

# Synthesis, structures, and properties of iridium(III) bis-cyclometallated complexes containing three-atom chelates

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Received 23 September 2007; received in revised form 4 December 2007; accepted 4 December 2007

Available online 15 December 2007

Dedicated to the memory of the late Professor F. Albert Cotton

## Abstract

Heating of  $[\text{Ir}(\eta^2\text{-ppy})_2(\text{MeCN})_2]\text{NO}_3$  (**1**, ppy = 2-phenylpyridine) in MeCN under reflux afforded  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-NO}_3)]$  (**2**). Treatment of **1** with 2-mercaptopyridine (Hmp), 6-methyl-2-hydroxypyridine (Hmhp), 6-chloro-2-hydroxypyridine (Hchp), trimethylacetic acid (Htma), benzoic acid (Hbz), 2-methylacrylic acid (Hma), and acetic acid (Hac) in the presence of excess  $\text{Et}_3\text{N}$  produced  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-XZY})]$  ( $\text{XZY}^- = \text{mp}^-$  (**3**),  $\text{mhp}^-$  (**4**),  $\text{chp}^-$  (**5**),  $\text{ac}^-$  (**6**),  $\text{bz}^-$  (**7**),  $\text{ma}^-$  (**8**),  $\text{tma}^-$  (**9**)). Crystal structures of **2**, **3**, **7**, **8**, and **9** have been characterized by X-ray diffraction. The inherent strain contained in the four-member rings,  $\{\text{Ir}(\eta^2\text{-XZY})\}$ , is apparently reflected in the long Ir–X and Ir–Y distances. The absorption and emission properties of nearly all the new complexes except **2** show small variations. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Iridium(III); Cyclometallated complexes; Chelate

## 1. Introduction

Recently, luminescent cyclometallated  $d^6$  transition metal complexes have been shown to exhibit an enormous potential for a range of photonic applications. In particular, organic light emitting devices (OLEDs) [1] based on the triplet emitters such as Ir(III) [2], Ru(II) [2c,2d,3], and Os(II) [2c,2d,4] as the organic dopants have been demonstrated with high efficiency. While extensive works have been done on a series of bis-cyclometallated Ir(III) complexes with 4- or 5-atom chelates [5,6],  $[(\eta^2\text{-}(\text{C}^{\wedge}\text{N})_2)\text{Ir}(\eta^2\text{-chelate})]$ , the isoelectronic Ir(III) analogues with 3-atom chelates ( $\text{XZY}^-$ ) have received relatively less attention [7]. Note the contrasting feature whereby all the 4- and 5-atom

chelates used in the complexes are hard (N, N), (N, O), and (O, O) donors, whereas all the reported 3-atom chelates are soft (S, S) and (Se, Se) ligands. This feature is understandable in terms of the inherent, much higher, strain contained in four-member rings (i.e.,  $\{\text{Ir}(\eta^2\text{-XZY})\}$ ), relative to those in five- or six-member rings, if all rings contain hard (N, N), (N, O), and (O, O) chelates [8]. Hence, the reported four-member examples containing only softer (S, S) and (Se, Se) chelates (ligands, Lewis bases) and soft 5d transition-metal atom (Lewis acid) are obviously stabilized in terms of the soft-base–soft-acid interaction according to the Pearson HSAB (hard and soft acids and bases) theory [9]. In this paper, however, we wish to report on the facile syntheses and crystal structures of bis-cyclometallated Ir(III) complexes with 3-atom (N, O), (N, S), and (O, O) chelates. Both photophysical and electrochemical properties of these apparently thermally stable complexes are also described.

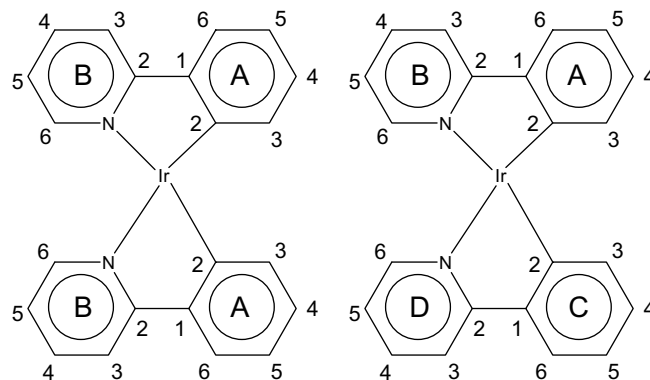
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## 2. Experimental

### 2.1. General information

All operations were carried out under prepurified  $N_2$  by means of standard Schlenk and vacuum-line techniques. Solvents were purified by standard procedures and distilled prior to use. All organic reagents, including 2-mercapto-pyridine (Hmp), 6-methyl-2-hydroxypyridine (Hmhp), 6-chloro-2-hydroxypyridine (Hchp), 1,1,1-trimethylacetic acid (Htma), benzoic acid (Hbz), 2-methylacrylic acid (Hma), and acetic acid (Hac) were purchased from Aldrich and used without further purification. The bis-cyclometalated iridium precursor complex,  $[Ir(\eta^2\text{-ppy})_2(\text{MeCN})_2]\text{-NO}_3$  (**1**, ppy = 2-phenylpyridine), was synthesized by the method reported by Watts et al. [10]. Two different atom labeling schemes for assignment of  $^1\text{H}$  NMR spectral signals for ppy are shown below for complexes with the presence or absence of a molecular  $C_2$  axis.  $^1\text{H}$  NMR spectra were acquired on a Bruker AVANCE 300 (300 MHz) spectrometer using the deuterated solvent as the lock and the residual solvent as the internal reference. IR spectra were recorded on a Perkin–Elmer Spectrum-One or Bruker TENSOR 27 FT-IR spectrophotometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Heraeus CHN-OS rapid elemental analyzer by the staff of the Instrument Center, National Cheng Kung University. The ESI–MS spectra of the iridium complexes dissolved in MeCN, mixed with some drops of aqueous  $\text{NH}_3$ , were measured on a Micromass Quattro Ultima mass spectrometer by the staff of the Instrument Center, National Chung Cheng University. UV–vis spectra were recorded with a Hewlett Packard 8453 instrument at room temperature using 1-cm path length quartz cell. Cyclic voltammetry (CV) was carried out in nitrogen-purged anhydrous  $10^{-3}$  M dichloromethane solution at room temperature with a CHI 600a voltammetric analyzer. Tetramethylammonium tetrafluoroborate ( $\text{TBABF}_4$ ) (0.1 M) was used as a supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an  $\text{Ag}/\text{AgNO}_3$  (MeCN) reference electrode with ferrocenium/ferrocene ( $\text{Fc}^{+/0}$ ) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV/s. Photoluminescence (PL) spectra were performed on Hitachi F-4500 luminescence spectrophotometer. Excited-state lifetimes were measured by a home-constructed time-resolved Laser spectrometer. The instrument consists a Quanta Ray GCR-170, pulsed Nd:YAG Laser, and used the third harmonic (355 nm, FWHM = 10 ns) as an excitation source. Emission signals were focused into an ARC SpectraPro-500 monochromator. The monochromator output was sent into a PMT (Hamamatsu, R928). The signal was then further amplified by a home made fast amplifier before being sent into a digitizer (LeCory 9350A). Decay traces were transferred to a personal computer loaded with the commercial software Origin 3.5. All experimental data

were fitted by a single exponential decay. Analytical TLC was carried out using Merck glass-backed 0.2 mm silica gel 60 F254 plates. Flash column chromatography was conducted using Merck silica gel 60 (230–400 mesh).



### 2.2. $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-NO}_3)]$ (**2**)

A solution of **1** (0.0505 g, 0.078 mmol) in MeCN (25 ml) was refluxed for 3 h. The solvent was then pumped off. Recrystallization from  $\text{CH}_2\text{Cl}_2$  at room temperature afforded the yellow product. Yield: 37 mg (84%). Anal. Calc. for  $\text{C}_{22}\text{H}_{16}\text{IrN}_3\text{O}_3$ : C, 46.97; H, 2.87; N, 7.47. Found: C, 46.87; H, 3.87; N, 8.34%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.80 (d, 2H,  $J = 5.8$  Hz,  $\text{H}^{6\text{B}}$ ), 7.96 (br, 4H,  $\text{H}^{3\text{B}}$  and  $\text{H}^{4\text{B}}$ ), 7.60 (d, 2H,  $J = 7.8$  Hz,  $\text{H}^{6\text{A}}$ ), 7.37 (br, 2H,  $\text{H}^{5\text{B}}$ ), 6.91 (d,  $\text{H}^{5\text{A}}$ ), 6.72 (br, 2H,  $\text{H}^{4\text{A}}$ ), 6.12 (d, 2H,  $J = 7.6$  Hz,  $\text{H}^{3\text{A}}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 1549 ( $\nu(\text{N}=\text{O})$ ), 1284 ( $\nu_a(\text{NO}_2)$ ), 1010 ( $\nu_s(\text{NO}_2)$ ).

### 2.3. $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-chelate})]$ (*chelate* $^- = \text{mp}^-$ (**3**), *mhp* $^-$ (**4**), *chp* $^-$ (**5**))

To a solution of **1** (ca. 0.16 mmol) in MeCN (15 ml) was added Hmp, Hmhp, or Hchp (ca. 0.4 mmol) and  $\text{Et}_3\text{N}$  (ca. 0.5 ml) stirred at room temperature for 30 min. The resulting solution was then heated under reflux overnight (ca. 8 h). The solvent was pumped off to produce the crude product. The crude product was further purified with a flash column chromatography and eluted with  $\text{CH}_2\text{Cl}_2$ . A clear yellow band was then collected and evaporated to dryness, affording the yellow crystalline product.

**3**. Yield: 79 mg (81%). Anal. Calc. for  $\text{C}_{27}\text{H}_{20}\text{IrN}_3\text{S}$ : C, 53.10; H, 3.30; N, 6.88. Found: C, 53.27; H, 3.35; N, 6.86%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.86 (d, 1H,  $J = 5.4$  Hz,  $\text{H}^{6\text{B}}$  or  $\text{H}^{6\text{D}}$ ), 8.03 (d, 1H,  $J = 5.7$  Hz,  $\text{H}^{6\text{D}}$  or  $\text{H}^{6\text{B}}$ ), 7.94 (m, 2H,  $\text{H}^{4\text{B}}$  and  $\text{H}^{4\text{D}}$ ), 7.79 (m, 2H,  $\text{H}^{3\text{B}}$  and  $\text{H}^{3\text{D}}$ ), 7.65 (m, 2H, mp), 7.20 (m, 2H,  $\text{H}^{6\text{A}}$  and  $\text{H}^{6\text{C}}$ ), 7.16 (t, 1H,  $J = 7.2$  Hz,  $\text{H}^{5\text{B}}$  or  $\text{H}^{5\text{D}}$ ), 7.12 (t, 1H,  $J = 7.1$  Hz,  $\text{H}^{5\text{D}}$  or  $\text{H}^{5\text{B}}$ ), 6.95 (t, 1H,  $J = 7.4$  Hz,  $\text{H}^{5\text{A}}$  or  $\text{H}^{5\text{C}}$ ), 6.79 (m, 4H with 2H from mp, 1H as  $\text{H}^{5\text{C}}$  or  $\text{H}^{5\text{A}}$ , and 1H as  $\text{H}^{4\text{A}}$  or  $\text{H}^{4\text{C}}$ ), 6.66 (t, 1H,  $J = 7.5$  Hz,  $\text{H}^{4\text{C}}$  or  $\text{H}^{4\text{A}}$ ), 6.35 (d, 1H,  $J = 7.3$  Hz,  $\text{H}^{3\text{A}}$  or  $\text{H}^{3\text{C}}$ ), 6.33 (d, 1H,  $J = 7.4$  Hz,  $\text{H}^{3\text{C}}$  or  $\text{H}^{3\text{A}}$ ). ESI–MS:  $m/z$  612 ( $(\text{M}+1)^+$ ).

4. Yield: 73 mg (75%). Anal. Calc. for  $C_{28}H_{22}IrN_3O$ : C, 55.25; H, 3.64; N, 6.90. Found: C, 55.27; H, 3.83; N, 6.82%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  8.97 (d, 1H,  $J = 5.7$  Hz,  $H^{6B}$  or  $H^{6D}$ ), 8.28 (d, 1H,  $J = 5.6$  Hz,  $H^{6D}$  or  $H^{6B}$ ), 7.94 (m, 2H,  $H^{4B}$  and  $H^{4D}$ ), 7.81 (m, 2H,  $H^{3B}$  and  $H^{3D}$ ), 7.63 (m, 2H,  $H^{6A}$  and  $H^{6C}$ ), 7.30 (t, 1H,  $J = 7.9$  Hz,  $H^{5A}$  or  $H^{5C}$ ), 7.24 (t, 1H,  $J = 6.2$  Hz,  $H^{5B}$  or  $H^{5D}$ ), 7.17 (t, 1H,  $J = 6.2$  Hz,  $H^{5D}$  or  $H^{5B}$ ), 6.89 (t, 1H,  $J = 7.5$  Hz, mhp), 6.87 (m, 2H,  $H^{5C}$  or  $H^{5A}$ ), 6.71 (m, 2H,  $H^{4A}$  and  $H^{4C}$ ), 6.29 (d, 1H,  $J = 7.5$  Hz, mhp), 6.21 (d, 1H,  $J = 7.1$  Hz,  $H^{3A}$  or  $H^{3C}$ ), 6.14 (d, 1H,  $J = 7.5$  Hz, mhp), 6.06 (d, 1H,  $J = 8.6$  Hz,  $H^{3C}$  or  $H^{3A}$ ), 2.14 (s, 3H, mhp). ESI-MS:  $m/z$  609 ( $M^+$ ).

5. Yield: 65 mg (43%). Anal. Calc. for  $C_{27}H_{19}ClIrN_3O$ : C, 51.55; H, 3.04; N, 6.68. Found: C, 55.27; H, 3.83; N, 6.82%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  8.90 (d, 1H,  $J = 5.6$  Hz,  $H^{6B}$  or  $H^{6D}$ ), 8.42 (d, 1H,  $J = 7.3$  Hz,  $H^{6D}$  or  $H^{6B}$ ), 7.95 (m, 2H,  $H^{4B}$  and  $H^{4D}$ ), 7.85 (m, 2H,  $H^{3B}$  and  $H^{3D}$ ), 7.62 (m, 2H,  $H^{6A}$  and  $H^{6C}$ ), 7.33 (t, 1H,  $J = 7.7$  Hz, chp), 7.22 (m, 2H,  $H^{5B}$  and  $H^{5D}$ ), 6.88 (m, 2H,  $H^{5A}$  and  $H^{5C}$ ), 6.72 (m, 2H,  $H^{4A}$  and  $H^{4C}$ ), 6.42 (d, 1H,  $J = 7.5$  Hz, chp), 6.27 (d, 1H,  $J = 7.8$  Hz,  $H^{3C}$  or  $H^{3A}$ ), 6.20 (d, 1H,  $J = 8.6$  Hz, chp), 6.13 (d, 1H,  $J = 7.6$  Hz,  $H^{3C}$  or  $H^{3A}$ ). ESI-MS:  $m/z$  629 ( $M^+$ ).

2.4.  $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-chelate})]$  (*chelate*<sup>−</sup> = *ac*<sup>−</sup> (**6**), *bz*<sup>−</sup> (**7**), *ma*<sup>−</sup> (**8**), *tma*<sup>−</sup> (**9**))

These complexes were prepared similarly as for the Ir analogues but using toluene as the solvent in place of MeCN.

6. Yield: 30 mg (34%). Anal. Calc. for  $C_{24}H_{19}IrN_2O_2$ : C, 51.51; H, 3.42; N, 5.01. Found: C, 51.69; H, 3.32; N, 5.06%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  8.84 (d, 2H,  $J = 4.8$  Hz,  $H^{6B}$ ), 7.93 (d, 2H,  $J = 8.0$  Hz,  $H^{3B}$ ), 7.86 (t, 2H,  $J = 7.7$  Hz,  $H^{4B}$ ), 7.57 (d, 2H,  $J = 7.6$  Hz,  $H^{6A}$ ), 7.33 (t, 2H,  $J = 6.3$  Hz,  $H^{5B}$ ), 6.83 (t, 2H,  $J = 7.1$  Hz,  $H^{5A}$ ), 6.64 (t, 2H,  $J = 7.3$  Hz,  $H^{4A}$ ), 6.07 (d, 2H,  $J = 7.5$  Hz,  $H^{3A}$ ), 1.98 (s, 3H,  $CH_3$ ). IR (KBr,  $cm^{-1}$ ): 1524 ( $\nu_a$  ( $COO^-$ )), 1411 ( $\nu_s$  ( $COO^-$ )).

7. Yield: 81 mg (80%). Anal. Calc. for  $C_{29}H_{21}IrN_2O_2$ : C, 56.02; H, 3.40; N, 4.51. Found: C, 56.32; H, 3.45; N, 4.53%.  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  8.87 (d, 2H,  $J = 5.4$  Hz,  $H^{6B}$ ), 8.04 (d, 2H,  $J = 7.4$  Hz, Ph), 7.96 (d, 2H,  $J = 8.0$  Hz,  $H^{3B}$ ), 7.85 (t, 2H,  $J = 7.8$  Hz,  $H^{4B}$ ), 7.62 (d, 2H,  $J = 7.6$  Hz,  $H^{6A}$ ), 7.53 (m, 1H, Ph), 7.43 (t, 2H,  $J = 7.4$  Hz, Ph), 7.27 (t, 2H,  $J = 6.3$  Hz,  $H^{5B}$ ), 6.88 (t, 2H,  $J = 7.3$  Hz,  $H^{5A}$ ), 6.70 (t, 2H,  $J = 7.3$  Hz,  $H^{4A}$ ), 6.14 (d, 2H,  $J = 7.6$  Hz,  $H^{3A}$ ). IR (KBr,  $cm^{-1}$ ): 1508 ( $\nu_a$  ( $COO^-$ )), 1414 ( $\nu_s$  ( $COO^-$ )).

8. Yield: 67 mg (71%). Anal. Calc. for  $C_{26}H_{21}IrN_2O_2$ : C, 53.32; H, 3.61; N, 4.78. Found: C, 53.34; H, 3.66; N, 4.72%.  $^1H$  NMR ( $CD_2Cl_2$ ):  $\delta$  8.79 (d, 2H,  $J = 4.7$  Hz,  $H^{6B}$ ), 7.93 (d, 2H,  $J = 7.5$  Hz,  $H^{3B}$ ), 7.85 (t, 2H,  $J = 7.1$  Hz,  $H^{4B}$ ), 7.58 (d, 2H,  $J = 7.3$  Hz,  $H^{6A}$ ), 7.31 (t, 2H,  $J = 4.9$  Hz,  $H^{5B}$ ), 6.84 (br, 2H,  $J = 7.4$  Hz,  $H^{5A}$ ), 6.81 (br, 1H,  $CH_2$ ), 6.65 (t, 2H,  $J = 7.2$  Hz,  $H^{4A}$ ), 6.08 (d, 2H,  $J = 7.7$  Hz,

$H^{3A}$ ), 6.00 (br, 1H,  $CH_2$ ), 1.89 (s, 3H,  $CH_3$ ). IR (KBr,  $cm^{-1}$ ): 1501 ( $\nu_a$  ( $COO^-$ )), 1413 ( $\nu_s$  ( $COO^-$ )). ESI-MS:  $m/z$  628 ( $(M+42)^+$ ).

9. Yield: 56 mg (58%). Anal. Calc. for  $C_{27}H_{25}IrN_2O_2$ : C, 53.89; H, 4.19; N, 4.66. Found: C, 53.85; H, 4.35; N, 4.63%.  $^1H$  NMR (300 MHz,  $CD_2Cl_2$ ):  $\delta$  8.78 (d, 2H,  $J = 5.7$  Hz,  $H^{6B}$ ), 7.96 (d, 2H,  $J = 7.9$  Hz,  $H^{3B}$ ), 7.88 (t, 2H,  $J = 7.7$  Hz,  $H^{4B}$ ), 7.60 (d, 2H,  $J = 7.7$  Hz,  $H^{6A}$ ), 7.34 (t, 2H,  $J = 6.5$  Hz,  $H^{5B}$ ), 6.85 (t, 2H,  $J = 7.6$  Hz,  $H^{5A}$ ), 6.67 (t, 2H,  $J = 7.6$  Hz,  $H^{4A}$ ), 6.11 (d, 2H,  $J = 7.7$  Hz,  $H^{3A}$ ), 1.18 (s, 9H,  $(CH_3)_3C$ ). IR (KBr,  $cm^{-1}$ ): 1509 ( $\nu_a$  ( $COO^-$ )), 1413 ( $\nu_s$  ( $COO^-$ )).

## 2.5. X-ray crystallography

All single crystals of **2**, **3**, **7**, **8**, and **9** were grown from  $CH_2Cl_2$ /hexane at ambient temperature. The single crystals of **7** were found in rod or block forms, designated as **7a** and **7b**, respectively. All crystals were also found suitable for X-ray analysis after they were mounted on a Nonius Kappa or a Bruker SMART APEX II CCD diffractometer, each with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The  $\theta$  range for data collection is 1.52–27.50° for **2**, 1.73–27.50° for **3**, 2.22–27.50° for **7a**, 2.33–27.50° for **7b**, 2.71–28.76° for **8**, and 2.00–28.72° for **9**. Of the 17572, 19386, 8444, 11721, 13157, and 23362 reflections collected for **2**, **3**, **7a**, **7b**, **8**, and **9**, 4249, 5061, 2567, 2618, 2679, and 5871 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structures were solved by the direct method and refined by least-squares cycles. All the non-hydrogen atoms were refined anisotropically. Almost all hydrogen atoms were either found from difference maps or geometrically located. All calculations were performed using SHELXTL-97 [11]. A crystallographic  $C_2$  axis is imposed in compounds **7a**, **7b**, and **8** through the Ir atom and the C12–C13 bond. In **8**, two equivalent C14 atomic positions were found, each with a 0.5 occupancy of  $CH_2$  (i.e., H14D–C14–H14E) and  $CH_3$  (i.e., C14(H14A)(H14B)–(H14C)). The other essential details of single-crystal data measurement and refinement are given in Table 1, and selected distances and angles are listed in Tables 2 and 3. Since both structures of **7a** and **7b** are similar, only the ORTEP of **7a** was shown. Thus, the perspective views for compounds **2**, **3**, **7a**, **8**, and **9** were shown in Figs. 1–5, respectively.

## 3. Results and discussion

### 3.1. Cyclometallated complexes containing (*O*, *O*), (*N*, *O*), and (*N*, *S*) donor ligands

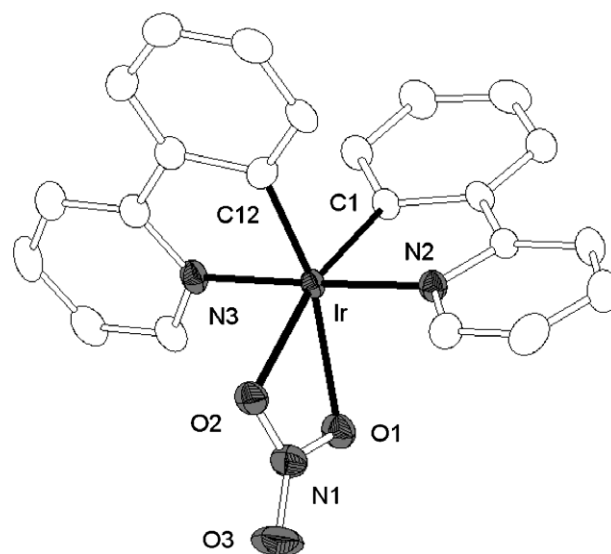
Treatment of mononuclear  $[Ir(\eta^2\text{-ppy})_2(\text{MeCN})_2]NO_3$  (**1**) with suitable chelating anions produced substituted complexes **2–9**. Apparently, the nitrate anion in **1** can serve as a chelate, enabling to replace two lightly ligated MeCN molecules in MeCN to form  $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-NO}_3)]$  (**2**). The

Table 1  
Crystallographic data

	<b>2</b>	<b>3</b>	<b>7a</b>	<b>7b</b>	<b>8</b>	<b>9</b>
Chem. formula	C <sub>22</sub> H <sub>16</sub> IrN <sub>3</sub> O <sub>3</sub>	C <sub>27</sub> H <sub>20</sub> IrN <sub>3</sub> S	C <sub>29</sub> H <sub>21</sub> IrN <sub>2</sub> O <sub>2</sub>	C <sub>29</sub> H <sub>21</sub> IrN <sub>2</sub> O <sub>2</sub>	C <sub>26</sub> H <sub>21</sub> IrN <sub>2</sub> O <sub>2</sub>	C <sub>27</sub> H <sub>25</sub> IrN <sub>2</sub> O <sub>2</sub>
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
FW	562.58	610.72	621.68	621.68	585.65	601.69
<i>T</i> , K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>	<i>C2/c</i>	<i>Pben</i>	<i>Aba2</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	30.0232(4)	9.7746(10)	14.6149(11)	12.4189(9)	12.5384(4)	10.7434(3)
<i>b</i> , Å	9.4160(1)	9.5295(9)	12.0898(9)	12.2054(9)	15.0371(5)	23.1210(6)
<i>c</i> , Å	14.6786(2)	23.659(2)	13.0841(10)	14.9516(11)	11.1258(4)	9.6655(3)
$\alpha$ , °	90	90.00	90.00	90.00	90.00	90.00
$\beta$ , °	116.4784(8)	93.981(2)	104.772(2)	90.00	90.00	108.8210(10)
$\gamma$ , °	90	90.00	90.00	90.00	90.00	90.00
<i>V</i> , Å <sup>3</sup>	3714.33(8)	2198.4(4)	2235.4(3)	2281.3(3)	2097.67(12)	2272.52(11)
<i>Z</i>	8	4	4	4	4	4
<i>D</i> <sub>calc.</sub> g cm <sup>-3</sup>	2.012	1.845	1.847	1.810	1.854	1.759
$\mu$ , mm <sup>-1</sup>	7.219	6.189	6.003	5.883	6.391	5.902
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.0409/0.1072	0.0373/0.0750	0.0209/0.0480	0.0214/0.0458	0.0296/0.0714	0.0276/0.0883
GOF on <i>F</i> <sup>2</sup>	1.068	1.147	1.037	1.035	1.067	0.746

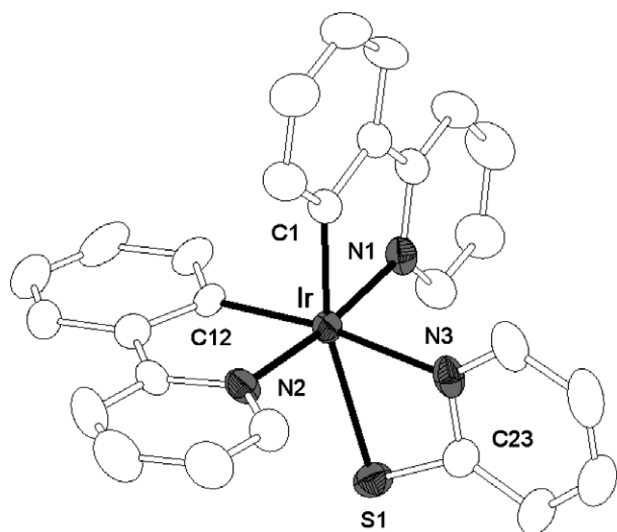
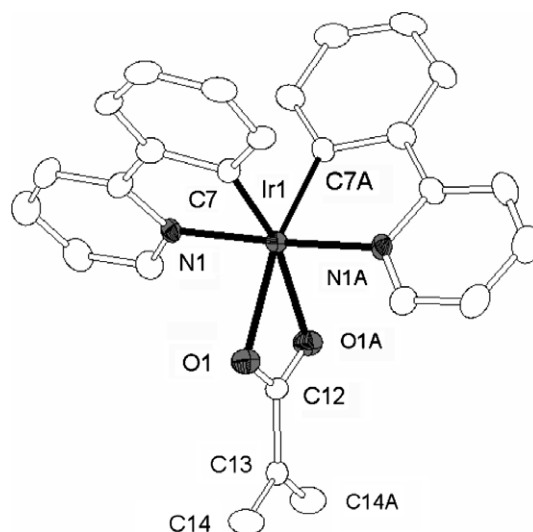
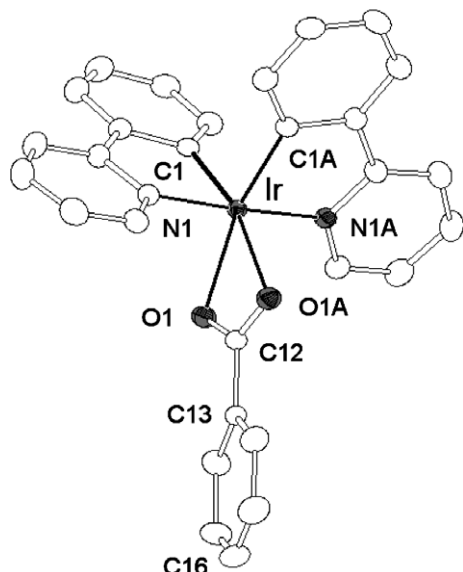
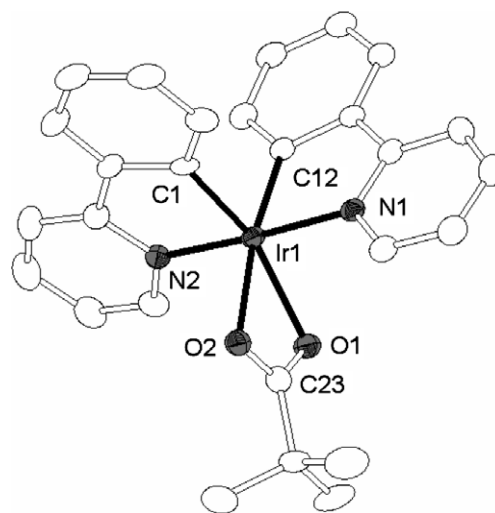
Table 2  
Selected bond lengths (Å) and bond angles (°) for **2**, **7a**, **7b**, **8**, and **9**

	<b>2</b>	<b>7a</b>	<b>7b</b>	<b>8</b>	<b>9</b>
<i>Bond lengths</i>					
Ir–O	2.254(3) 2.227(3)	2.240(2)	2.239(2)	2.237(4)	2.283(2) 2.216(2)
Ir–N	2.037(3) 2.040(4)	2.028(2)	2.028(2)	2.038(4)	2.050(3) 2.021(3)
Ir–C	1.985(4) 1.986(6)	1.983(3)	1.980(3)	1.983(5)	1.992(3) 1.994(3)
<i>Bond angles</i>					
O(1)–Ir–O(2)	57.5(1)	58.54(8)	58.75(7)	59.1(1)	58.15(8)
N(1)–Ir–N(2)	177.8(1)	177.2(1)	177.5(1)	176.7(1)	174.8(1)
C(1)–Ir–C(2)	87.6(2)	88.8(1)	87.7(1)	86.3(2)	85.2(1)
C–Ir–N	80.4(2) 81.3(1)	80.9(1)	80.9(1)	81.0(2)	80.6(1) 80.6(1)
C–Ir–N'	97.5(2) 97.7(2)	97.1(1)	97.3(1)	96.5(2)	97.3(1) 94.3(1)

Fig. 1. Perspective view of [Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-NO<sub>3</sub>)] (**2**).Table 3  
Selected bond lengths (Å) and bond angles (°) for **3**

	<b>3 (X=N, S)</b>
<i>Bond lengths</i>	
Ir–X	N, 2.127(4) S, 2.509(1)
Ir–N	2.044(4) 2.035(4)
Ir–C	2.007(5) 1.997(5)
<i>Bond angles</i>	
X–Ir–X'	66.3(1)
N(1)–Ir–N(2)	173.1(2)
C(1)–Ir–C(2)	90.2(2)
C–Ir–N	80.8(2) 80.9(2)
C–Ir–N'	94.5(2) 94.0(2)

conversion from complex **1** to **2** can be monitored by means of the related spectral data. Following the conversion, a typical IR N–O stretching band around 831 cm<sup>-1</sup>, assigned for the free nitrate anion in **1**, disappeared gradually and three new bands of 1549 (*v*(N=O)), 1284 (*v<sub>a</sub>*(NO<sub>2</sub>)), 1010 (*v<sub>s</sub>*(NO<sub>2</sub>)), assigned for the chelating nitrate, grew [12]. The two ligated MeCN signals also faded away in the respective <sup>1</sup>H NMR spectra. Truly, the structure was later confirmed by X-ray crystallography, as described below. A striking difference in solubility between complexes **1** and **2** in an organic solvent is also observed. Complex **1** is insoluble in CH<sub>2</sub>Cl<sub>2</sub>. Upon formation of η<sup>2</sup>-NO<sub>3</sub>, complex **2** becomes very soluble in this solvent. As expected, treatment of **1** with the apparently stronger chelates of mp<sup>-</sup>, mhp<sup>-</sup> and chp<sup>-</sup> in MeCN resulted in ready substitution of two MeCN ligands and formation

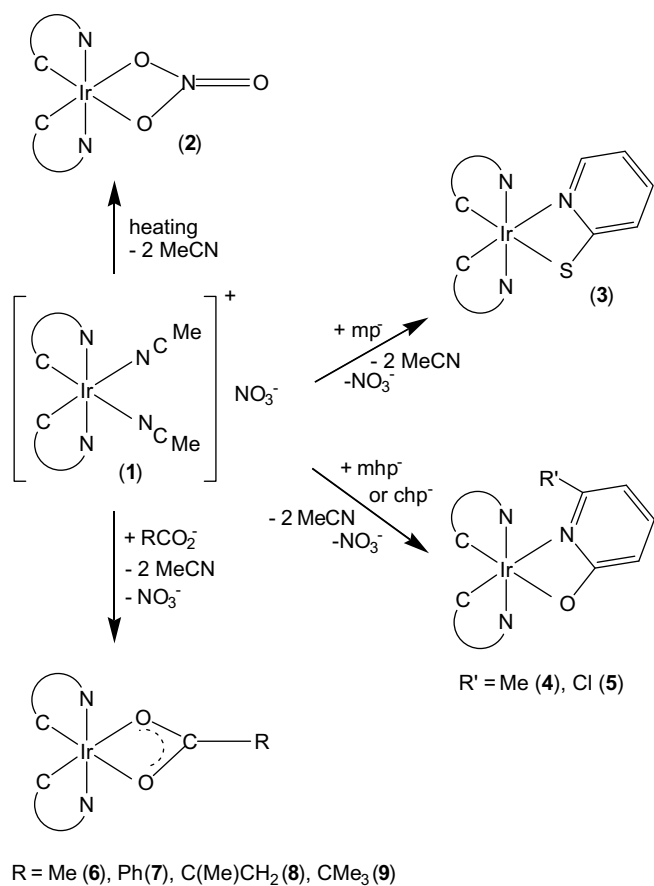
Fig. 2. Perspective view of  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-mp})]$  (**3**).Fig. 4. Perspective view of  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-ma})]$  (**8**).Fig. 3. Perspective view of  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-bz})]$  (**7**).Fig. 5. Perspective view of  $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-tma})]$  (**9**).

of complexes **3–5**. It was soon found that the easy conversion can also be performed in toluene to produce complexes **6–9**. Scheme 1 summarizes the new reactions of complex **1** with (O, O), (N, O), and (N, S) chelates. All the new products have been fully characterized by spectroscopic methods and elemental analyses. The assignments of the  $^1\text{H}$  NMR signals for the coordinated ppy ligands of the new complexes, **6**, **8**, and **9**, are straightforward, for they contain a symmetrical axis of  $C_2$  and no extra aromatic substituents in their chelates [7,8]. However, the much complicated signals, displayed by complexes, **3–5**, and **7**, can be assigned with aids from COSY experiments.

The solid-state structures of **2**, **3**, **7**, **8**, and **9** have been unambiguously established by X-ray crystallography and shown in Figs. 1–5, respectively. To the best of our knowl-

edge, **7–9** are the first reported structures containing  $\{\text{Ir}(\eta^2\text{-carboxylato})\}$  in the literature, although the chosen single crystal of **9** was of lower quality as reflected in the poorer agreement factor (Table 1). Selected bond lengths and angles for complexes with (O, O) chelates, **2**, **7a**, **7b**, **8**, and **9** are compiled in Table 2 and those for the (N, S) chelate are compiled separately in Table 3 for comparison.

The geometry around Ir in each of the complexes is distorted octahedral with two mutually *trans* pyridyl groups and the  $\eta^2\text{-XYZ}$  being opposite to the phenyl rings. The average Ir–C (1.986 Å for **2**, 2.002 Å for **3**, 1.983 Å for **7a**, 1.980 Å for **7b**, 1.983 Å for **8**, and 1.993 Å for **9**) and Ir–N(ppy) (2.039 Å for **2**, 2.040 Å for **3**, 2.028 Å for **7a**, 2.028 Å for **7b**, 2.038 Å for **8**, and 2.036 Å for **9**) are normal by comparison with other Ir(III) bis-ppy complexes [5h,6a,6l,6m,6n]. The average Ir–O distances (2.241 Å for



Scheme 1.

**2**, 2.240 Å for **7a**, 2.239 Å for **7b**, 2.237 Å for **8**, and 2.283 Å for **9** are significantly longer than those of 2.194 Å in [Ir<sub>2</sub>(η<sup>2</sup>-ppy)<sub>4</sub>(μ:η<sup>2</sup>,η<sup>2</sup>-ox)] (**10**) [5h], 2.146 Å in [Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-acac)] (**11**) [6a], 2.169 Å in [Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-pmo)] (**12**) [6l], and 2.146 Å in [Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-mao)] (**13**) [6n], where ox<sup>-</sup> is oxalato; acac<sup>-</sup> is acetylacetonato; pmo<sup>-</sup> is 1-phenyl-3-methyl-4-isobutryl-1H-pyrazol-5-olato; and mao<sup>-</sup> is 3-methylpentane-2,4-dionato. Quite obviously, the longer distances between Ir and the donor atoms in our complexes

with 3-atom XYZ chelates, compared with those in either complex **10** with a 4-atom chelate or complexes **11–13** with 5-atom chelates, do reflect the much higher ring strain.

### 3.2. Photophysical study

The absorption and photoluminescence data of all the iridium(III) complexes in CH<sub>2</sub>Cl<sub>2</sub> solutions are summarized in Table 4. Three typical photoluminescence spectra of **3**, **4**, and **6** are depicted in Fig. 6. The strong absorption bands in the ultraviolet region at about 250–280 nm with distinct vibronic features are assigned to the spin-allowed intraligand <sup>1</sup>π–π\* transitions. The next lower energy in the shoulder region of <sup>1</sup>π–π\* transitions at about 280–350 nm can be ascribed to the typical spin-allowed metal-to-ligand charge-transfer (<sup>1</sup>MLCT) transition, while typical extinction coefficients at peak wavelengths are in the range 4500–5200 M<sup>-1</sup> cm<sup>-1</sup> [13]. The weak shoulders extending into the visible region at 350–500 nm are believed to be associated with both spin-orbit coupling enhanced <sup>3</sup>π–π\* and <sup>3</sup>MLCT (spin-forbidden metal-to-ligand charge-transfer) transitions, and typical extinction coefficients at peak wavelengths are in the range 4200–4800 M<sup>-1</sup> cm<sup>-1</sup>.

Highly intensive green luminescence was observed for our new iridium complexes in CH<sub>2</sub>Cl<sub>2</sub> with λ<sub>max</sub> at 505–523 nm and acetone with λ<sub>max</sub> at 518–524 nm. It appears that complex **2** is unique, showing λ<sub>max</sub> at 505 nm in CH<sub>2</sub>Cl<sub>2</sub> and a 11-nm hypsochromic shift from that found for [Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-acac)] (**11**) (λ<sub>max</sub> = 516 nm [6a]), whereas all other complexes, **3–9**, show λ<sub>max</sub> > 516 nm and a small (2–7 nm) bathochromic shift. Since complex **2** emits light with λ<sub>max</sub> at 520 nm in acetone, a large solvent effect is also observed. However, unfortunately as indicated by the low quantum yield as 0.0001 (Table 4), the intensity of the emission band from **2** is the lowest among the eight complexes studied (cf. Fig. 6). Following the shortest excited-state lifetime of less than 10 ns for **2**, compared with those of 113–253 ns for other complexes (Table 4), it appears that the excited state of **2** is quenched more easily.

Table 4  
λ<sub>max</sub> of UV–vis and photoluminescence data of iridium(III) complexes

Complex	Absorbance <sup>a</sup>	Emission		
	λ <sub>max</sub> /nm (ε) <sup>b</sup>	λ <sub>max</sub> /nm	Φ <sub>degassed</sub> <sup>d</sup>	τ/ns <sup>a</sup>
<b>2</b>	254(233.0), 394(88.8), 423(79.0)	505 <sup>a</sup> (520) <sup>c</sup>	0.0001	<10
<b>3</b>	264(40.4), 370(5.2), 449(2.3), 485(0.8)	521 (524)	0.0029	165
<b>4</b>	261(45.3), 367(3.7), 398(2.5), 458(1.6)	520 (521)	0.0365	116
<b>5</b>	260(42.7), 372(2.6), 398(1.8), 452(1.3)	518 (518)	0.0058	223
<b>6</b>	262(62.5), 397(6.2), 454(4.9)	518 (521)	0.2338	253
<b>7</b>	262(62.1), 423(6.2)	522 (520)	0.1031	113
<b>8</b>	263(34.3), 400(3.35), 460(2.82)	521 (520)	0.1984	118
<b>9</b>	264(32.0), 365(3.4), 398(2.3), 485(1.8)	523 (519)	0.1335	253

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution (concentration = 10<sup>-5</sup> M).

<sup>b</sup> The unit of ε is 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>.

<sup>c</sup> In acetone solution.

<sup>d</sup> The quantum yields (Φ) in degassed CH<sub>2</sub>Cl<sub>2</sub> solution were measured at 298 K with *mer*-[Ir(η<sup>2</sup>-ppy)<sub>2</sub>(η<sup>2</sup>-acac)] (Φ = 0.34) as a standard.

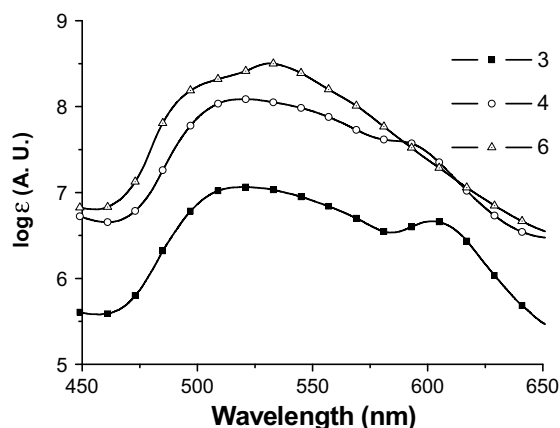


Fig. 6. Emission spectra of **3**, **4**, and **6** in  $\text{CH}_2\text{Cl}_2$  at room temperature.

As revealed previously by electrochemistry and theoretical calculations of related cyclometallated Ir(III) complexes [51,6a,14,15], the influence of ancillary ligands of bis-cyclometallated iridium complexes is on the HOMO energy level. Quite obviously, the chelates (such as  $\eta^2$ -nitrate) at stronger ligand field strength than acac may lower the HOMO energy levels and the corresponding complexes show a blue shift, whereas those (such as mp, mhp, chp, or carboxylate) at weaker ligand field strength than acac may raise the energy levels and the complexes show a red shift.

### 3.3. Electrochemical study

The electrochemical behavior of all new iridium(III) complexes in  $\text{CH}_2\text{Cl}_2$  was performed. Complexes **2**, **3**, **6**, and **8** undergo an irreversible oxidation with  $E_p^a = 746$ , 425, 607, and 588 mV, respectively, whereas the other complexes display a quasi-reversible oxidation (Table 5). The features can be attributed into the instability of the oxidized species. No reduction processes were observed within the solvent cathodic potential limit. The energy level of the HOMO was calculated by following the published procedure [16], while that of the LUMO was evaluated from the long-wavelength absorption edge using the theory reported [17]. As shown in Table 5, the summarized

Table 5  
Electrochemical data, HOMO, LUMO, and energy gap of iridium(III) complexes

Complex	$E_{1/2}^{\text{ox}}$ (mV) <sup>a</sup>	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>c</sup>	Energy gap (eV)
<b>4</b>	411	-5.2	-2.9	2.3
<b>5</b>	476	-5.4	-3.1	2.3
<b>7</b>	451	-5.4	-3.1	2.3
<b>9</b>	440	-5.3	-3.0	2.3

<sup>a</sup>  $E_{1/2}^{\text{ox}} = 1/2(E_p^a + E_p^c)$  (vs.  $\text{Ag}/\text{Ag}^+$ ), referenced against ferrocene/ferrocenium as internal standard.

<sup>b</sup> Data were collected in  $\text{CH}_2\text{Cl}_2$  solution containing 0.001 M iridium(III) complexes by cyclic voltammograms.

<sup>c</sup> LUMO = HOMO + energy gap.

HOMO, LUMO, and energy gap data of complexes **4**, **5**, **7**, and **9** are very close to each other, except the redox potentials. This feature is apparently supportive to the previous theoretical results that the ancillary ligands only influence the HOMO energy levels [51,6a,14,15]. Further, the  $E_{1/2}$  data of iridium(III) complexes **5** and **7** exhibit higher values (451–476 mV) than others (411–440 mV). This fact implies that despite the similar energy gap of these complexes, the different substitute groups at different sites on the chelate ligands have a significant effect on their molecular orbital energy. When an electron-donating group such as Me to replace Cl of chp, and <sup>t</sup>Bu to replace Ph of bz, the  $E_{1/2}$  shifts negatively to 411 mV for **4** from that of 476 mV for **5**, and 440 mV for **9** from that of 451 mV for **7**.

## 4. Conclusion

This work reports detailed synthesis, structures, and electrochemical and photophysical properties of eight green-emitting iridium(III) metal complexes **2–9** containing bis-cyclometallated ppy ligands and an  $\eta^2$ -chelate in (O, O), (N, O), or (N, S) donor (Scheme 1). Each of the iridium complexes is endowed with a four-membered chelate ring,  $\{\text{Ir}(\eta^2\text{-chelate})\}$ . The physical properties of the complexes support the theoretical results that the ancillary ligands only influence the HOMO energy levels, reported previously [51,6a,14]. However, the absorption and emission properties of nearly all the new complexes except **2** show small variations (Table 4). It is demonstrated in the article that a nitrate can serve as an  $\eta^2$ -chelate (cf. **2** in Fig. 1). This complex is unique, emitting light at  $\lambda_{\text{max}} = 505$  nm, but suffering the low quantum yield and the instability of the oxidized intermediate species in  $\text{CH}_2\text{Cl}_2$ . Like **1**, the complexes containing (N, O) or (N, S) chelate also suffer the low quantum yields, but the complexes of carboxylates are different, showing high quantum yields (0.103–0.234) (Table 4). Based on the electrochemical behavior (cf. Table 5), it appears that either an aryl group (e.g., Ph) or a sterically bulky group (e.g., <sup>t</sup>Bu) on a carboxylate moiety,  $\{-\text{CO}_2^-\}$ , can stabilize or protect the oxidized intermediate species so that both **7** and **9** exhibit a quasi-reversible oxidation whereas both **6** and **8** undergo an irreversible oxidation. Further OLED-related fabrication using some of the complexes reported here is in progress.

## 5. Supporting information available

Crystallographic data for complexes **2**, **3**, **7a**, **7b**, **8**, and **9** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 658877, 658878, and 658880–658883, respectively, in CIF format. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Acknowledgements

The work has been supported financially by the National Science Council of the Republic of China, Project NSC 95-2113-M-006-012-MY3. We are also grateful to Professor I-Jy Chang and her group for measuring the life-time of the iridium complexes, reported herein.

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