



Three cationic iridium(III) complexes with 1,10-phenanthroline or compounds containing 1,10-phenanthroline unit as auxiliary ligands: Synthesis and application in polymer light-emitting diodes



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ABSTRACT

Three yellow-green phosphorescent cationic iridium(III) complexes $[(\text{CBT})_2\text{Ir}(\text{phen})]\text{PF}_6$, $[(\text{CBT})_2\text{Ir}(\text{BCP})]\text{PF}_6$ and $[(\text{CBT})_2\text{Ir}(\text{o-phen})]\text{PF}_6$ were synthesized (**phen**: 1,10-phenanthroline, **BCP**: bathocuproine, **o-phen**: 2-(4-tert-butylphenyl)-5-(4-(1-ethyl-*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenyl)-1,3,4-oxadiazole, **CBT**: 2-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)benzo[*d*]thiazole). All of them were successfully applied in polymer light-emitting diodes: ITO/PEDOT: PSS (40 nm)/PVK: PBD: complex (mass ratios 100: 40: *x*, *x* = 1.0, 3.0, and 5.0) (80 nm)/CsF (1.5 nm)/Al (100 nm). The maximum luminances were 8733 cd m⁻², 8878 cd m⁻² and 13019 cd m⁻², the maximum luminance efficiencies were 13.7 cd A⁻¹, 12.5 cd A⁻¹ and 17.5 cd A⁻¹ respectively. Because the steric hindrance of two methyls increase the distance between central Ir³⁺ and **BCP**, and the conjugated plane of 1,10-phenanthroline unit in **BCP** are distorted by two benzene rings, the flow of electrons are partly hindered, $[(\text{CBT})_2\text{Ir}(\text{BCP})]\text{PF}_6$ exhibits the lowest electroluminescent performances. Due to the electron-transporting functional group 2,5-diphenyl-1,3,4-oxadiazole and hole-transporting functional group carbazole providing good bipolar property, $[(\text{CBT})_2\text{Ir}(\text{o-phen})]\text{PF}_6$ exhibits the best electroluminescent performances.

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1. Introduction

In recent years, phosphorescent cationic iridium(III) complexes (CICs) have attracted considerable research interest due to their attractive physical and chemical properties, such as 100% theoretical internal quantum efficiency, moderate excited state lifetime (~μs), tunability of emission spectra via various ligands, high stability, ease of synthesis and purification with high yields, and so on [1–6]. They have been successfully applied in light-emitting electrochemical cells (LECs) [1–5], organic [6–9] and inorganic [10–12] light-emitting diodes (LEDs), bioimaging [13–15], chemical sensing [16–22], data recording and security protection [23], etc. Among these applications, organic light-emitting diodes (OLEDs, including small molecule and polymer light-emitting diodes) are very important electroluminescent (EL) devices and developed rapidly

due to their potential applications in the next-generation full-color flat-panel displays, liquid crystal display backlights and solid lighting sources [2–4,6–9].

To research and understand the factors affecting the applicability and efficiency of cationic iridium(III) complexes in OLEDs are very important and necessary. In previous research, some factors have become clear, for example, dendritic and long chain-like alkyls are beneficial to improving solubility, anti-crystallization and compatibility with host materials [7,24]. Hole-transporting and electron-transporting functional groups, especially the bipolar units containing both of them with more balanced hole and electron fluxes are beneficial to improving EL performances [6,7,24]. In report of J. M. Fernández-Hernández et al., [25] the stereoisomerism of cationic iridium(III) complexes affecting on color and efficiency of their EL devices was investigated. Last year, the photoluminescent (PL) and electroluminescent properties of cationic iridium(III) complexes with different organic anions were comparatively studied by D. Ma et al [8]. However, some other relevant factors are still unknown and worthwhile to be

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continuedly investigated, such as type, number and position of functional groups on organic ligands, the effect of different auxiliary ligands, the comparative advantages of mononuclear and polynuclear cationic iridium(III) complexes, and so on.

1,10-Phenanthroline (**phen**), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (also known as bathocuproine, **BCP** [26]) and 2-(4-tert-butylphenyl)-5-(4-(1-ethyl-*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenyl)-1,3,4-oxadiazole (**o-phen** [6,24,27]) all were widely used as electron-transporting materials (both **BCP** and **o-phen** are compounds containing 1,10-phenanthroline unit) [28], at the same time, they all are commonly used as the neutral auxiliary ligands in metal complexes [4,6,24,27,29]. In order to promote the EL performances of luminescent metal complexes, using carrier-transporting functional ligands in them is a common strategy [29]. **Phen**, **BCP** and **o-phen** all are usable ligands for phosphorescent cationic iridium(III) complexes, at the same time, all of them are coordinated to iridium(III) ion through N–N atoms of 1,10-Phenanthroline unit, however, the different effects and respective functions of them on phosphorescent cationic iridium(III) complexes are unknown. In this work, three cationic iridium(III) complexes were designed and synthesized by all using 2-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)benzo[*d*]thiazole (**CBT**) as the main ligands, and **phen**, **BCP**, or **o-phen** as the auxiliary ligands. Because **CBT** is the same main ligands in three complexes, the different effects and respective functions of three different auxiliary ligands on physical and chemical properties of the complexes are distinguishable. After their thermal stability, electrochemical properties, ultraviolet–visible (UV–vis) absorption spectra and PL spectra being carefully and comparatively investigated, three cationic iridium(III) complexes all were used as phosphorescent dopants in polymer light-emitting diodes (PLEDs).

2. Experimental

2.1. General information

Chemicals and reagents were purchased from commercial sources and used without further purification unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer operating at 400 MHz and 100.6 MHz respectively, tetramethylsilane (TMS) was used as internal standard. Mass spectra (MS) were obtained on an Agilent 1100 LC/MSD TOF liquid chromatography mass spectrometer (LC-MS) with an electrospray ionization (ESI) interface using acetonitrile as matrix solvent. Elemental analyses (EA) were performed on a Vario EL III Elemental Analysis Instrument. UV–vis absorption spectra were measured on an Agilent 8453 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Jobin Yvon FL3-21 spectrofluorometer at room temperature. Differential scanning calorimetry (DSC) curves were obtained on a Netzsch DSC200 analyzer at a heating rate $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 after the first heating cycles of the iridium(III) complexes from room temperature to $250\text{ }^\circ\text{C}$ under the same conditions. Thermogravimetry (TG) curves were obtained on a Netzsch STA 449F3 thermal analyzer at a heating rate $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 . Cyclic voltammetry (CV) was performed on a computer-controlled CHI660D electrochemical analyzer with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as reference electrode, in anhydrous and Ar-saturated acetonitrile solutions of the cationic iridium(III) complexes at $1 \times 10^{-3}\text{ mol L}^{-1}$ at a scanning rate of 100 mV s^{-1} using 0.1 mol L^{-1} tetra-*n*-butylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) as supporting electrolyte. Ferrocene (Fc, 4.8 eV under vacuum) was used as the internal standard.

2.2. Synthesis and characterization of the cationic iridium(III) complexes

The synthetic routes to the cationic iridium complexes are shown in Scheme 1, experimental details and characterization data are given in the following.

2.2.1. Synthesis of $(\text{CBT})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CBT})_2$

Compounds 2-(9-(2-ethylhexyl)-9*H*-carbazol-3-yl)benzo[*d*]thiazole (**CBT**) and $(\text{CBT})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CBT})_2$ were synthesized according to the procedures reported previously by us [10]. The dimer product was directly used for the next step after being dried in vacuum without further purification and characterization.

2.2.2. Synthesis of $[(\text{CBT})_2\text{Ir}(\text{phen})]\text{PF}_6$

A mixture of $(\text{CBT})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CBT})_2$ (0.84 g, 0.40 mmol) and 1,10-phenanthroline (**phen**, 0.17 g, 0.84 mmol) in glycol (30 mL) was stirred at $150\text{ }^\circ\text{C}$ in argon for 16 h. After being cooled to room temperature, an orange-red solution was obtained, and then 10 mL aqueous solution of NH_4PF_6 (0.4 mol L^{-1}) was added in. The resultant orange floccules were filtered, washed with water and then dried in vacuum. The pure product was obtained by silica gel column chromatography, eluting with a mixture of CH_2Cl_2 and acetonitrile (10:1, volume ratio). Yield 90.3% (0.97 g, 0.72 mmol), orange-yellow solid. ^1H NMR (400 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, δ/ppm): 8.74 (d, 2H, $^3J = 8.0\text{ Hz}$, ArH), 8.57 (s, 2H, ArH), 8.42 (s, 2H, ArH), 8.18 (s, 2H, ArH), 8.08 (d, 2H, $^3J = 8.0\text{ Hz}$, ArH), 7.80–7.87 (m, 4H, ArH), 7.39 (t, 2H, $^3J = 7.6\text{ Hz}$, ArH), 7.21 (d, 6H, $^3J = 8.0\text{ Hz}$, ArH), 6.87 (t, 2H, $^3J = 8.0\text{ Hz}$, ArH), 6.47 (dd, 2H, $^3J = 13.0\text{ Hz}$, $^4J = 5.2\text{ Hz}$, ArH), 5.81 (dd, 2H, $^3J = 18.2\text{ Hz}$, $^4J = 7.2\text{ Hz}$, ArH), 3.63 (d, 4H, $^3J = 6.8\text{ Hz}$, $-\text{N}-\text{CH}_2-$), 1.50–1.62 (m, 2H, $-\text{CH}<$), 0.75–1.10 (m, 16H, alkyl-H), 0.73 (t, 6H, $^3J = 6.4\text{ Hz}$, $-\text{CH}_3$), 0.50 (t, 6H, $^3J = 7.2\text{ Hz}$, $-\text{CH}_3$). ^{13}C NMR (100.6 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, δ/ppm): 181.4, 150.8, 149.5, 147.9, 147.0, 144.3, 141.0, 139.4, 131.3, 131.2, 131.1, 130.8, 130.7, 128.7, 127.8, 127.8, 126.6, 125.8, 125.3, 123.1, 120.0, 119.8, 119.6, 119.6, 116.7, 112.8, 112.8, 109.4, 47.3, 47.2, 38.7, 38.6, 30.6, 30.4, 28.2, 28.16, 23.8, 23.8, 23.0, 22.9, 14.0, 13.9, 10.5, 10.3. MS (m/z , ESI^+) 1195.40 (100); calc. for $\text{C}_{66}\text{H}_{62}\text{IrN}_6\text{S}_2$ ($[\text{M}-\text{PF}_6]^+$) 1195.41, found 1195.40. Anal. Calc. for $\text{C}_{66}\text{H}_{62}\text{F}_6\text{IrN}_6\text{PS}_2$: C, 59.13; H, 4.66; N, 6.27%. Found: C, 59.39; H, 4.68; N, 6.53%.

2.2.3. Synthesis of $[(\text{CBT})_2\text{Ir}(\text{BCP})]\text{PF}_6$

2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (being widely known as bathocuproine, **BCP**) was obtained from commercial sources. $[(\text{CBT})_2\text{Ir}(\text{BCP})]\text{PF}_6$ was synthesized via the same method as $[(\text{CBT})_2\text{Ir}(\text{phen})]\text{PF}_6$. 0.84 g (0.40 mmol) $(\text{CBT})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CBT})_2$ and 0.30 g (0.84 mmol) **BCP** were used, and 1.08 g (0.71 mmol) $[(\text{CBT})_2\text{Ir}(\text{BCP})]\text{PF}_6$ was obtained, yield 88.5%, orange solid. ^1H NMR (400 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, δ/ppm): 8.45 (d, 1H, $^3J = 7.2\text{ Hz}$, ArH), 8.42 (d, 1H, $^3J = 6.8\text{ Hz}$, ArH), 7.99 (d, 2H, $^3J = 8.0\text{ Hz}$, ArH), 7.85–7.93 (m, 4H, ArH), 7.51–7.58 (m, 12H, ArH), 7.35 (t, 4H, $^3J = 7.6\text{ Hz}$, ArH), 7.17 (t, 4H, $^3J = 7.6\text{ Hz}$, ArH), 7.00–7.07 (m, 2H, ArH), 6.29 (s, 2H, ArH), 6.21 (d, 1H, $^3J = 8.0\text{ Hz}$, ArH), 6.13 (d, 1H, $^3J = 8.0\text{ Hz}$, ArH), 3.65–3.69 (m, 4H, $-\text{N}-\text{CH}_2-$ on 2-ethylhexyl), 2.19 (s, 6H, $-\text{CH}_3$ on **BCP**), 1.51–1.65 (m, 2H, $-\text{CH}<$ on 2-ethylhexyl), 0.85–1.09 (m, 16H, alkyl-H), 0.67 (t, 6H, $^3J = 6.4\text{ Hz}$, $-\text{CH}_3$ on 2-ethylhexyl), 0.57 (t, 3H, $^3J = 7.2\text{ Hz}$, $-\text{CH}_3$ on 2-ethylhexyl), 0.45 (t, 3H, $^3J = 7.2\text{ Hz}$, $-\text{CH}_3$ on 2-ethylhexyl). ^{13}C NMR (100.6 MHz, CDCl_3 , $25\text{ }^\circ\text{C}$, δ/ppm): 181.4, 181.3, 164.6, 164.6, 151.4, 151.4, 151.3, 150.2, 150.1, 150.1, 149.7, 149.6, 149.5, 149.4, 146.3, 146.2, 143.7, 140.7, 135.4, 131.1, 130.5, 129.9, 129.6, 129.5, 129.2, 127.8, 127.6, 127.5, 125.7, 124.9, 123.3, 123.1, 119.9, 119.7, 119.6, 119.5, 119.3, 117.2, 117.1, 116.9, 111.7, 111.6, 109.3, 47.3, 47.1, 38.7, 38.5, 30.7, 30.5, 28.5, 28.4, 27.0, 23.8, 23.7, 22.9, 14.0, 13.2, 10.3, 10.0. MS (m/z , ESI^+) 1375.50 (100); calc. for $\text{C}_{80}\text{H}_{74}\text{IrN}_6\text{S}_2$ ($[\text{M}-\text{PF}_6]^+$) 1375.50, found 1375.50. Anal. Calc. for $\text{C}_{80}\text{H}_{74}\text{F}_6\text{IrN}_6\text{PS}_2$: C, 63.18; H, 4.90; N, 5.53%. Found: C, 63.36; H,

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