Study on a novel emitter based on rhenium complex: Synthesis, molecular structure, photophysical feature and electroluminescence performance

Haiyan Yan*, Kaichang Kou, Wan Pu

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

In the present work, we report a diamine ligand of 2-(4-chlorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (CPO) which owns a large conjugation plane and an electron-pulling moiety of 1,3,4-oxadiazole group. Its corresponding Re(I) complex of $Re(CO)_3(CPO)Br$ is also synthesized and studied in detail, including single crystal structure, electronic structure, photophysical performance, thermal stability and electrochemical property. Experimental data suggest that Re(I) localizes in the center of a distorted octahedral coordination sphere, and the π–π attraction between CPO ligands makes $Re(CO)_3(CPO)Br$ molecules take a highly-ordered arrangement. Upon photoexcitation, $Re(CO)_3(CPO)Br$ shows a yellow emission peaking at 540 nm with quantum yield of 0.13 and excited state lifetime on microsecond scale. Theoretical calculation then points out that the emission comes from the triplet excited state of ML&LLCT, where ML&LLCT means metal-to-ligand-charge-transfer and ligand-to-ligand-charge-transfer. Further experimental result suggests that $Re(CO)_3(CPO)Br$ owns a high decomposition temperature of 300 °C and a band gap of 2.27 eV with HOMO and LUMO energy levels of −5.39 eV and −3.12 eV, respectively. The optimal electroluminescence device using $Re(CO)_3(CPO)Br$ as the emissive dopant renders an emission peaking at ~555 nm with maximum brightness of 3520 cd/m² and maximum current efficiency of 7.2 cd/A.

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1. Introduction

The requirement for optoelectronic applications, such as organic light-emitting diodes (OLEDs), solar cells and optical sensors, has sparked the research interest in phosphorescent transition metal complexes, as suggested by Yersin and coworkers [1–3]. Among the numerous candidates, phosphorescent iridium complexes have shown promising potential due to their tunable emitting wavelength, high photoluminescence (PL) quantum yield, short excited state lifetime and good stability [4]. However, further study and literature reports indicate that most phosphorescent iridium-based emitters suffer badly from intense self-quenching at high concentrations, leading to device efficiency roll-off. What is more, the synthetic and purification procedures are generally complicated. Thus, the strong appeal of developing other superior emitters with slight self-quenching effect and simple synthetic procedure, along with the need for further understanding on the correlation between molecular structure and luminescence (photoluminescence and electroluminescence) performance, has

activated a continuous progress in the design and synthesis of luminescent transition metal complexes.

Gordon, Walsh, Lundin and coworkers have devoted their efforts to phosphorescent rhenium(I) complexes owing to their promising performance such as high PL quantum yield, short excited state lifetime, along with the potentiality of achieving an internal quantum efficiency of 100% [5–8]. The promising results convinced their potential as a functional material for OLEDs. The correlation between molecular structure and photophysical feature has also been explored. For example, Li and coworkers have investigated the substituent effect of electron–donor/acceptor groups in N–N ligands on the PL and EL performance of their corresponding $Re(CO)_3(N–N)X$ complexes, where N–N and X stand for diamine ligand and halogen atom, respectively [9–10]. It has been reported that the introduction of electron-donor, such as carbazole group, into the ligand can improve the EL performance [9], and the large conjugation plane is helpful to balance the charge injection and achieve efficient energy transfer [10].

Gordon and Blackman have also performed a density functional theory (DFT) calculation on Re(I), Ru(II) and Cu(I) complexes based on dipyrido[3,2-a:2 ',3 '-c]-phenazine, which provides a perspective insight for those complexes [11]. The definitive work by Meyer has discussed the correlation between photophysical property

* Corresponding author. Tel.: +86 015353554745.
  E-mail address: hyyan01@163.com (H. Yan).

(energy gap law) and substituent groups in diamine ligands [12]. Generally, the occupied frontier molecular orbitals (MOs) of Re(CO)$_3$(N–N)X complexes own predominant metal character of dπ (Re), while the unoccupied frontier MOs are essentially π^* orbital of diamine ligand. The onset electronic transition could be assigned to the one from occupied frontier MOs to unoccupied ones, showing metal-to-ligand-charge-transfer (MLCT) character. It is also concluded that the extent of diamine ligand distortion has some effect on the energy gap between excited and ground states.
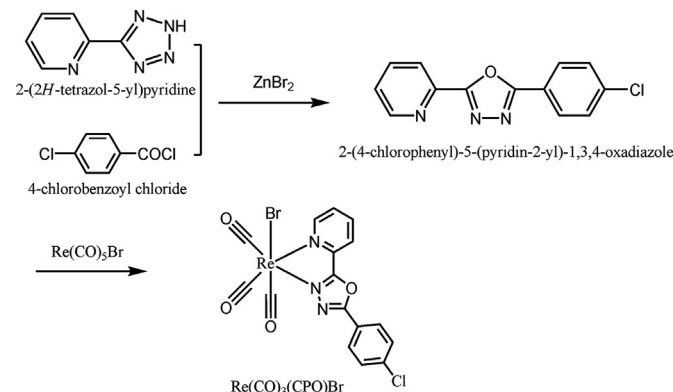
Enlightened by above results, we decide to introduce an oxadiazole group into the diamine ligand, trying to find to correlation between the photophysical property and ligand conjugation chain. In the present work, we design and synthesize a diamine ligand of 2-(4-chlorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (CPO) which owns a large conjugation plane and an electron-pulling moiety of 1,3,4-oxadiazole group, aiming to realize a promising emitter with good PL and EL performance. Its molecular structure, photophysical property, electrochemical and thermal features are measured and discussed in detail. In addition, its potential for EL application is also investigated.

2. Experimental details

The synthetic route for the N–N ligand of 2-(4-chlorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (CPO) and its corresponding Re(I) complex of Re(CO)$_3$(CPO)Br is depicted in Scheme 1. The staring reagents of 4-chlorobenzoyl chloride, NaN$_3$, ZnBr$_2$, 2-cyanopyridine 4,4',4"-tris[3–methylphenylphenylamino] triphenylamine (m-MT-DATA), 4,4 -bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), 4,4'-dicarbazolyl-1,1'-biphenyl (CBP), 4,7-diphenyl-1,10-phenanthroline (Bphen), tris(8-hydroxy-quinoline)aluminum (Alq$_3$) and Re(CO)$_5$Br were obtained from Aldrich Chemical Co. and used as received. The starting material of 2-(2 H-tetrazol-5-yl)pyridine was synthesized according to a literature procedure [13]. All organic solvents have been redistilled for purification.

2.1. Synthetic procedure of CPO

The synthetic route for the N–N ligand of CPO can be described as follows [13,14]. The mixture of 10 mmol of 2-(2 H-tetrazol-5-yl) pyridine, 11 mmol of 4-chlorobenzoyl chloride and 30 mL of pyridine was heated to reflux under N$_2$ protection for 30 h. After cooling, the transparent solution was poured into 300 mL of cold water. The solid residue was collected and recrystalized in hot ethanol. The crude product was further purified on a silica gel column to yield 0.15 g of white solid. ^{1}HNMR (300 MHz, CDCl$_3$): δ 7.27 (1 H, m), 7.44 (2 H, m), 7.79 (1 H, m), 8.03 (1 H, t), 8.12 (1 H, t), 8.25 (1 H, d, J=6.0), 8.63 (1 H, d, J=3.6). Anal. Calcd. For

C$_{13}$H$_8$N$_3$OCl: C, 60.60; H, 3.13; N, 16.31. Found: C, 60.52; H, 3.26; N, 16.44.

2.2. Synthetic procedure of Re(CO)$_3$(CPO)Br

The synthetic route for the Re(I) complex of Re(CO)$_3$(CPO)Br can be described as follows [15]. The mixture of 5 mmol of CPO, 5 mmol of Re(CO)$_5$Br and 20 mL of redistilled toluene was heated to reflux for 10 hours under N$_2$ protection. After cooling, the solvent of toluene was removed by rotary evaporation. The solid residue was firstly purified by the recrystalization from hot ethanol. The crude product was further purified on a silica gel column to yield 0.21 g of yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.28 (1 H, m), 7.46 (2 H, m), 7.81 (1 H, m), 8.02 (1 H, t), 8.16 (1 H, t), 8.24 (1 H, d, J=6.0), 8.74 (1 H, d, J=3.6). Anal. Calcd. for C$_{16}$H$_8$BrN$_3$O$_4$ClRe: C, 31.62, H, 1.33, N, 6.91. Found: C, 31.76, H, 1.45, N, 7.07. The molecular structure of Re(CO)$_3$(CPO)Br was then further proven by single crystal XRD which will be later discussed in detail.

2.3. Construction procedure of EL devices

EL devices using Re(CO)$_3$(CPO)Br as the emissive dopant were constructed by resistive heating method under a chamber pressure of ~4×10^{-4} Pa onto clean indium tin oxide (ITO) glass substrates [9,16]. Before use, the ITO substrates were cleaned by sonication in detergent solution, water, and ethanol sequentially. After being dried by nitrogen flow, the ITO substrates were treated with oxygen plasma for 1 min. The thicknesses of functional layers and the evaporation speed of individual materials were monitored with a quartz crystal monitor in vacuum.

2.4. Apparatus and measurement methods

^{1}H NMR spectra were taken on a Varian INOVA 300 spectrometer. Elemental analysis data were obtained from a Carlo Erba 1106 elemental analyzer. Single crystal data of Re(CO)$_3$(CPO)Br were measured on a Siemens P4 single crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo Kα radiation at 298 K, under operating voltage of 50 kV and current of 30 A, respectively. All hydrogen atoms were calculated. Singlet excitation and density functional theory (DFT) calculation were performed on Re(CO)$_3$(CPO)Br at RB3PW91/SBKJC level in vacuum [11,17–20]. The molecular structure obtained from single crystal data was used as the initial structure. The graphical presentation for frontier MOs was generated by wxMacMolPlt software package with contour value of 0.020. The percentage composition of frontier MOs and the first ten singlet electronic transitions were finished by VMODes program (see its description via http://www.d.umn.edu/~vnemykin/VMODes/VMODes.htm). UV–vis absorption spectra were measured by a Shimadzu UV-3101PC spectrophotometer. PL and excitation spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. PL quantum yield was measured according to a literature method [21]. Excited state lifetime data were measured by a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd:yttrium aluminium garnet (YAG) laser as the excitation source. Thermogravimetric analysis on Re(CO)$_3$(CPO)Br was taken on a thermal analysis instrument of SDT2960 (TA Instruments, New Castle, DE) with heating rate of 10 °C per minute. Cyclic voltammerty (CV) measurement of Re(CO)$_3$(CPO)Br was run on a CHI830b electrochemical workstation (CH Instruments, Shanghai Chenhua Instrument Corporation, China) in a three-electrode cell, using a platinum-sheet working electrode, a platinum-wire counter electrode and a silver/silver nitrate (Ag/Ag$^+$) reference electrode. The measurement was recorded in CH$_3$CN solution (~10^{-3} M) with

Scheme 1. The synthetic procedure for CPO ligand and its Re(I) complex of Re(CO)$_3$(CPO)Br.