Theoretical insight on electronic structure and photophysical properties of a series of cyclometalated iridium(III) complexes bearing the substituted phenylpyrazole with different electron-donating or electron-accepting groups

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Abstract

By using the density functional theory (DFT) and time-dependent density functional theory (TDDFT), the electronic structure and photophysical properties of a series of cyclometalated iridium(III) complexes bearing the substituted phenylpyrazole have been theoretically investigated. All studied iridium(III) complexes have the distorted octahedral geometry with *cis*-C,C, *cis*-O,O, and *trans*-N,N chelate disposition. The lowest lying singlet → singlet absorptions of all studied iridium(III) complexes are respectively located at 405 nm, 387 nm, 382 nm, 370 nm, and 387 nm. The calculated emission wavelengths for all studied iridium(III) complexes are 654 nm, 513 nm, 506 nm, 505 nm and 499 nm, respectively. The calculated emission wavelength for complex **4** at the CAM-B3LYP level is in good agreement with the experimental value. From the theoretical results, it can be seen that the electron-donating substituent groups have the important effect on the electronic structure and photophysical properties of all studied iridium(III) complexes. We hope that this study can provide valuable guidance for the design of new phosphorescent organic light-emitting diodes (OLEDs) materials.

Graphic abstract

Keywords DFT · TDDFT · OLEDs · Iridium · Phosphorescence

1 Introduction

In the last two decades, due to the benefits of relatively short excited-state lifetimes, high photoluminescence efficiency, good colour tunability, general thermal, and electrochemical stability, phosphorescent transition metal complexes of Ir(III), Pt(II), Os(II), Cu(I) and so on have been widely explored [1–6]. Especially, phosphorescent cyclometallated iridium(III) complexes have already been extensively investigated for many applications, such as organic light-emitting diodes (OLEDs), solar cells, sensors, and bioimaging [7–12]. The phosphorescence quantum yield is enhanced beyond that achievable with fluorescent emitters due to the strong spin–orbit coupling induced by the iridium atom, which allows for mixing of singlet and triplet excited states through efficient intersystem crossing [13, 14].

Many researchers have extensively investigated the color tuning via the molecular design of Ir(III) complexes to realize full-color displays. Generally speaking, one strategy is to vary the heterocycle, the degree of conjugation in the C^N ligand, and/or the ancillary ligand. Another strategy is to alter substituents on the cyclometalated phenyl, the coordination heterocycle, or the ancillary ligands. F.Q. Bai et al. have designed and studied many iridium(III) complexes with different substituent groups, which indicates that the substituent groups could be propitious to produce better performance of iridium(III) materials [15, 16]. B.Q. Liu et al. have studied a series of neutral cyclometalated Ir(III) complexes bearing substituted N-heterocyclic carbene (NHC) ligands for high-performance yellow OLED application [17]. The influence of the electron-donating or electron-withdrawing substituents on their photophysical properties have been explored. In recent years, tetraphenylimidodiphosphinate (tpip) derivatives with polar P=O bonds and phenyl rings have been used as ancillary ligands to obtain Ir(III) complexes for efficient OLEDs because they could increase the electron mobility of the complexes and improve their corresponding electroluminescent performances [18, 19]. L.M. Groves et al. have studied a series of Ir(III) complexes based on phenylpyrazole (ppz) derivatives with electron-withdrawing groups (–F, –CF₃, –OCF₃, and –SF₅), which revealed a broad, featureless emission peak that ranged between 510 and 560 nm [20]. Z.G. Niu et al. have synthesized and fully characterized seven cyclometalated iridium(III) complexes Ir1–Ir7 based on phenylpyrazole derivatives as main ligands and tetraphenylimidodiphosphinate (tpip) as the ancillary ligand [21]. Via variation of the main ligands, the emission colors for complexes Ir1–Ir7 can be adjusted from blue to yellow in CH₂Cl₂ solutions. It is known that the control of the optical physical process must ensure the structural

similarity, so that the expected increase of the radiative decay rate can ensure the improvement of the overall efficiency [22, 23]. Hence, on the basis of complex Ir6 [21], we have theoretically designed four complexes and investigated their electronic structure and photophysical properties by density functional theory (DFT) and time-dependent density functional theory (TDDFT) method.

2 Computational method

The ground state geometry for each molecule was optimized by density functional theory (DFT) method with hybrid Hartree–Fock/density functional model (PBE0) based on the Perdew–Burke–Erzenrhof (PBE) [24, 25]. On the basis of the ground- and excited-state equilibrium geometries, the time-dependent DFT (TDDFT) approach was applied to investigate the absorption and emission spectral properties. The “double- ξ ” quality basis set LANL2DZ associated with the pseudopotential was employed on atom Ir [26, 27]. The 6–31G(d,p) basis set was used for nonmetal atoms in the gradient optimizations. Furthermore, the stable configurations of these complexes can be confirmed by frequency analysis, in which no imaginary frequency was found for all configurations at the energy minima. All calculations were performed with the polarized continuum model (PCM) in CH₂Cl₂ medium. All calculations were performed with the Gaussian 09 software package [28].

3 Results and discussion

3.1 Geometries in the ground state S₀ and triplet excited state T₁

The sketch map of iridium(III) complexes 1–5 have been presented in Fig. 1a, and the optimized ground state geometric structure for complex 1 is shown in Fig. 1b along with the numbering of some key atoms. The main optimized geometric parameters of the ground state (S₀) and the lowest lying triplet excited state (T₁) have been summarized in Table 1.

These cyclometalated iridium(III) complexes are based on the substituted phenylpyrazole derivatives as main ligands and tetraphenylimidodiphosphinate (tpip) as the ancillary ligand. The coordination geometry of the iridium center in each complex is a distorted octahedral geometry with *cis*-C,C, *cis*-O,O, and *trans*-N,N chelate disposition. The lengths of Ir–C1, Ir–C2, Ir–N1 and Ir–N2 of complex 4 are close to those in reported data [21]. The lengths of Ir–C1 and Ir–C2 of complexes 1–5 are 1.98 or 1.99 Å. The lengths of Ir–N1

Fig. 1 **a** Sketch map of the structures of iridium(III) complexes **1–5**. **b** Vertical view (left) and side view (right) of the optimized geometrical structure of iridium(III) complex **1**

and Ir–N2 of complexes **1–5** are 2.00 or 2.01 Å. The lengths of Ir–O1 and Ir–O2 of complexes **1–5** are 2.23 or 2.24 Å. The bond angles C1–Ir–O2, C2–Ir–O1 and N1–Ir–N2 of complexes **1–5** are at the range from 170° to 177°. The dihedral angles C1–N1–O2–N2 and C2–N1–O1–N2 of complexes **1–5** are smaller than 3°, which indicates that all these iridium complexes possess a distorted octahedral configuration.

Beside, to investigate the changes of the geometrical structures upon excitation, the calculated geometrical parameters of T_1 state for complexes **1–5** have been provided in Table 1. The bond lengths Ir–C1 and Ir–C2 of complexes **1–5** in T_1 state are slightly smaller than those in S_0 state. The bond angles C1–Ir–O2, C2–Ir–O1 and N1–Ir–N2 of complexes **1–5** in T_1 state have slight change in contrast to those in S_0 state. The dihedral angle C1–N1–O2–N2 of complexes **1–5** in T_1 state are larger than those in S_0 state. It is interesting to note that the dihedral angle C2–N1–O1–N2 of complex **1** in T_1 state is smaller than that of S_0 state. However, the dihedral angles C2–N1–O1–N2 of complex **2–5** in T_1 state are obviously larger than those of S_0 state.

3.2 Molecular orbital properties

The frontier molecular orbital (FMO) components and the energy level have been investigated to describe the electronic and photophysical properties. Figure 2 shows the HOMOs and LUMOs distribution (iso-surface value 0.02), energy levels, and energy gaps between of LUMO and HOMO ($\Delta E_{L \rightarrow H}$) of the complexes **1–5**. The detailed

Table 1 Main optimized geometry parameters for complexes **1–5**

	1		2		3		4		5	
	S_0	T_1	S_0	T_1	S_0	T_1	S_0 PBE0/Exptl. ^a	T_1	S_0	T_1
Bond length (Å)										
Ir–C1	1.98	1.98	1.99	1.96	1.99	1.96	1.98/1.98	1.96	1.99	1.96
Ir–C2	1.98	1.97	1.99	1.96	1.99	1.96	1.98/1.99	1.96	1.99	1.96
Ir–N1	2.01	2.02	2.00	2.01	2.01	2.01	2.01/2.00	2.01	2.01	2.01
Ir–N2	2.01	2.01	2.01	2.01	2.01	2.01	2.01/2.00	2.01	2.00	2.01
Ir–O1	2.24	2.23	2.24	2.24	2.24	2.24	2.23/2.17	2.23	2.23	2.23
Ir–O2	2.24	2.28	2.23	2.24	2.24	2.24	2.23/2.22	2.23	2.23	2.21
Bond angle (°)										
C1–Ir–O2	171.49	171.75	170.43	172.82	170.68	169.44	170.51/171.78	169.76	171.45	169.31
C2–Ir–O1	170.79	171.57	172.86	169.92	170.68	169.44	170.51/168.86	169.76	170.73	170.16
N1–Ir–N2	175.56	176.26	176.02	176.40	175.92	175.83	175.78/176.23	175.75	175.57	175.91
Dihedral angle (°)										
C1–O1–O2–C2	11.81	11.04	11.12	9.25	12.49	12.69	12.74/11.48	12.45	11.95	12.39
C1–N1–O2–N2	1.94	2.70	2.14	5.65	1.88	5.43	1.92/6.35	5.20	1.90	4.97
C2–N1–O1–N2	2.02	1.13	1.55	4.03	1.60	4.67	1.65/2.02	4.46	2.00	4.75

^aReference [21]

Fig. 2 Molecular orbital diagrams and HOMO and LUMO energies for complexes **1–5**

information of FMO compositions for complexes **1–5** at the PBE0/6–31G(d,p) + LANL2DZ level has been listed in Tables S1–S5 (Supplementary Materials). It can be seen from Fig. 2 and Tables S1–S5 (Supplementary Materials) that the HOMO of complex **1** resides mainly on the L1 ligand, however, the HOMO of complexes **2–5** are mainly located at Ir atom and L1 ligand. For example, the HOMO of **2** distributes over the d-orbital of Ir (34%) and the π -orbital of L1 ligand (63%). The LUMO of complexes **1–5** resides mostly on the L1 ligand, for example, complex **1** has the 93% antibonding π^* -orbital of the L1 ligand. It is known that the different R substituent groups on the main ligand have different electron-donating and electron-accepting abilities, that is, the order of electron-donating ability $-\text{N}(\text{CH}_3)_2 > -\text{CH}_3 > -\text{H}$, the order of electron-accepting ability $-\text{H} < -\text{F} < -\text{NO}_2$. In comparison with complex **1**, it can be seen that the introduction of the electron-donating substituents ($-\text{N}(\text{CH}_3)_2$ and $-\text{CH}_3$) or electron-accepting ones ($-\text{F}$ and $-\text{NO}_2$) can slightly raise or lower the HOMO and LUMO energy levels. It is particularly interesting to note that the order of HOMO or LUMO energy levels is **1** > **2** > **3** > **4** > **5**. Obviously, the HOMO and LUMO energy levels of complex **1** are the largest ones among these studied complexes. Furthermore, the $\Delta E_{\text{L} \rightarrow \text{H}}$ value (3.78 eV) of **1** is the smallest one among complexes **1–5**. In addition, complex **4** has the largest $\Delta E_{\text{L} \rightarrow \text{H}}$ value 4.22 eV in these studied complexes. Complex **5** has the smallest HOMO and LUMO level, that is, -5.59 eV and -1.67 eV, respectively. The HOMO of **5** distributes over the d-orbital of Ir (35%) and the π -orbital of L1 ligand (60%). Meanwhile, the LUMO of **5** resides mostly on the L1 ligand (99%).

3.3 Absorption spectra

The PBE0 method has been used to calculate the absorption properties of complexes **1–5** on the basis of the optimized ground state geometries. Table S6 (Supplementary Materials) presents the vertical electronic excitation energies, oscillator strengths (f), dominant orbital excitations and their assignments of the S_0 and T_1 states. The stimulated absorption spectra of complexes **1–5** in CH_2Cl_2 solvent based on the TDDFT calculations has been described in Fig. 3.

As shown in Table S6, the lowest lying singlet $\rightarrow$ singlet absorption of **1–5** are located at 405 nm ($f=0.1175$), 387 nm ($f=0.0507$), 382 nm ($f=0.0523$), 370 nm

Fig. 3 Simulated absorption spectra in CH_2Cl_2 medium for complexes **1–5**

($f=0.0610$) and 387 nm ($f=0.0208$), respectively. It can be seen that the calculated absorption wavelength for complex **4** is comparable with the experimental value [19]. In contrast to complexes **2–5**, complex **1** has an obviously large absorption peak at about 288 nm wavelength, which originates from the contributions HOMO $\rightarrow$ LUMO + 2 (34%) and HOMO $\rightarrow$ LUMO + 6 (25%) electron transition configurations. In addition, complex **1** has also a small absorption peak at 398 nm. The lowest lying absorption of complex **1** is obviously redshifted in contrast to that of complex **3**, which is due to the strong electron-donating substituent group $-\text{N}(\text{CH}_3)_2$. Complexes **2–4** have the similar absorption curve shape with two peaks at about 243 nm and 310 nm, respectively. In contrast to that of complex **3**, the lowest lying absorption of **1** is obviously red-shifted, which is consistent with the variation of the $\Delta E_{\text{L} \rightarrow \text{H}}$ values, which indicates that the substitute groups $-\text{N}(\text{CH}_3)_2$ has the obvious effect on the lowest lying singlet $\rightarrow$ singlet absorption wavelengths. The lowest lying absorption for complexes **1–5** have the different transition configuration contributing to the $\text{S}_0 \rightarrow \text{S}_1$ state. For example, the lowest lying absorption for complex **1** has the HOMO $\rightarrow$ LUMO (39%) and HOMO $\rightarrow$ LUMO + 1 (49%) transition configuration and intraligand charge transfer (ILCT) [$\pi(\text{L}1) \rightarrow \pi^*(\text{L}1)$] character. The lowest lying absorption for complex **3** has the HOMO $\rightarrow$ LUMO + 1 (94%) transition configuration and metal to ligand charge transfer (MLCT)/ILCT character. This shows that the different substituent groups have important influence on the transition character. Complex **5** with the strong electron-accepting substituent $-\text{NO}_2$ has the weakest absorption intensity in comparison with other four complexes. It can be seen that there is an obvious difference between the absorption spectrum of complex **1** and that of **5**, which indicates that the electron-donating substituent $-\text{N}(\text{CH}_3)_2$ and electron-accepting substituent $-\text{NO}_2$ have the different effect on the absorption properties of iridium(III) complexes.

3.4 Phosphorescence property

To check the computational method, five different density functionals (B3LYP [29], CAM-B3LYP [30], M052X [31], M062X [32], and PBE0 [33]) were used to calculate the emission of complex **4**. A better agreement with experimental data was obtained for CAM-B3LYP relative to the other four functionals. The calculated emission wavelengths for complex **4** at B3LYP, CAM-B3LYP, M052X, M062X and PBE0 levels are 526, 505, 457, 436 and 526 nm, respectively, with the deviations of 32, 11, 37, 58 and 32 nm from the measured value of 494 nm [19]. It is obvious that the CAM-B3LYP functional leads to a more satisfactory result. Hence, we have employed the CAM-B3LYP functional for further emission spectral calculations. On the basis of the optimized triplet excited-state geometries, the emission properties of complexes **1–5** in CH_2Cl_2 medium obtained using the TDDFT/CAM-B3LYP method are shown in Table 2. For comparison, the available experimental value has also been listed in Table 2. The plots of the molecular orbitals related to emissions of complexes **1–5** have been depicted in Table 3. In addition, partial frontier molecular orbital compositions (%) of complexes **1–5** in the T_1 state have been provided in Table S7 (Supplementary Materials).

From Table 2 it can be seen that the calculated lowest energy emissions of complex **1** is obviously red-shifted in comparison with that of **3**, which shows electron-donating substituent group $-\text{N}(\text{CH}_3)_2$ has great effect on the phosphorescence emission wavelength. The emission transition characters for complex **1** are assigned to triplet intraligand charge transfer ($^3\text{ILCT}$) [$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$]. In addition, compared to complex **3**, the calculated lowest energy emissions of **2** is also slightly red-shifted, which originates from the $\text{L} \rightarrow \text{H}$ (43%) and $\text{L} + 1 \rightarrow \text{H} - 1$ (24%) transition configuration with triplet metal to ligand charge transfer ($^3\text{MLCT}$)/triplet intraligand charge transfer ($^3\text{ILCT}$) and $^3\text{ILCT}$ characters. However, the introduction of electron-accepting substituent group $-\text{F}$ in complex **4** has no obvious influence on the phosphorescence emission properties, that is, **3** and

Table 2 Phosphorescent emissions of complexes **1–5** in CH_2Cl_2 at the TDDFT calculations, together with the experimental wavelength (nm) available

	λ (nm)/E (eV)	Configuration	Assignment	Nature	Expt. ^a
1	654/1.89	$\text{L} \rightarrow \text{H}$ (71%)	$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$	$^3\text{ILCT}$	
2	513/2.41	$\text{L} \rightarrow \text{H}$ (43%)	$\pi^*(\text{L}1) \rightarrow \text{d}(\text{Ir}) + \pi(\text{L}1)$	$^3\text{MLCT}/^3\text{ILCT}$	494 ^a
		$\text{L} + 1 \rightarrow \text{H} - 1$ (24%)	$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$	$^3\text{ILCT}$	
3	506/2.44	$\text{L} \rightarrow \text{H}$ (41%)	$\pi^*(\text{L}1) \rightarrow \text{d}(\text{Ir}) + \pi(\text{L}1)$	$^3\text{MLCT}/^3\text{ILCT}$	
		$\text{L} + 1 \rightarrow \text{H} - 1$ (25%)	$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$	$^3\text{ILCT}$	
4	505/2.45	$\text{L} \rightarrow \text{H}$ (41%)	$\pi^*(\text{L}1) \rightarrow \text{d}(\text{Ir}) + \pi(\text{L}1)$	$^3\text{MLCT}/^3\text{ILCT}$	
		$\text{L} + 1 \rightarrow \text{H} - 1$ (26%)	$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$	$^3\text{ILCT}$	
5	499/2.48	$\text{L} \rightarrow \text{H}$ (37%)	$\pi^*(\text{L}1) \rightarrow \text{d}(\text{Ir}) + \pi(\text{L}1)$	$^3\text{MLCT}/^3\text{ILCT}$	
		$\text{L} + 1 \rightarrow \text{H} - 1$ (16%)	$\pi^*(\text{L}1) \rightarrow \pi(\text{L}1)$	$^3\text{ILCT}$	

^aReference [21]

Table 3 Transitions responsible for the emissions at 654, 513, 506, 505 and 499 nm for complexes **1–5**, respectively, simulated in CH₂Cl₂ medium

	1	2	3	4	5
L + 1
L
H
H-1

4 have the similar phosphorescence emission properties. Besides, the introduction of electron-accepting substituent group –NO₂ in complex **5** leads to the slight blueshift of phosphorescence emission wavelength, however, possessing the similar transition character to complex **3**. As shown in Table 3 and Table S7, the HOMO and LUMO of complex **1** mainly distribute on the L1 ligand. However, the emission transition characters for complexes **2–5** are assigned to LUMO → HOMO and LUMO + 1 → HOMO–1 transition configurations characterized as triplet metal-to-ligand charge transfer (³MLCT) and ³ILCT. The HOMO of complexes **2–5** are mainly located on the Ir atom and L1 ligand. For example, the HOMO of complex **2** is distributed on the Ir atom (30%) and L1 ligand (66%). Therefore, the introduction of the different electron-donating substituents or electron-accepting ones probably have different effect on the phosphorescence properties.

3.5 Phosphorescence quantum yield

The emission quantum yield (Φ) can be affected by the competition between k_r (radiative decay rate) and k_{nr} (nonradiative decay rate), i.e. $\Phi = k_r / (k_r + k_{nr})$. To increase the quantum yield, k_r should be increased and k_{nr} should be decreased simultaneously or respectively [34, 35]. Moreover, k_r is also theoretically related to the mixing between S₁ and T₁, which is proportional to the spin–orbit coupling (SOC) and

inversely proportional to the energy gaps between the S₁ and T₁ states according to the following formula [36, 37]:

$$k_r \approx \gamma \frac{\langle \psi_{S_1} | H_{S_0} | \psi_{T_1} \rangle^2 \mu_{S_1}^2}{(\Delta E_{S_1-T_1})^2} \quad (1)$$

$$\gamma = 16\pi^3 10^6 n^3 E_{em}^3 / 3h\epsilon_0$$

where H_{S_0} is the Hamiltonian for the spin–orbit coupling, μ_{S_1} is the transition dipole moment in the S₀ → S₁ transition, $\Delta E_{S_1-T_1}$ is the energy gaps between the S₁ and T₁ states, E_{em} represents the emission energy in cm^{–1} and n , h , and ϵ_0 are the refractive index, Planck's constant and the permittivity in a vacuum, respectively. Accordingly, the variation of quantum yield (Φ) can be qualitatively analyzed in theory from the above formula.

It is known that the phosphorescence quantum yield could be increased by a larger ³MLCT composition and thus the intersystem crossing (ISC). Additionally, for iridium atom, the direct involvement of the d(Ir) orbital enhances the first-order SOC in the T₁ → S₀ transition and thus ISC, which would result in a drastic decrease of the radiative lifetime and avoid the nonradiative process [38]. In Table 4, we have listed the ³MLCT contributions which were calculated to be 1.42%, 11.71%, 11.82%, 10.47% and 11.42% for complexes **1–5**, respectively. The ³MLCT contribution of **1** is the smallest one among these complexes. It is also known that the phosphorescence quantum yield

Table 4 The contribution of $^3\text{MLCT}$ (%) in the T_1 state and the energy gaps between the S_1 and T_1 states ($\Delta E_{S_1-T_1}$) (in eV), along with the transition dipole moment in the $S_0 \rightarrow S_1$ transition μ_{S_1} , theradiative decay rate k_r ($\times 10^5 \text{ s}^{-1}$) and nonradiative decay rate k_{nr} ($\times 10^5 \text{ s}^{-1}$), together with the measured lifetime τ [μs] and quantum yield Φ [%] for the studied complex **4** in CH_2Cl_2 solution

	$^3\text{MLCT}$	$\Delta E_{S_1-T_1}$	μ_{S_1}	Φ^a	τ^a	k_r	k_{nr}
1	1.42	0.6805	1.5673				
2	11.71	1.4502	0.6640				
3	11.82	0.4650	0.6591				
4	10.47	0.5438	0.7440	30.9	2.75	1.12	2.51
5	11.42	0.4762	0.2650				

^aReference [21]

are inversely proportional to the $\Delta E_{S_1-T_1}$ [39]. Namely, a minimal $\Delta E_{S_1-T_1}$ is required for enhancing the ISC rate, leading to the increased k_r . The $\Delta E_{S_1-T_1}$ for these complexes are also listed in Table 4, along with the μ_{S_1} values. The results give 0.6805, 1.4502, 0.4650, 0.5438 and 0.4762 eV for the $\Delta E_{S_1-T_1}$, respectively, for complexes **1–5**. From the discussion above, it is obvious that a lower $\Delta E_{S_1-T_1}$ and larger $^3\text{MLCT}$ contributions and higher μ_{S_1} values may account for a larger k_r according to Eq. (1). F.Q. Bai et al. have concluded that electron-withdrawing substituent groups on cyclometalating ligands cannot completely decide the final quantum efficiency [23], which is also seen from complexes **4** and **5** in our study. From the data in Table 4, it can be seen that the complex **3** probably possesses the largest k_r value among these studied complexes.

4 Conclusions

A series of cyclometalated iridium(III) complexes bearing the substituted phenylpyrazole have been studied by using DFT/TDDFT method to explore the electronic structure and photophysical properties. Theoretical calculation results show that the obtain bond lengths Ir–C1, Ir–C2, Ir–N1 and Ir–N2 of complex **4** from theoretical calculation have good agreement with the crystallographic data. The $\Delta E_{L \rightarrow H}$ values increase in the order of **1** (3.78 eV) < **5** (3.92 eV) < **2** (4.09 eV) < **3** (4.13 eV) < **4** (4.22 eV). Both the lowest lying singlet $\rightarrow$ singlet absorption wavelength and the lowest energy emission of complex **1** with the substitute groups $-\text{N}(\text{CH}_3)_2$ have the obvious redshift in contrast to other four complexes. According to the theoretical result, complex **3** could possesses the largest k_r value among these studied complexes. It is anticipated that this study will be useful for designing novel Ir(III) complexes applied to OLEDs field.

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Declarations

Conflict of interest There are no conflicts to declare.

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