

Tuning the Photophysical and Excited State Properties of Phosphorescent Iridium(III) Complexes by Polycyclic Unit Substitution

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Two novel N-embedded polycyclic units functionalized phosphorescent iridium(III) complexes (Ir-1 and Ir-2) with substituents in different positions have been prepared. Complex Ir-1 bearing the substituent at the 3-position shows a distinct blue shift single-peak emission (524 nm) with a higher luminescence efficiency ($\Phi_{\text{PL}} = 42\%$) and shorter emission lifetime ($\tau = 282$ ns) by comparison with 4-position substitution based complex Ir-2 ($\Phi_{\text{PL}} = 23\%$, $\tau = 562$ ns), which exhibits a dual-peak emission

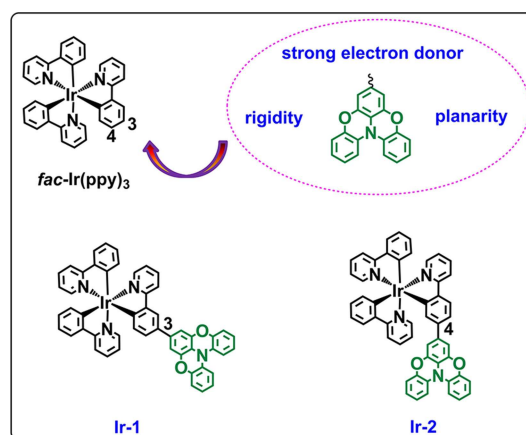
(564 nm and 602 nm), and phosphorescence color can be tuned from green to yellow. In addition, DFT calculations demonstrate that unusual ligand-to-metal charge transfer ($^3\text{LMCT}$) excited state property can be found in Ir-2, which is in contrast to metal-to-ligand charge transfer ($^3\text{MLCT}$) excited state character in Ir-1. This result can be attributed to strong electron-donating character and 4-position substitution effect of the unit.

1. Introduction

During the past decades, transition metal complexes^[1–32] are widely used in the fields of functional materials. Among them, phosphorescent iridium(III) complexes as luminescent materials have attracted more and more attentions due to their stable chemical structures, and excellent optical performances. In particular, functionalization of the cyclometalating ligand (CN ligand) can effectively control of spatial geometries, energy levels (HOMO and LUMO) and excited state characters of iridium(III) complexes, and thus further tune of photophysical properties of complexes, containing phosphorescence color, efficiency and lifetime, etc. One of simplest modification method is to introduce different substituents (electron-donating or electron-withdrawing) into CN ligand to regulate photophysical properties of complexes.^[33–35] Moreover, the orbital analyses further suggest that the position of the substituent on CN ligand is also important for affecting electronic structure of the ligand. Nevertheless, most phosphorescent iridium(III) complexes usually show various common charge transfer characters in the lowest triplet excited state (T_1), such as metal-to-ligand charge transfer ($^3\text{MLCT}$), intraligand charge transfer

($^3\text{ILCT}$) and ligand-to-ligand charge transfer ($^3\text{LLCT}$) excited states characters, but little for ligand-to-metal charge transfer ($^3\text{LMCT}$) character. Moreover, as a catalyst, metal complexes with $^3\text{LMCT}$ excited state characters have recently been proved to be very effective in the field of photocatalytic organic synthesis.^[36–37] To gain unusual $^3\text{LMCT}$ character based novel phosphorescent Iridium(III) complexes, we are focus on N-embedded dioxygen-bridged polycyclic unit^[38–39] with certain planarity, rigidity and strong electron-donating ability (Scheme 1), which may induce new $^3\text{LMCT}$ excited states character. So it is anticipated that introduction of the unit into phosphorescent iridium(III) complex can regulate energy levels, excited state and photophysical properties.

Herein, we choose a classic green phosphorescent iridium (III) complex $\text{fac-Ir}(\text{ppy})_3$ (ppy = 2-phenylpyridine) as model complex, and then synthesize two novel tris-cyclometalated



Scheme 1. The structures of N-embedded polycyclic unit functionalized Iridium(III) complexes Ir-1 and Ir-2. (number 3 and number 4 represent the carbon position on the benzene ring, respectively).

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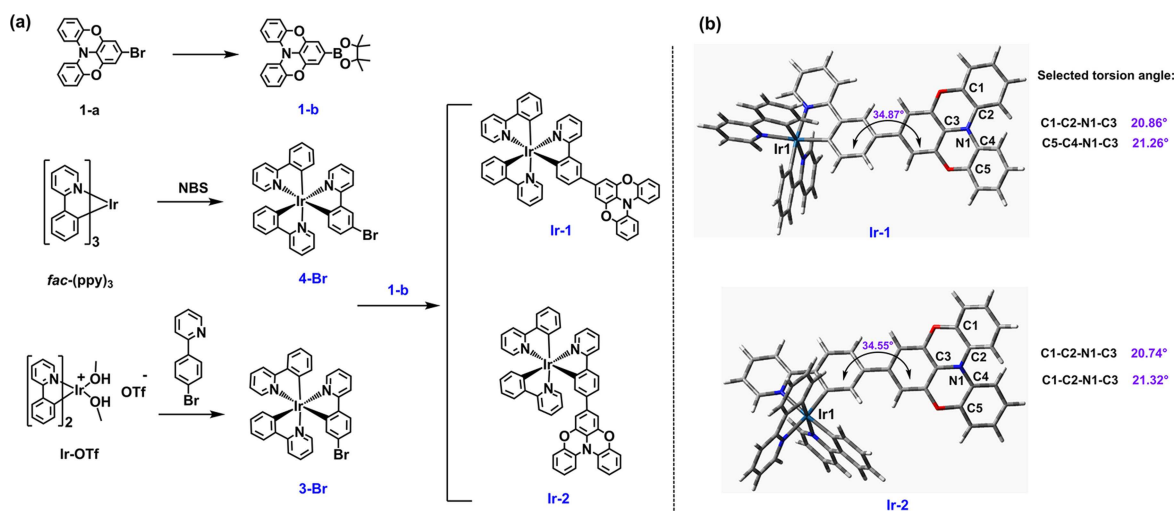


Figure 1. Calculated optimized structures of the complex Ir-1 and Ir-2.

heteroleptic Iridium(III) complexes (Ir-1 and Ir-2) by introduction of N-embedded dioxygen-bridged polycyclic unit into 3- and 4-positions of phenyl ring of one ppy ligand (Scheme 1), respectively. It is found that Ir-1 shows a distinct blue shift single-peak emission with a higher luminescence efficiency and shorter emission lifetime by comparison with Ir-2, which exhibits a dual-peak emission. In addition, unusual $^3\text{LMCT}$ excited state character can be found in Ir-2, which is in contrast to $^3\text{MLCT}$ excited state property in Ir-1. This result can be attributed to a strong electron-donating character and 4-position substitution effect of N-embedded polycyclic unit.

2. Results and Discussion

Although their single crystal structures can not be obtained, optimized structure from DFT calculations at the B3LYP/6-31G (d) level clearly displays their spatial geometries (Figure 1b). It is found that Iridium(III) center is coordinated by two same CN ligands (ppy) and another N-embedded dioxygen-bridged polycyclic unit based CN ligand through distorted octahedral coordination geometry. In addition, N-embedded polycyclic unit of Ir-1 (torsion angles: 20.86° and 21.26°) shows very similar planarity by comparison with that of Ir-2 (torsion angles: 20.74° and 21.32°). The dihedral angle between the planar unit and the benzene ring of 2-phenylpyridine from Ir-1 (34.87°) is also the same as that of Ir-2 (34.55°) (Figure 1b). Besides, molecular polarity of Ir-1 is significantly different from that of Ir-2. Calculated dipole moment (μ) of excited state in Ir-1 (4.2346 D) is larger than that in Ir-2 (3.8716 D). In contrast, calculated μ of ground state in Ir-1 (6.8785 D) is smaller than that in Ir-2 (7.9280 D) (Figure S2 and Table S1).

As shown in Figure 2a, the spin-allowed $\pi \rightarrow \pi^*$ (LC) transitions of the ligands based intense absorption bands are below 300 nm, and various charge-transfer (CT) transitions (MLCT, LLCT or ILCT) based weak low-energy absorption bands locate in the region of 310–500 nm. Notably, the lowest energy

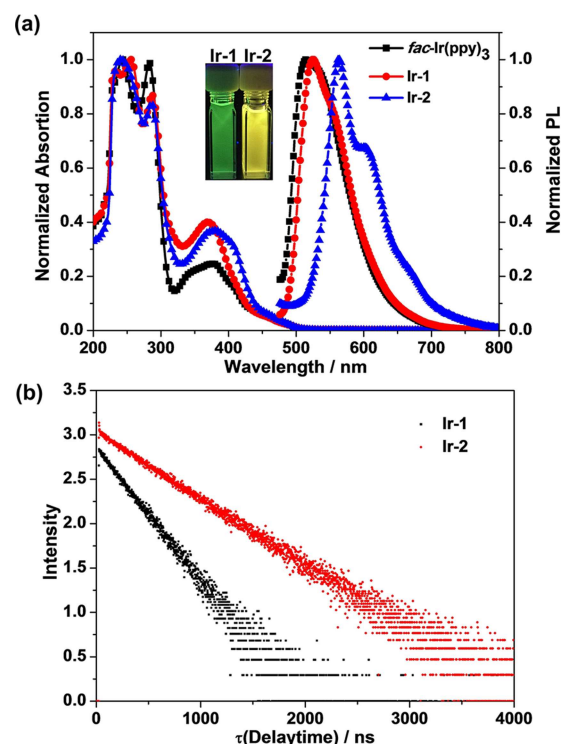


Figure 2. (a) Absorption and PL spectra of Ir-1 and Ir-2 and (b) their emission decay curve measured in degassed dichloromethane solution.

absorption bands of Ir-2 are clearly red-shifted relative to those of Ir-1, demonstrating that 4-position of N-embedded polycyclic unit substitution can efficiently lower excited-state energy level, whereas 3-position substitution has little effect on the excited state energy level.

A similar pattern of change is also reflected in their PL spectra in CH_2Cl_2 solution (Figure 2a). Ir-2 ($\lambda = 564$ and 602 nm) shows a significantly red shift dual-peak emission compared with Ir-1 ($\lambda = 524$ nm) with a single-peak emission. Additionally, Ir-1 displays a higher luminescence efficiency ($\Phi_{\text{PL}} = 42\%$) and

Table 1. Photophysical data of Ir(III) complexes.

Complexes	Absorption ^[a] λ/nm $\lg \epsilon$	PL ^[a] /nm	Φ_p ^[a]	τ ^[a] /ns	$E_{1/2}^{\text{ox}}$ /eV	E_g ^[b] /eV	HOMO/ LUMO ^[b] /eV
Ir-1	232(4.75), 242(4.74), 256(4.77), 274(4.64), 288(4.70), 332(4.26), 370(4.37), 410(4.01), 450(3.49)	524	0.42	282	0.25/ 0.46	2.50	-5.05/-2.55
Ir-2	240(4.92), 274(4.80), 286(4.84), 330(4.31), 380(4.48), 410(4.39), 450(3.76)	564,602	0.23	562	0.31/ 0.43	2.45	-5.11/-2.66

[a] Recorded in degassed CH_2Cl_2 (3×10^{-5} M) at 298 K with an excitation wavelength of 370 nm. Φ_p is referred to absolute quantum yields of phosphorescence determined by employing an integrating sphere. [b] The HOMO(eV) = $-e(E_{\text{onset}}^{\text{ox}} + 4.8)$, $E_g = 1240/\lambda$, λ is absorption wavelength threshold. LUMO(eV) = $E_g + \text{HOMO}$

shorter emission lifetime ($\tau = 282$ ns) than those of **Ir-2** ($\Phi_{\text{PL}} = 23\%$, $\tau = 562$ ns) (Figure 2b and Table 1). This result suggests that 3-position of N-embedded polycyclic unit substitution can efficiently improve optical properties.

In addition, electrochemical properties of both complexes were measured by cyclic voltammetry in their CH_2Cl_2 solutions (Figure 3 and Table 1). Two oxidation potentials (Iridium(III) center and N-containing unit) are found in **Ir-1** and **Ir-2**, which is different from only one oxidation potential for Iridium(III) center in *fac*-Ir(ppy)₃. It is noted that oxidation potentials for the Iridium(III) centers of two N-embedded polycyclic unit functionalized complexes (**Ir-1**: 0.46 V and **Ir-2**: 0.43 V) both show obvious red shift than that of *fac*-Ir(ppy)₃ (0.32 V). Besides, the oxidation potential for N-embedded polycyclic unit in **Ir-1** (0.25 V) displays a remarkable blue shift in comparison with that in **Ir-2** (0.31 V) (Figure 3 and Table 1). As a result, the HOMO energy level of complex can be increased more by 3-position of substitution than by 4 position, that is, the HOMO value (-5.05 eV) of **Ir-1** is larger than that of **Ir-2** (-5.54 eV).

To investigate the effects of N-embedded polycyclic unit and its substitution position on the excited state properties of two complexes discussed above, DFT calculations were carried out for **Ir-1** and **Ir-2** (Figure 4, Figure S3 and Table S2). The T_1 of **Ir-1** originates from both HOMO-1 \rightarrow LUMO (52%) and HOMO \rightarrow LUMO (36%) transitions, whereas **Ir-2** exhibits only a HOMO \rightarrow LUMO (64%) transition in T_1 (Figure 4 and Table S2). The HOMO of **Ir-1** is mainly located in N-embedded polycyclic unit and phenyl ring of CN ligand and Iridium(III) center (contribution of

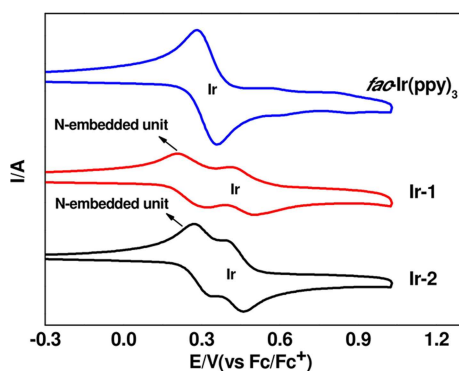


Figure 3. Cyclic voltammograms of **Ir-1**, **Ir-2** and *fac*-Ir(ppy)₃ in degassed CH_2Cl_2 under the scan rate of 100 mV s^{-1} .

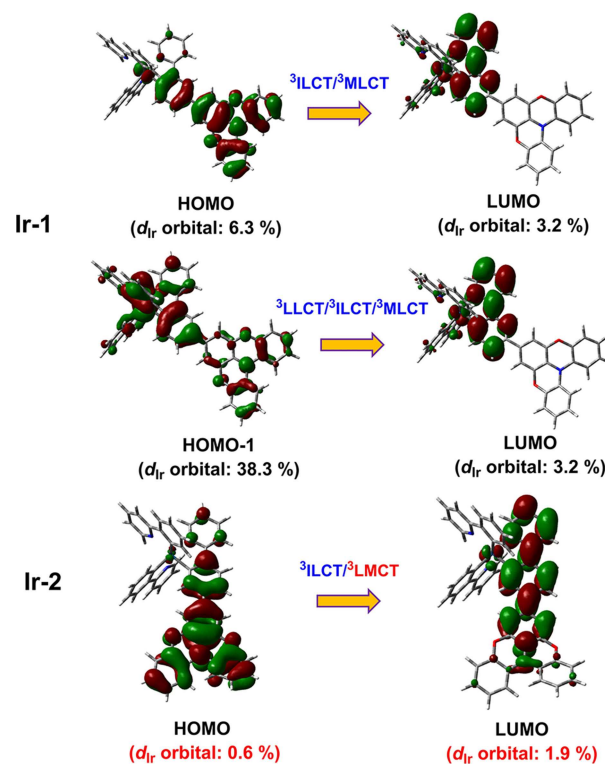


Figure 4. The optimized geometries and orbital transitions of **Ir-1** and **Ir-2** at the lowest triplet excited state (T_1).

d orbitals: 6.3%), the HOMO-1 mainly resides in Iridium(III) center (contribution of d orbitals: 38.3%) and phenyl ring of the CN ligands, and the LUMO is mainly distributed in 2-phenyl pyridine and Iridium(III) center (contribution of d orbitals: 3.2%). Interestingly, the HOMO of **Ir-2** is mainly located in N-embedded polycyclic unit and phenyl ring of CN ligand whereas a little on Iridium(III) center (contribution of d orbitals: 0.6%), and the LUMO mainly resides in 2-phenyl pyridine, phenyl ring and embedded nitrogen atom of CN ligand and Iridium(III) center (contribution of d orbitals: 1.9%). As a result, the T_1 transition of **Ir-2** exhibits $^3\text{ILCT}$ and unusual $^3\text{LMCT}$ characters (Figure 4 and Table S2). This result is significant different from complexes **Ir-1** with typical $^3\text{ILCT}$, $^3\text{LLCT}$ and $^3\text{MLCT}$ characters (Figure 4). It is suggested that different positions of N-embedded polycyclic unit substitution has a great influence on the excited state properties.

3. Conclusions

We have prepared two N-embedded polycyclic unit Iridium(III) complexes functionalized in different position (3- and 4-). It is found that the strong electron-donating character of the unit and its substitution position effect both have a great influence on excited state and photophysical properties of Iridium(III) complexes. Notably, unusual $^3\text{LMCT}$ excited state character can be found in 4-position substitution based complex, which is in contrast to $^3\text{MLCT}$ excited state character in 3-position substitution based complex. The preliminary research results indicate that 4-position of strong electron-donating substitution is a useful strategy for the design of novel phosphorescent Iridium(III) complexes with $^3\text{LMCT}$ excited state character.

Experimental Section

Synthesis and Characterization of 1-b

Intermediate 1-a was synthesized according to literature procedures.^[22] 1-a (0.352 g, 1 mmol), Bis(pinacolato)diboron (0.379 g, 1.5 mmol), Pd(dppf)₂Cl₂ (0.0229 g, 0.03 mmol) and CH₃COOK (0.9814 g, 10 mmol) were charged to a 100 mL schlenk tube, followed by 15 mL 1, 4-Dioxane. The mixture was heated to 110 °C for 24 h under N₂. The resulting solution was saturated with water and extracted with CH₂Cl₂ three times. The combined organic phase was dried and concentrated in vacuum, and target product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether 1:3 (v/v) to afford green solid (1-b), 337 mg (85%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 1.8 Hz, 1H), 7.30 (t, J = 3.7 Hz, 1H), 6.95 (s, 2H), 6.89 (m, 6H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃): 147.22, 144.81, 128.89, 123.91, 123.62, 123.44, 117.53, 117.24, 114.71, 83.89, 25.06, 24.87. C₂₄H₂₂BNO₄ calcd: C, 72.20; N, 3.51; H, 5.55. Found: C, 72.11; N, 3.48; H, 5.61. EI-MS (m/z): 400.02 (M⁺, 100%).

Synthesis and Characterization of Complex 4-Br

5 mL NBS (0.019 g, 0.107 mmol) dichloromethane solution was added to the solution of fac-Ir(ppy)₃ (0.065 g, 0.1 mmol) in 15 mL dichloromethane, then the resulting mixture was stirred for 15 hours at room temperature, and was extracted with water and dichloromethane, and the organic layer was concentrated, then target product was purified by column chromatography on silica gel with CH₂Cl₂/hexane 1:3 (v/v) to afford yellow solid, 0.058 g (80%). ¹H NMR (CDCl₃): 7.88 (d, J = 3.1 Hz, 2H), 7.82 (d, 1H), 7.73 (d, J = 2.1 Hz, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.59 (m, 3H), 7.53 (t, J = 5.1, 1.6 Hz, 2H), 7.48 (d, 1H), 6.87(m, 10H), 6.71 (d, J = 2.0 Hz, 1H). ¹³C NMR (CDCl₃): 151.66, 147.24, 146.97, 145.30, 143.74, 138.70, 136.35, 136.20, 132.49, 130.58, 130.04, 129.07, 123.65, 122.69, 122.16, 121.32, 120.23, 120.01, 119.08, 118.41. C₃₃H₂₃BrIrN₃ calcd: C, 54.02; N, 5.73; H, 3.16. Found: C, 53.98; N, 5.71; H, 3.21. EI-MS (m/z): 734.06(M⁺, 80%).

Synthesis and Characterization of Complex Ir-1

A mixture of 4-Br (0.073 g, 0.1 mmol), 1-b (0.048 g, 0.12 mmol), K₂CO₃ (2.2 g, 16 mmol) and tetra-(triphenylphosphine)-palladium (0.001 g, 0.001 mmol), followed 8 mL of water and 16 mL of dioxane. The mixed solution was heated to 100 °C for 24 h under N₂. The resulting solution was cooled to room temperature and

concentrated in vacuum, extracted with water and dichloromethane, and the organic layer was concentrated, then target product was purified by column chromatography on silica gel with CH₂Cl₂/hexane 1:3 (v/v) to afford yellow solid, 0.074 g (80%). ¹H NMR (CD₂Cl₂): 8.06 (t, J = 7.1 Hz, 1H), 7.97 (d, J = 7.9 Hz, 2H), 7.87 (d, 1H), 7.72 (m, 6.2 Hz, 5H), 7.63 (m, J = 5.4 Hz, 3H), 7.38 (d, 2H), 6.97 (m, 13H), 6.85 (m, 6H). ¹³C NMR (CD₂Cl₂): 166.39, 166.06, 147.27, 147.17, 145.42, 143.78, 137.17, 136.77, 136.32, 129.71, 127.58, 124.05, 123.46, 122.39, 122.16, 121.59, 119.96, 119.03, 118.89, 117.25, 114.69, 108.52. C₅₁H₃₃IrN₄O₂ calcd: C, 66.15; N, 6.05; H, 3.59. Found: C, 66.11; N, 6.02; H, 3.63. EI-MS (m/z): 926.25(M⁺, 30%).

Synthesis and Characterization of Complex 3-Br

Ir-OTf (0.146 g, 0.225 mmol) and 2-(4-bromophenyl)pyridine (0.116 g, 0.5 mmol) were charged to a 100 mL schlenk tube, followed by ethanol (50 mL). The mixture was heated to 80 °C for 24 h under N₂. The combined organic phase was dried and concentrated in vacuum, and target product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether 1:2 (v/v) to afford yellow solid, 133 mg (70%). ¹H NMR (CDCl₃): 7.87 (m, 3H), 7.62 (m, 5H), 7.49 (m, 4H), 7.03 (m, J = 2.1 Hz, 1H), 6.87 (m, J = 1.8 Hz, 9H), 6.77 (d, J = 7.3 Hz, 1H). ¹³C NMR (CDCl₃): 147.14, 147.04, 146.95, 139.13, 137.15, 136.98, 136.16, 136.08, 130.10, 129.94, 125.27, 124.04, 123.89, 122.92, 122.23, 121.94, 121.86, 120.22, 120.03, 118.96, 118.90, 118.83. C₃₃H₂₃BrIrN₃ calcd: C, 54.02; N, 5.73; H, 3.16. Found: C, 53.97; N, 5.71; H, 3.20. EI-MS (m/z): 734.12(M⁺, 100%).

Synthesis and Characterization of Complex Ir-2

A mixture of 3-Br (0.073 g, 0.1 mmol), 1-b (0.048 g, 0.12 mmol), K₂CO₃ (2.2 g, 16 mmol) and tetra-(triphenylphosphine)-palladium (0.001 g, 0.001 mmol), followed 8 mL of water and 16 mL of dioxane. The mixed solution was heated to 100 °C for 24 h under N₂. The resulting solution was cooled to room temperature and concentrated in vacuum, extracted with water and dichloromethane, and the organic layer was concentrated, then target product was purified by column chromatography on silica gel with CH₂Cl₂/hexane 1:5 (v/v) to afford yellow solid (Ir-1) 0.074 g, yield 80%. ¹H NMR (400 MHz, CDCl₃): 7.87 (t, 3H), 7.66 (m, 3H), 7.55 (m, 6H), 7.31 (d, J = 7.9 Hz, 2H), 7.04 (m, 2H), 6.90 (m, J = 6.1, 4.0 Hz, 15H), 6.58 (s, 2H). ¹³C NMR (CDCl₃): 166.83, 166.75, 166.19, 161.65, 161.13, 160.71, 147.12, 147.00, 145.02, 143.65, 143.56, 143.48, 137.27, 137.13, 135.90, 134.54, 130.08, 129.88, 123.33, 121.89, 120.06, 119.80, 118.87, 118.77, 118.34, 117.45, 114.56, 109.68. C₅₁H₃₃IrN₄O₂ calcd: C, 66.15; N, 6.05; H, 3.59. Found: C, 66.09; N, 6.01; H, 3.64. EI-MS (m/z): 926.22(M⁺, 30%).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: N-embedded complexes · polycyclic units · phosphorescence · iridium complexes · photophysical properties

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