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Color tuning of iridium(III) complexes containing 2-phenylbenzothiazole-based cyclometalated ligands for application in highly efficient organic light-emitting diodes

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ABSTRACT

By introducing a carbazolyl or diphenylamino substituent into the cyclometalated ligand, replacing the ancillary ligand of acetylacetone into 2-picolinic acid, or employing a homoleptic molecular structure, six complexes $(TM1 \sim 6)$ bearing a similar molecular skeleton of yellow-emissive bis(2-phenylbenzo[d]thiozolato-N, C^{2})iridium (III) (acetylacetonate) (Ir-bt) have been acquired. In despite of their different types of ancillary ligand, or different homoleptic or heteroleptic molecular structures, TM1~3 bearing carbazolyl-modified cyclometalated ligands all emit vellow photoluminescence (PL) with their PL maximum (λ_{PLmax}) locating at 555–565 nm. Nevertheless, for TM4~6 bearing diphenylamino-modified cyclometalated ligands, they show red PL emission whose $\lambda_{PLmax} = 618-636$ nm, which is significantly red-shifted than that of Ir-bt. Note that the PL emission of these diphenylamino-modified iridium chelates can be fine-tuned by alteration on its ancillary ligand, or using a homoleptic structure. By taking advantage of the excellent thermal stability and relatively high PL efficiencies of TM3 and TM6, organic light-emitting diodes devices (OLEDs) using them as phosphorescent guests show relatively high electroluminescence performance. The TM3-based device can emit highly efficient yellow light with CIE coordinates of (0.43, 0.56), a maximum current efficiency (η_{Lmax}) of 54.2 cd·A⁻¹, and a maximum power efficiency (η_{Pmax}) of 48.9 lm W⁻¹, which is one of the highest reported power efficiency data of yellow PhOLEDs; the **TM6**-based device can emit orange emission with CIE coordinates of (0.57, 0.42), $\eta_{\rm Lmax}$ of 18.6 cd·A⁻¹, and $\eta_{\rm Pmax}$ of 14.3 lm·W⁻¹.

1. Introduction

Electrophosphorescent iridium(III) complexes have shown great application prospect in displays and lighting sources due to their high luminous efficiencies as well as flexible color tunability [1-4]. As red emission is a key component for full-color display applications, and yellow materials play an irreplaceable role in the fabrication of binary white organic light-emitting diodes (OLEDs) [5,6], the development of high-performance red and yellow iridium(III) complexes is of great significance [7–10].

Bis(2-phenylbenzothiozolato- $N_{c}C^{2'}$)iridium(III) (acetylacetonate) [(bt)₂Ir(acac), **Ir-bt**] is a typical yellow-emitting phosphorescent

material ($\lambda_{PLmax} = 557$ nm, $\phi_{PL} = 0.26$) [11]. Recently, enormous research effort has been devoted to the structural modification on **Ir-bt**, so that complexes with other luminescent colors or further enhanced yellow electroluminescence (EL) performance can be acquired [12–28]. The results indicated that while little substituent effect is generally observed on the color-tuning when structural modifications are carried on the benzothiazole moiety of the phenylbenzothiazole (**bt**) cyclometalated ligand [12–17], distinct color-tuning can be realized by grafting substituents on the phenyl segment of the **bt** ligand of **Ir-bt** [18–26]. However, despite the fact that many **Ir-bt**-based complexes showing diversified PL emission colors have been constructed successfully [12–28], so far there is only one example of **Ir-bt**-based complex

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that can emit red phosphorescence via substituent effect: in 2004, by introducing an electron-donating methoxy group (CH₃O-) into the *met*-*a*-position of the phenyl moiety of **bt**, Chang et al. developed an **Ir-bt**-based red phosphor whose λ_{PLmax} locates at 605 nm [19].

On the other hand, although up to date, yellow PhOLEDs with maximum external quantum efficiency (EqE_{max}) approaching 30% [13], high maximum current efficiency (η_{Lmax}) over 137 cd·A⁻¹ [29], or high maximum power efficiency (η_{Pmax}) over 98 lm·W⁻¹ [30] have been realized successfully, most of the reported yellow PhOLEDs suffer from obvious efficiency roll-off [31], which is unfavorable for their practical application in lighting sources. To acquire high-performance PhOLEDs, an effective strategy is constructing double-emitting-layered devices by doping the guest compound into two different types of host material with good hole- and electron-transporting abilities, respectively, so that the carrier recombination region can be limited successfully within the two emitting layers, leading to more balanced carrier-transportation and lowered leakage current [32,33].

In recent years, our research group has made great efforts to elucidate the substituent effects on the PL and EL properties of **Ir-bt**-based phosphors [24,34,35]. Our experimental findings revealed that by grafting a *tert*-butyl, phenyl or (4-*tert*-butyl)phenyl at the *para*-position of the phenyl segment of **bt**, highly efficient yellow or orange-yellow phosphors can be constructed [24,34]. But different from the findings of Chang et al. when a phenyl or a 4-methoxyphenyl is grafted at the *meta*-position of the phenyl of **bt**, the resultant iridium complexes only show a negligible color-tuning effect, although significantly improved film formation and morphology stability can be acquired [35]. Based on the fact that the electron-donating capability of phenyl and 4-methoxyphenyl groups is lower than that of methoxy group, we infer that if a substituent with stronger electron-donating capability is introduced into the *meta*-position of the phenyl of **bt**, the resultant iridium complexes may have their PL emission bands red-shifted to the red region.

As carbazole and diphenylamine units have been demonstrated to show not only relatively strong electron-donating ability, but also good hole-transporting capability and thermal stability [22,23,36,37], herein, we graft a carbazol-9-yl or a diphenylamino substituent at the meta-position of the phenyl of bt cyclometalated ligand. Moreover, to gain insight into the impact of the ancillary ligand on the emission color of the chelates, heteroleptic complexes bearing two carbazol-9-yl or diphenylamino modified bt-based cyclometalated ligands and one acetylacetone (acac) or 2-picolinic acid ancillary ligand, and homoleptic complexes bearing three carbazol-9-vl or diphenylamino modified bt-based cyclometalated ligands are constructed. For the three carbazol-9-yl-modified objective complexes (TM1~3), a negligible color-tuning effect is observed, and all the three complexes emit yellow photoluminescence (PL) with their PL maximum (λ_{PLmax}) locating at 555–565 nm. However, for the three diphenylamino-modified objective complexes (TM4~6), their PL emission bands are significantly red-shifted than that of Ir-bt, leading to red PL emission with λ_{PLmax} of 618-636 nm. Besides, by alterating the ancillary ligand, or using a homoleptic structure, the PL emission band of these Ir-bt-based complexes can be further fine-tuned. By using the carbazol-9-yl-modified TM3 as the guest phosphor, a high-performance yellow PhOLED with CIE coordinates of (0.43, 0.56), a maximum current efficiency (η_{Lmax}) of 54.2 cd·A⁻¹, a maximum power efficiency (η_{Pmax}) of 48.9 lm·W⁻ , and satisfactory efficiency roll-off is realized successfully. An orange PhOLED using the diphenylamino-modified TM6 as the guest is also demonstrated to show moderate EL performance with CIE coordinates of (0.57, 0.42), η_{Lmax} of 18.6 cd·A⁻¹, and η_{Pmax} of 14.3 lm·W⁻¹.

2. Experimental

2.1. General information

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer. High resolution MS spectra were obtained from a Q-

TOF Priemier ESI mass spectrometer (Micromass, Manchester, UK). Thermogravimetric analysis (TGA) was performed on a TGA Q500 instrument. UV-Vis absorption and photoluminescence (PL) spectra were recorded on a SHIMADZU UV-2100 spectrophotometer and a PerkinElmer LS55 fluorescence spectrophotometer, respectively. The absolute PL quantum yield (PLQY) data of the doped films were determined with an integrating sphere (IS80 from Labsphere) together with a digital photometer (S370 from UDT) under excitation of 340 nm. Cyclic voltammetry (CV) measurements were performed on a PARSTAT 2273 electrochemical workstation using a platinum plate, a Ag/AgNO₃ (0.1 $mol \cdot L^{-1}$ in acetonitrile) electrode and a platinum wire as the working electrode, quasi-reference electrode and counter electrode in CH2Cl2 solution with 0.1 mol· L^{-1} tetrabutylammonium perchlorate as the supporting electrolyte. The crystallographic data for TM1, TM3 and TM6 were deposited into the Cambridge Structural Database (CCDC 1943633, 1943634 and 1943635). Single crystal X-ray diffraction data of the complexes were obtained on an Xcalibur E X-ray single crystal diffractometer equipped with graphite monochromator Mo-K α (λ = 0.71073 Å) radiation. The data collection was executed using the CrysAlisPro program. The structures were determined using direct method and successive Fourier difference syntheses (SHELXS-97) and refined using full-matrix least squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Packing analysis of the crystal cells was carried out using the Mercury program. Density functional theory (DFT) calculations were performed using the Gaussian 09 software by employing B3LYP with LANL2DZ basis set for Ir atom, and 6-31G(d) basis sets for C, H, S, N and O atoms. All the geometries were confirmed as stationary structures by the presence of only real frequencies at the same level of theory. Orbital energies were calculated within the framework of the IEF-PCM Model in CH₂Cl₂ media based on the optimized geometries.

2.2. OLED fabrication and measurements

All OLEDs were fabricated on pre-patterned indium-tin oxide (ITO) coated glass substrate with an ITO sheet resistance of 15 Ω /sq, and the emission area was 0.1 cm². The ITO-coated substrate was cleaned in an ultrasonic bath with acetone, isopropyl alcohol, de-ionized water in sequence. After 20 min ozone treatment on ITO, a 1,1-bis[4-[N,N'-di(ptolyl)amino]phenyl]cyclohexane (TAPC) layer (40 nm) was deposited on ITO. Then the two light-emitting layers of the target iridium complex doped in 4,4',4"-tri(N-carbazolyl)triphenylamine (TCTA) or 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) with thickness of 10 nm were evaporated in sequence, followed by the evaporation of 1,3,5-tris (1-phenyl-1H-benzo[d]imidazole-2-yl)benzene (TPBi) (40 nm), LiF (1 nm), and Al (100 nm) successively. The vacuum was 1×10^{-5} Pa during the deposition of organic-component layers. The current densityvoltage-luminance (J-V-L) characteristics of the devices were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. The EL spectra of the OLEDs were measured with a Hitachi F-4600 spectrophotometer. 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 Spectrascan PR650 spectrophotometer.

2.3. Synthesis

All the reagents involved in the synthetic procedure were commercially available and used without further purification unless otherwise stated. All the solvents were of analytical grade and freshly distilled prior to use. The synthetic routes of objective molecules **TM1**~**TM6** are shown in Scheme 1. The synthetic details of ligands and intermediates are provided in Supporting Information.

2.3.1. General procedure for the synthesis of dichloro-bridged iridium(III) complexes [24a]

A mixture of IrCl₃·nH₂O (1 mmol), the corresponding cyclometalated ligands (2.4 mmol), 2-ethoxyethanol (30 mL) and water (10 mL) was refluxed under argon for 24 h. Then the mixture was cooled down to room temperature, and the precipitate was filtered and washed with 10 mL of 1 mol·L⁻¹ HCl and 3×15 mL methanol in sequence, and dried in vacuum. The crude product was used in the next step without further purification.

2.3.2. General procedure for the synthesis of $(C^N)_2$ Ir(acac) complexes [24a]

The chloro-bridged dimer complex (0.2 mmol), acetylacetone (0.6 mmol), sodium carbonate (2 mmol) and 30 mL 2-ethoxyethanol were refluxed under argon for 12 h. After the mixture was cooled down, the precipitates were collected and purified by flash chromatography through silica column using *n*-hexane/dichloromethane (1/2) as the eluent, followed by recrystallization for more than three times to afford the objective complexes with satisfied purity. The complexes were dried at 100 °C under vacuum of 1.5 kPa for 24 h.

2.3.3. General procedure for the synthesis of $(C^{\wedge}N)_2$ Irpic complexes [38]

The corresponding chloro-bridged dimer complex (0.2 mmol), sodium carbonate (2 mmol) and picolinic acid (0.6 mmol) were dissolved in 30 mL 1,2-dicholorethane, and the reaction mixture was stirred for 6 h at 90 °C under argon. Then the solvent was removed under reduced pressure, and the precipitates were collected and purified by flash chromatography through a silica column using *n*-hexane/EtOAc (5/1) as the eluent, followed by recrystallization for more than three times to afford the objective complexes with satisfied purity. The complexes were dried at 100 °C under vacuum of 1.5 kPa for 24 h.

2.3.4. General procedure for the synthesis of fac- $Ir(C^N)_3$ complexes [39] A mixture of chloro-bridged dimer complex (0.2 mmol), the

corresponding cyclometalated ligands (0.8 mmol), AgCF₃SO₃ (0.4 mmol), and xylene (30 mL) were placed in a pressure-resistant reaction vessel and stirred for 12 h at 130 °C. Then the solvent was removed under reduced pressure, the precipitates were collected and purified by flash chromatography through silica column using *n*-hexane/dichloromethane (1/2) as the eluent, followed by recrystallization for more than three times to afford the objective complexes with satisfied purity. The complexes were dried at 100 °C under vacuum of 1.5 kPa for 24 h.

2.3.5. Bis[2-(3-(9H-carbazol-9-yl)phenyl)benzothiazole-N,C^{2'}]iridium (III) (acetyl acetonate) (TM1)

Orange solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 56.2%, m.p.: 305-310 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.22 (d, J = 8.0 Hz, 2H, ArH), 8.13 (d, J = 8.0 Hz, 4H, ArH), 7.93 (d, J = 8.0 Hz, 2H, ArH), 7.87 (d, J = 1.6 Hz, 2H, ArH), 7.56–7.46 (m, 8H, ArH), 7.41–7.36 (m, 6H, ArH), 7.28–7.24 (m, 2H, ArH), 6.90 (dd, J = 8.0 Hz, 4.0 Hz, 2H, ArH), 6.68 (d, J = 8.0 Hz, 2H, ArH), 5.24 (s, 1H, –CH), 1.89 (s, 6H, –CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 186.0, 179.7, 150.8, 147.6, 143.1, 141.0, 136.4, 131.5, 131.3, 128.9, 127.7, 125.8, 125.6, 124.0, 123.1, 122.6, 120.40, 120.2, 119.6, 110.1, 101.9, 28.4. ESI-MS: m/z 1065.1880 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1065.1885.

2.3.6. Bis[2-(3-(9H-carbazol-9-yl)phenyl)benzothiazole-N,C^{2'}]iridium (III) (picolin ate) (TM2)

Orange solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 62.5%, m.p.: >280 °C. ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 8.42 (d, J = 8.4 Hz, 2H, ArH), 8.33–8.18 (m, 8H, ArH), 8.13 (d, J = 5.2 Hz, 1H, ArH), 8.06 (d, J = 7.6 Hz, 1H, ArH), 7.87 (t, J = 6.0 Hz, 1H, ArH), 7.62–7.40 (m, 10H, ArH), 7.30–7.21 (m, 4H, -picH + ArH), 7.15–7.11 (m, 2H, -picH + ArH), 6.83 (d, J = 8.0 Hz, 1H, ArH), 6.59 (d, J = 8.0 Hz, 1H, ArH), 6.19 (d, J = 8.4 Hz, 1H, ArH), 5.76 (s, 2H, ArH). ESI-MS: m/z 1066.1858 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1066.1789.



Scheme 1. Molecular structures and synthetic routes of the objective iridium complexes TM1~6.

2.3.7. fac-Tris[2-(3-(9H-carbazol-9-yl)phenyl)benzothiazole-N,C^{2'}] iridium(III) (TM3)

Yellow solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 42%, m.p.: >280 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.13 (d, J = 8.0 Hz, 6H, ArH), 7.92–7.90 (m, 6H, ArH), 7.43 (d, J = 8.0 Hz, 6H, ArH), 7.39–7.31 (m, 9H, ArH), 7.27–7.24 (m, 6H, ArH), 7.17 (dd, J = 10.0, 2.0 Hz, 3H, ArH), 7.05–7.01 (m, 6H, ArH), 6.84 (d, J = 8.4, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 178.6, 156.6, 152.3, 142.0, 141.2, 137.4, 132.7, 131.1, 130.6, 127.5, 125.8, 125.2, 124.6, 123.1, 122.8, 120.3, 119.9, 119.6, 110.0. ESI-MS: m/z 1341.2404 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1341.2395.

2.3.8. Bis[3-(benzo[d]thiazol-2-yl)-N,N-diphenylaniline-N,C^{2'}]iridium (III) (acetyl acetonate) (TM4)

Red solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 51.3%, m.p.: 212–215 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.09 (d, J = 7.6 Hz, 2H, ArH), 7.82 (d, J = 7.6 Hz, 2H, ArH), 7.46–7.40 (m, 6H, ArH), 7.22–7.15 (m, 8H, ArH), 7.06–7.00 (m, 8H, ArH), 6.92 (t, J = 8.0 Hz, 4H, ArH), 6.46 (dd, J = 8.4 Hz, 2 Hz, 2H, ArH), 6.27 (d, J = 8.4, 2H, ArH), 5.17 (s, 1H, –CH), 1.81 (s, 6H, –CH₃). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 185.7, 179.9, 150.8, 147.9, 142.7, 142.4, 141.3, 135.8, 131.5, 129.1, 127.9, 127.3, 125.1, 123.4, 122.3, 122.19, 122.0, 120.2, 101.7, 28.5. ESI-MS: m/z 1069.2193 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1069.2198.

2.3.9. Bis[3-(benzo[d]thiazol-2-yl)-N,N-diphenylaniline-N,C^{2'}]iridium (III) (picolin ate) (TM5)

Red solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 50.6%, m.p.: >280 °C. ¹H NMR (400 MHz, DMSO- d_6) δ (ppm): 8.27 (d, J = 8.0 Hz, 1H, ArH), 8.18 (d, J = 8.0 Hz, 1H, ArH), 8.14–8.10 (m, 2H, ArH), 7.99 (d, J = 7.6 Hz, 1H, ArH), 7.94 (d, J = 5.2 Hz, 1H, ArH), 7.79 (t, J = 7.2 Hz, 1H, ArH), 7.54–7.44 (m, 4H, ArH), 7.41 (t, J = 8.0, 1H, ArH), 7.28–7.21 (m, 8H, -picH + ArH), 7.15–7.11 (m, 1H, ArH), 7.01–6.94 (m, 12H, ArH), 6.62 (dd, J = 10.4, 2.0 Hz, 1H, ArH), 6.54 (dd, J = 8.0, 2.0 Hz, 1H, ArH), 6.44 (d, J = 8.0 Hz, 1H, ArH), 6.19 (d, J = 8.0, 1H, ArH), 6.05 (d, J = 8.4, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 181.4, 178.7, 173.1, 153.2, 149.9, 149.8, 148.7, 147.9, 147.7, 143.7, 142.5, 142.0, 141.9, 141.4, 138.0, 135.7, 135.1, 131.9, 131.2, 129.3, 129.1, 128.9, 128.4, 128.1, 127.9, 127.1, 125.8, 125.0, 123.5, 123.3, 123.1, 122.6, 122.4, 122.2, 122.0, 121.2, 117.9, 37.1, 32.0, 30.1, 29.7, 29.4, 27.1, 22.7, 14.2. ESI-MS: m/z 1092.1991 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1092.1994.

2.3.10. fac-Tris[3-(benzo[d]thiazol-2-yl)-N,N-diphenylaniline-N,C^{2'}] iridium(III) (TM6)

Red solid, recrystallized from a mixture of dichloromethane and methanol. Yield: 28.6%, m.p.: >280 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.80 (d, J = 8.0 Hz, 3H, ArH), 7.42 (d, J = 2.4 Hz, 3H, ArH), 7.23–7.16 (m, 15H, ArH), 7.02 (d, J = 7.6 Hz, 12H, ArH), 6.93–6.88 (m, 9H, ArH), 6.70–6.68 (m, 6H, ArH), 6.59 (d, J = 8.0, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 178.8, 155.8, 152.4, 147.8, 141.5, 141.4, 140.9, 136.9, 132.7, 129.8, 129.0, 127.0, 124.6, 123.2, 123.1, 122.4, 121.8, 119.8. ESI-MS: m/z 1347.2879 (M + Na)⁺; Calcd. for (M_w + Na)⁺: 1347.2864.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic procedure of the parent compound **Ir-bt** can be found in our previous report [24a]. The six objective complexes of **TM1**~6 are synthesized following the similar procedures reported in references [40] [24a,38-40]. Their molecular structure is characterized by ¹H NMR, ¹³C NMR, and HR-ESI-MS spectrometry. Besides, the molecular structure of **TM1**, **TM3** and **TM6** is further verified by single crystal X-ray diffraction. It should be pointed out that the ¹³C NMR spectrum data of compound TM2 is not available due to its poor solubility in common solvents.

The single crystal samples of TM1, TM3 and TM6 are obtained by slow vapor diffusion of methanol into their CH2Cl2 solution. The ORTEP drawing of the crystal structure and the crystallographic refinement parameters as well as selected bond length/angle data of the three complexes are given in Fig. S1, Tables S1 and S2. All the three complexes display a distorted octahedral geometry around the metal center. In the heteroleptic complex **TM1**, its two C[\]N ligands show a C.C-*cis*, N.N-*trans* configuration; but in the case of homoleptic complexes TM3 and TM6, fac-configurations are observed. As generally, iridium(III) complexes bearing a fac-configuration show better thermal stability than those with a mer-configuration [41], TM3 and TM6 are expected to display better thermostability, hence better photoelectric performance than the other four complexes. In TM1, the average bond lengths of Ir–C, Ir–N and Ir–O are 2.000(4) Å, 2.059(3) Å and 2.142(3) Å respectively. The longer Ir-O bond is due to the strong trans-effect of Ir-C bond. On the other hand, the average bond lengths of Ir-C and Ir-N in TM3 and TM6 are 2.015(4) Å, 2.162(3) Å and 2.017(3) Å, 2.164(3) Å, respectively. The similarity of Ir-C and Ir-N in their bond lengths suggests a nearly identical coordination environment around the Ir center in these homoleptic complexes [42].

The intermolecular packing pattern of the three objective compounds in their crystals is depicted in Fig. 1. In the single crystal structure of **TM1**, only a weak "edge-to-face" interaction between the two C^AN ligands (3.518(2) Å) is discernible, suggesting that no severe π - π interactions exist in the crystal sample of **TM1**. In the case of **TM3**, relatively weak π - π interactions are observed, because the distances between the benzothiazole and benzothiazole rings, as well as carbazole and carbazole rings, are 3.846(2) Å and 3.798(3) Å, respectively. However, in **TM6**, relatively strong π - π stacking can be observed, because the intermolecular interplanar distance between its benzothiazole and benzothiazole rings is as short as 3.648(2) Å. Accordingly, the carbazolyl-modified complexes should show more alleviated concentration quenching than their diphenylamino-modified counterparts.

3.2. Photophysical properties

The UV-Vis absorption spectra and photoluminescence (PL) spectra of all the complexes studied here are depicted in Fig. 2 and Fig. 3, and representative data are summarized in Table 1. For the purpose of comparison, the absorption spectrum of Ir-bt is also given. All these complexes exhibit two distinguishable absorption bands in their absorption spectra, namely, an intense absorption band at 280-380 nm and a weak one at 380-550 nm. For the intense absorption band, TM1~3 show quite analogous spectral profiles, and TM4~6 show similar absorption spectra. But the latter three complexes all possess a red-shifted absorption band than that of TM1~3. Consequently, this absorption band is safely assigned to the ${}^{1}\pi$ - π^{*} transition of the C^{\wedge}N ligand [11]. In the case of the weak absorption band, TM1~3 shows similar absorption onsets with that of Ir-bt, but the absorption onsets of TM4~6 are all observed to be bathochromically shifted than those of TM1~3 and Ir-bt, indicative of the lower optical bandgaps (E_g) of TM4~6 than those of TM1~3 and Ir-bt. Besides, for complexes bearing either carbazolyl- or diphenylamino-modified $C^{\wedge}N$ ligands, the ones with a homoleptic-structure show the largest $E_{g}s$, while the ones bearing an ancillary ligand of acac show the smallest $E_{g}s$.

Consistent with the absorption characteristics, with regard to the PL spectra, the carbazolyl-substituted complexes TM1~3 show yellow emission with their λ_{PLmax} locating at 555–565 nm, which is similar to the parent compound **Ir-bt** ($\lambda_{PLmax} = 557$ nm). However, TM4~6 bearing stronger electron-donating diphenylamino substituents display red or even deep-red emission with λ_{PLmax} of 617–636 nm, which is significantly red-shifted than that of **Ir-bt**. Additionally, the heteroleptic-structured **TM1** and **TM4** using acac as the ancillary ligand are both observed to show the utmost red-shifted PL band, but the homoleptic-structured **TM3** and **TM6** have their PL bands located at the



Fig. 1. Crystal packing diagrams of TM1, TM3 and TM6.



Fig. 2. Normalized absorption spectra of the complexes studied here in 10^{-5} mol L⁻¹ CH₂Cl₂ solution at 298 K.



Fig. 3. Normalized PL spectra of the complexes studied here in 10^{-5} mol L⁻¹ CH₂Cl₂ solution at 298 K under irradiation of 420 nm.

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Photophysical data of the complexes studied here.

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Compounds	$\lambda_{\rm abs} ({\rm nm})^{a}$	$\lambda_{PLmax} (nm)^{a}$	$\phi_{ ext{PL}}$
Ir-bt	313, 327, 358, 447, 488	557	-
TM1	293, 310, 330, 415, 452, 490	565	8.9%
TM2	292, 327, 396, 447	559	26.5%
TM3	293, 325, 345, 404, 436, 480	555	23.1%
TM4	308, 416, 520	636	25.0%
TM5	309, 319, 398, 506	631	25.3%
TM6	308, 438, 505	618	25.2%

^a Determined in 10^{-5} mol L⁻¹ CH₂Cl₂ solution at 298 K.

^b Absolute PL quantum yields of the 5 wt% doped film samples (with poly (methyl methacrylate) (PMMA) as the host) determined using an integrating sphere at 298 K.

highest energy region among **TM1~3** and **TM4~6**, respectively. The more red-shifted λ_{PLmax} of the acac-comprising complexes should be attributed to the lower ligand field of acac than that of either the C^{Λ} ligand or picolinic acid, through which a low crystal field splitting energy, hence a reduced energy gap of the complexes can be achieved [43].

Based on these experimental findings, it can be deduced that the introduction of strong electron-donating substituents into the *meta*-site of the phenyl moiety of **bt** ligand would result in complexes with redshifted PL emission, and the magnitude of the spectral redshift correlates highly with the electron-donating ability of the substituents. Further fine-tuning on the PL emission band could be realized through replacing one of the $C^{\Lambda}N$ ligand in homoleptic complexes with picolinic acid or acetylacetone to construct corresponding heteroleptic-structured complexes.

Subsequently, the absolute photoluminescence quantum yields (PLQYs) of the complexes are measured by doping 5 wt% of **TM1~6** into a poly(methyl methacrylate) (PMMA) matrix (data summarized in Table 1). The results show that except for **TM1** (PLQY: 8.9%), **TM2~6** all show a relatively high PLQY (23–25%), which is propitious to their EL performance.

3.3. Electrochemical and thermal properties

The electrochemical properties of these complexes are investigated by cyclic voltammetry (CV) in an argon purged 5×10^{-4} mol L⁻¹ CH₂Cl₂ solution with the Fc/Fc⁺ redox couple as reference, and the voltammograms are shown in Fig. 4, data are summarized in Table 2. During the anodic scan, all the six complexes exhibit reversible oxidation waves, implying that they have good electrochemical stability. In the scanning region of -0.2–0.85 V, the carbazolyl-modified TM1~3 all display a one-electron oxidation characteristics. Consequently, the HOMO energy levels of TM1~3 are estimated to be -5.37, -5.42, -5.25 eV, respectively. According to the corresponding data of HOMO energy level and



Fig. 4. Cyclic voltammograms of TM1~6. The oxidation potentials are determined relative to Ag/Ag⁺ in 5×10^{-4} mol·L⁻¹ CH₂Cl₂ solution, using ferrocene as external reference.

Table 2

Electrochemical and thermal data of the complexes studied here.

Compounds	E ^{ox a} _{1/2}	Eg (eV) ^b	HOMO ^c (eV)	LUMO ^d (eV)	HOMO ^e (eV)	LUMO ^e (eV)	E _g (eV)	$T_d^{f}(^{\circ}C)$
Ir-bt	0.51	2.23	-5.31	-3.08	-5.28	-1.80	3.48	326
TM1	0.57	2.18	-5.37	-3.19	-5.23	-1.96	3.27	356
TM2	0.62	2.25	-5.42	-3.17	-5.33	-2.05	3.28	338
TM3	0.45	2.21	-5.25	-3.04	-5.28	-1.94	3.34	443
TM4	0.13	1.97	-4.93	-2.96	-4.77	-1.86	2.91	313
TM5	0.20	2.00	-5.00	-3.00	-4.87	-1.95	2.92	349
TM6	0.08	2.14	-4.88	-2.74	-4.82	-1.82	3.00	342

 $^{
m a}$ Oxidation potential values are measured in CH_2Cl_2 solution containing 5 imes 10 $^{-4}$ mol L $^{-1}$ of the iridium complexes, potential values are reported versus Fc/Fc $^+$. ^b E_{g} are estimated from the onset wavelength of the optical absorption bands.

^c HOMO energies are deduced from the equation HOMO = -(4.8 + Eox 1/2).

^d LUMO energies are obtained from the equation $LUMO = HOMO + E_g$.

^e Obtained from B3LYP calculations within the framework of the IEF-PCM model in CH₂Cl₂.

 $^{\rm f}$ Temperature with 5 wt % loss.

 E_g , the LUMO energy levels of **TM1~3** are estimated to be -3.19, -3.17and -3.04 eV in sequence. Note that the energy level data of both the HOMO and LUMO of TM1~3 are close to that of the parent complex Irbt (HOMO: -5.31 eV; LUMO: -3.08 eV) [24a]. Therefore, the absorption onset and PL emission color of TM1~3 are similar to those of Ir-bt.

However, in similar scanning region of -0.1-0.75 V, the diphenylamino-decorated $TM4{\sim}6$ all display a two-electron oxidation profile. The ones with lower oxidation potentials are assigned to the oxidation of iridium (III/IV) metal center as well as the C^N ligand; whereas the ones with higher oxidation potentials are attributed to the oxidation of the triphenylamine moiety of the C^N ligand [44].

Consequently, on the basis of the first oxidation potentials $(E_{1/2}^{0x})$, the HOMO energy levels of TM4~6 are calculated to be -4.93, -5.00 and -4.88 eV, respectively; and the LUMO energy levels of TM4~6 are estimated to be -2.96, -3.00 and -2.74 eV in sequence. In comparison with TM1~3 and Ir-bt, TM4~6 all show dramatically elevated HOMO and slightly elevated LUMO energy levels. Hence the reduced E_{g} and red-shifted PL band of TM4~6 than those of TM1~3 should be mainly attributed to the more elevated HOMO energy levels of $TM4 \sim 6$ than TM1~3 originating from the stronger electron-donating capability of diphenylamino group than the carbazol-9-yl group at the meta-site of the phenyl moiety of bt.



Fig. 5. Isodensity plots of the HOMOs and LUMOs for TM1~6.

Thermogravimetric analysis (TGA) (data summarized in Table 2) shows that except for TM4 ($T_d = 313$ °C), all these objective complexes show better thermal stability than the reference compound of Ir-bt (T_d : >330 °C vs 326 °C) [24a], implying that the incorporation of carbazole and diphenylamine units with the C^{\wedge}N ligand can effectively improve the thermal stability of the resultant chelates. Furthermore, the homoleptic complexes TM3 and TM6 are both found to show higher T_d s than their acetylacetone-comprising counterparts, confirming that the homoleptic complexes show better thermal stability.

3.4. DFT theoretical calculation

To gain insights into the effect of substituents and auxiliary ligands on the E_g and energy levels of the complexes, density functional theory (DFT) calculations are performed on **TM1~6** with the Gaussian09 software. The electronic density distribution of the HOMOs and LUMOs of **TM1~6** is depicted in Fig. 5, and the calculated HOMO and LUMO energy level data are summarized in Table 2. Although the calculated LUMOs are significantly shallower than those estimated from experimental data, the similar variation trends in both LUMO energy level and E_g of the complexes between the calculation results and experiment findings illustrates the reliability of our computation results.

As depicted in Fig. 5, the carbazolyl and diphenylamino substituents are both observed to participate in the HOMO of the chelates, whereas the LUMOs mainly locate on the 2-phenylbenzothiazole segment, indicating that the substituents should have a major effect on the HOMO energy levels of the complexes. This is consistent with the electrochemical characterization results. Further calculation on the orbital compositions of the HOMO of **TM1~6** (shown in Table S1) reveals that the substituents have an obvious contribution to the HOMOs (41.5–64.2%), while the contributions from Ir-d orbitals are only 11.7–26.3%. In addition, for all the target compounds, the HOMO- \rightarrow LUMO transitions show a d(Ir) + π (sub + C[\]N) \rightarrow π *(C[\]N) configuration, implying that the transition process possesses a metal-to-ligand charge-transfer (MLCT) characteristics.

3.5. Electroluminescence properties

Based on the photophysical and thermal stability experimental

results, TM3 and TM6 are selected as the phosphorescent guests to fabricate PhOLEDs with single or double light-emitting-layer (EML). The configuration of the single-EML devices is: ITO/TAPC (40 nm)/ 26DCzPPy:TM3 or TM6 (x wt%) (10 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm); and the configuration of the double-EML devices is: ITO/ TAPC (40 nm)/TCTA: TM3 or TM6 (x wt%) (10 nm)/26DCzPPy: TM3 or TM6 (x wt%) (10 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm), where TAPC serves as the hole-transporting layer; 26DCzPPy and TCTA serve as the host materials for TM3 or TM6 with electron- and holetransporting capability, respectively; TPBi serves as the electrontransporting layer. The two emission layers in double-EML devices have identical doping levels. The devices based on TM3 and TM6 are named as device I and II, respectively; a~e represents single-EML devices, and f~j stands for double-EML devices with different doping levels. For TM3-based devices, the doping levels are 3 wt%, 4 wt%, 5 wt %, 6 wt%, 7 wt%; for TM6-based devices, the doping levels are 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, respectively. The relative energy level alignments of the devices I and II, and the molecular structure of the materials used are shown in Fig. 6.

For single- and double-EML OLEDs based on the same guest phosphor with similar doping levels, their EL spectra are almost identical (Fig. 7), implying that the presence and absence of a hole-transporting EML has negligible impact on the EL process of the guests. All the TM3-based devices Ia~j, regardless of their different doping levels of 3-7 wt%, exhibit yellow EL with CIE coordinates of (0.43, 0.56). The dopant-concentration independent EL spectra suggest that there only exist weak intermolecular interactions in TM3. The EL spectra of devices Ia~j (λ_{ELmax} = 558 nm) match well with the corresponding PL spectra of **TM3** in diluted CH₂Cl₂ solution ($\lambda_{PLmax} = 555$ nm), suggestive of the analogous luminescence processes of EL and PL. In contrast, the λ_{ELmax} of the TM6-based devices II is concentration-dependent. With increasing dopant concentration from 2 wt % to 6 wt %, the corresponding EL spectrum is bathochromic-shifted gradually from 590 nm to 601 nm. Note that the all the **TM6**-based devices have their λ_{ELmax} blue-shifted for 16-26 nm than the PL spectrum of TM6 in diluted CH₂Cl₂ solution $(\lambda_{PLmax} = 618 \text{ nm})$, which is tentatively ascribed to the higher environmental polarity of CH₂Cl₂ than either the TCTA or the 26DCzPPy host. To validate this conjecture, PL spectra of binary host-guest films of TM3 or TM6 in 26DCzPPy or TCTA with similar doping levels of the



Fig. 6. The relative energy level alignments of the devices I and II and the molecular structure of the materials used.



Fig. 7. EL spectra of device I and device II.

PhOLEDs are recorded. As depicted in Fig. S2, in both the two hosts, regardless of the different doping levels, the λ_{PLmax} of the **TM3**-based films locates at 558 nm; but in both 26DCzPPy and TCTA, with increasing concentration of **TM6** from 2 wt% to 6 wt%, the resultant films have their λ_{PLmax} slightly red-shifted, which should be ascribed to

the concentration quenching of **TM6** [24b], or the higher molecular polarity of **TM6** than 26DCzPPy or TCTA. It is noteworthy that when doped in 26DCzPPy, the **TM6**-based films show slightly red-shifted λ_{PLmax} than those doped in TCTA with similar doping levels (e.g., at doping level of 4 wt%, λ_{PLmax} is 598 nm in TCTA host, but 603.5 nm in 26DCzPPy host). Consequently, the concentration-dependent EL spectra of these **TM6**-based devices II should originate from the concentration quenching of **TM6**, the higher molecular polarity of the guest **TM6** than the hosts, leading to orange EL with their CIE coordinates shifted from (0.53, 0.42) to (0.59, 0.41).

In addition, for the 3 wt%-doped devices Ia and If and 2 wt%-doped devices IIa and IIf, an extra EL band at the blue-light region of 380–450 nm is observed. According to Fig. S2, the blue EL of these low doping-level devices should be assigned to the emission from the hosts of 26DCzPPy and/or TCTA due to the inefficient host-guest energy transfer. It should be pointed out that the energy transfer efficiency in the TM3-based samples are much higher than that in the TM6-based ones, because more effective spectral overlap exists between the absorption spectrum of TM3 and PL emission spectra of 26DCzPPy or TCTA (vide Fig. S3). Additionally, according to the device energy level diagram, TM3 shows a better trapping effect on both hole and electron carriers [45], while TM6 only acts as a trap for holes, and no distinct electrons trapping may occur on it.

The corresponding current density-voltage-luminance (J-V-L) and current efficiency-current density-power efficiency characteristics of these devices are shown in Fig. 8 and Fig. 9, some representative data are summarized in Table 3. All the TM3-based devices I exhibit low turn-on voltage of 3.1-3.2 V, suggesting that the presence of an extra 10 nmthick EML and the different guest concentrations have negligible effects on the turn-on voltages of these devices. The single-EML devices of Ia~e can emit bright yellow light with the maximum brightness (L_{max}) of 33390-44910 cd $m^{-2},$ and the highest brightness is obtained at a doping-level of 5 wt%. In the case of the double-EML devices, they all show much higher maximum brightness than their single-EML counterparts. Note that an expressive L_{max} of 60860 cd \cdot m⁻² is achieved in the 5 wt% doped device Ih. In addition to L_{max} , the maximum current efficiency (η_{Lmax}) and power efficiency (η_{Pmax}) of the 5 wt%-doped double-EML device are also observed to be much higher than those of the 5 wt %-doped single-EML device (η_{Lmax} : 54.2 vs 50.6 cd A⁻¹; η_{Pmax} : 42.9 vs 39.5 $\text{Im} \cdot \text{W}^{-1}$), while the η_{Pmax} data of 41.8 $\text{Im} \cdot \text{W}^{-1}$ and 48.9 $\text{Im} \cdot \text{W}^{-1}$ are separately obtained in single-EML device Ie (7 wt%) and double-EML device Ig (4 wt%), confirming that the double-EML device structure can lead to much improved EL performance. Note that to our knowledge, the η_{Pmax} value of 48.9 lm·W⁻¹ is one of the highest reported power efficiency data of yellow PhOLEDs [5,20,30,31,46-52].

It should be pointed out that all these yellow devices, either single-EML or double-EML, display rather low efficiency roll-off. In fact, a high η_L of 51.4 cd·A⁻¹ could be even achieved at 1000 cd·m⁻² for device Ih (5 wt%), and the efficiency roll-off is only as low as 5.17%, indicative of its potential applications for white OLED lighting sources.

Analogous to devices I, the **TM6**-based devices II also display low turn-on voltage of 3.2–3.4 V (*vide* Table 3), regardless of their different device structures and dopant concentrations. The L_{max} of the five devices IIa~e with single EML is 9960–14350 cd·m⁻², which are much inferior to the corresponding L_{max} data of the double-EML devices (14330–19870 cd·m⁻²). For single-EML and double-EML devices, the best performance is both acquired in the 4 wt%-doped devices. The η_{Lmax} of devices IIc and IIh is 14.9 cd·A⁻¹ and 18.6 cd·A⁻¹, respectively. In the double-EML device IIg, relatively low efficiency roll-off is observed, since its η_L is determined to be 14.1 cd·A⁻¹ at 1000 cd·m⁻².

All these EL characterization results indicate that **TM3** is a very promising yellow phosphorescent emitter for white OLEDs applications. Although **TM6** could also display moderate EL performance, it shows inferior EL performance to that of **TM3**. This may be ascribed to the more properly matched energy levels and higher energy transfer efficiency between the selected hosts and **TM3**, and more alleviated



Fig. 8. Current density-voltage-luminance(*J-V-L*) characteristics of device I (a, b) and device II (c,d).

intermolecular interactions of TM3 than TM6.

4. Conclusions

In summary, a series of novel **Ir-bt** derivatives are developed by introducing an electron-donating carbazolyl or diphenylamino substituent into its cyclometalated ligand, and using 2-picolinic acid instead of acetylacetone as the ancillary ligand or employing a homoleptic structure. Through this strategy, the emission color of the objective iridium complexes could be tuned from yellow to red, and the magnitude of the spectral red-shift can be not only adjusted through the electron-donating



Fig. 9. Current efficiency-current density-power efficiency characteristics of device I (a,b) and device II (c,d).

ability of the substituents, but also be fine-tuned through the alteration of the acetylacetone into picolinic acid or the corresponding C^AN ligand. PhOLEDs with the carbazol-9-yl-modified **TM3** or the diphenylamino-modified **TM6** as phosphors show relatively high EL performance. The **TM3**-based yellow devices show $\eta_{\rm Lmax}$ of 54.2 cd·A⁻¹, $\eta_{\rm Pmax}$ of 48.9 lm·W⁻¹ and CIE coordinates of (0.43, 0.56), together with satisfactory efficiency roll-off. Note that the $\eta_{\rm Pmax}$ data of 48.9 lm·W⁻¹ is one of the highest reported power efficiency data for yellow PhOLEDs. The **TM6**-based orange devices show $\eta_{\rm Lmax}$ of 18.6 cd·A⁻¹, $\eta_{\rm Pmax}$ of 14.3 lm·W⁻¹

Table 3

EL characteristics of device I and device II based on TM3 and TM6.

TM3	device Ia	device Ib	device Ic	device Id	device Ie	device If	device Ig	device Ih	device Ii	device Ij
Dopant ratio (wt%)	3	4	5	6	7	3	4	5	6	7
λ_{ELmax} (nm)	557	558	557	557	557	558	558	558	559	559
V _{turn-on} (V) ^a	3.2	3.1	3.1	3.1	3.1	3.3	3.2	3.2	3.2	3.2
L _{max} (cd⋅m ⁻²) ^b	33390	39420	44910	41670	38660	47230	55420	60860	55240	52800
$\eta_{Lmax} (cd \cdot A^{-1})^{c}$	31.5	46.0	50.6	44.6	45.1	44.0	53.9	54.2	48.0	45.9
$\eta_{\text{Pmax}} (\text{lm} \cdot \text{W}^{-1})^{\text{d}}$	18.4	33.4	39.5	37.7	41.8	37.3	48.9	42.9	42.7	38.8
$\eta_L (cd \cdot A^{-1})^e$	31.4	43.7	46.7	42.1	41.2	42.1	50.1	51.4	43.8	43.6
CIE (x, y)	0.42, 0.56	0.43, 0.57	0.42, 0.57	0.42, 0.57	0.42, 0.57	0.42, 0.56	0.43, 0.57	0.43, 0.56	0.43, 0.56	0.43, 0.56
TM6	device IIa	device IIb	device IIc	device IId	device IIe	device IIf	device IIg	device IIh	device IIi	device IIj
Dopant ratio (wt%)	2	3	4	5	6	2	3	4	5	6
λ _{ELmax} (nm)	592	596	597	602	601	590	598	598	603	601
V _{turn-on} (V) ^a	3.2	3.2	3.1	3.2	3.2	3.3	3.4	3.4	3.3	3.3
L _{max} (cd⋅m ⁻²) ^b	9960	12600	14350	13640	12240	14330	18030	19870	18540	16620
$\eta_{Lmax} (cd \cdot A^{-1})^{c}$	12.6	13.8	14.9	13.5	13.4	18.4	16.7	18.6	16.2	15.6
$\eta_{\text{Pmax}} (\text{lm} \cdot \text{W}^{-1})^{\text{d}}$	8.2	10.8	10.3	10.9	11.1	14.4	13.8	14.3	14.1	14.1
$\eta_L (cd \cdot A^{-1})^e$	7.7	9.4	12.2	10.6	10.4	10.3	12.0	14.1	12.2	11.4
CIE (x, y)	0.54, 0.42	0.57, 0.42	0.58, 0.42	0.58, 0.41	0.58, 0.41	0.53, 0.42	0.56, 0.43	0.57, 0.42	0.59, 0.41	0.59, 0.41

 $^{\rm a}\,$ The driven voltages of the device at 1 cd $\cdot m^{-2}.$

^b Maximum brightness of the device.

^c Maximum current efficiencies of the device.

^d Maximum power efficiencies of the device

^e current efficiencies of the device at 1000 cd \cdot m⁻².

and CIE coordinates of (0.57, 0.42). All these preliminary studies reveal that this rational molecular design strategy is a simple yet effective means to realize color tunability as well as the enhancement of EL performance of iridium complexes.

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.

CRediT authorship contribution statement

Jingjing Liu: Investigation, Writing - original draft, Data curation. Ming Li: Formal analysis, Visualization, Validation. Zhiyun Lu: Conceptualization, Methodology, Funding acquisition, Writing - review & editing. Yan Huang: Project administration, Supervision. Xuemei Pu: Software, Methodology, Investigation. Liang Zhou: Resources, Investigation.

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Appendix A. Supplementary data

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