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Research paper

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New yellow-emitting iridium(III) complexes containing 2-phenyl-2Hindazole-based ligands for high efficient OLEDs with EQE over 25%

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RTICLE INFO	A B S T R A C T
gwords: dium (III) complexes ellow photoluminescence ganic light-emitting diodes T calculations	Six new pidz-based bis-cyclometalated Ir(III) complexes (Ir1-Ir6) have been synthesized and characterized. These complexes contain 2-phenyl-2H-indazole (pidz, 2a), 2-(4-fluorophenyl)–2H-indazole (fpidz, 2b), 2-(p-tolyl)–2H-indazole (ch ₃ pidz, 2c), 2-(4-(trifluoromethyl)phenyl)–2H-indazole (cf ₃ pidz, 2d), 2-(2,4- difluorophenyl)–2H-indazole (2,4-f ₂ pidz, 2e) and 2-(3,5-difluorophenyl)–2H-indazole (3,5-f ₂ pidz, 2f) as cyclo- metalated (C [^] N) ligands, and acetylacetone (acacH) as ancillary ligand. The crystal structure of Ir2 has been determined by X-ray analysis. Different substituents of C [^] N ligand in Ir2-Ir6 induce either a bathochromic or hypsochromic shift in the absorption spectra relative to the parent complex Ir1 . The phenomenon is further well explained by DFT calculation and electrochemical study. All of the iridium(III) complexes are yellow emissive with quantum yields of 13 1–32.3% and lifetimes of 1.32–1.77 us in solution at room temperature. We de-

monstrate that their emission originates from a hybrid ${}^{3}MLCT/{}^{3}ILCT$ excited state on the basis of the experimental and theoretical investigation. The corresponding yellow-emitting devices based on complexes Ir1, Ir2 and Ir4 can produce efficient electrophosphorescence with a luminance efficiency of 35.1–52.2 cdA⁻¹, a power efficiency of 20.8–32.1 lm·W⁻¹ and an external quantum efficiency of up to 25.6%. All these EL data definitely suggest the bulky –CF₃ skeleton in the doped materials could benefit the fabrication of high-efficiency phosphorescent OLEDs.

1. Introduction

Cyclometalated iridium(III) complexes have been widely employed to fabricate organic light emitting diodes (OLEDs) on account of their relatively short phosphorescence lifetimes, high quantum efficiencies, good thermal stability, and excellent color tunability [1-3]. In particular, yellow iridium(III)-based phosphorescent emitters play an important role in the full color display applications and the high-efficiency two-color (light blue, yellow/orange) WOLEDs (white organic light emitting diodes) [4-6]. To successfully achieve yellow emissions, the cyclometalated ligands should possess a medium-sized π system, because smaller or larger π systems can result in blue or red emissions [7]. Therefore, researchers designed different sizes of hetero-atoms ligands, including C,N-heterocyclic rings [8–11], N,N-heterocyclic rings [12-17], S,N-heterocyclic rings [18-20] and O,N-heterocyclic rings [8,21]. Among these, a kind of commonly used ligand is N,N-heterocyclic compound, such as pyrazine [12], benzoimidazole [13-15], imidazopyridine [16], pyrimidine [17], and phthalazine [22]. To date,

benzoimidazole-based cyclometalated ligands have been extensively studied [23–31], because this type of ligand framework can offer an easy manipulation of donors, substituents and chain length for many specific applications [32]. As the isomer of benzoimidazole, benzoindazole should also has these similar advantages. Surprisingly, it appears that cyclometalated Ir(III) complexes using the benzoindazole-based ligands are rarely reported in the literature, especially the yellowemissive ones.

In 2018, our group firstly reported a series of novel 2-phenyl-2Hindazole-based Ir(III) complexes, $(h-1-pidz)_2Ir(tpip)$, $(f-1-pidz)_2Ir(tpip)$ and $(cf_3-1-pidz)_2Ir(tpip)$, emitting in the yellow region with a peak at 556–576 nm [33]. Unfortunately, using complexes $(f-1-pidz)_2Ir(tpip)$ and $(cf_3-1-pidz)_2Ir(tpip)$ as dopants, both phosphorescent OLEDs exhibited device performances with EQE_{max} values of only 9.0 and 10.7%. To improve the efficiency of this class of complexes, in this work, we further design three new pidz-based derivatives (**2c**, **2e** and **2f**) by introducing methyl group and fluorine group to the parent ligand (**2a**). In the meanwhile, we employ the other two reported ligands (**2b** and **2d**)

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Scheme 1. Synthetic routes of Ir(III) complexes Ir1-Ir6.



Fig. 1. Chemical structures of complexes Ir1-Ir6.



Fig. 2. (a) Perspective diagram of complex **Ir2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity; (b) Selected non-covalent C–H··O contacts (dashed red lines). Atoms involved in hydrogen bonds are shown as balls of arbitrary radii. All other atoms and covalent bonds are represented as wires or sticks. Symmetry codes: x, 1/2-y, -1/2 + z; 1/2-x, 1-y, -0.5 + z.

as the cyclometalated ligands and acetylacetone (acacH) as the ancillary ligand to synthesize a series of iridium(III) complexes (**Ir1-Ir6**) (Scheme 1). Their photophysical and electrochemical properties have been studied systematically. The lowest energy electronic transitions and the lowest triplet excited states have been calculated using density functional theory (DFT) and time-dependent DFT (TD-DFT). All these Ir (III) complexes produce the expected yellow emission in CH₂Cl₂ solution (Fig. 1). Cyclometalated iridium(III) complexes (**Ir1, Ir2** and **Ir4**) have been employed as emitters to construct yellow-emitting OLEDs (**D1, D2** and **D4**), which display good EL performance with an external quantum efficiency of up to 25.6%.

2. Results and discussion

2.1. Structural description

The single crystal structure of **Ir2** was obtained through X-ray diffraction analysis, and the ORTEP diagram is shown in Fig. 2a. The crystallographic data and structure refinement details are listed in Table S1, with selected bond lengths and bond angles collected in Table S2. Single crystal structure of **Ir2** was deposited to Cambridge Crystallographic Data Centre (CCDC) with deposition number of 1967686.

As shown in Fig. 2a, the iridium metal center adopts a distorted octahedral coordination geometry with the C and N atoms of the cyclometalated ligands and the two O atoms of the ancillary ligand. The nitrogen atoms in the cyclometalated ligands are *trans* conformation with respect to one another, while the two carbon atoms are *cis* dispositions. All of the Ir-C (1.963(8) – 2.036(8)Å), Ir – N (2.040(7) – 2.053(7) Å) and Ir – O (2.128(6) – 2.136(5) Å) bond lengths are close to those in previously reported iridium complexes [34]. The bite angle of O1–Ir1–O2 (86.6(2)°) in a six-membered chelate ring is much larger than that of C13–Ir1–N1 (80.0(3)°) or C26–Ir1–N3 (80.0(3)°) in a five-membered chelate ring. In addition, the adjacent non-covalent contacts in the crystal structure are presented in Fig. 2b, including intramolecular hydrogen bond (C2–H2··O2, 2.48 Å) and intermolecular hydrogen bond (C9–H9··O2, 2.42 Å; C20–H20··O1, 2.57 Å).

2.2. Photophysical properties

The UV–vis absorption and photoluminescence (PL) emission spectra of all complexes in CH_2Cl_2 solution at room temperature are depicted in Fig. 3, and the corresponding photophysical data are provided in Table 1. The strong absorption bands in the range of 220–320 nm match those of the free ligands (Fig. S3), and thus can be attributed to the spin-allowed ligand-centered (¹LC) $\pi \rightarrow \pi^*$ transitions. The weaker absorption bands at ca. 320–500 nm are ascribed to a mixture of metal to ligand (Ir to C^N) charge transfer (¹MLCT) and intraligand (C^N to C^N) charge transfer (¹ILCT) transitions on the basis of TD-DFT analysis. With the same ancillary ligand, the UV–vis absorption spectra of these complexes are perturbed by the substituent

patterns on cyclometalated ligands. For example, **Ir2** (420 nm) and **Ir4-Ir6** (424 nm, 418 nm, 420 nm) exhibit a relatively blue-shifted absorption band than **Ir1** (427 nm), which is due to the electron-withdrawing effect exerted by the fluorine substituent. On the contrary, **Ir3** (429 nm) with electron-donating $-CH_3$ group gives rise to a slightly redshifted absorption band compared to **Ir1** (427 nm).

All of the iridium complexes reported here are yellow-emitting in solution at room temperature. Their emission spectra display structured profiles comprising ³MLCT transitions with maxima at 554–570 nm, and the vibronic progression with shoulder peaks at 588–608 nm [35–36]. For the purpose of comparison, we take **Ir1** (564 nm) as the parent complex. Changing the substituents (-F, $-CH_3$, $-CF_3$) on cyclometalated ligands in **Ir2-Ir4** (554 nm, 558 nm, 570 nm) have a moderate impact on the emission wavelength. However, complexes **Ir5** (565 nm) and **Ir6** (566 nm) exhibit nearly identical emission spectra, suggesting that substituions at the 2,4- and 3,5-positions have a minimal influence on the luminescence. The different behavior indicates that the substituents on the phenyl of C^N ligands play an important role in positioning the emission profile.

Remarkably, the $\Phi_{\rm em}$ of fluorinated complexes **Ir2** and **Ir4-Ir6** are higher than that of un-fluorinated analogues **Ir1** and **Ir3** (Table 1). This is dependent on the fact that the presence of the C – F bonds could lead to the reduced radiationless deactivation rate in comparison with that seen with C – H bonds [33,37]. Subsequently, their radiative decay rate (k_r) and the nonradiative decay rate (k_{nr}) were estimated from the $\Phi_{\rm em}$ and τ values. It is noteworthy that **Ir4** bearing –CF₃ group on the C^N ligands, has the largest k_r and the smallest k_{nr}, resulting in the highest quantum yield in the series.

2.3. Theoretical calculations

In order to further understand the lowest-energy electronic transitions, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed on **Ir1-Ir6**. The calculated energy levels and the most representative molecular frontier orbital diagrams for these complexes are presented in Fig. 4 and Fig. S1, respectively. The calculated spin-allowed electronic transitions are provided in Table 2. The electron density distributions are summarized in Table S3.

For all the complexes, the calculations clearly show that the HOMO is located more on the iridium center (47.92 ~ 51.68%) and the phenyl ring (41.21 ~ 45.88%) from C^N ligands. The LUMO and LUMO + 1 are very similar, dominated by the whole C^N ligands (96.18 ~ 96.97% and 96.20 ~ 96.83%). Hence, the low-energy absorption transitions (HOMO \rightarrow LUMO, HOMO \rightarrow LUMO + 1) of **Ir1-Ir6** can be ascribed as the ¹MLCT transition from the *d* orbital of iridium to π^* orbital of the C^N ligand, supporting the experimental assignment of the absorption tails.

Upon the introduction of electron-donating methyl group on the C^N ligand from **Ir1** to **Ir3**, the HOMO and LUMO are destabilized by 0.058 and 0.042 eV. In contrast, fluorinating the pidz ligand from **Ir1** to **Ir2**, the HOMO and LUMO are stabilized by 0.154 and 0.032 eV. Changing



Fig. 3. UV-vis absorption (a) and PL emission (b) spectra of complexes Ir1-Ir6 in CH₂Cl₂ solution at room temperature.

Table 1				
Photophysical	data	of	complexes	Ir1-Ir6.

Complex	Absorption ^a λ_{abs} (nm) ϵ (10 ⁴ cm ⁻¹ ·M ⁻¹)	Emission $\lambda_{em}^{a}(nm)$	$\Phi_{em}^{\ \ b}(\%)$	$\tau^{a}(\mu s)$	$k_r^c (10^5 s^{-1})$	$k_{nr}^{c}(10^{5} \text{ s}^{-1})$
Ir1	251(2.20), 304(1.58), 315(1.47), 355(0.57), 427(0.38)	564, 597(sh)	40.8	1.57	2.60	3.77
Ir2	248(2.32), 303(1.86), 311(1.86), 348(0.89), 387(0.69), 420(0.31)	554, 588(sh)	58.6	1.57	3.73	2.64
Ir3	255(2.23), 309(1.85), 319(1.79), 353(0.84), 394(0.60), 429(0.35)	558, 593(sh)	33.1	1.32	2.51	5.07
Ir4	246(2.86), 303(1.98), 314(1.92), 358(0.74), 395(0.63), 424(0.37)	570, 608(sh)	74.2	1.77	4.19	1.46
Ir5	241(3.53), 302(2.49), 313(2.45), 349(1.18), 386(0.86), 418(0.43)	565, 603(sh)	64.7	1.68	3.85	2.10
Ir6	241(3.48), 303(2.54), 312(2.50), 353(1.23), 389(0.92), 420(0.37)	566, 605(sh)	68.8	1.69	4.07	1.85

^a Data were collected from degassed CH_2Cl_2 solutions at 298 K. ^b Absolute emission quantum yields measured in degassed CH_2Cl_2 solution. ^c Radiative decay rate (k_{rr}) and nonradiative decay rate (k_{rr}) were estimated from the measured quantum yields and lifetimes.

the –F to –CF₃, 2,4-F₂ and 3,5-F₂ substituents, the HOMOs of **Ir4-Ir6** are further lowered with similar values of $-5.387 \sim -5.549$ eV. However, the energetic difference between the LUMO orbitals of **Ir4-Ir6** is very large, from -1.709 to -1.866 eV. In the case of the energy gap, the order is **Ir3** < **Ir1** < **Ir6** < **Ir4** < **Ir2** < **Ir5**, correlating well with the experimental low-energy absorption bands. The finding indicates the electron-donating group (–CH₃) can shrink the energy gap, while the electron-withdrawing group can enlarge it, especially 2,4-F₂ substituents.

To understand the nature of the transitions in the emission profile, the TD-DFT calculations were also carried out to study their lowest triplet excited state (T₁) characters, and the relevant information is presented in Table 2. For complexes **Ir1-Ir6**, their T₁ are ascribed to spin–orbit-induced mixings of several transitions, but with major contributions from HOMO-1 \rightarrow LUMO + 1 (**Ir1-Ir3**, **Ir5** and **Ir6**) and HOMO-1 \rightarrow LUMO (**Ir4**). Base on the electron density distribution information in Table S3, HOMO-1 are located on Ir *d*-orbital, C^N ligands and ancillary ligands, while LUMO and LUMO + 1 are largely dominated on C^N ligands. Consequently, their (T₁) states have ³MLCT/³ILCT/³LLCT characteristics, which is in line with the vibronically structured bands observed in the emission spectra.

2.4. Electrochemical properties

The electrochemical properties of all the complexes were measured by cyclic voltammetry in CH_2Cl_2 solution (0.1 M *n*-Bu₄NClO₄) and the electrochemical waves are given in Fig. 5. On the basis of their oxidation potentials and absorption spectra, the HOMO and LUMO energy levels are estimated and included in Table 3, as well as compared with the theoretical data. All complexes exhibit complicated quasi-reversible or irreversible oxidation processes, which is presumably caused by the reaction or decay products resulting from multiple oxidation processes centered on iridium and cyclometalated ligands [38]. However, no reduction process due to the ligands was observed within the solvent cathodic potential limit.

In order to gain the HOMO energy levels, we hence focused on the first oxidation waves of Ir1-Ir6. From Table 3, the onset oxidation potentials (E_{onset}^{ox}) of these iridium complexes are 0.67–0.80 V (vs Fc/ Fc⁺). Three complexes exhibit quasi-reversible oxidation processes $(Ir2, \Delta E_p = 103 \text{ mV}, i_{pc}/i_{pa} = 0.55; Ir5, \Delta E_p = 106 \text{ mV}, i_{pc}/i_{pa} = 0.17;$ Ir6, $\Delta E_p = 122 \text{ mV}, i_{pc}/i_{pa} = 1.73$. Apparently, with the electronwithdrawing fluorine-substituted ligands, Ir2 and Ir4-Ir6 show more positive oxidation potentials relative to **Ir1**, resulting in the stabilization of the HOMO orbitals. Nevertheless, Ir3 consisting of the electrondonating -CH₃ ligands displays the opposite situation, which in turn leads to much higher HOMO energy levels. According to the equation of HOMO = $- [E_{onset}^{ox} + 4.8]$ eV [39], the HOMO energy levels are deduced to be $-5.47 \sim -5.60$ eV. The calculated results reveal the above order is Ir2, Ir4-Ir6 < Ir1 < Ir3, which was consistent with the DFT-calculated values. Therefore, these electrochemical features provide evidence that the chemical modification of cyclometalated ligands affects the energy levels of HOMO. Additionally, the energy levels of the LUMO are obtained from the HOMO and E_{opt.g} values. From Table 3, it can be observed that the experimental LUMO energy levels are lower than the theoretical ones, but they have the same order, that is Ir4 < Ir6 < Ir5 < Ir2 < Ir1 < Ir3.

2.5. Electroluminescence devices

To illustrate electroluminescence (EL) properties of **Ir1**, **Ir2** and **Ir4** as the phosphorescent emitter, the corresponding monochrome devices **D1**, **D2** and **D4** were fabricated with the following configurations via vacuum thermal evaporation: ITO/MoO₃ (5 nm) / TAPC (30 nm) / 2,6-DCzPPy : Ir complex (8 wt%, 10 nm) / TmPyPB (40 nm) / LiF (1 nm) / Al (100 nm). The schematic energy level diagrams of electrophosphorescent devices and the molecular structures of materials used in these devices are depicted in Fig. 6. MoO₃ acts as a hole-injection layer (HIL), TPAC [4,4'-(cyclohexane-1,1-diyl)bis(*N*,*N*-di-*p*-tolylaniline)] as a hole-transport layer (HTL), TmPyPb [1,3,5-tri[(3-pyridyl)-phen-3-yl] benzene] as an electron-transport layer (ETL), and LiF as an electron-



Fig. 4. Calculated energy levels and energy gaps for complexes Ir1-Ir6. The molecular orbital diagrams of complex Ir1 are plotted as representative.

Table 2

Contributions,	oscillator	strengths a	nd transition	characters	of single	t and tri	plet transition	s for com	plexes Ir1	-Ir6.

Complex		Major assignments	Transition	Character	Oscillation Strength
Ir1 Ir2	S ₁ T ₁ S ₁ T ₁	HOMO → LUMO + 1 HOMO-1 → LUMO + 1 HOMO → LUMO + 1 HOMO-1 → LUMO + 1	¹ MLCT/ ¹ ILCT ³ MLCT/ ³ LLCT ¹ MLCT/ ¹ ILCT ³ MLCT/ ³ ILCT/ ³ LLCT	$\begin{split} d\pi_{ir/pidz} & \rightarrow \pi^*{}_{pidz} \\ d\pi_{ir/pidz/acac} & \rightarrow \pi^*{}_{pidz} \\ d\pi_{ir/pidz} & \rightarrow \pi^*{}_{fpidz} \\ d\pi_{ir/fpidz/acac} & \rightarrow \pi^*{}_{fpidz} \end{split}$	0.1048 0 0.1104 0
Ir3	S ₁ T ₁	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO} \ + \ 1 \\ \text{HOMO-1} \rightarrow \text{LUMO} \ + \ 1 \end{array}$	¹ MLCT/ ¹ ILCT ³ MLCT/ ³ ILCT/ ³ LLCT	$d\pi_{Ir/ch3pidz} \rightarrow \pi^*_{ch3pidz}$ $d\pi_{Ir/ch3pidz/acac} \rightarrow \pi^*_{ch3pidz}$	0.1130 0
Ir4	S ₁ T ₁	$HOMO \rightarrow LUMO$ $HOMO-1 \rightarrow LUMO$	¹ MLCT/ ¹ ILCT ³ MLCT/ ³ ILCT/ ³ LLCT	$\begin{array}{l} d\pi_{\rm Ir/cf3pidz} \rightarrow \pi^*{}_{cf3pidz} \\ d\pi_{\rm Ir/cf3pidz/acac} \rightarrow \pi^*{}_{cf3pidz} \end{array}$	0.0946 0
Ir5	S ₁ T ₁	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO} \ + \ 1 \\ \text{HOMO-1} \rightarrow \text{LUMO} \ + \ 1 \end{array}$	¹ MLCT/ ¹ ILCT ³ MLCT/ ³ ILCT/ ³ LLCT	$\begin{array}{l} d\pi_{Ir/2,4-f2pidz} \twoheadrightarrow \pi^{*}{}_{2,4-f2pidz} \\ d\pi_{Ir/2,4-f2pidz/acac} \twoheadrightarrow \pi^{*}{}_{2,4-f2pidz} \end{array}$	0.0855 0
Ir6	S ₁ T ₁	$\begin{array}{l} \text{HOMO} \rightarrow \text{LUMO} \ + \ 1 \\ \text{HOMO-1} \rightarrow \text{LUMO} \ + \ 1 \end{array}$	¹ MLCT/ ¹ ILCT ³ MLCT/ ³ ILCT/ ³ LLCT	$\begin{array}{l} d\pi_{\rm Ir/3,5\mbox{-}f2pidz} \rightarrow \pi^*{}_{3,5\mbox{-}f2pidz} \\ d\pi_{\rm Ir/3,5\mbox{-}f2pidz/acac} \rightarrow \pi^*{}_{3,5\mbox{-}f2pidz} \end{array}$	0.0915 0

injection layer (EIL). In addition, 2,6-DCzPPy layers doped with Ir(III) complexes act as the emissive layer (EML).

The EL spectra, current density-luminance-voltage (J-L-V), current efficiency-luminance (η_c -L) and external quantum efficiency-luminance (EQE-L) characteristics of devices (8 wt% doping level) are shown in Fig. 7. The key device performance data are summarized in Table 4. At a driving voltage of 8 V, the normalized EL spectra of these devices D1, D2 and D4 show the maximum emission peak at 556–570 nm, together with a shoulder peak at 590–610 nm (Fig. 7a). The Commission Internationale de L'Eclairage (CIE) color coordinates are (0.47, 0.49) for D1, (0.47, 0.47) for D2 and (0.47, 0.47) for D4. All of these values correspond to the yellow region of the CIE chromaticity diagram. In each case, the close resemblance between the EL and PL spectra indicates that the triplet excitons of the phosphors are the same type and the energy can be transferred from 2,6-DCzPPy to the emitters in the EML. For all devices, the turn on voltages (V_{turn-on}) are 3.9–4.0 V and the maximum luminance (L_{max}) are 8508–15295 cd·m⁻² at 12.6-13.9 V (Fig. 7b). In the series, device D4 exhibits the best device performance with a luminance efficiency ($\eta_{c,max}$) of 52.2 cd·A⁻¹, a power efficiency ($\eta_{p,max}$) of 32.1 lm·W⁻¹ and a maximum external quantum efficiency (EQE_{max}) of 25.6%. The two other devices exhibit a $\eta_{c,max}$ of 35.1 cd·A⁻¹, a $\eta_{p,max}$ of 20.8 lm·W⁻¹ and EQE_{max} of 17.3% for **D1**, and a $\eta_{c,max}$ of 40.3 cd·A⁻¹, a $\eta_{p,max}$ of 26.9 lm·W⁻¹ and EQE_{max} of 19.8% for D2 (Fig. 7c-d). These results reveal that the overall efficiency parameters are D4 > D2 > D1, which may be attributed to a higher PL triplet yield of the former as compared to the latter series [40]. Moreover, it should be highlighted that the bulky –CF₃ groups of dopant Ir4 in the EML can restrain the self-quenching of luminescence, thus improving device performance.

3. Conclusion

A novel series of bis-cyclometalated pidz-based iridium complexes along with acacH as the ancillary ligand were synthesized and characterized. In the cyclometalated ligands, the phenyl ring was either unsubstituted or substituted with electron-donating groups $(-CH_3)/$ electron-withdrawing groups (-F, $-CF_3$, 2,4-F₂ and 3,5-F₂). The influence of these substituents on the structure–property relationships of iridium complexes was systematically investigated through photophysical and electrochemical studies, as well as theoretical calculations. The yellow OLEDs by using the complexes **Ir1**, **Ir2** and **Ir4** as triplet emitters achieved good device performance with the external quantum efficiencies of 17.3–25.6%. This work not only can represent a new approach to develop high-efficient pidz-based iridium(III) complexes, but also provide some important information in designing two-color (light blue, yellow/orange) WOLEDs.

4. Experimental

4.1. General

All reactions were performed under nitrogen atmosphere. All of the reagents were purchased from commercial sources and used without further purification, unless stated otherwise. 2-Phenyl-2H-indazole (pidz, 2a), 2-(4-fluorophenyl)-2H-indazole (fpidz, 2b) and 2-(4-(trifluoromethyl)phenyl)-2H-indazole (cf3pidz, 2d) were synthesized according to our previous paper [34]. ¹H NMR spectra were recorded on a Bruker AM 400 MHz instrument, and chemical shifts were reported in ppm relative to Me₄Si as internal standard. MALDI-TOF-MS spectra were recorded on a Bruker Autoflex ^{II}TM TOF/TOF instrument. The elemental analyses were measured on a Vario EL Cube Analyzer system. UV-vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F-7000 spectrophotometer in degassed CH₂Cl₂ solutions at room temperature and corrected for the detector response. Luminescence lifetimes were measured on a HORIBA FL-3 fluorescence spectrometer and the data were treated as one-order exponential fitting using OriginPro 8 software. The absolute photoluminescence quantum yield (Φ_{em}) was measured on a HORIBA FL-3 fluorescence spectrometer equipped with an integrating sphere. Radiative decay constants (kr) were calculated using



Fig. 5. Cyclic voltammograms for complexes Ir1-Ir6 in CH₂Cl₂ solution (0.1 M *n*-Bu₄NClO₄). The scan rate was 100 mV·s⁻¹ and ferrocene was used as a reference.

Electrochemical and theoretical data of complexes Ir1-Ir6.

Complex	$E_{onset}^{ox a}(V)$	$\Delta E_{\rm p}^{\ b}({\rm mV})$	$i_{\rm pc}/i_{\rm pa}{}^c$	$E_{\text{opt},g}^{d}(\text{eV})$	$E_{\rm HOMO}/E_{\rm LUMO}^{e}({\rm eV})$	$E_{\rm HOMO}/E_{\rm LUMO}^{f}(\rm eV)$
Ir1	0.69	_g	_g	2.90	-5.49/-2.59	-5.23/-1.64
Ir2	0.74	103	0.55	2.95	-5.54/-2.59	-5.38/-1.67
Ir3	0.67	_g	_g	2.89	-5.47/-2.58	-5.17/-1.60
Ir4	0.77	_g	_g	2.92	-5.57/-2.65	-5.49/-1.87
Ir5	0.80	106	0.17	2.97	-5.60/-2.63	-5.55/-1.71
Ir6	0.79	122	1.73	2.95	-5.59/-2.64	-5.39/-1.78

^a The first oxidation processes, and values are reported to Fc/Fc⁺. ^b The peak separation. ^c The peak current ratios. ^d Calculated from the UV–vis absorption edges $(E_{opt,g} = 1240/\lambda_{onset})$. ^e Deduced from the equation $E_{HOMO} = -[E_{onset}^{ox} + 4.8]$ eV and LUMO = HOMO + $E_{opt,g}$, respectively. ^f Obtained from theoretical calculations. ^g Irreversible.

the equation Φ_{em} / τ , where τ is the excited-state lifetime of the sample, and subsequently, nonradiative decay constants (k_{nr}) were calculated using the relationship k_{nr} = (1 - Φ_{em}) / τ [41].

4.2. X-ray crystallography

X-ray diffraction data were collected with an Agilent Technologies Gemini A Ultra diffractometer equipped with graphite-monochromated Mo-K α radiation (λ = 0.7107 Å) at room temperature. Data collection and reduction were processed with CrysAlisPro software [42]. The structure was solved using Superflip [43] and refined using SHELXL – 2014 [44] within Olex2 [45].

4.3. Theoretical calculations

All calculations were carried out with Gaussian 09 software package [46]. The density functional theory (DFT) and time-dependent DFT (TDDFT) were employed with no symmetry constraints to investigate the optimized geometries and electron configurations with the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid density functional theory [47–49].

4.4. Electrochemistry

Cyclic voltammetry (CV) was performed on a CHI 1210B electrochemical workstation, with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag/AgCl electrode as the reference electrode, and 0.1 M *n*-Bu₄NClO₄ as the supporting electrolyte. The redox potentials are reported relative to an external ferrocene/ferrocenium (Fc/Fc⁺) reference.

4.5. OLED fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 10 Ω ·sq⁻¹. The deposition rate for organic compounds is 1–2 Å·s⁻¹. The phosphor and the host 2,6DCzPPy were co-evaporated to form emitting layer from two separate sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å·s⁻¹ and then by evaporation of Al metal with a rate of 3 Å·s⁻¹. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

4.6. Synthesis

4.6.1. 2-(p-tolyl)–2H-indazole (ch₃pidz, 2c)

Aminotoluene (500 mg, 4.67 mmol) and 2-nitrobenzaldehyde (715 mg, 4.67 mmol) were added in EtOH (15 mL) and refluxed for 5 h. After the solvent was removed in vacuo, the obtained yellow compound **1c** was dissolved in P(OEt)₃ (10 mL) and heated at 110 °C for 8 h. The solvent was removed, and the resulting residue was purified by column chromatography on silica gel, eluted with EtOAc / hexanes (1:100, v/v) to give compound **2c** (585 mg, yield: 60.2%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 7.74 ~ 7.92 (m, 3H), 7.70 (dt, J = 8.4, 0.8 Hz, 1H), 7.28 ~ 7.38 (m, 3H), 7.11 (ddd, J = 8.4, 6.4, 0.8 Hz, 1H), 2.42 (s, 3H).

Compounds **2e** and **2f** were obtained in good yields by following the procedure described for **2c**.





Fig. 6. Energy level diagram of phosphorescent OLEDs and their molecular structures of used materials.



Fig. 7. Characteristics of devices D1, D2 and D4: (a) normalized EL spectra at 8 V; (b) luminance–voltage–current density curves; (c) current efficiency–luminance curves; (d) external quantum efficiency–luminance curves.

 Table 4

 EL performances of single-EML devices D1, D2 and D4.

Device	Emitter	$V_{turn-on}^{a}(V)$	L_{\max}^{b} [cd·m ² (V)]	$\eta_{c,\max}^{c}(\mathrm{cd}\ \mathrm{A}^{1})$	$\eta_{p,\max}^{c}(\operatorname{Im} W^{1})$	$EQE_{\max}^{c}(\%)$	EL ^d (nm)	CIE ^e (x, y)
D1	Ir1	3.9	8508(12.6)	35.1	20.8	17.3	562, 600(sh)	(0.47, 0.49)
D2	Ir2	4.0	9916(13.4)	40.3	26.9	19.8	556, 590(sh)	(0.47, 0.47)
D4	Ir4	3.9	15295(13.9)	52.2	32.1	25.6	570, 610(sh)	(0.47, 0.47)

^a Turn-on voltage recorded at a luminance of 1 cd·m⁻². ^b Maximum luminance. ^c Data at maximum and 1000 cd·m⁻² for current efficiency ($\eta_{c,max}$), power efficiency ($\eta_{p,max}$) and EQE_{max} , respectively. ^d Values were collected at 8 V. ^e CIE (Commission Internationale de l'Eclairage) coordinates at 8 V.

7.68 (d, J = 8.5 Hz, 1H), 7.46 ~ 7.59 (m, 2H), 7.33 ~ 7.40 (m, 1H), 7.12 (dd, J = 8.3, 6.8 Hz, 1H), 6.84 (tt, J = 8.6, 2.2 Hz, 1H).

4.6.3. 2-(3,5-difluorophenyl)-2H-indazole (3,5-f2pidz, 2f)

¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.25 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 6.67 ~ 6.85 (m, 3H).

5. General procedure for the Ir(III) complexes Ir1-Ir6.

The cyclometalated Ir(III) dichloro-bridged dimmers $[(C^N)_2 Ir(\mu-Cl)]_2$ were synthesized according to the method reported by Nonoyama [50]. And then the complexes **Ir1-Ir6** were prepared by the reaction of Ir(III) dichloro-bridged dimmers, 8.0 equiv of acetylacetone (acacH) and 5.0 equiv of sodium carbonate in 2-ethoxyethanol at 120 °C. After the reaction was completed, the mixture was diluted with water and extracted multiple times with DCM. The combined organic phase was concentrated and the residue was purified by column chromatography to provide the desired complexes **Ir1-Ir6**.

(pidz)₂Ir(acac) (Ir1) (76 mg, 45.3%), yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (2 s, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.67 (dd, J_1 = 0.8 Hz J2 = 8.8 Hz, 2H), 7.41 (dd, J_1 = 0.8 Hz J_2 = 8.0 Hz, 2H), 7.30 ~ 7.35 (m, 2H), 7.22 ~ 7.25 (m, 2H), 6.84 ~ 7.88 (m, 2H), 6.59 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 2H), 6.13 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 2H), 5.26 (s, 1H), 1.94 (s, 6H). MALDI-TOF calcd for C₃₁H₂₅IrN₄O₂: 678.161 ([M + H]⁺), found: 678.300, 577.070 (M – acac). Anal. calcd for C₃₁H₂₅IrN₄O₂: C, 54.94; H, 3.72; N, 8.27%; Found: C, 54.95; H, 3.73; N, 8.28%.

(fpidz)₂Ir(acac) (Ir2) (65 mg, 38.3%), yellow solid. ¹H NMR

(400 MHz, CDCl₃) δ 8.52 (2 s, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.33 ~ 7.39 (m, 4H), 7.24 (t, J = 6.8 Hz, 2H), 6.58 (dt, J_1 = 2.8 Hz, J_2 = 8.4 Hz, 2H), 5.74 (dd, J_1 = 2.8 Hz, J_2 = 9.2 Hz, 2H), 5.28 (s, 1H), 1.81 (s, 6H). MALDI-TOF calcd for C₃₁H₂₃F₂IrN₄O₂: 714.142 ([M + H]⁺), found: 714.231, 613.025 (M – acac). Anal. calcd for C₃₁H₂₃F₂IrN₄O₂: C, 52.17; H, 3.25; N, 7.85%; Found: C, 52.18; H, 3.27; N, 7.86%.

(ch₃pidz)₂Ir(acac) (Ir3) (72 mg, 43.6%), yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.27 ~ 7.35 (m, 4H), 7.15 ~ 7.25 (m, 2H), 6.66 (dd, J = 8.0, 1.2 Hz, 2H), 5.94 (d, J = 1.0 Hz, 2H), 1.95 (s, 6H), 1.78 (s, 6H). MALDI-TOF calcd for C₃₃H₂₉IrN₄O₂: 706.192 ([M + H]⁺), found: 706.328, 605.141 (M – acac). Anal. calcd for C₃₃H₂₉IrN₄O₂: C, 56.15; H, 4.14; N, 7.94%; Found: C, 56.17; H, 4.13; N, 7.97%.

(cf₃pidz)₂Ir(acac) (Ir4) (62 mg, 40.6%), yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.55 (2 s, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.34 ~ 7.42 (m, 4H), 7.24 ~ 7.28 (m, 2H), 6.75 (dd, J_1 = 1.2 Hz, J_2 = 8.8 Hz, 2H), 5.84 (d, J = 1.2 Hz, 2H), 5.27 (s, 1H), 1.81 (s, 6H). MALDI-TOF calcd for C₃₃H₂₃F₆IrN₄O₂: 814.135 ([M + H]⁺), found: 814.316, 713.177 (M-acac). Anal. calcd for C₃₃H₂₃F₆IrN₄O₂: C, 48.71; H, 2.85; N, 6.88%; Found: C, 48.69; H, 2.86; N, 6.86%.

(2,4-f₂pidz)₂Ir(acac) (Ir5) (69 mg, 42.9%), yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 7.34 ~ 7.38 (m, 2H), 6.75 (dd, J = 8.4, 1.6 Hz, 2H), 5.84 (d, J = 1.6 Hz, 2H), 5.27 (s, 1H), 1.81 (s, 2H). MALDI-TOF calcd for C₃₁H₂₁F₄IrN₄O₂: 750.123 ([M + H]⁺), found: 750.251, 649.024 (M – acac). Anal. calcd for C₃₁H₂₁F₄IrN₄O₂: C, 49.66; H, 2.82; N, 7.47%; Found: C, 49.67; H, 2.81; N, 7.48%.

(3,5-f₂pidz)₂Ir(acac) (Ir6) (78 mg, 48.1%), yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.24 ~ 7.28 (m, 2H), 6.46 ~ 6.51 (m, 2H), 5.54 (dd, J = 8.4, 2.2 Hz, 2H), 5.28 (s, 1H), 1.82 (s, 6H). MALDI-TOF calcd for C₃₁H₂₁F₄IrN₄O₂: 750.123 ([M + H]⁺), found: 750.246, 649.032 (M – acac). Anal. calcd for C₃₁H₂₁F₄IrN₄O₂: C, 49.66; H, 2.82; N, 7.47%; Found: C, 49.69; H, 2.80; N, 7.49%.

CRediT authorship contribution statement

Zhuo Liu: Conceptualization, Investigation, Writing - original draft. Rui-Lian Yang: Investigation, Visualization. Xiao-Han Yang: Formal analysis, Data curation. Jing-Lan Cao: Investigation, Validation. Xu-Ru Fan: Investigation, Validation. Shui-Xing Wu: Software, Formal analysis, Funding acquisition. Zhi-Gang Niu: Methodology, Resources, Supervision, Funding acquisition. Gao-Nan Li: Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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