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Synthesis, characterization and photophysical properties of two heteroleptic 2-(4,6-difluorophenyl)pyridyl iridium(III) complexes with amidate ancillary ligands

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ABSTRACT

Two novel iridium(III) complexes containing 2-(4,6-difluorophenyl)pyridyl cyclometalating ligand and amidate ancillary ligands were synthesized and characterized by NMR and X-ray crystallographic methods. Photophysical properties including UV–vis absorption and photoluminescence spectra were studied, indicating that the electronic properties of the amidate ancillary ligand exhibit a significant effect on the emitting excited states of these iridium(III) amidate complexes and thus lead to different emission colors.

In recent years, iridium(III) complexes containing cyclometalating ligands have been studied intensively as promising candidates for phosphorescent emitters in OLEDs [1–8]. These complexes have been shown to exhibit high quantum efficiencies due to strong spin-orbital coupling of iridium center, which leads to mixing of singlet and triplet excited states and subsequent harvesting of “spin-forbidden” triplet states for photon emission [1–3]. Generally, there are two major kinds of iridium(III) emitters: homoleptic $Ir(C^\wedge N)_3$[9–12] and heteroleptic $(C^\wedge N)_2Ir(LX)$ [13–19] complexes (C^N denotes a cyclometalating ligand, such as 2-phenylpyridine etc.; LX denotes a monoanionic ancillary ligand such as acetylacetonate and picolinate etc.). Homoleptic Ir(III) complexes, with three identical cyclometalating ligands, have been shown to possess high photoluminescent efficiencies and their internal efficiencies can reach 100% in principle. In heteroletpic Ir(III) emitters, usually two main cyclometalating ligands, associated with an ancillary ligand, cooperatively coordinate to an iridium center. The efficiency and color of the Ir(III) emitters can be readily tuned by the variation of electronic and/or steric properties of cyclometalating ligands as well as ancillary ligands, resulting in a broad range of readily tunable emission color bands.

The commonly used ancillary ligands include acetylacetonate, picolinate, *N*-methylsalicyliminyl, triazolate and others [20–23]. As a result of our continuing effort, we have shown that amides are able to bind to iridium center via κ^2 mode and thus form a four-membered metallocycle. Consequently, a number of photoluminescent Ir(III) complexes with several amidate ancillary ligands have been synthesized and characterized, and have been demonstrated to exhibit high photoluminescent efficiencies and quite wide color bands [24,25]. On the other hand, iridium complexes containing 2-(4,6-difluorophenyl) pyridyl (dfppy) cyclometalating ligand have been shown to exhibit distinct photopysical properties from classical iridium phenylpyridyl complexes due to the involvement of small, strongly electronegative fluorine atoms that can effectively alter the energy level of the HOMO and LUMO orbitals of the complexes [26–30]. In line with these studies, we report herein the synthesis, characterization and photophysical properties of two unprecedented iridium(III) complexes containing 2-(4,6-difluorophenyl)pyridine as cyclometalating ligand and amides as the ancillary ligand (Scheme 1, complexes **2** and **3**). These complexes have shown good photoluminescence. The substituent effect of amide on photophysical properties was recognized.

Cyclometalating ligand dfppy was synthesized by using Suzuki coupling reaction (Scheme 1a). Dichloro-bridged complex **1** $[(dfppy)_2IrCl]_2$ was obtained by reaction of dfppy ligand with $IrCl_3$ according to a general procedure (Scheme 1b) [31]. Into a Schlenk tube containing complex **1**, amide ligand and sodium methanolate were added CH_2Cl_2 solvent under dinitrogen atmosphere (Scheme 1c). The mixture was stirred at room temperature for 48 h. After work-up, column chromatography, and recrystallization, yellow crystals **2** and **3** were obtained.

These two complexes have been fully characterized by ^1H, ^{13}C and ^{19}F NMR methods, and X-ray crystallography where possible. Chemical shifts and splittings of signals in ^1H, ^{13}C and ^{19}F NMR for complexes **2** and **3** are consistent with the formation of the $[dfppy]_2Ir$ (amidate) complexes. For instance, for complex **2** ^1H chemical shifts in the aromatic range and splitting patterns are consistent with relevant Ir(III) 2-(4,6-difluorophenyl)pyridyl complexes previously reported

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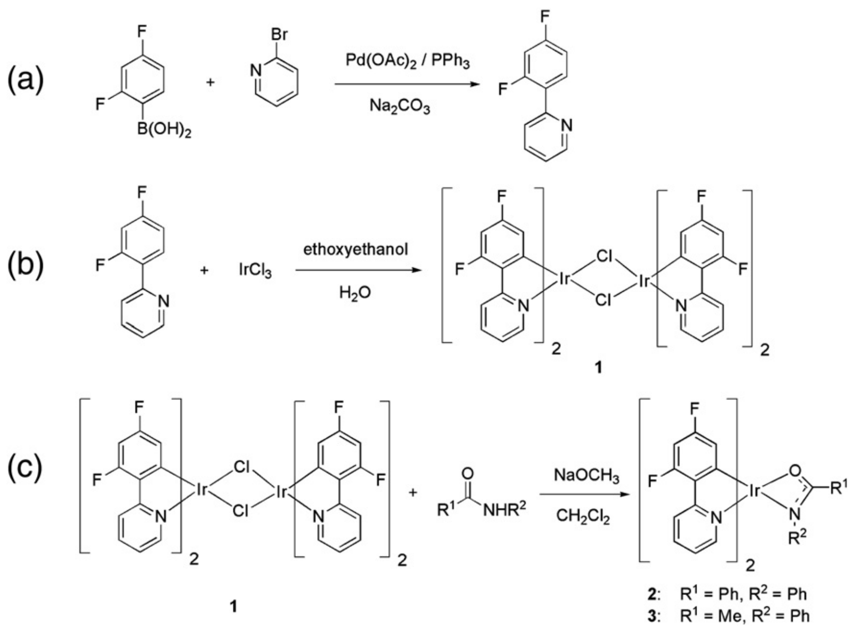


Scheme 1. Synthesis of Ir(III) complexes with amidate ancillary ligands.

by Thompson, Park and Chi groups [26–30] and Ir(III) amidate complexes reported by us [24,25]. The typical chemical shift at 179.19 in ^{13}C NMR spectrum is characteristic of the amidate carbon atom in the four-membered metallocycle. Furthermore, the ^{19}F chemical shifts at 111.14 and 110.78 are attributed to the two 6-F atoms of the two 4,6-difluorophenylpyridyl ligands and the dd splitting at 109.11 is attributed to the two 4-F atoms [26–30]. Due to the different chemical environments for the two 4,6-difluorophenylpyridyl ligands (with one C *trans* to amidate nitrogen atom and the other C' *trans* to amidate oxygen atom), there are slight differences for the chemical shifts of the four fluorine atoms. Finally, X-ray crystallographic structure presents the most convincing and intuitional evidence (vide infra). For complex **3**, additional evidence in the ^{1}H NMR spectrum is the chemical shift at 2.11 (s, 3H) for acetamidate α-methyl hydrogens, and this methyl carbon atom is found at 23.85 in ^{13}C NMR spectrum of complex **3** (for more information, please refer to the supplementary material).

To unambiguously elucidate the structure, single crystal X-ray diffraction analysis was done for complex **2**, as shown by Fig. 1. Complex **2** adopts an octahedral geometry with the two dfppy ligands located in a cis *C*, *C'* and trans *N*, *N'* manner. This orientation has been previously reported for analogous heteroleptic complexes containing Ir-bis(ppy) and Ir-bis(dfppy) fragment. The other two coordination positions have been occupied by amidate O and N atoms, forming a four-membered metallocycle. The Ir1 – C11, Ir1 – C22, Ir1 – N1 and Ir1 – N2 bond lengths of 1.989, 2.012, 2.045 and 2.044 Å are consistent

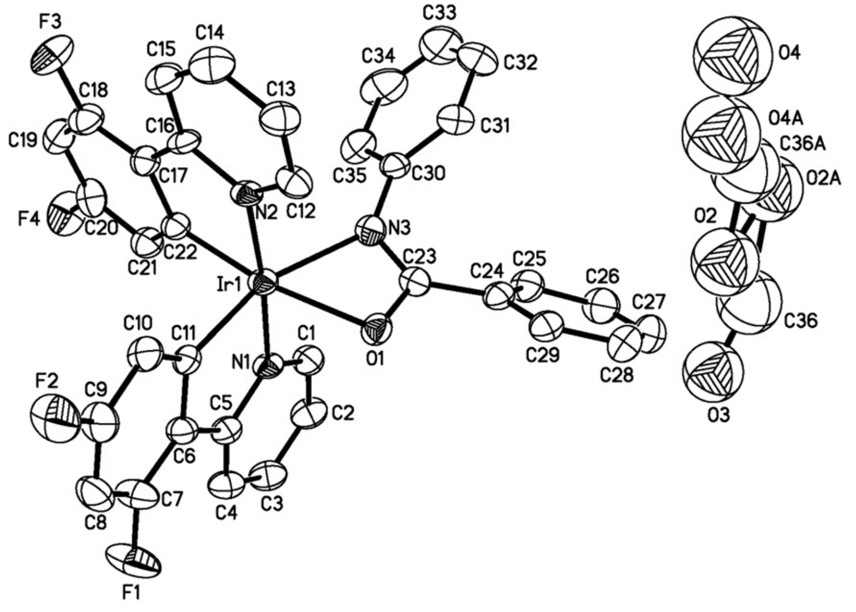
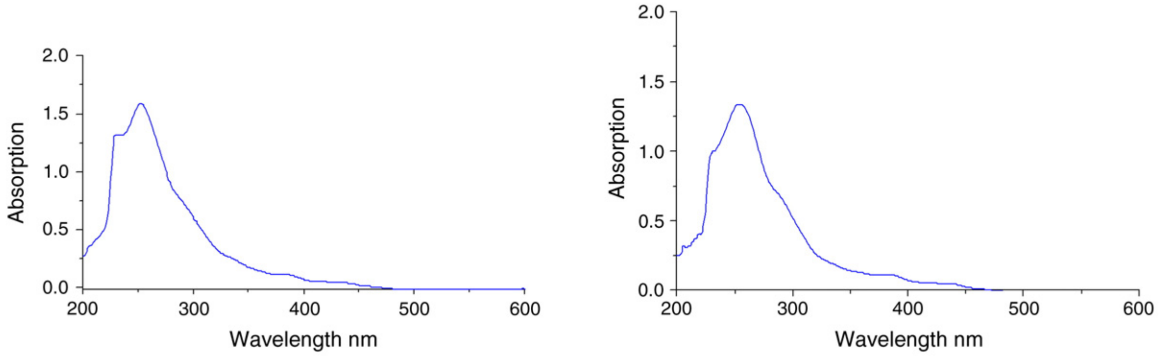
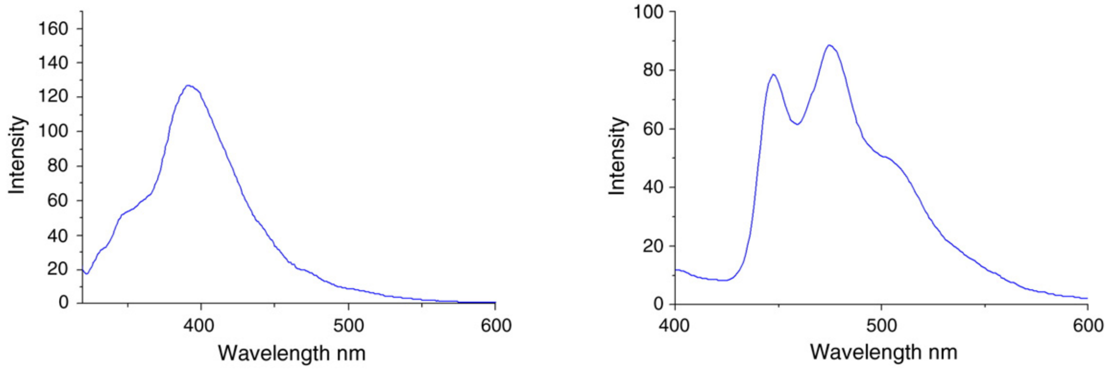


Fig. 1. ORTEP diagram of complex **2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ir(1) – C(11) 1.989(6), Ir(1) – N(1) 2.045(4), Ir(1) – C(22) 2.012(5), Ir(1) – N(2) 2.044(4), Ir(1) – O(1) 2.207(4), Ir(1) – N(3) 2.154(5), C(23) – O(1) 1.294(6), N(3) – C(23) 1.308(7), C(22) – Ir(1) – N(2) 81.2(2), C(11) – Ir(1) – N(1) 80.8(2), N(3) – Ir(1) – O(1) 59.66(16), C(11) – Ir(1) – C(22) 90.7(2), N(1) – Ir(1) – N(2) 174.97(16).



(a) UV-vis Absorption spectrum of complex **2**.

(b) UV-vis Absorption spectrum of complex **3**.



(c) Emission spectrum of complex **2.**

(d) Emission spectrum of complex **3.**

Fig. 2. UV–vis absorption and normalized photoluminescent emission spectra of complexes **2** and **3** at a concentration of 10^{-5} mol/L in CH_2Cl_2 solution at 298 K.

with other complexes containing Ir-(dfppy) fragment [26–30,32]. The Ir1 – N3 and Ir1 – O1 bond lengths are 2.154 and 2.207 Å, in agreement with those of other Ir(III) amidate complexes reported by us previously [24,25].

Complexes **2** and **3** show similar absorption spectra, as reflected by the shape of Fig. 2a and b and absorption wavelengths in Table 1. However, the emission spectra for complexes **2** and **3** are distinct from each other. Complex **2** shows a significant maximum emission at 394 nm (purple light emission, Fig. 2c) whereas complex **3** features two significant emission bands at 448 and 478 nm (blue light emission, Fig. 2d) [27,28]. It is noteworthy that the purple emission of complex **2** is quite unprecedented for such heteroleptic Ir(III) complexes in the literature. In addition, these results suggest that excitation of complexes **2** and **3** should involve a common transition (possibly a metal-to-ligand charge transfer) [27–29,33], but there is significant differences for the emitting excited states for complexes **2** and **3**. In view of the two lower-energy emission bands for complex **3**, the energy levels of emitting states for complex **3** should be substantially lower than that for complex **2**. DFT calculation results [34] indicate that the energy level of HOMO of the triplet complex **2** is much higher than that for complex **3** (−0.110 vs. −0.154), therefore validating the fact that shorter wavelength has been observed for complex **2**.

Table 1
Summary of photophysical properties of complexes **2** and **3.**

Complex	Absorption bands (nm)	Emission (maximum, nm)
2	229, 252, 380	394
3	229, 254, 383	478

Additionally, there should be significant inter-ligand energy transfer during emission process of complex **3**, resulting in the stabilization of the emitting states and subsequently a second longer emission wavelength [29]. But this inter-ligand energy transfer process should be unfavorable for complex **2**. According to the inter-ligand energy transfer theory, much more stable LX^3 state is predicted for complex **3** than for complex **2**. This is reasonable because there is better delocalization of electrons in benzamidate ligand due to the incorporation of phenyl group in complex **2** and subsequently it should be more energy-costly to form the LX^3 state for complex **2**. This explains why inter-ligand energy transfer process is unfavorable for complex **2**.

In conclusion, we report here the synthesis and characterization of two novel $Ir(dfppy)_2$ complexes with different amidate ancillary ligands. These complexes show distinct emission colors, demonstrating the crucial role of the electronic properties of ancillary ligands on photoluminescent properties. The dichotomy of photophysical properties has been proposed to be caused by the more delocalized nature of benzamidate ligand.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.05.035.

References

[1] H. Yersin, Highly Efficient OLEDs with Phosphorescent Materials, Wiley-VCH, Weinheim, Germany, 2008.

[2] K. Müllen, U. Scherf, Organic Light Emitting Devices: Synthesis, Properties and Applications, Wiley-VCH, Weinheim, Germany, 2006.

[3] H. Klauk, Organic Electronics: Materials, Manufacturing and Applications, Wiley-VCH, Weinheim, Germany, 2006.

[4] Z. Chen, Z. Bian, C. Huang, Functional Ir^{III} compexes and their applications, Adv. Mater. 22 (2010) 1534–1539.

[5] Y. Chi, P. Chou, Transition-metal phosphors with cyclometalating ligands: fundamentals and applications, Chem. Soc. Rev. 39 (2010) 638–655.

[6] C. Ulbricht, B. Beyer, C. Friebe, A. Winter, U.S. Schubert, Recent developments in the application of phosphorescent iriudm(III) complex systems, Adv. Mater. 21 (2009) 4418–4441.

[7] Y. You, S.Y. Park, Phosphorescent iridium(III) complexes: toward high phosphorescence quantum efficiency through ligand control, Dalton Trans. (2009) 1267–1282.

[8] S. Kappaun, C. Slugovc, E.J.W. List, Phosphorescent organic light-emitting devices: working principle and iridium based emitter materials, Int. J. Mol. Sci. 9 (2008) 1527–1547.

[9] T. Hofbeck, H. Yersin, The triplet state of *fac*-$Ir(ppy)_3$, Inorg. Chem. 49 (2010) 9290–9299.

[10] A. Endo, C. Adachi, Photoluminescence characteristics of tris(2-phenylquinoline) iridium(III) dispersed in an iridium complex host layer, Chem. Phys. Lett. 483 (2009) 224–226.

[11] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, Synthesis and characterization of facial and meridional tris-cyclometalated iridium(III) complexes, J. Am. Chem. Soc. 125 (2003) 7377–7387.

[12] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, Homoleptic cyclometalated iridium complexes with highly efficient red phosphorescence and application to organic light-emitting diode, J. Am. Chem. Soc. 125 (2003) 12971–12979.

[13] J.C. Deaton, R.H. Young, J.R. Lenhard, M. Rajeswaran, S. Huo, Photophysical properties of the series *fac*- and *mer*-(1-phenylisoquinolinato-$N^\wedge C^{2'})_x$ (2-phenylpyridinato-$N^\wedge C^{2'})_{3-x}$Iridium(III) ($x = 1–3$), Inorg. Chem. 49 (2010) 9151–9161.

[14] A.R. McDonald, M. Lutz, L.S. Chrzanowski, G.P.M. Klink, A.L. Spek, G. van Koten, Probing the mer- to fac-isomerizatin of tris-cyclometalated homo- and heteroleptic (C, N)3 iridium(III) complexes, Inorg. Chem. 47 (2008) 6681–6691.

[15] T. Karatsu, E. Ito, S. Yagai, A. Kitamura, Radiative and nonradiative processes of meridional and facial isomers of heteroleptic iridium-trishelete complexes, Chem. Phys. Lett. 424 (2006) 353–357.

[16] Q. Zhao, C. Jiang, M. Shi, F. Li, T. Yi, Y. Cao, C. Huang, Synthesis and photophysical, electrochemical, and electrophosphorescent properties of a series of iridium(III) complexes based on quinoline derivatives and different beta-diketonate ligands, Organometallics 25 (2006) 3631–3638.

[17] K.R.J. Thomas, M. Velusamy, J.T. Lin, C. Chien, Y. Tao, Y.S. Wen, Y. Hu, P. Chou, Efficient red-emitting cyclometalated iridium(III) complexes containing lepidine-based ligands, Inorg. Chem. 44 (2005) 5677–5685.

[18] Y. Su, H. Huang, C. Li, C. Chien, Y. Tao, P. Chou, S. Datta, R. Liu, Highly efficient red electrophosphorescent devices based on iridium isoquinoline complexes: remarkable external quantum efficiency over a wide range of current, Adv. Mater. 15 (2003) 884–888.

[19] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, Highly phosphorescent bis-cyclometalated iridium complexes: synthesis, photophysical characterization, and use in organic light emitting diodes, J. Am. Chem. Soc. 123 (2001) 4304–4312.

[20] J. Li, P.I. Djurovich, B.D. Alleyne, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, Synthesis and characterization of cyclometalated Ir(III) complexes with pyrazolyl ancillary ligands, Polyhedron 23 (2004) 419–428.

[21] T. Tsuzuki, N. Shirasawa, T. Suzuki, S.Z. Tokito, Color tunable organic light-emitting diodes using pentafluorophenyl-substituted iridium complexes, Adv. Mater. 15 (2003) 1455–1458.

[22] V.V. Grushin, N. Herron, D.D. LeCloux, W.J. Marshall, V.A. Petrov, Y. Wang, New, efficient electroluminescent materials based on organometallic Ir complexes, Chem. Commun. (2001) 1494–1495.

[23] L. Famigni, A. Barbieri, C. Sabtini, B. Ventura, F. Barigelletti, Photochemistry and photophysics of coordination compounds: iridium, Top. Curr. Chem. 281 (2007) 143–203.

[24] W. Yang, H. Fu, Q. Song, M. Zhang, Y. Ding, Amidate iridium(III) bis(2-pyridyl) phenyl complexes: application examples of amidate ancillary ligands in iridium (III)-cyclometalated complexes, Organometallics 30 (2011) 77–83.

[25] W. Wang, T. Zhu, G. Chen, C. Li, H. Di, C. Ren, Y. Ding, Synthesis, characterization and photoluminescence of poly(VK-$(ppy)_2$Ir(*N*-phMA)), Synth. Met. 158 (2008) 1022–1027.

[26] R.D. Costa, G. Fernandez, L. Sanchez, N. Martin, E. Orti, H.J. Bolink, Dumbbell-shaped dinuclear iridium complexes and their application to light-emitting electrochemical cells, Chem. Eur. J. 16 (2010) 9855–9863.

[27] C. Adachi, R.C. Kwong, P.I. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, S.R. Forrest, Endothermic energy transfer: a mechanism for generating very efficient high-energy phosphorescent emission in organic materials, Appl. Phys. Lett. 79 (2001) 2082–2084.

[28] A.F. Rausch, M.E. Thompson, H. Yersin, Matrix effects on the triplet state of the OLED emitter Ir(4,6-$dFppy)_2$(pic) (Firpic): investigations by high-resolution optical spectroscopy, Inorg. Chem. 48 (2009) 1928–1937.

[29] Y. You, S.Y. Park, Inter-ligand energy transfer and related emission change in the cyclometalated heteroleptic iridium complex: facile and efficient color tuning over the whole visible range by the ancillary ligand structure, J. Am. Chem. Soc. 127 (2005) 12438–12439.

[30] C.H. Yang, Y.M. Cheng, Y. Chi, C.J. Hsu, F.C. Fang, K.T. Wong, P.T. Chou, C.H. Chang, M.H. Tsai, C.C. Wu, Blue-emitting heteroleptic iridium(III) complexes suitable for high-efficiency phosphorescent OLEDs, Angew. Chem. Int. Ed. 46 (2007) 2418–2421.

[31] M. Nonoyama, Benzo[*h*]quinolin-10-yl-*N* iridium(III) complexes, Bull. Chem. Soc. Jpn. 47 (1974) 767–768.

[32] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M.E. Thompson, Synthesis and characterization of phosphorescent cyclometalated iridium complexes, Inorg. Chem. 40 (2001) 1704–1711.

[33] A.F. Rausch, M.E. Thompson, H. Yersin, Blue light emitting Ir(III) compounds for OLEDs — new insights into ancillary ligand effects on the emitting triplet state, J. Phys. Chem. A 113 (2009) 5927–5932.

[34] All geometry optimizations were performed by using Gaussian03 program. Density functional theory method B3LYP was used, in combination with a combined basis set in which Ir was described by LANL2DZ and 6-31 G(d) was used for the other atoms. For more information, please refer to supplementary data.