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Efficient yellow–green light-emitting cationic iridium complexes based on 1,10-phenanthroline derivatives containing oxadiazole-triphenylamine unit

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ABSTRACT

Cationic iridium(III) complexes with 1,10-phenanthroline (phen) derivatives containing oxadiazole-triphenylamine, oxadiazole or triphenylamine unit used as neutral auxiliary ligands, with the formula of $[Ir(ppy)_2(op\text{-}phen)][PF_6]$ (**C1**), $[Ir(ppy)_2(o\text{-}phen)][PF_6]$ (**C2**), and $[Ir(ppy)_2(p\text{-}phen)][PF_6]$ (**C3**) (ppy = 2-phenylpyridine) were synthesized, respectively. The complexes exhibit high thermal stability and were used as phosphorescent dopants in polymer light-emitting diodes (PLEDs) with the configuration of ITO/PEDOT: PSS/PVK (70): PBD (30): complex (*x*, wt.%)/TPBI/CsF/Al. The complexes **C1, C2** and **C3** exhibit high electroluminescent performances with the maximum luminance efficiencies of 30.6 cd/A, 28.4 cd/A and 26.3 cd/A, respectively. The Commission Internationale de L'Eclairage (CIE) color coordinates of all complexes are (0.41, 0.55) corresponding to the yellow-green region. The complex **C1** containing bipolar unit of oxadiazole-triphenylamine exhibits higher efficiency due to its balance of hole and electron fluxes.

1. Introduction

Cationic iridium complexes have attracted considerable interest in recent years due to their unique photophysical properties and applications in light-emitting electrochemical cells (LECs) [1–9] and organic light-emitting diodes (OLEDs, including small-molecule and polymer light-emitting diodes) [10–16]. LECs usually require only a single emissive layer without extra layers and use ionic charges to facilitate electronic charge injection from the electrodes into the active layer [1–9]. So LECs can offer several advantages such as simpler device architecture, independence on active layer thickness and being used with air-stable electrodes [1–9]. Nevertheless, some grievous drawbacks such as slow response, severe excited-state quenching due to being composed of neat film of emissive materials, have hindered their practical applications [10–16]. Comparatively, such drawbacks can be significantly suppressed in OLEDs [10–16]. For example, Plummer et al. used a cationic iridium complex as yellow-emitting dopant in polymer light-emitting diodes (PLEDs) which achieved a maximum current efficiency of 22.5 cd/A [10]. Wong et al. reported a sublimable cationic iridium complex being used as dopant in small-molecule OLEDs with a maximum current efficiency of 19.7 cd/A [11]. Up to now, the cationic iridium complexes emitting from blue to red [10–16], white [13] and even near-infrared [15] in OLEDs all were reported.

As being mentioned above, the performances of cationic iridium complexes in OLEDs are noticeable and comparable with those of some neutral iridium complexes. Moreover, cationic iridium complexes can be more easily synthesized and purified with much higher yield (usually above 80%) than neutral iridium complexes [1–16]. However, there are still some disadvantages of cationic iridium complexes used as phosphorescent dopants in OLEDs: 1) cationic iridium complexes, composed of organic complex cation and inorganic acid anion such as PF_6, $ClO_4$and BF_4, usually are incompatible with organic host materials and result in the phase segregation between the host and dopants [11]; 2) cationic iridium

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complexes usually have low solubility in ordinary organic solvents such as toluene, chlorobenzene, chloroform, although they are probably soluble in strong polar solvents such as acetonitrile and N,N-dimethylformamide (DMF), however, strong polar solvents can erode the bottom organic layer in solution-processing and result in decreasing the device performances. Moreover, it is also difficult to fabricate OLEDs via vacuum-deposition due to poor sublimability of cationic iridium complexes [11].

To function as effective phosphorescent dopants in OLEDs like neutral iridium complexes, above mentioned issues of cationic iridium complexes need to be addressed. Although the inorganic acid anions such as PF_6, ClO_4 and BF_4 were found to facilitate electronic charge injection from the electrodes into the active layer in LECs [1–9], however, this effect can be neglected in OLEDs because the doping concentration usually is very low and carrier transport layers are used. So the function and mass ratio of inorganic acid anions can be disregarded in designing cationic iridium complexes for OLEDs. Theoretically, some properties of cationic iridium complexes such as solubility in organic solvents, miscibility with organic host materials and amorphous nature would be improved when using irregular and solubilizing organic ligands, which are advantages to their being used in OLEDs [17]. Similar to neutral iridium complexes, the device performances of cationic iridium complexes would be improved when carrier-transporting units such as triphenylamine, carbazole and oxadiazole were contained in their ligands [17–19].

1,10-Phenanthroline (phen) derivatives are conventional auxiliary ligands for luminescent complexes due to its large conjugated area and good electron fluidity [3,20]. However, some properties such as carrier-transporting property, solubility and thermal stability still need to be further improved [17]. Recently, orange-red light-emitting cationic iridium complexes with 1,10-phenanthroline derivatives containing oxadiazole or carbazole unit were synthesized according to aforementioned strategies [21]. In this work, 1,10-phenanthroline was further modified by bipolar carrier-transporting unit of oxadiazole-triphenylamine as auxiliary ligand in cationic iridium complex which was used as phosphorescent dopant in PLEDs.

2. Experimental

2.1. General information

Chemicals and reagents were obtained from commercial sources and used without further purification unless otherwise stated. Column chromatography was carried out on silica gel (200–300 mesh). Yields refer to the isolated pure compound. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300 spectrometer operating at 300 MHz or a Bruker AV400 spectrometer operating at 400 MHz, tetramethylsilane (TMS) was used as internal standard. Mass spectra (MS) were obtained from a Bruker Esquire HCT PLUS liquid chromatography mass spectrometer (LC-MS) with an electrospray ionization (ESI) interface using MeCN as the matrix solvent. The IR spectra were recorded in KBr on a Shimadzu FTIR-8201PC spectrometer. Elemental analyses (EA) were performed on Vario EL Elemental Analysis Instrument. UV–Vis absorption spectra were recorded on a HP8453E spectrophotometer. Photoluminescence (PL) spectra were recorded on a Fluorolog–3 spectrophotometer. Differential scanning calorimetry (DSC) curves were obtained on a Netzsch DSC200 analyzer via two heating cycles at a heating rate of 10 °C min^{-1} in N_2 atmosphere. Thermogravimetry (TG) curves were obtained on a Netzsch TG209 thermal analyzer at a heating rate of 20 °C min^{-1} in N_2. Cyclic voltammetry (CV) was performed on a computer-controlled CHI800C electrochemical analyzer with the cationic iridium complexes dissolved in anhydrous and Ar-saturated MeCN solutions containing 0.1 mol L^{-1} tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte at a scanning rate of 50 mV s^{-1}. A glass carbon electrode was used as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire as counter electrode. Ferrocene (4.8 eV under vacuum) was used as the internal standard.

2.2. Synthesis and characterization

2.2.1. Synthesis of dichloro-bridged iridium dimer (**$[(ppy)_2Ir(\mu\text{-}Cl)_2Ir(ppy)_2]$**) [2,4]

$IrCl_3 \cdot 3H_2O$ with 2.2 equiv of 2-phenylpyridine (ppy) in a mixed solvent of 2-ethoxyethanol and deionized water (3:1) was heated at 110 °C under Ar for 24 h. The yellow–green solid product was directly used for the next step after being dried in vacuum without further purification and characterization.

2.2.2. Synthesis of 1,10-phenanthroline derivatives

4-(5-(4-(1-Ethyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl)-1,3,4-oxadiazol-2-yl)-N,N-diphenylaniline (**op-phen**): synthesized according to the previously reported procedures [22].

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 9.16 (d, 2H, $^3J = 2.4$ Hz, ArH), 9.06 (d, 1H, $^3J = 7.2$ Hz, ArH), 8.62 (d, 1H, $^3J = 8.4$ Hz, ArH), 8.33 (d, 2H, $^3J = 8.0$ Hz, ArH), 7.95 (t, 4H, $^3J = 8.8$ Hz, ArH), 7.70–7.75 (m, 2H, ArH), 7.33 (t, 4H, $^3J = 7.6$ Hz, ArH), 7.10–7.20 (m, 8H, ArH), 4.69 (q, 2H, $^3J = 7.2$ Hz, $-CH_2-$), 1.64 (t, 3H, $^3J = 7.2$ Hz, $-CH_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 165.2, 163.4, 152.3, 151.4, 149.0, 146.7, 144.8, 144.1, 136.8, 133.0, 130.8, 130.6, 129.8, 128.4, 128.3, 127.3, 125.9, 125.5, 125.1, 124.7, 123.8, 123.0, 121.0, 120.0, 115.6, 41.96, 16.15; FTIR (KBr, cm^{-1}): 3443, 2360, 2333, 2027, 1657, 1593, 1487, 1418, 1384, 1334, 1269, 1118, 1070, 1042, 1008, 989, 864, 818, 740, 697, 620, 546; Element anal. calcd. for $C_{41}H_{29}N_7O$ (%): C, 77.46; H, 4.60; N, 15.42; found (%): C, 77.52; H, 4.55; N, 15.47.

2-(4-Ttert-butyl)phenyl)-5-(4-(1-ethyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenyl)-1,3,4-oxadiazole (**o-phen**): synthesized according to the previously reported procedures [20]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 9.17–9.18 (m, 2H, ArH), 9.05 (dd, 1H, $^3J = 4.0$ Hz, $^4J = 1.8$ Hz, ArH), 8.62 (dd, 1H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, ArH), 8.36 (dd, 2H, $^3J = 6.8$ Hz, $^4J = 1.8$ Hz, ArH), 8.08–8.11 (m, 2H, ArH), 7.94–7.97 (m, 2H, ArH), 7.70–7.73 (m, 2H, ArH), 7.56–7.59 (m, 2H, ArH), 4.72 (q, 2H, $^3J = 7.2$ Hz, $-CH_2-$), 1.65 (t, 3H, $^3J = 7.2$ Hz, $-CH_3$), 1.38 (s, 9H, $-C(CH_3)_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 165.2, 163.9, 155.8, 152.2, 149.3, 148.1, 145.1, 144.4, 137.1, 133.4, 130.6, 130.5, 128.2, 127.4, 127.0, 126.3, 125.4, 125.2, 124.2, 123.8, 122.8, 121.0, 120.0, 41.96, 35.27, 31.24, 16.18; FTIR (KBr, cm^{-1}): 3445, 2365, 2335, 2026, 1642, 1612, 1572, 1444, 1384, 1353, 1269, 1115, 1052, 1011, 861, 743, 619, 569; Element anal. calcd. for $C_{33}H_{28}N_6O$ (%): C, 75.55; H, 5.38; N, 16.02; found (%):C, 75.18; H, 5.47; N, 15.77.

4-(1-Ethyl-1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)-N,N-diphenylaniline (**p-phen**): synthesized according to the previously reported procedures [23]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 9.11–9.20 (m, 2H, ArH), 9.04 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, ArH), 8.55 (dd, 1H, $^3J = 8.4$ Hz, $^4J = 1.4$ Hz, ArH), 7.62–7.69 (m, 2H, ArH), 7.58 (d, 2H, $^3J = 8.6$ Hz, ArH), 7.26–7.36 (m, 4H, ArH), 7.16–7.21 (m, 6H, ArH), 7.08 (t, 2H, $^3J = 7.2$ Hz, ArH), 4.64 (q, 2H, $^3J = 7.2$ Hz, $-CH_2-$), 1.59 (t, 3H, $^3J = 7.2$ Hz, $-CH_3$); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 153.6, 149.5, 148.9, 147.6, 147.2, 144.7, 144.2, 136.7, 130.6, 130.4, 129.6, 128.0, 125.3, 124.7, 124.2, 123.9, 123.5, 123.0, 122.6, 122.3, 120.0, 41.96, 16.12; FTIR (KBr, cm^{-1}): 3380, 2357, 2330, 2051, 2027, 1662, 1594, 1490, 1467, 1443, 1384, 1333, 1270, 1118, 1042, 1010, 865, 741, 700, 622, 548; Element anal. calcd. for $C_{33}H_{25}N_5$ (%): C, 80.63; H, 5.13; N, 14.25; found (%):C, 80.54; H, 5.17; N, 14.29.