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PAPER

A butterfly-like yellow luminescent Ir(III) complex and its application in highly efficient polymer light-emitting devices[†]

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A novel butterfly-like Ir(III) complex is designed, synthesized, and characterized for highly efficient yellow phosphorescent polymer-based light-emitting diodes (PLEDs). The device shows a maximum external quantum efficiency of 19.2%, luminance efficiency of 40 cd A^{-1} and Commission International de L'Eclairage (CIE) color coordinates of (0.49, 0.50) at J = 1.2 mA cm⁻².

Introduction

Ir(III) complexes are one kind of promising phosphorescent emitters which have attracted intensive study in recent years.¹ Due to their efficient intersystem crossing owing to the large spin-orbital coupling mediated by the heavy metal core, Ir(III) complexes feature unmatched photoluminescence efficiencies. relatively short (ms range) phosphorescence lifetimes and versatile color tuning abilities via ligand control. Typically, Ir(III) complexes can emit blue to red phosphorescence upon opto- or electro-stimulating.²⁻⁴ However, reports of yellow luminescent Ir(III) complexes remain relatively rare. In recent years, due to the emerging demand for white light illumination, mixing yellow with blue luminescence or phosphorescence has become an important choice in the fabrication of white light emitting diodes (LEDs).5-7 Furthermore, yellow constitutes one of the most sensitive colors to human eyes and is widely used in traffic signals, wild field rescues or art decoration. Therefore, the fabrication of yellow light emitting Ir(III) complexes is quite essential in both the scientific and the practical view. Due to this, the application of efficiently emitting Ir(III) complexes in polymer-based light emitting diodes (PLEDs) has made significant progress in recent years. Compared with the standard vacuum evaporation-based organic light emitting diodes (OLEDs), PLEDs feature improved large-area display or illumination ability, as well as facile and inexpensive solution processing

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† Electronic supplementary information (ESI) available: Crystallographic information, TG curve, PL spectra. See DOI: 10.1039/c2jm34992b methods. However, until now, PLEDs still faced the problem of the relatively low device efficiency of fluorescent polymer-emitting layers. One solution is that the mixture of phosphorescent Ir(III) complexes in polymer-emitting layers may provide a significant breakthrough in obtaining both large display area and high device efficiency.8 In this regard, improvement of the luminance efficiency (Φ_p) is a prerequisite for the successful application of Ir(III) complex based PLEDs. However, other factors such as the electron or hole transport and injection abilities, solubilities, and film-forming properties of Ir(III) complex will also affect the electroluminesence (EL) performance of the PLED devices significantly. In this article, we report a butterfly-like bright yellow luminescent Ir(III) complex based on a carbazole-substituted tridentate N^C^N ligand. Its application in PLEDs gives a maximum external quantum efficiency of 19.2%, which is among the highest quantum efficiency for yellow light PLED ever reported.9

Experimental

General details

The ¹H NMR spectra were recorded on a Varian/Mercury-Plus 300 NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Elemental analyses (C, H, N) were tested on a Vario EL instrument. Mass spectra were determined by AccuTOF CS JMS-T100CS spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-2450 spectrometer. The photoluminescence (PL) spectra were recorded on an Edinburgh Analytical Instruments FLS920 spectrometer. The emission quantum yield of the complex was measured in degassed CH₂Cl₂ solution, using Rhodamine 6G in degassed ethanol as the standard. Cyclic voltammetry (CV) was performed on a CHI760D electrochemical workstation at room temperature using 0.1 mol L⁻¹ tetra(*n*-butyl) ammonium hexafluorophosphate (TBAP) as the supporting electrolyte and degassed CH₂Cl₂ as the solvent. The ferrocenium/ ferrocene couple was used as the internal standard.

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The new ligand L1 (1,3-bis(1-(6-(9*H*-carbazol-9-yl)hexyl)-1*H*benzo[*d*]imidazol-2-yl)benzene) was synthesized by introducing carbazole groups with long alkyl chains on a tridentate N^C^N ligand, and then the butterfly-like Ir(III) complex 1 (Scheme 1) was synthesized from IrCl₃ with L1 and 2-phenylpyridine (ppy).¹⁰ Both the ligand and complex were characterized by means of ¹H NMR, MS, and elemental analyses. The synthetic details are as follows:

Synthesis of 1,3-bis(1*H*-benzo[*d*]imidazol-2-yl)benzene (MBImB). Isophthalic acid (1.66 g, 10 mmol) and benzene-1,2diamine (2.16 g, 20 mmol) were dissolved in 15 mL polyphosphoric acid and 15 mL phosphoric acid. The mixture was heated to 190 °C for 12 h, then cooled to 100 °C and poured into water. The precipitate was filtered and then recrystallized with 50% ethanol as a white product with yield of 72%. ¹H NMR (300 MHz, dimethyl sulfoxide (DMSO), TMS) δ 9.03 (s, 1H), 8.24 (dd, J = 7.8, 1.7 Hz, 2H), 7.72 (t, J = 7.8 Hz, 1H), 7.66–7.55 (m, 4H), 7.25–7.16 (m, 4H), 1.11–1.00 (m, 1H). electrospray ionization mass spectrometry (ESI-MS) *m/z*: 310.1.

Synthesis of 9-(6-bromohexyl)-9*H*-carbazole (Br-Cz). Carbazole (1.67 g, 10 mmol), 1,6-dibromohexane (5.5 mL, 36 mmol), tetrabutylammonium bromide (TBAB) (160 mg, 0.5 mmol), and aqueous NaOH (50%, 1 g) were added to benzene (5 mL). The mixture was stirred at room temperature for 48 h. The organic phase was separated and washed by water (2 × 30 mL) and then dried with MgSO₄. The solvent was removed *in vacuo*, and the residue was purified by flash column chromatography using petroleum ether (boiling range 60–90 °C) : ethyl acetate = 10 : 1 as eluent to afford white needle crystals (2.38 g, 60%). ¹H NMR (300 MHz, CDCl₃, TMS) δ 8.10 (d, *J* = 7.7 Hz, 2H), 7.50–7.37 (m, 4H), 7.25–7.19 (m, 2H), 4.32 (t, *J* = 7.1 Hz, 2H), 3.37 (t, *J* = 6.7 Hz, 2H), 1.92 (t, *J* = 12.3, 6.1 Hz, 2H), 1.82 (dd, *J* = 14.6, 6.7 Hz, 2H), 1.53–1.35 (m, 4H). ESI-MS *m/z*: 330.1.

Synthesis of 1,3-bis(1-(6-(9*H*-carbazol-9-yl)hexyl)-1*H*-benzol*d*] imidazol-2-yl)benzene (L1). The benzimidazole derivatives MBImB (2.5 mmol), the bromide Br-Cz (5 mmol), aqueous NaOH (50%, 0.5 g) and TBAB (80 mg, 0.25 mmol) were dissolved in 20 mL butanone. The mixture was heated to reflux for 8 h, and the resulting precipitate complex was collected. White power with yield of 86% was obtained. ¹H NMR (300 MHz, DMSO, TMS) δ 8.07 (dd, J = 14.4, 9.4 Hz, 5H), 7.86 (d, J = 7.7Hz, 2H), 7.65 (dt, J = 5.3, 3.3 Hz, 3H), 7.52 (d, J = 7.3 Hz, 2H), 7.41–7.16 (m, 12H), 7.09 (t, J = 7.2 Hz, 4H), 4.16 (dt, J = 13.5, 6.9 Hz, 8H), 1.50 (s, 8H), 1.02 (s, 8H). ESI-MS *m/z*: 809.6.

Preparation of Ir(III) complex (1). Under N₂ atmosphere, IrCl₃·4H₂O (370 mg, 1 mmol) was added to a solution of the ligand L1 (1.1 mmol) in methanol (20 mL). The mixture was heated to 75 °C for 8 h and then cooled to room temperature. The green precipitates were filtered, washed with chloroform 3 times and then with ether 3 times. Crude dichloro-bridged iridium dimers ([Ir(L1)Cl₂]₂) were obtained. The complex was insoluble in common organic solvents and was therefore used without purification for further preparation. After that, the mixture of the dimers and 2-phenylpyridine (ppy, 1 g) in 15 mL glycerol was heated by microwave irradiation (600 W) for 10 min. After the mixture was cooled to room temperature, the addition of water resulted in the formation of an orange precipitate, which was collected by filtration and washed with water and ether. The purification was performed by flash column chromatography using CH₂Cl₂ and CHCl₃ as eluent to afford complex 1 with a yield of 26%. ¹H NMR (300 MHz, CD₂Cl₂, TMS) δ 10.51 (dd, J = 5.5, 1.2 Hz, 1H), 8.15–8.04 (m, 5H), 7.86 (d, J = 7.8 Hz, 2H), 7.68 (dd, J = 9.0, 4.0 Hz, 1H), 7.52–7.32 (m, 10H), 7.21 (dd, J = 11.5, 8.7, 7.7 Hz, 9H), 6.94 (dd, J = 8.2, 7.1 Hz, 2H), 6.55–6.46 (m, 1H), 6.27 (t, J = 7.4 Hz, 1H), 6.21 (d, J = 8.2 Hz, 2H), 5.73 (d, J = 8.2 Hz, 2H), 5.74 (dJ = 7.6 Hz, 1H), 4.71–4.54 (m, 4H), 4.27 (t, J = 7.0 Hz, 4H), 2.08-1.98 (m, 4H), 1.91-1.81 (m, 4H), 1.29 (s, 4H). ESI-MS m/z:



Scheme 1 Synthesis of the ligand L1 and complex 1.

1154.8. Anal. calcd (%) for C₆₇H₅₉IrN₇Cl: C, 67.63; H, 8.24; N, 5.00; found: C, 67.90; H, 7.84; N, 5.27.

PLED fabrication and measurement

Devices based on the iridium(III) complex 1 with a structure of indium tin oxide (ITO)/Poly(3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT:PSS) (4083)/EML (Emitting Material Layer) (80 nm)/CsF (1.5 nm)/Al (100 nm) were fabricated. PVK poly(*N*-vinylcarbazole) : PBD (2-tert-butylphenyl-5biphenyl-1,3,4-oxadiazole) (100:40) doped with 1, 2, 4, 8% of iridium complex 1 were used as EML. All raw materials were purchased commercially. ITO glass substrates were washed in turn with acetone, substrate cleaning detergent, deionized water and isopropyl alcohol, then oven dried. The cleaned substrates were treated with oxygen plasma to improve the work function of ITO. After that, a 40 nm thick PEDOT:PSS film was spin-coated onto the pre-cleaned and dried ITO glass and baked in a vacuum oven at 80 °C for 8 h. Then the PVK, PBD and complex 1 with different ratios were dissolved separately in chlorobenzene and spin-coated on top of the dried PEDOT:PSS layer to obtain an emitting layer (80 nm) inside a glove box under vacuum. The assembly was then annealed for 20 min at 100 °C. Subsequently, a layer of CsF (1.5 nm) and a layer of Al (100 nm) were vacuum evaporated at 3×10^{-4} Pa on top of the EML polymer layer. Except for the PEDOT:PSS, which was spin-coated in air, other processes were performed in the glove box. EL spectra and current density-voltage-luminance (J-V-L) characteristics were collected by a PR705 photometer and a Keithley 236 source meter, respectively. The external quantum efficiency was calibrated in an integrating sphere (Labsphere, IS080).

Results and discussion

Optimized geometrical structure of complex 1

Fig. 1 shows the coordination unit structure of complex 1, optimized by theoretical calculations with HOMO or LUMO orbitals highlighted. The calculations were performed using the B3LYP hybrid functional implemented in the Gaussian-03 suite of programs.¹¹ The basis sets used were 6-31G(d) for C, H, N and LanL2DZ for Ir. We can see that the central ion, Ir³⁺, is six coordinated by three nitrogen atoms and two carbon atoms from L1 and ppy, and one chlorine atom helps to satisfy the octahedral coordination sphere. Two of the nitrogen atoms and one of the carbon atoms are offered by the ligand L1, forming N^C^N type coordination, and the other nitrogen and carbon atoms are



Fig. 1 Schematic representation of the optimized geometrical structure and HOMO (left), LUMO (right) orbitals of complex 1.

contributed by the ancillary ligand ppy. The planes of the primary and ancillary ligands are almost perpendicular (dihedral angle is 100°). The Ir–C bond lengths between Ir^{3+} and L1 and between Ir^{3+} and ppy are 2.005 and 2.036 Å, respectively, which are much shorter than Ir–N_{ppy} (2.160 Å) and Ir–Cl (2.481 Å) bonds.

UV-Vis absorption and photoluminescent properties

To examine the photophysical properties of the complex, UV-Vis and PL spectra were measured. The UV-Vis spectrum of complex **1** in CH₂Cl₂ shows the ¹MLCT (metal-to-ligand charge transfer) band at 404, 427 and 477 nm, in addition to the π - π * transition at 266 nm for ppy and 294, 347 nm for the **L1** ligand (Fig. 2a). Besides these, the band around 510–550 nm can be assigned as a ³MLCT band characteristic of Ir(III) complex. Fig. 2b shows the emission spectra of the complexes in solid state and in CH₂Cl₂ solution (1×10^{-5} mol L⁻¹) at 298 K. As shown in Fig. 2b, the solid and solvent (CH₂Cl₂, 1×10^{-5} mol L⁻¹) state complex **1** exhibit intense luminescence with a maximum at 570 and 558 nm, respectively. The CIE coordinates for the two emissions are calculated to be (0.50, 0.50) and (0.49, 0.50), falling into the yellow light region.

A noteworthy observation is that the photoluminescent quantum yield (Φ) for complex **1** is quite outstanding, reaching 77% in CH₂Cl₂ when using Rhodamine 6G as the standard. This indicates efficient intra- and intermolecular energy transfer in the complex. The luminescent lifetimes (τ) of the complex were measured in air at 298 K and 77 K, as 131 and 1241 ns, respectively. We can see that low temperature significantly reduces nonradiative pathways for triplets and increases the lifetime of the luminescence in the Ir(III) complex.





Electrochemical properties

The CV responses for the complex dissolved in CH₂Cl₂ are presented in Fig. 3. We can see that the complex has single reversible oxidative wave between 1.73 and 1.96 V vs. normal hydrogen electrode (NHE) and between 0.80 and 1.33 vs. ferrocene, which may be formally attributed to the oxidation of the iridium metal centre [Ir^{3+/4+}]. In addition, the complex has two reduction peaks which belong to the reduction of the cyclometallated ligand and ancillary ligand ppy. According to the equation $E_{\text{HOMO}} = -(E_{\text{ox}(vs. Fe/Fc+}) + 4.8)$ eV and $E_{\text{LUMO}} =$ $-(E_{\text{HOMO}} + E_g)$,¹² the HOMO and LUMO of complex 1 in CH₂Cl₂ were calculated to be -6.13 and -3.71 eV, respectively.

Theoretical calculations

To understand the nature of the electrochemical and optical properties of the complex, we used density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations to examine the frontier orbitals and electronic transitions in complex **1**. From Fig. 1, we can see that the HOMO orbitals of the complex comprise contributions mainly from the iridium atom, the chlorine atom and the phenyl ring of the ppy ligands, while the LUMO orbitals are mainly contributed by the benzene and pyridine rings of the cyclometalated ligands (Table S1†). The delocalization of the HOMO and LUMO orbitals of the complex is consistent with the experimental evidence from electrochemistry and photoluminescence.

The calculated TD-DFT singlet state transitions support the assignment of the absorption bands from the experimental data. The absorption bands above 400 nm are mainly assigned to the energy transitions between the frontier orbitals, *i.e.* between the d orbitals of Ir(III) center and π^* orbitals of the ligand. Therefore, these peaks are generally endowed with MLCT characters.

Electrophosphorescent properties

The iridium complex 1 which exhibited high photoluminescent quantum yield at room temperature was selected for PLED device fabrication. The device structure used is ITO/ PEDOT:PSS(4083)/EML(80 nm)/CsF(1.5 nm)/Al(100 nm), in which ITO was used as the anode, PVK : PBD (100 : 40) doped with 1, 2, 4, 8% of iridium complex as the emitter and CsF/Al as the cathode.

Devices with the iridium complex emit strong orange-yellow light with an emission maximum at 570 nm (Fig. 4a). We can see



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Fig. 4 Electroluminescent performance of the PLED devices based on complex 1.

that the maximum emission wavelength and the shape of the electroluminescent spectra are nearly the same as those in the photoluminescent spectra, which illustrates that both EL and PL originate from the same emitting core. The CIE coordinates of the devices and other details are listed in Table 1. We can see that all the electroluminescence falls into the orange-yellow region.

Fig. 4b and c show the luminance–voltage–current (L–C–I) and the external quantum efficiency–current density–power efficiency characteristics of the devices, respectively. All devices show low turn-on voltages between 4.7 and 7.0 V. The device with a doping ratio of 4% appears to show the highest performance, with brightness of 7455 cd m⁻² at 9.3 V, external quantum efficiency (EQE) of 19.2% and luminance efficiency (LE) of 40.1 cd A⁻¹.

 Table 1
 Detailed electroluminescent performance of the PLED devices based on complex 1

EML	Doping ratio	Devices ID	The maxima of efficiency							
			LE (cd A ⁻¹)	QE (%)	Voltage (V)	Current Density (mA cm ⁻²)	Lumin (cd.m ⁻²)	Lmax.(cd m ⁻²)	Turn on voltage (V)	CIE(x, y)-2 mA
	1%	5824	13.70	6.60	6.50	0.16	23.0	1700	4.70	0.451,0.494
PVK:PBD:I rcomplex	2%	5822	33.60	16.10	8.80	1.50	511.0	5700	5.00	0.478,0.505
	4%	5838	40.10	19.20	9.30	1.20	500.0	7455	5.50	0.493,0.500
	8%	5823	30.80	14.80	11.50	1.60	497.00	5650	7.00	0.500,0.493

Compared with Ir(III) complexes with similar structures, the electroluminescent performance of the PLED devices based on complex **1** is substantially higher, which can be mainly explained by the efficient hole transport and injection ability, due to the introduction of carbazole groups on the Ir(III) complex,¹³ as well as the good solubility and film-forming property due to the introduction of long alkyl chains.

Conclusions

In conclusion, a highly efficient yellow-emitting iridium(III) complex is assembled from a carbazole-substituted benzimidazole-based N^C^N type ligand. The fabricated PLEDs based on the complex showed maximum external quantum efficiency and luminance efficiency of 19.1% and 40.2 cd A^{-1} , respectively. These performances of the Ir(III) complex are some of the highest ever reported for yellow emitting PLEDs. The combination of good efficiency and color specificity elevates the material to a promising candidate for phosphorescent dopants of PLEDs, especially in the fabrication of white-light display or illumination devices.

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