, δ): 8.38 (d, 3H), 7.91 (t, 1H), 7.77 (d, 1H), 7.61 (d, 1H), 7.31 (d, 1H), 7.22 (d, 1H), 7.03 (d, 1H), 6.96 (d, 1H), 6.49 (m, 2H), 5.86 (d, 1H), 5.68 (d, 1H), 0.33 (s, 18H) ppm. ¹³C NMR (85 MHz, CDCl₃, δ): -1.45, -1.41, -1.24, 97.7, 97.9, 98.1, 98.12, 98.4, 98.6, 104.7, 114.29, 114.3, 114.6, 114.8, 116.2, 116.5, 120.2, 123.1, 126.5, 127.4, 127.5, 127.6, 127.8, 128.0, 138.5, 146.7, 148.8, 149.7, 150.7, 153.0, 153.6, 154.3, 155.6, 159.7, 163.5, 164.3 HRMS (FAB⁺) *m/z* calcd for C₃₈H₃₂F₁₁IrN₆Si₂ (M⁺) 1030.07, found 1030.4.

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