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Photophysical Properties of Highly Efficient Blue-Green Emitting Cationic Iridium (III) Complexes Containing Two 2-Phenylbenzothiazole Ligands and One Diphosphine Ligand

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Two novel phosphorescent heteroleptic cationic Ir(III) complexes, Ir(bt)$_2$(dmpe) (Ir1) and Ir (bt)$_2$(dppe) (Ir2), where bt is 2-phenylbenzothiazole, dmpe is 1,2-bis(dimethylphosphino)ethane, and dppe is 1,2-bis(diphenylphosphino)ethane, were designed and synthesized. Their photophysical and electrochemical properties and the X-ray structure of the Ir1 complex were investigated. The prepared Ir(III) complexes exhibited blue-green emissions at 503-538 nm with vibronic fine structures in dichloromethane solution and PMMA film, implying that the lowest excited states are dominated by ligand-based $^3\pi$-π^* transitions. The π-acceptor ability of the diphosphine ancillary ligand leads to blue-shift emission. The room temperature photoluminescent quantum yields (PLQYs) of Ir1 and Ir2 were 52% and 45%, respectively, in dichloromethane solution. These high PLQYs resulted from steric hindrances by the bulky cationic iridium complexes. The crystal structure of Ir1 was determined by X-ray crystallography, which revealed that central iridium adopted a distorted octahedral structure coordinated with two bt ligands (N^C) and one dmpe ligand (P^P) showing *cis* C-C and *trans* N-N dispositions. The bent nature of the dmpe ligand resulted in a relatively wide bite angle of 83.83° of P-Ir-P.

Key Words : Cationic iridium complex, Blue-green phosphorescence, Phosphorescent iridium complex, Phosphorescent material, High quantum yield

Introduction

Cyclometallated Ir(III) complexes have attracted wide interest because of their unique photophysical properties and their applications as emitters in organic light-emitting diodes (OLEDs)[1] and light-emitting electrochemical cells (LECs).[2] LECs offer more advantages than multilayered OLEDs because they consist of a single light emitting layer that can be easily produced from solution. Single layered LECs do not rely on electron and hole injection layers and hence enable the use of high work function electrode materials for their fabrication. In such devices, no ion conducting material is needed since these metal complexes are intrinsically ionic. These features make LECs a more promising candidate than OLEDs for the next generation of low cost lighting and display applications.

Cyclometallated Ir(III) complexes can be divided into two classes, namely, neutral and cationic complexes. Neutral Ir(III) complexes contain cyclometallated ligands and an anionic ligand, such as an acetylacetonate anion.[3] This class of Ir(III) complexes has received extensive study due to their possible applications in highly efficient organic electroluminescence devices. Cationic Ir(III) complexes are cationic salts with counter anions that demonstrate rich photophysical properties, ionic character and good solubility in polar solvents.[4] Most of the reported cationic Ir(III) complexes were produced with focus on the tuning photophysical properties, especially of changing emission wavelengths from blue to red.[5] Unlikely neutral Ir(III) complexes, cationic Ir(III) complexes contain mobile counter ions that facilitate charge transport across films, and thus, can be used as the single active component of charged luminescent materials in LECs. However, stable phosphorescent cationic Ir(III) complexes with high quantum yields (QYs) are relatively rare and solution-processable efficient cationic Ir(III) complexes remain a challenge. Recently Ma D. *et al.*[6] described cationic Ir(III) complexes with bulky counter boracic anions and enhanced photoluminescent quantum yields (PLQYs). Furthermore, complexes with larger counter anions were found to show higher PLQYs since distances between molecules were increased and intermolecular interactions and molecular aggregation were decreased, which inhibited concentration quenching and led to substantial PLQY increases. Based on these results, we considered that bulky cationic Ir(III) complexes, like cationic Ir(III) complexes with large counter anions, could be used to increase intermolecular distances and avoid concentration quenching. In the present study, we undertook the syntheses of bulky cationic Ir(III) complexes in order to increase PLQYs. We prepared two novel cationic iridium complexes [Ir(bt)$_2$(dmpe)]Cl and [Ir(bt)$_2$(dppe)]Cl (bt = 2-phenylbenzothiazole, dmpe = 1,2-bis(dimethylphosphino)ethane and dppe = 1,2-bis(diphenylphosphino)ethane) using flexible diphosphine ligands. Here we describe the syntheses, structural, photophysical, and electrochemical properties of the prepared cationic Ir(III) complexes. We found that we were able to tune the emission in the blue-green range, presumably because of the presence of π–accepting diphosphine ancillary ligands with high PLQYs.

Experimental Section

Materials and Synthesis. All reagents and solvents were purchased from Sigma-Aldrich Chemicals or Acros Organics and used as received. $IrCl_3·3H_2O$ was purchased from Alfa Aesar. All solvents were purified and distilled prior to use.

Synthesis of [(bt)$_2$Ir(dmpe)]Cl (Ir1). The cyclometallated iridium(III) μ-chloro bridged dimer [(bt)$_2$Ir(μ-Cl)]$_2$ was prepared as described by Nonoyama with modification.[7] Briefly, $IrCl_3·3H_2O$ (0.71 g, 2 mmol) and 2-phenylbenzothiazole (1.27 g, 6 mmol) were dissolved in a mixture of 2-ethoxyethanol/water (24 mL; 3:1 v/v) and heated at 125 °C for 24 h. The reaction mixture was cooled to room temperature and the precipitate collected. The dimer product so obtained was washed with ethanol and hexane, and dried in vacuum (0.88 g, 68%). The Iridium(III) μ-chloro bridged dimer (0.25 g, 0.2 mmol) and 1,2-bis(dimethylphosphino) ethane (dmpe) (0.1 g, 0.6 mmol) were dissolved in methanol/dichloromethane (6 mL; 2:3 v/v). The mixture was refluxed for 8 h and then the solvent was removed by evaporation. The crude product was subjected to flash column chromatography (methanol:dichloromethane = 1:20) to give Ir1 as yellow solid. Yield: 78.5% (0.22 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, 1H, $J = 7.8$ Hz), 7.80 (d, 1H, $J = 7.5$ Hz), 7.70 (t, 2H, $J = 15.6$ Hz), 7.60 (d, 1H, $J = 6.9$ Hz), 7.12 (m, 3H), 1.84 (s, 6H), 1.59 (d, 2H, $J = 8.1$ Hz).

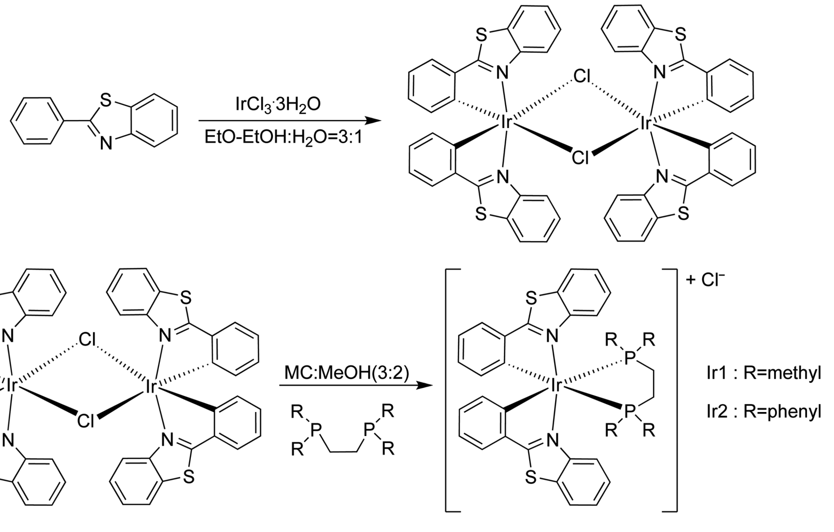
Synthesis of [(bt)$_2$Ir(dppe)]Cl (Ir2). This compound was prepared using a method identical to that used for Ir1 but using 1,2-bis(diphenylphosphino)ethane (dppe). Yield: 81.5% (0.31 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, 1H, $J = 7.8$ Hz), 7.52 (t, 3H, $J = 18.7$ Hz), 7.16 (m, 4H), 6.93 (m, 3H), 6.65 (t, 6H, $J = 15.6$ Hz), 6.30 (d, 1H, $J = 7.5$ Hz), 2.32 (s, 2H).

Characterization. ^{1}H NMR spectra were recorded on Varian Mercury 300 MHz spectrometer using $CDCl_3$ as solvent. UV-visible spectra were recorded on a Jasco V-570 spectrophotometer, and photoluminescence spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. Quantum yields were calculated using the equation $\Phi_s = \Phi_r(\eta_s{}^2A_rI_s/\eta_r{}^2A_sI_r)$ where notations have the usual meanings.[8] Cyclic voltammetry (CV) was performed using a Bioanalytical Systems CV-50W voltametric analyzer at potential scan rates of 50-100 mV s^{-1} in a 0.1 M solution of tetra(*n*-butyl)ammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous dichloromethane. An Ag/$AgNO_3$ (0.1 M) electrode was used as the reference electrode, and a Pt wire was used as the counter electrode. The working electrode was a Pt disc electrode (0.2 cm^2). Potentials are reported relative to the ferrocene/ferrocenium (Cp_2Fe/Cp_2Fe^+) redox couple as an internal reference (0.45 V *vs* SCE) in a nitrogen atmosphere.[9] Thermal analyses were carried out on a Metter Toledo TGA/SDTA 851e analyzer in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

X-ray Crystallography. X-ray intensity data were obtained using a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 174 K. Structures were solved using SHELXS-97 and refined by full-matrix least-squares calculation on F^2 using SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms ($B_{iso} = 1.2\ B_{eq}$ and $1.5\ B_{eq}$).

Results and Discussion

Synthesis and Structural Properties. Treatment of $IrCl_3·xH_2O$ with 3.0 equivalents of 2-phenylbenzothiazole (bt) in 2-ethoxyethanol/water solution gave the iridium(III) μ-chloro bridged precursor [(bt)$_2$Ir(μ-Cl)]$_2$ which was further reacted with 1,2-bis(dimethylphosphino)ethane (dmpe) or 1,2-bis(diphenylphosphino)ethane (dppe) to yield the cationic



Scheme 1. Synthetic procedure of Ir(III) complex Ir1 and Ir2.

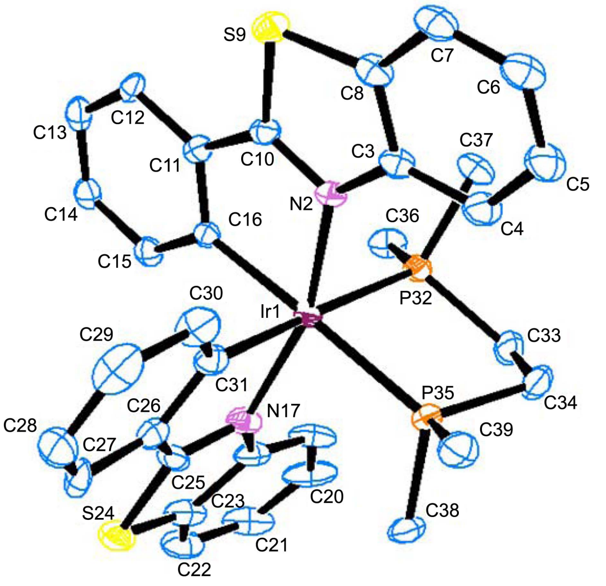


Figure 1. ORTEP drawing with an atom labeling scheme showing 20% thermal ellipsoids of Ir1.

cyclometallated iridium(III) complexes as chloride salts, that is, $[(bt)_2Ir(dmpe)]Cl$ (Ir1) or $[(bt)_2Ir(dppe)]Cl$ (Ir2) at yields of 78.5 and 81.5%, respectively. The synthetic procedure is shown in Scheme 1. The synthesized complexes, Ir1 and Ir2, are air and moisture-stable yellow solids and are soluble in polar organic solvents.

Table 1. Crystal data and structure refinement parameters for Ir1

Complex	Ir1
Chemical formula	$C_{32}H_{32}N_2P_2S_2Ir$
Formula weight (amu)	762.86
Crystal description	red
Crystal size (mm)	0.22 × 0.21 × 0.20
Crystal system	Monoclinic
Space group	*C*2/*c*
T (K)	296(2)
Wavelength (Å)	0.71073
a (A°) & α (°)	31.072(2) & 90.00
b (A°) & β (°)	14.7920(11) & 126.391(3)
c (A°) & γ (°)	18.5375(14) & 90.00
Volume (Å^3) & Z	6858.7(9) & 8
D_{calc} (Mg/m^3)	1.478
μ (mm^{-1})	4.130
θ Range(°)	1.60 to 28.29
T_{max} & T_{min}	0.610 & 0.506
Index ranges	$-41 \le h \le 19$; $-19 \le k \le 12$; $-13 \le l \le 24$
Reflections collected/unique	30829/8229 [R(int) = 0.1021]
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0655, wR2 = 0.1786
R indices (all data)	R1 = 0.0838, wR2 = 0.1872
Data/Restraints/parameters	8229/0/352
Goodness-of-fit on F^2	1.143
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	7.324 and −1.654

Table 2. Selected bond lengths (Å) and angles (°) for Ir1

Bond length [Å]		Bond angle [deg]	
Ir(1)-C(16)	2.078(8)	C(16)-Ir(1)-(31)	90.0(3)
Ir(1)-C(31)	2.110(10)	C(16)-Ir(1)-N(2)	78.5(3)
Ir(1)-N(17)	2.084(8)	N(17)-Ir(1)-N(2)	161.9(3)
Ir(1)-N(2)	2.095(6)	C(16)-Ir(1)-N(17)	88.7(3)
Ir(1)-P(35)	2.346(2)	P(35)-Ir(1)P(32)	83.83(8)
Ir(1)-P(32)	2.352(2)	C(31)-Ir(1)-P(32)	174.6(3)
		N(2)-Ir(1)-P(35)	105.8(2)

A single crystal of Ir1 was obtained from a chloroform/n-hexane solution. The structure of Ir1 was determined by X-ray diffraction. Figure 1 shows the ORTEP view of the Ir1 complex. Table 1 presents X-ray crystallographic data, and Table 2 selected bond lengths and bond angles. As depicted in Figure 1, the iridium(III) center in Ir1 adopts a distorted octahedral coordination geometry containing *cis* C-C and *trans* N-N atoms, which concurs with those reported for cationic iridium(III)[11] and neutral iridium(III) complexes.[12] However, Ir-N distances were longer than the values (2.03-2.05 Å) reported for Ir(III) complexes,[13] whereas Ir-P distances in Ir1 (2.346-2.352 Å) were shorter than those reported for other iridium(III)-phosphine complexes (2.420-2.432 Å).[14] This shorter Ir-P bond indicates greater bond strength. The strong bond is expected to destabilize the ligand field d-d excited state and reduce its interference to the radiative process from the lower lying exited state. This could explain why the Ir1 complex is an efficient phosphor with high quantum yields.[15]

Photophysical Characterization. The UV-vis absorption spectra of Ir1 and Ir2 in dichloromethane solution (~10^{-5} M) at 298 K are shown in Figure 2. The resulted data are summarized in Table 3. The Ir1 and Ir2 complexes displayed strong absorption bands between 250-300 nm, which were attributed to the spin-allowed ligand-centered (LC) $^1\pi$-π^* transition.[16] In addition, weaker absorption tails were observed at wavelengths longer than 360 nm and assigned to an admixture of ^{1}MLCT (metal-to-ligand charge transfer) and ^{3}MLCT and ligand-based $^3\pi$-π^* states.[17] The admixture of a

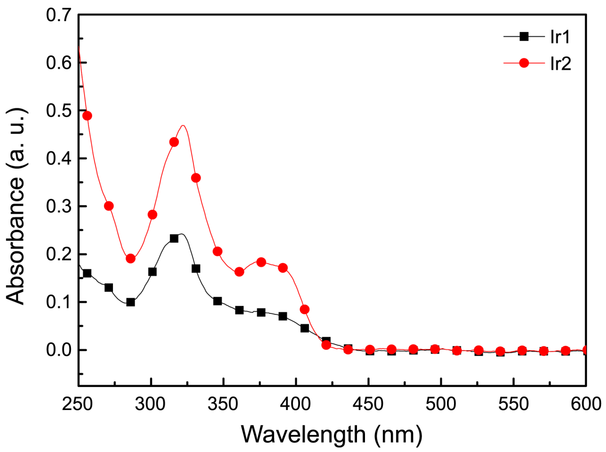


Figure 2. Absorption spectra of Ir1 and Ir2 in solution (1.0×10^{-5} M in CH_2Cl_2).

Table 3. Photophysical and thermal properties for Ir1 and Ir2

Complexes	Absorption λ (nm)[a] (ε, × 10^3 $M^{-1}cm^{-1}$)	Emission λ_{max} (nm) 298 K[a]	Emission λ_{max} (nm) Film[b]	Φ[c] (%)	T_d[d] (°C)	Remarks
$(bt)_2Ir(dmpe)$(Ir1)	262(0.13), 297(0.12), 319(0.16), 347(0.09), 384(0.05), 410(0.03)	503, 536	508, 538	52	301	This work
$(bt)_2Ir(dppe)$(Ir2)	259(0.36), 301(0.21), 322(0.36), 340(0.14), 378(0.13), 397(0.11)	503, 538	506, 541	45	338	This work
$(bt)_2Ir(acac)$	269, 313, 327, 408, 447, 493, 540	557		26		Ref. (21)
$(bt)_2Ir(pic)$	206, 326, 355, 388, 437, 475	541		37		Ref. (21)
$(bt)_2Ir(acac)$	314, 327, 403, 442	557				Ref. (22)
$(bt)_2Ir(acac)$		570, 610				Ref. (23)

[a]All data were measured in CH_2Cl_2 solution (concentration = 1 × 10^{-5} M). [b]Film was doped in PMMA with 5 wt % of Ir(III) complex. [c]$Ir(tpy)_3$ (0.40) was used as an external reference. [d]T_d was decomposition temperature.

high-lying ^{1}MLCT state with ^{3}MLCT and $^3\pi$-π^* states is induced by the heavy iridium atom and by the presence of closely-spaced π-π* and MLCT states.[18] Moreover, the low-energy absorption bands of Ir1 (384 and 410 nm) were red-shifted versus those of Ir2 (378 and 397 nm) due to the presence of an electron donating methyl group on the ancillary ligand in Ir1, resulting in the weaker π-accepting ability of dmpe compared to that of dppe.

Figure 3 shows the photoluminescence (PL) spectra of the Ir1 and Ir2 in solution (~10^{-5} M in dichloromethane) and in film. The film PL spectra were obtained from using poly-(methylmethacrylate) (PMMA) films doped with iridium complexes (wt. 5%). PL spectra in solution and film clearly showed vibronic fine structures and two well resolved peaks. For example, Ir1 exhibited emissions at 503 and 536 nm in solution with similar intensities, implying that its lowest excited states are dominated by ligand-based $^3\pi$-π^* transitions.[19] Film PL spectra resembled those of solutions except for a small red-shift (2-8 nm), which was probably caused by greater intermolecular interactions due to smaller distances between molecules in films.[20]

Table 3 lists the PL results of Ir1 and Ir2 complexes and of reported analogs containing the same main ligand (bt) but different ancillary ligands, and thus, provides an overview of the emission wavelengths of cyclometallated iridium complexes. Ir1 and Ir2 complexes emitted blue-green phosphorescence, which was 54-67 nm blue-shifted emission versus those of $(bt)_2Ir(acac)$ and $(bt)_2Ir(pic)$ which are neutral cyclometallated iridium(III) complexes containing bt main ligand. This result suggests that the diphosphine ancillary ligand has the ability to tune the emission colour of cationic iridium complexes to the blue. We believe this could be because the π-accepting character of the diphosphine ancillary ligand increases associated MLCT energy levels and thereby causes a blue-shift.[24] The room temperature quantum yields (QY) of the Ir1 and Ir2 complexes were 52 and 45%, respectively. Wu C. *et al.*[25] reported the photophysical properties of cationic Ir(III) complexes with soft anions and found QY values were sensitive to ligand size and counter ion nature, and found that greater steric hindrances increased QYs by increasing distance between iridium complexes. Moreover, soft salts, such as PF_6^{-1} salts, have higher QYs than halide salts because larger anion sizes increase intermolecular distances. Although Ir1 and Ir2 complexes were produced as chloride salts, they exhibited PLQYs of up to 52% and 45%, respectively. These high QY values could be due to the prevention of phosphor deactivation by the inhibition of energy transfer between complexes by strong Ir-P bonds and the steric effects of the bulky bt and diphosphine ligands. The dmpe ligand in Ir1 caused a relatively wide P-Ir-P bite angle. The bite angle of the biphosphine ligand in Ir1 was 83.83° (Table 2), which is larger than those reported for cationic complexes containing a biimine ligand (75-78°)[5a,b] or neutral Ir(III) complexes containing a pyridyltetrazole ligand (75-77°).[26]

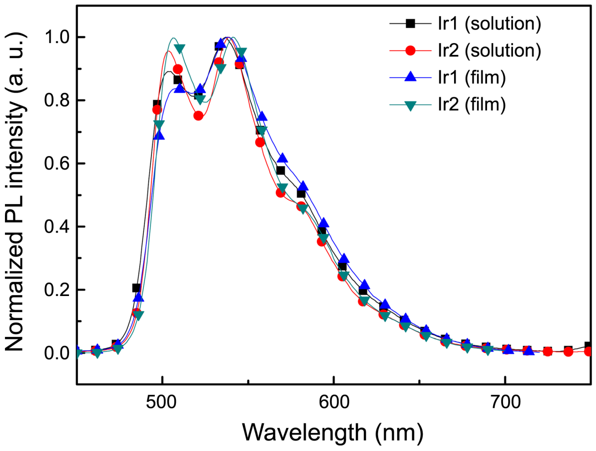


Figure 3. Photoluminescence spectra of Ir1 and Ir2 in solution (1 × 10^{-5} M in CH_2Cl_2) and 5 wt % doped in PMMA film excited at 380 nm.

Electrochemical and Thermal Properties. Electrochemical behaviours were examined in dichloromethane solution by cyclic voltammetry (CV). The data obtained relative to the ferrocenium/ferrocene redox couple are shown in Table 4. Ir1 and Ir2 showed irreversible oxidation potentials at 1.28 and 1.26 V, respectively. The oxidation potentials are believed to be due to the iridium cationic site and a contribution from the cyclometallated phenyl fragment.[27] HOMO energy levels were calculated using the equation, $E_{HOMO} = -e(E_{ox,onset} + 4.4)(eV)$ where $E_{ox,onset}$ is the

Table 4. Electrochemical properties for Ir1 and Ir2

Complex	$E_{ox}{}^{a}$ (V)	HOMO^{b} (eV)	LUMO^{c} (eV)	ΔE^{c} (eV)
Ir1	1.28	−5.58	−2.93	2.65
Ir2	1.26	−5.56	−2.91	2.65

^{a}Data measured in CH_2Cl_2 solution containing 1×10^{-3} M Ir(III) complexes. ^{b}Potential values were reported *vs.* Fc/Fc^{+}. $^{c}\Delta E$ collected by UV-Vis spectrophotometer.

onset oxidation potential. LUMO levels were calculated from HOMO levels and optical band gap (E_g) values using $E_{LUMO} = E_{HOMO} + E_g$. Optical band gaps were obtained using $E_g = 1240/\lambda_{edge}$, where λ_{edge} is the absorption spectrum onset value.[28]

The thermal stabilities of Ir1 and Ir2 were examined by thermogravimetric analysis (TGA). Decomposition temperatures in a nitrogen atmosphere at the 5% weight loss were 301 °C and 338 °C for Ir1 and Ir2, respectively (Table 3), which are sufficiently high for electronic applications.

Conclusions

We synthesized two novel blue-green emitting cationic iridium(III) complexes, that is, $[(bt)_2Ir(dmpe)]Cl$ (Ir1) and $[(bt)_2Ir(dppe)]Cl$ (Ir2), and analyzed their photophysical properties to determine their potential suitabilities as phosphors in LEC and OLED devices. The incorporation of a diphosphine ancillary ligand (dmpe or dppe) led to a blue-shift in emission, which is presumed to be due to the π-acceptor ability of the diphosphine ancillary ligand. The Ir1 and Ir2 complexes produced were found to be thermo-stable and soluble in organic solvents, and to have photoluminescence quantum yields (PLQYs) of over 45% in dichloromethane solution. These high PLQYs are believed to be due to steric hindrance by bulky bt and bent diphosphine ligands. Our results show the synthesized cationic iridium(III) complexes have high PLQYs and desirable photophysical properties, and thus, that they have potential use in high efficiency solution-processed electroluminescent devices.

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References

1. (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley D. D. C.; Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* (London) **1999**, *397*, 121. (c) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585. (d) Tseng, R. J.; Chiechi, R. C.; Wudl, F.; Yang, Y. *Appl. Phys. Lett.* **2006**, *88*, 093512. (e) Fan, C.; Miao, J.; Jiang, B.; Yang, C.; Wu, H.; Qin, J.; Cao, Y. *Org. Elect.* **2013**, *14*, 3392. (f) Wang, L.; Wu, Y.; Shan, G.-G.; Geng, Y.; Zhang, J.-Z.; Wang, D.-M.; Yang, G.-C.; Su, Z.-M. *J. Mater. Chem. C* **2014**, *2*, 2859. (g) Teng, M.-Y.; Zhang, S.; Jin, W.-M.; Li, T.-Y.; Liu, X.; Xu, Q.-L.; Lin, C.; Zheng, Y.-X.; Wang, L.; Zuo, J.-L. *Dyes and Pigments* **2014**, *105*, 105.
2. (a) Lee, J. K.; Yoo, D. S.; Handy, E. S.; Rubner, M. F. *Appl. Phys. Lett.* **1996**, *69*, 1686. (b) Sinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J. J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763. (c) Bolink, H. J.; Cappelli, L.; Cheylan, S.; Coronado, E.; Costa, R. D.; Lardie, N.; Nazeeruddin, M. K.; Orti, E. *J. Mater. Chem.* **2007**, *17*, 2976. (d) Rudmann, H.; Rubner, M. F. *J. Appl. Phys.* **2011**, *90*, 4338. (e) Sunesh, C. D.; Mathai, G.; Cho, Y.-R.; Choe, Y. *Polyhedron* **2013**, *57*, 77. (f) Zhang, J.; Zhou, L.; Al-Attar, H. A.; Shao, K.; Wang, L.; Zhu, D.; Su, Z.; Bryce, M. R.; Monkman, A. P. *Adv. Funct. Mater.* **2013**, *23*, 4667. (g) Sunesh, C. D.; Mathai, G.; Choe, Y. *Org. Elect.* **2014**, *15*, 667.
3. (a) You, Y.; Soo, Y. P. *J. Am. Chem. Soc.* **2005**, *127*, 12438. (b) Dedeian, K.; Shi, J.; Shepherd, N.; Forsythe, E.; Morton, D. C. *Inorg. Chem.* **2005**, *44*, 4445. (c) Kappaun, S.; Sax, S.; Eder, S.; Möller, K. C.; Waich, K.; Niedermair, F.; Saf, R.; Mereiter, K.; Jacob, J.; Müllen, K.; List, E. J. W.; Slugovc, C. *Chem. Mater.* **2007**, *19*, 1209. (d) Seo, H.-J.; Yoo, K.-M.; Song, M.; Park, J. S.; Jin, S.-H.; Kim, Y. I.; Kim, J.-J. *Org. Elect.* **2010**, *11*, 564. (e) Fan, C.; Zhu, L.; Jiang, B.; Zhong, C.; Ma, D.; Qin, J.; Yang, C. *Org. Elect.* **2013**, *14*, 3163. (f) Cao, H.; Sun, H.; Yin, X.; Shan, G.; Su, Z.; Zhong, R.; Xie, W.; Li, P.; Zhu, D. *J. Mater. Chem. C* **2014**, *2*, 2150.
4. (a) Wong, W.-Y.; Zhou, G.-J.; Yu, X.-M.; Kwok, H.-S.; Lin, Z. *Adv. Funct. Mater.* **2007**, *17*, 315. (b) Angelis, F. D.; Fantacci, S.; Evans, N.; Klein, C.; Zakeeruddin, S. M.; Moser, J.-E.; Kalyanasundaram, K.; Bolink, H. J.; Gra1tzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* **2007**, *46*, 5989. (c) Geiß, B.; Lambert, C. *Chem. Commun.* **2009**, 1670.
5. (a) Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 8723. (b) Zhao, Q.; Liu, S.; Shi, M.; Wang, C.; Yu, M.; Li, L.; Li, F.; Yi, T.; Huang, C. *Inorg. Chem.* **2006**, *45*, 6152. (c) Auffrant, A.; Barbieri, A.; Barigelletti, F.; Lacour, J.; Mobian, P.; Collin, J.-P.; Sauvage, J.-P.; Ventura, B. *Inorg. Chem.* **2007**, *46*, 6911. (d) Yun, S.-J.; Seo, H.-J.; Song, M.; Jin, S.-H.; Kim, Y. I. *Bull. Korean Chem. Soc.* **2012**, *33*, 3645.
6. Ma, D.; Duan, L.; Wei, Y.; He, L.; Wang, L.; Qiu, Y. *Chem. Commun.* **2014**, 530.
7. Nonoyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767.
8. Joshi, H. S.; Jamshidi, R.; Tor, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 2722.
9. Fang, K.-H.; Wu, L.-L.; Huang, Y.-T.; Yang, C.-H.; Sun, I.-W. *Inorganica Chimica Acta* **2006**, *359*, 441.
10. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
11. (a) Cao, H.-T.; Shan, G.-G.; Zhang, B.; Li, P.; Sun, S.-L.; Su, Z.-M. *J. Mol. Struct.* **2012**, *1026*, 59. (b) Hu, T.; Duan, L.; Qiao, J.; He, L.; Zhang, D.; Wang, R.; Wang, L.; Qui, Y. *Org. Elect.* **2012**, *13*, 1948. (c) Shavaleev, N. M.; Scopelliti, R.; Grätzel, M.; Nazeeruddin, M. K. *Inorg. Chim. Acta* **2013**, *396*, 17.
12. Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304.
13. (a) Song, Y.-H.; Yeh, S.-J.; Chen, C.-T.; Chi, Y.; Liu, C.-S.; Yu, J.-K.; Hu, Y.-H.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Adv. Funct. Mater.* **2004**, *14*, 1221. (b) Huang, Y.-T.; Chuang, T.-H.; Shu, Y.-L.; Kuo, Y.-C.; Wu, P.-L.; Yang, C.-H.; Sun, I.-W. *Organimetallics* **2005**, *24*, 6230.
14. Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, R. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713.
15. (a) Lin, C.-H.; Chang, Y.-Y.; Hung, J.-Y.; Lin, C.-Y.; Chi, Y.; Chung, M.-W.; Lin, C.-L.; Chou, P.-T.; Lee, G.-H.; Chang, C.-H.; Lin, W.-C. *Angew. Chem. Int. Ed.* **2011**, *50*, 3182. (b) Luo, S.-X.; Wei, L.; Zhang, X.-H.; Lim, M. H.; Lin, K. X. V.; Yeo, M. H. V.; Zhang, W.-H.; Liu, Z.-P.; Young, D. J.; Hor, T. S. A. *Organometallics* **2013**, *32*, 2908.
16. (a) Lo, S. C.; Shipley, C. P.; Bera, R. N.; Harding, R. E.; Cowley, A. R.; Burn, P. L.; Samuel, I. D. W. *Chem. Mater.* **2006**, *18*, 5119.

(b) Ho, C. L.; Wong, W. Y.; Zhou, G. J.; Xie, Z.; Wang, L. *Adv. Funct. Mater*. **2007**, *17*, 2925.

17. (a) Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem*. **1991**, *95*, 629. (b) Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem*. **1991**, *95*, 629. (c) Columbo, M. C.; Hauser, A.; Güdel, H. U. *Top. Curr. Chem*. **1994**, *171*, 143.
18. (a) Garces, F. O.; King, K. A.; Watts, R. *J. Inorg. Chem*. **1998**, *27*, 3464. (b) Wang, Y.; Herron, N.; Grushin, V. V.; LeCloux, D.; Petrov, V. *Appl. Phys. Lett*. **2001**, *79*, 449.
19. Seo, H.-J.; Heo, Y.-M.; Jin, S.-H.; Yook, K. S.; Lee, J. Y.; Kang, S. K.; Kim, Y.-I. *J. Luminescence* **2010**, *130*, 1694.
20. Tang, H.; Li, Y.; Zhao, B.; Yang, W.; Wu, H.; Cao, Y. *Org. Elect*. **2012**, *13*, 3211.
21. Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem*. **2001**, *40*, 1704.
22. Chang, W.-C.; Hu, A. T.; Duan, J.-P.; Rayabarapu, D. K.; Cheng, C.-H. *J. Organomet. Chem*. **2004**, *689*, 4882.
23. Cole, J. M.; Bowes, K. F.; Clark, I. P.; Low, K. S.; Zeidler, A.; Parker, A. W.; Laskar, I. R.; Chen, T.-M. *Cryst. Growth. Des*. **2013**, *13*, 1826.
24. Ma, A.-F.; Seo, H.-J.; Jin, S.-H.; Yoon, U. C.; Hyun, M. H.; Kang, S. K.; Kim, Y.-I. *Bull. Korean Chem. Soc*. **2009**, *30*, 2754.
25. Wu, C.; Chen, H.-F.; Wong, K.-T.; Thompson, M. E. *J. Am. Chem. Soc*. **2010**, *132*, 3133.
26. (a) Hwang, F.-M.; Chen, H.-Y.; Chen, P.-S.; Liu, C.-S.; Chi, Y.; Shu, C.-F.; Wu, F.-I.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem*. **2005**, *44*, 1344. (b) Wu, L.-L.; Yang, C.-H.; Sun, I.-W.; Chu, S.-Y.; Kao, P.-C.; Huang, H.-H. *Organimetallics* **2007**, *26*, 2017.
27. Sengottuvelan, N.; Yun, S.-J.; Kim, D.-Y.; Hwang, I.-H.; Kang, S. K.; Kim, Y.-I. *Bull. Korean Chem. Soc*. **2013**, *34*, 167.
28. Du, B.; Wang, L.; Wu, H.; Yang, W.; Zhang, Y.; Lin, R.; Sun, M.; Peng, J.; Cao, Y. *Chem. Eur. J*. **2007**, *13*, 7432.