Optical Materials 47 (2015) 173–179

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

High efficient OLEDs based on novel Re(I) complexes with phenanthroimidazole derivatives

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ARTICLE INFO

Article history:
Received 25 January 2015
Received in revised form 30 April 2015
Accepted 10 May 2015
Available online 3 June 2015

Keywords:
Rhenium complex
Phenanthroimidazole
Phosphorescence
Electroluminescence
High efficiency
OLEDs

ABSTRACT

Novel rhenium(I) [Re(I)] complexes with phenanthroimidazole ligands were successfully designed, synthesized and characterized. The Re(I) complexes displayed intense phosphorescence with yellow or orange color around 540–580 nm at room temperature with relatively short lifetimes. The phosphorescent simple-structure OLEDs using these Re(I) complexes as dopants exhibited low turn-on voltage of 3.5–3.6 V, maximum current efficiencies of 18.7–21.1 cd A^{-1} and maximum power efficiencies of 13.3–18.9 lm W^{-1}, which were amongst the highest reported for OLEDs based on Re(I) complexes with phenanthroline ligands as emitters. The excellent performances are due to the bulky steric Re(I) complexes with short lifetime and good electron-transporting ability, which may improve the electron injection and result in greater balance between electron and hole fluxes. The results suggest that these complexes have potential application in OLEDs.

1. Introduction

Phosphorescent organic light-emitting diodes (OLEDs) have been extensively studied since the pioneering work by Ma and Forrest et al. in 1998 [1,2]. Compared with conventional fluorescent OLEDs, in which only singlet excitons are luminescent and thus the internal emission efficiency is limited to 25%, phosphorescent OLEDs can harness both singlet and triplet excitons for light emission, thereby approaching an internal efficiency of 100% [3–6]. Therefore, heavy-metal phosphorescent materials have become important research objectives of many chemists for achieving highly efficient OLEDs. Iridium(III) [Ir(III)] [7,8], and platinum(II) [Pt(II)] [9,10] complexes have been mainly exploited in OLEDs. As another class of phosphorescent luminescent material-Rhenium(I) [Re(I)] complex, its d^6 electronic configuration is coincident with that of the corresponding Ir(III) system. Re(I) complexes possess many advantages such as high room temperature (RT) phosphorescence quantum yield, relatively short excited state lifetime and excellent thermal, chemical, and photochemical stability, so many researchers pay considerable attention to this field. Rigid 1,10-phenanthroline is a classic chelating bidentate ligand for transition metal ions that show potential applications due to its high charge transfer mobility [11,12]. So far, some Re(I) complexes with phenanthroline ligands have been reported for being employed as emitters in OLEDs. For example, Ma and Liu et al. first reported efficient devices based on (1,10-phenanthroline)Re$(CO)_3$Cl as emitter with a maximum current efficiency of 6.67 cd A^{-1} [13]. Li et al. fabricated highly efficient device using a functionalized (1-ethyl-2-(4′-triphenylamino)imidazo[4,5-*f*] 1,10-phenanthroline)Re$(CO)_3$Br complex as emitter with efficiencies of 17.6 cd $A^{-1}$and 9.2 lm W^{-1} [14]. Subsequently, our group reported more efficient OLEDs based on (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)Re$(CO)_3$Br emitter with maximum current efficiency of 21.8 cd A^{-1}, which was ascribed to the exceptional molecular structure [15]. In brief, Re(I) complexes with phenanthroline ligands as phosphorescent materials for application in OLEDs exhibited flourishing trends.

It is well-known that for organic semiconductors, conductivities of emissive materials with electron-transporting properties are generally lagging behind the hole-transporting materials. Thus, development of better emissive materials with electron-transporting properties is an important approach for performance enhancement. Moreover, the imidazole ring possesses a great electronic transmission capacity. Here, we developed a serials of new Re(I) materials based on 1,10-phenanthroimidazole due to its good electron-transporting properties. By attaching bulky rigid

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http://dx.doi.org/10.1016/j.optmat.2015.05.013
0925-3467/

phenyl group to N-1 position of the imidazole, three novel Re(I) complexes with 1*H*-imidazo[4,5-*f*][1,10]phenanthroline ligands, i.e., (1,2-diphenyl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline) Re(CO)$_3$Br (Re-DPIP), 2-(4-fluorophenyl)-1-phenyl-1*H*-imidazo [4,5-*f*][1,10] phenanthroline Re(CO)$_3$Br (Re-FPIP) and 2-(4-methoxyphenyl) -1-phenyl-1*H*-imidazo[4,5-*f*][1,10]phenanthroline Re(CO)$_3$Br (Re-MPIP), were designed, synthesized and structurally characterized. The photophysical, electrochemical and electroluminescent (EL) properties of the Re(I) complexes were also investigated in detail. The OLEDs based on these Re(I) complexes as doped emitters exhibited very high efficiencies.

2. Experimental

2.1. Reagents and physical measurements

Commercially available reagents and starting materials were used for synthesis of the Re(I) complexes without further purification. Solvents were purified and dried by standard procedures prior to use. NMR spectra were recorded on a Bruker AC 500 spectrometer with tetramethylsilane (TMS) as an internal reference. Mass spectroscopy (MS) was performed on AB SCIEX API 3200 spectrometer. Elemental analysis was performed on Vario EL III CHNS instrument. IR spectra were recorded with samples as KBr pellets using NICOLET-IS5 FTIR spectrophotometer. UV–vis absorption and PL spectra of the Re(I) complexes in CH_2Cl_2 solution of 1.0×10^{-5} mol L^{-1} were completed on a PerkinElmer Lambda 900 spectrophotometer and LS 55 fluorescence spectrophotometer, respectively. Luminescence decay data were obtained with a 355 nm light generated from the third-harmonic-generator pump, using a pulsed Nd:yttrium aluminum garnet (YAG) laser as the excitation source. Cyclic voltammetry experiments were conducted using a CHI 660D electrochemical analyzer with a scan rate of 100 mV s^{-1}. All measurements were carried out at RT unless otherwise specified.

2.2. Synthesis of the Re(I) complexes

2.2.1. Synthesis of 1,10-phenanthroline-5,6-dione

1,10-Phenanthroline-5,6-dione was synthesized according to general procedures [16]. Yield: 72%. MS (ESI): *m/z* 211.3 [M+H$^+$]. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 9.13(s, 2H), 8.51(d, *J* = 8.00 Hz, 2H), 7.61–7.60(t, 2H).

2.2.2. Synthesis of 1,2-diphenyl-1H-imidazo[4,5-f][1,10]phenanthroline (DPIP)

The mixture of 1,10-phenanthroline-5,6-dione 1.01 g (4.8 mmol), NH$_4$OAc 1.48 g (19.2 mmol), was dissolved in 15 mL of HOAc. Under N$_2$ atmosphere, benzaldehyde (0.5 mL, 4.8 mmol) and aniline (0.4 mL, 4.8 mmol) were added in sequence and then the mixture was heated to reflux for 6 h. Then the mixture was poured into cold water, extracted with CH_2Cl_2 and dried with anhydrous magnesium sulfate. After the evaporation of solvent, the crude product was further purified by recrystallization from EtOH with light yellow crystal. Yield: 52.5%. MS (ESI): *m/z* 373.5 [M+H$^+$]. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 9.20–9.19(m, 1H), 9.16–9.14(m, 1H), 9.05–9.04(m, 1H), 7.77–7.75(m, 1H), 7.67–7.65(m, 3H), 7.64–7.62(m, 2H), 7.58–7.53(m, 2H), 7.44–7.42(m, 1H), 7.35–7.27(m, 4H).

2.2.3. Synthesis of 2-(4-fluorophenyl)-1-phenyl-1H-imidazo[4,5-f][1,10] phenanthroline (FPIP)

The synthesized procedure was similar to that of DPIP. Ashy-yellow crystal. Yield: 74.2%. MS (ESI): *m/z* 391.3 [M+H$^+$]. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 9.20–9.19(m, 1H), 9.13–9.11(m, 1H), 9.05–9.04(m, 1H), 7.78–7.75(m, 1H), 7.71–7.68(m, 3H), 7.66–7.64(m, 2H), 7.58–7.53(m, 2H), 7.43–7.41(m, 1H), 7.30–7.28(m,1H), 7.03–6.99(m, 2H).

2.2.4. Synthesis of 2-(4-methoxyphenyl)-1-phenyl-1H-imidazo[4,5-f][1,10] phenanthroline (MPIP)

The synthesized procedure was similar to that of DPIP. Yellow crystal. Yield: 63.5%. MS (ESI): *m/z* 403.4 [M+H$^+$]. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 9.22–9.20(m, 1H), 9.15–9.13(m, 1H), 9.05–9.04(m, 1H), 7.78–7.75(m, 1H), 7.68–7.63(m, 3H), 7.55–7.50(m, 4H), 7.43–7.41(m, 1H), 7.30–7.27(m, 1H), 6.84–6.83(m, 2H), 3.80(s, 3H).

2.2.5. Synthesis of Re-DPIP

DPIP (78.2 mg, 0.21 mmol) and Re(CO)$_5$Br (81.2 mg, 0.2 mmol) were refluxed in 20 mL of toluene for 5 h under nitrogen atmosphere. After the mixture was cooled to RT, the solvent was removed and the resulting yellow solid was purified by silica-gel column chromatography with acetic ether and petroleum ether as mobile phase. Yield: 88%. Yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ 9.33(s, 1H), 9.29(m, 1H), 9.25(m, 1H), 8.03–8.00(t, 1H), 7.76–7.67 (m, 5H), 7.581–7.557(t, 2H), 7.49(d, *J* = 7.50 Hz, 2H), 7.106–7.073(m, 3H). Elemental analysis for $C_{28}H_{19}BrN_4O_3Re$. Calcd: C, 46.35; H, 2.64; N, 7.72; Found: C, 46.39; H, 2.61; N, 7.76.

2.2.6. Synthesis of Re-FPIP

The synthesized procedure was similar to that of Re-DPIP. Yellow powder. Yield: 83%. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, TMS): δ 9.42–9.39(t, 2H), 9.31–9.29(t, 1H), 8.03–8.01(t, 1H), 7.83(d, *J* = 8.00 Hz, 3H), 7.78(d, *J* = 7.00 Hz, 2H), 7.70(d, *J* = 8.50 Hz, 1H), 7.66–7.63(t, 2H), 7.59–7.57(t, 3H). Elemental analysis for $C_{28}H_{18}BrFN_4O_3Re$. Calcd: C, 45.23; H, 2.44; N, 7.53; Found: C, 45.29; H, 2.46; N, 7.49.

2.2.7. Synthesis of Re-MPIP

The synthesized procedure was similar to that of Re-DPIP. Yellow powder. Yield: 85%. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, TMS): δ 9.43(d, *J* = 7.50 Hz, 1H), 9.39(s, 1H), 9.26(s, 1H), 8.01–7.99(t, 1H), 7.75(d, *J* = 7.50 Hz, 2H), 7.68(d, *J* = 8.50 Hz, 1H), 7.62(d, *J* = 8.00 Hz, 2H), 7.56(s, 1H), 7.47–7.44(t, 3H), 6.89(d, *J* = 8.00 Hz, 2H), 3.84(s, 3H). Elemental analysis for $C_{29}H_{21}BrN_4O_4Re$. Calcd: C, 46.10; H, 2.80; N, 7.41; Found: C, 46.33; H, 2.78; N, 7.45.

2.3. Device Fabrication and EL measurements

OLEDs were fabricated through vacuum deposition of the materials at about 1×10^{-6} Torr onto ITO-coated glass substrates with a sheet resistance of 25 Ω sq^{-1}. The ITO-coated substrates were routinely cleaned by ultrasonic treatment in solvent and then cleaned by exposure to a UV-ozone ambient. All organic layers were deposited in succession without breaking vacuum. The devices were prepared with the following structures of ITO/TAPC (20 nm)/CBP: Re(I) complexes (30 nm)/TPBi (50 nm)/Liq (2 nm)/Al (150 nm), in which TAPC [1,1-bis[4-[*N,N*′-di(*p*-tolyl)amino]phenyl]cyclohexane], CBP (4,4′-N,N′-dicarbazolebiphenyl), and TPBi [1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene] were used as hole-transporting layer, host, and electron-transporting layer, respectively, and Liq/Al as the composite cathode. Deposition rates and thicknesses of the layers were monitored *in situ* using oscillating quartz monitors. Thermal deposition rates for organic materials, Liq and Al were ~1, ~1 and ~10 Å s^{-1}, respectively. EL spectra were measured by a PR 655 spectra scan spectrometer. The luminance–current–voltage (*L–I–V*) characteristics were recorded simultaneously with the measurement of EL spectra by combining the spectrometer with a