

Synthesis, photophysical and electrophosphorescent properties of a novel fluorinated rhenium(I) complex

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ABSTRACT

A novel fluorinated rhenium complex, i.e., Re-BFPP (BFPP, 2, 3-bis(4-fluorophenyl)pyrazino[2,3-*f*][1,10]phenanthroline) was designed, synthesized and characterized by ¹H NMR and mass spectroscopy. The light-emitting and electrochemical properties of this complex were studied. The organic light-emitting diodes (OLEDs) employing Re-BFPP as a dopant emitter with the structures of ITO/m-MTDATA (10 nm)/NPB (20 nm)/CBP: X wt.% Re-BFPP (30 nm)/Bphen (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm) were successfully fabricated and a broad electroluminescent peak at 553 nm was observed. The 10 wt.% Re-BFPP doped device exhibited the maximum luminance of 6342 cd/m² and a peak current efficiency of 17.9 cd/A, corresponding to the power efficiency of 8.1 lm/W.

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1. Introduction

Tremendous potentials in organic light-emitting diodes (OLEDs) have triggered intensive research endeavors to develop efficient phosphorescent materials owing to their excellent performances and promising applications in OLEDs for full-color flat panel displays and lighting sources [1–5]. In OLEDs based on phosphorescent materials, both singlet and triplet excitons contribute to light emission due to intersystem crossing of the singlet to the triplet excited state manifold resulting from strong spin–orbit coupling induced by heavy metal atom, and then the internal quantum efficiency of OLEDs based on phosphorescent emitters can approach 100% theoretically [6]. So far, highly efficient OLEDs based on Ir(III) [7–9], Pt(II) [10], Os(II) [11] complexes have been extensively studied since the pioneering work by Forrest et al. in 1998 [12]. As another class of phosphorescent materials, Re(I) complexes present many virtues such as relatively short excited state lifetime (<1 μs), excellent thermal and photochemical stability and so on [13,14]. In addition, the d⁶ electronic configuration of Re(I) is coincident with that of the corresponding Os(II) and Ir(III) systems. So Re(I) complexes are also anticipated to exhibit excellent electroluminescent (EL) performances, but OLEDs that

utilize them as the phosphorescent emitters are less investigated [15–18]. Furthermore, fluorinated substituents in the ligand can result in higher photoluminescence (PL) efficiency, reduced self-quenching of luminescence, outstanding volatility and so on [19–21]. These promising results stimulate our interest in exploring these types of Re-complexes. In this paper, a novel fluorinated tricarbonyl rhenium(I) complex, i.e., Re-BFPP (BFPP, 2,3-bis(4-fluorophenyl)pyrazino[2,3-*f*][1,10]phenanthroline) was designed, synthesized and its electrochemical characterizations, photophysical and EL properties were elaborated.

2. Experimental

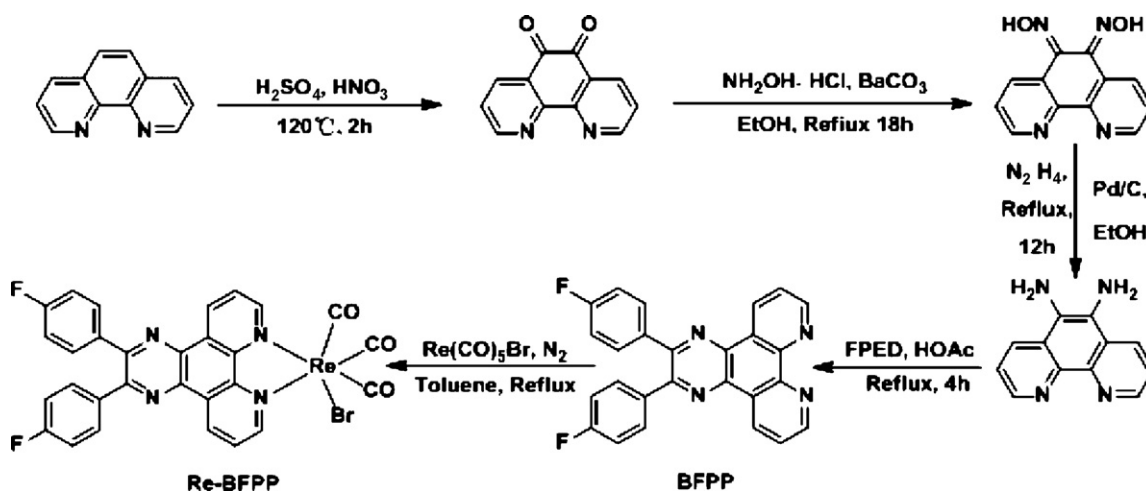
2.1. General information

¹H NMR spectra were recorded on a Bruker AC 500 spectrometer with tetramethylsilane (TMS) as an internal reference. Mass spectroscopy (MS) was performed on an Agilent 1100 LC/MSD Trap VL spectrometer. UV–vis absorption spectrum was obtained on a PerkinElmer Lambda 900 spectrophotometer. PL spectra were measured on a PerkinElmer LS 55 fluorescence spectrophotometer. The luminescent lifetime of Re-BFPP in solid state was detected by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a Third-Harmonic-Generator (THG) 355 nm output. Cyclic voltammetry (CV) experiments were conducted using a CHI832B electrochemical analyzer.

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Scheme 1. Synthetic pathways of Re-BFPP. FPED: 1,2-bis(4-fluorophenyl)ethane-1,2-dione.

2.2. Synthesis

2.2.1. Synthesis of BFPP

1,10-Phenanthroline-5,6-diamine was synthesized according to the generally modified procedures [22,23]. Yield: 52%. ^1H NMR (DMSO, TMS): 8.827 (t, $J=2.57$ Hz, 2H), 7.785 (t, $J=4.32$ Hz, 2H), 6.225 (s, 4H).

1,10-Phenanthroline-5,6-diamine (1.05 g, 5.0 mmol) and 1,2-bis(4-fluorophenyl)ethane-1,2-dione (1.48 g, 6.0 mmol) were refluxed in 25 mL of glacial acetic acid for 4 h under nitrogen atmosphere. The mixture was cooled to room temperature (RT) and filtered. The resulting solid was washed by ammonia and water and recrystallized by methanol to obtain light white solid powders. Yield: 85%. ^1H NMR (CDCl_3 , TMS): 7.336–7.653 (m, 6H), 7.691 (d, $J=7.69$ Hz, 4H), 8.575 (d, $J=3.98$ Hz, 2H), 8.975 (d, $J=7.86$, 2HHZ→2H); MS (APCI): m/z 420.98 [$\text{M}+\text{H}^+$].

2.2.2. Synthesis of Re-BFPP

BFPP (0.088 g, 0.21 mmol) and pentacarbonylbromorhenium (0.081 g, 0.2 mmol) were refluxed in 20 mL of toluene for 6 h under nitrogen atmosphere. After the mixture was cooled to RT, the solvent was removed and the resulting yellow solid was purified by chromatography on silica gel. Yield: 82%. ^1H NMR (CDCl_3 , TMS): 7.436–7.684 (m, 6H), 7.746 (d, $J=7.5$ Hz, 4H), 8.772 (d, 2H, $J=4.13$ Hz), 8.956 (d, $J=7.91$ Hz, 2H).

2.3. Fabrication and EL measurements of OLEDs

The devices were fabricated on patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of $25 \Omega \text{sq}^{-1}$ by thermal evaporation in vacuum chamber at 2×10^{-4} Pa. The devices were prepared with the following structures of ITO/m-MTDATA (10 nm)/NPB (20 nm)/CBP: X wt.% Re-BFPP (30 nm)/Bphen (10 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm). Here, 4,4',4''-tris[3-methylphenyl (phenyl)amino]triphenylamine (m-MTDATA), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB), 4,7-diphenyl-1,10-phenanthroline (Bphen), and tris(8-hydroxyquinoline)aluminum (Alq₃) were used as hole injection layer, hole transporting layer, exciton blocking layer and electron transporting layer, respectively, and LiF/Al as the composite cathode. Deposition rates and thicknesses of the layers were monitored in situ using oscillating quartz monitors. The evaporating rates were kept at $0.5\text{--}1 \text{ \AA s}^{-1}$ for organic layers and LiF layer, and 10 \AA s^{-1} for Al cathode, respectively. EL spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The

luminance–current–voltage ($L\text{--}I\text{--}V$) characteristics were measured with a 3645 DC power supply combined with a spot photometer and were recorded simultaneously with measurements.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathways of the Re-complexes are outlined as shown in Scheme 1. 1,10-phenanthroline-5,6-dione was prepared as yellow needles with the yield of 82% according to a slightly modified method reported in Ref. [22]. 1,10-phenanthroline-5,6-dione dioxime was synthesized by condensation of this diketone with hydroxylamine. Due to its poor solubility, the resulting dioxime was not purified further before conversion to the corresponding diamine. Subsequently, 1,10-phenanthroline-5,6-diamine was obtained by catalytic reduction of the dioxime. Then this diamine was treated with 1,2-bis(4-fluorophenyl)ethane-1,2-dione to obtain BFPP. BFPP can be obtained as pure light white solid by recrystallization with overall yield of over 80%. Finally, Re-BFPP was obtained by direct complexation of BFPP with $\text{Re}(\text{CO})_5\text{Br}$ in refluxing toluene under nitrogen atmosphere with good yield. Except 1,10-phenanthroline-5,6-dione dioxime, other compounds exhibited good solubility in common solvents such as dichloromethane, chloroform and dimethyl sulfoxide. Thus the characterizations by ^1H NMR and MS were easily accomplished.

3.2. Photophysical properties

The UV–vis absorption spectrum of Re-BFPP in CH_2Cl_2 and PL spectra of Re-BFPP in CH_2Cl_2 and film are shown in Fig. 1. The intense absorption bands at $\lambda < 300$ nm are mainly attributed to the spin-allowed $^1\pi\text{--}\pi^*$ ligand-centered transitions. The moderately intense absorption bands extending into the visible region from 340 to 480 nm are tentatively assigned to an admixture of metal-to-ligand charge transfer states, $d\pi(\text{Re}) \rightarrow \pi^*(\text{BFPP})$ ($^1\text{MLCT}$ and $^3\text{MLCT}$). Re-BFPP emits intensively with yellow phosphorescence peaked at 580 nm in CH_2Cl_2 and 585 nm in film, which can be assigned to radiative transitions from $^3\text{MLCT}$ level [24]. The PL quantum yield of Re-BFPP measured in deaerated dichloromethane is 1.5% by using quinine sulfate as a reference [14]. The emission decay curve of Re-BFPP in solid state is shown in Fig. 2. Phosphorescence decay follows the single exponential equation: $y = A_1 \times \exp(-x/t_1) + y_0$, where A_1 is the initial intensity of phosphorescence decay, t_1 the phosphorescence decay lifetime and y_0 the

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