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Efficient electrophosphorescence from low-cost copper(I) complex

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Abstract

Light-emitting devices, using a high-phosphorescent copper(I) complex [Cu(phen)(POP)]PF_6 [POP = Bis-[(2-diphenyl-phosphino)phenyl]ether and phen = 1,10-phenanthroline] as dopant and emitting center have been investigated, in different device architectures involving single layer devices using the blend of poly(*N*-vinylcarbazole) (PVK) and 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) as host and heterostructure multi layer devices using PVK as host. The maximum luminance of the phosphorescent devices reached 1400 cd/m^2 and the highest luminance efficiency exceeded 1 cd/A for single layer devices and higher luminescence efficiency up to 1.8 cd/A for multi layer ones. Efficient electrophosphorescent OLEDs can be developed by using low-cost Cu(I) complex as guest and polymer as host material.

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1. Introduction

Extensive research on organic electroluminescence (EL) in recent years has improved both the reliability and the efficiency of LEDs, which has been applied commercially in cell phones. However, new materials with better properties are still in great need to fully realize the advantages that organic and polymer LED technology can potentially offer and to overcome the disadvantages of current materials such as high costs and environment pollution. Heavy-metal complexes that enable the otherwise transition from spin-forbidden triplet-state to ground-state (phosphorescence), due to the spin–orbit coupling effect induced by heavy atoms, are attractive for organic light-emitting devices (OLEDs), especially for the improvement of device efficiency [1–13]. It has been demonstrated that efficient electrophosphorescence was obtained from a class of heavy-metal complexes that feature metal-to-ligand-charge-transfer (MLCT) excited states with relatively short phosphorescence lifetime [2]. Particularly, most of them derive from d^6 transition metals ca. Ir(III) [3–7], Ru(II) [8,9], Re(I) [10], and Os(II) [11,12] and few from d^8 transition metals ca. Pt(II) [1,13]. The devices based on $Ir(ppy)_3$ (ppy = 2-phenylpyridine) and its derivatives exhibited the highest external quantum efficiency of 19% in all reported EL materials. However, there are still some potential drawbacks of Ir(III)-based devices, including the high costs and the poor resource (the content of metal Ir in the earth's crust is about 10^{-7}%). Existing alternatives, such as Ru(II), Re(I) and Os(II) also have the same inherent limitation. Therefore it is worthwhile to develop some alternatives containing cheap metals to circumvent these difficulties.

An attractive alternative, Cu(I) coordination compound, is emerging in the form of d^{10} transition metal compounds. In fact, Cu(I) diimine compounds exhibit MLCT excited state properties that are completely comparable to $Ru(bpy)_3^{2+}$, a well-known MLCT compound [8,9]. Cu(I) diimine compounds have been found and investigated since the early 1950s [14], however they did not draw the attention of organic EL community due to their low emission

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efficiency (<1%) at room temperature [15–19]. We have reported EL devices based on a high phosphorescence tetranuclear Cu(I) complex $Cu_4 (C\equiv Cph)_4L_2$ (L = 1,8-bis(diphenylphosphino)-3,6-dioxaoctane), but due to the poor energy collection of phosphor in devices, only low efficiency (<0.1%) was obtained [20]. The structure of $Cu_4(C\equiv Cph)_4L_2$ was too complex to be put into practical application, and further photochemical and device study on $Cu_4(C\equiv Cph)_4L_2$ showed that an unexpected decomposition occurred upon photo irradiation and in EL process. Another tetrameric copper(I)-amide cluster $[CuN(Si(CH_3)_3)_2]_4$ was also applied as the emitting center of OLEDs with the maximum external quantum efficiency of 0.2% [21]. Recently, a simple mixed-ligand Cu(I) 2,9-dimethyl-1,10-phenanthroline complex [Cu(dmp)(POP)]-BF_4 [POP = Bis[(2-diphenylphosphino)phenyl]ether] is reported to exhibit good stability, unusually high efficient and long-lived PL in solution [22] ($\lambda_{max} = 570$ nm, with the efficiency of ca. 15% and the lifetime of ca. 15 μs), which is comparable to other electrophosphorescent metal complexes such as $Ir(ppy)_3$. We believe [Cu(dmp)(POP)]BF_6 and its derivatives have great potentials to be candidates for current electrophosphorescence materials. For this aim, the electroluminescence properties of Cu-based OLEDs of different architectures are investigated.

2. Experimental

2.1. Materials

PVK and PBD were purchased from Aldrich and poly(3,4-ethylene dioxythiophene) (PEDOT) from Bayer Chemical Company and used as received. Cu(I) complex [Cu(phen)(POP)]PF_6 (inset in Fig. 1) was synthesized by the reaction of $[Cu(NCCH_3)_4]PF_6$ with bis[2-(diphenylphosphino)phenyl]ether and 1,10-phenanthroline in CH_2Cl_2 for 3 h at room temperature, and then purified by crystallization as yellow crystals. The structure of [Cu(phen)(POP)]PF_6 was confirmed by ^1H NMR, IR spectroscopy, elemental analysis, and XRD.

2.2. UV–vis and PL spectra

UV–vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out by RF-5301PC. The films for photoluminescence (PL) experiments were formed on pre-cleaned quartz plate at air atmosphere. Doped PC was dissolved in chloroform at a concentration of 10 mg/ml.

2.3. Preparation of EL devices and testing

The LEDs fabricated in this work had two configurations. One was Single layer LEDs with the structure of ITO/PEDOT(100 nm)/40 wt.% PVK–PBD: *x* wt.% [Cu(phen)(POP)]PF_6(80 nm)/LiF(0.5 nm)/Al(200 nm) and the other was heterostructure multi layer LEDs with the structure of ITO/PEDOT(100 nm)/PVK: *x* wt.% [Cu(phen)(POP)]PF_6(80 nm)/PBD(50 nm)/Alq_3(45 nm)/LiF(0.5 nm)/Al(200 nm). Indium–tin-oxide (ITO)-coated glass with a sheet resistance of <50 Ω/□ was used as substrate. The substrate was pre-patterned by photolithography to give an effective device size of 4 mm^2. Pre-treatment of ITO includes a routine chemical cleaning using detergent and alcohol in sequence, followed by oxygen plasma cleaning. The poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was coated from a water dispersion yielding a 100 nm thick layer after drying (ca. 105 °C; 5 min). Active layers were spin-coated from chloroform solution containing *x* wt.% dyes in 10 mg/ml PVK or PVK–PBD blend on PEDOT:PSS to give a film with the thickness of 80–100 nm. The cathode LiF (0.5 nm) and Al (200 nm) was deposited by thermo-evaporation. The electroluminescence was recorded by a PR65-spectrometer. Current–voltage and light intensity measurements were made at room temperature and ambient condition.

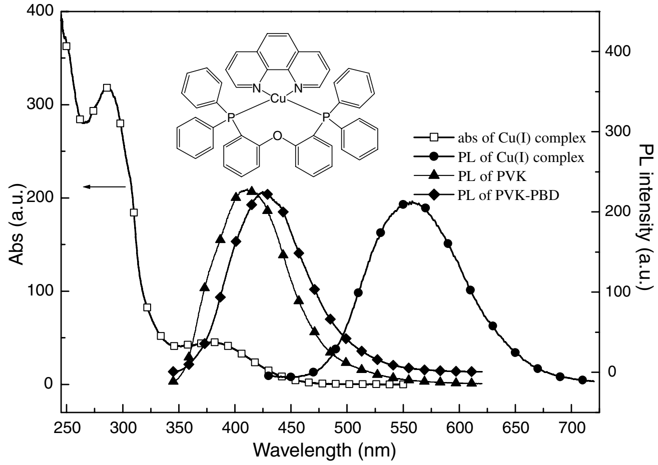

Fig. 1. Normalized spectra of absorption of [Cu(phen)(POP)]PF_6 in solution (CH_2Cl_2) and photoluminescence of [Cu(phen)(POP)]PF_6: polycarbonate (PC) blend film excited at 350 nm, and photoluminescence spectra of PVK and PVK–PBD in thin film excited at 325 nm. Inset: the molecular structure of $[Cu(phen)(POP)]^+$. Anal. Calcd for $C_{48}H_{36}CuF_6N_2OP_3$ (i.e. [Cu(phen)(POP)]PF_6): C, 62.17; H, 3.91; N, 3.02. Found: C, 62.08; H, 3.99; N, 2.92. Crystal data for [Cu(phen)(POP)]PF_6 are deposited at the Cambridge Crystallographic Data Centre (CCDC) and the deposition number is CCDC 224679.

3. Results and discussion

The absorption and photoluminescence (PL) spectra for [Cu(phen)(POP)]PF_6 are given in Fig. 1. The ligand π–π^* absorption band is centered at 285 nm and the MLCT singlet absorption band is centered at 385 nm. The diluted chloroform solution of [Cu(phen)(POP)]PF_6 shows weak luminescence as excitation at both π–π^* and ^{1}MLCT absorption band. However, the crystal of [Cu(phen)(POP)]PF_6 and a doped polycarbonate (PC) film shows a bright yellow light emission with the maximum emission