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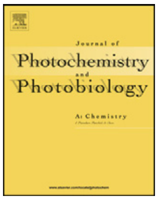

Synthesis and characterization of novel rhenium (I) complexes with large Stokes shift for applications in organic electroluminescent devices

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ABSTRACT

Two novel tricarbonyl rhenium(I) (Re(I)) complexes with versatile building block (1,10-phenanthroline), i.e., Re-PPhen and Re-FPPhen (PPhen, 3,8-diphenyl-1,10-phenanthroline; FPPhen, 3,8-bis(4-fluorophenyl)-1,10-phenanthroline), were designed, synthesized and structurally characterized by FTIR, ^{1}H NMR and mass spectroscopy. The photophysical properties of two complexes were investigated in detail. The absorption bands centered at ca. 255–350 and 380–550 nm from two complexes were attributed to the ligand-centered $\pi \rightarrow \pi^*$ electronic transition and the metal-to-ligand charge transfer $d\pi(\mathrm{Re}) \rightarrow \pi^*(\mathrm{ligand})$ (MLCT) transition, respectively. Re-PPhen and Re-FPPhen exhibited broad ^{3}MLCT maximum emission around 572–580 nm with the full width of half maximum of ca. 90 nm. These complexes displayed a unique feature that was a remarkably high Stokes shift up to about 240 nm. Both of two complexes showed high photoluminescence quantum efficiencies (0.11, 0.13) and short luminescent lifetimes (0.21, 0.16 μs), respectively. Re-PPhen and Re-FPPhen were thermally stable with high decomposition temperature in the range of 355–365 °C corresponding to 5% weight loss, indicating that two complexes were stable enough to be sublimated to fabricate organic electroluminescent devices. The electroluminescent devices based on doped Re-FPPhen complex showed very high luminance of 9293 cd m^{-2} and reasonable luminance efficiency of 9.4 cd A^{-1}. All evidences showed that Re-PPhen and Re-FPPhen were potential candidates for applications in organic electroluminescent devices.

1. Introduction

Organic light-emitting diodes (OLEDs) possess latent application prospects in eco-friendly flat-panel displays and energy-saving solid-state lightings owing to rapid progress in material design and device fabrication [1–8]. Of the light-emitting organic materials available, phosphorescent materials are particularly captivating because they can harvest light from both singlet and triplet excitons, enabling the devices with close to 100% internal quantum efficiency. Therefore, many research groups have aimed at the development of efficient light-emitting phosphorescent materials based on iridium [9–15], platinum [16–21], osmium [22,23] and, more recently, copper [24,25] complexes. Among them, iridium(III) (Ir(III)) complexes are still the most efficient and mainly exploited. However, with the aim to further extend the scope of luminescent materials, many works have been focused on the rhenium(I) (Re(I)) complexes [26,27], of which its d^6 electronic configuration is coincident with that of the corresponding Ir(III) system.

For the purpose of design and synthesis of high efficiently luminescent complexes, it is important to select ligands with appropriate frontier molecular orbitals thus to allow efficient electronic transitions occurring between different energy states associated with both central metal atom and chelating ligands. Substituent effects provide an efficient means by which luminescence can be fine tuned, a fact that has been recognized for related Ir(III) complexes [9,10]. Most Re(I) complexes studied for light emission have a bidentate heteroaromatic diimine ligand, such as 1,10-phenanthroline [28–30], 2,2′-bipyridine [31], 2-(2-pyridine)-benzimidazole [32] and 4,5-diazafluorene [33,34]. Among them, Re(I) complexes with rigid 1,10-phenanthroline derivatives display outstanding luminescent properties [35]. It's well known that 1,10-phenanthroline is a classic chelating bidentate ligand for transition metal ions that has played an important role in the development of coordination chemistry [36,37].

Inspired by those, two novel Re(I) complexes based on decorated 1,10-phenanthroline, i.e., Re-PPhen (3,8-diphenyl-1,10-phenanthroline Re(CO)$_3$Br) and Re-FPPhen (3,8-bis(4-fluorophenyl)-1,10-phenanthroline Re(CO)$_3$Br), were designed, synthesized, and structurally characterized. In order to investigate their potential applications in the OLEDs, their optical

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properties and thermal stabilities were also measured and elucidated. What drew special attention was that both two complexes displayed a remarkably high Stokes shift up to about 240 nm, which could effectively alleviate self-absorption and would be very favorable to light emission. The OLEDs using the Re-FPPhen complex as dopant exhibited excellent electrophosphorescent performances.

2. Experimental

2.1. Materials and instruments

Commercially available reagents were used without further purification unless otherwise stated. $Re(CO)_5Br$ was available from Alfa Aesar. Solvents were dried by standard procedures prior to use. ^1H NMR spectra were recorded on a Bruker AC 500 spectrometer. Chemical shifts were reported in ppm down field from tetramethysilane with the solvent resonance as the internal standard. Mass spectroscopy (MS) was carried out on an Agilent 1100 LC/MSD Trap VL spectrometer. Elemental analysis was performed on Vario EL III CHNS instrument. FTIR spectra were recorded with samples as KBr pellets using WQF 200 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was undertaken under nitrogen atmosphere at a heating rate of 10 °C min^{-1} on a PerkinElmer Diamond TG–DTA 6300 thermal analyzer. UV–vis absorption spectra were obtained on a PerkinElmer Lambda 900 spectrophotometer. Photoluminescent (PL) spectra were measured on a PerkinElmer LS 55 fluorescence spectrophotometer. The PL quantum yields (PLQYs) of two Re(I) complexes were measured according to the reference's method [26]. The luminescent lifetime of two Re(I) complexes 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 355 nm output. All measurements were carried out at room temperature (RT).

2.2. Synthesis of Re(I) complexes

2.2.1. Synthesis of 3,8-dibromo-1,10-phenanthroline

A mixture of 1,10-phenanthroline (1.25 g, 6.94 mmol), pyridine (5 mL), and sulfur monochloride (1.83 mL) dissolved in 50 mL of 1-chlorobutane was stirred and bromine (1.12 mL) was dropped simultaneously. Then the mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature, and the yellow solid formed was separated. An aqueous solution of NaOH and chloroform was added to the solid. The extracted solution was evaporated and purified by silica-gel column chromatography and subsequently recrystallization by benzene. Then the white solid product was obtained with the yield of 30%. MS (APCI): m/z 339 [M+H$^+$]; ^1H NMR (500 MHz, $CDCl_3$): 9.15(d, J = 2.3 Hz, 2H), 8.51(d, J = 2.23 Hz, 2H), 7.63(s, 2H).

2.2.2. Synthesis of 3,8-diphenyl-1,10-phenanthroline (PPhen)

A mixture of phenylboronic acid (366 mg, 3 mmol), 3,8-dibromo-1,10-phenanthroline (423 mg, 1.25 mmol), tetrakis (triphenylphosphine)palladium(0) (111.5 mg, 0.097 mmol), aqueous sodium carbonate (2.0 M, 1.5 mL), ethanol (1.5 mL) and toluene (4.5 mL) was degassed and placed under nitrogen. The reaction mixture was heated at 115 °C for 24 h. After the mixture was cooled to RT, then extracted with dichloromethane, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over neutral alumina to give a white solid of PPhen. Yield: 61.1%; MS (APCI): m/z 333.4 [M+H$^+$]; IR(KBr, cm^{-1}): 3043, 1603, 1485, 760, 690; ^1H NMR (500 MHz, $CDCl_3$): 9.15(s, 2H), 8.11(s, 2H), 7.85–7.77(m, 4H), 7.72–7.63(m, 4H), 7.62(d, J = 7.02 Hz, 2H), 6.62(t, 2H).

2.2.3. Synthesis of 3,8-bis(4-fluorophenyl)-1,10-phenanthroline (FPPhen)

The procedure is similar to that of 3,8-diphenyl-1,10-phenanthroline. Yield: 55%; MS (APCI): m/z 369.38 [M+H$^+$]; IR(KBr, cm^{-1}): 3045, 1601, 1512, 835; ^1H NMR (500 MHz, CD_2Cl_2): 9.17(s, 2H), 8.32(s, 2H), 7.85(d, J = 8.06 Hz, 2H), 7.51–7.40(m, 4H), 7.33–6.97(m, 4H).

2.2.4. Synthesis of Re-PPhen

PPhen (0.07 g, 0.21 mmol) and $Re(CO)_5Br$ (0.081 g, 0.2 mmol) were refluxed in 25 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 silica-gel column chromatography. Yield: 32.5%. IR(KBr, cm^{-1}): 2023, 1925, 1890, 764, 696; ^1H NMR (500 MHz, $CDCl_3$): 9.60(s, 2H), 8.65(s, 2H), 7.81–7.80(m, 4H), 7.64–7.61(m, 4H), 7.58(d, 2H), 6.68(t, J = 7.35 Hz, 2H); Elemental analysis for $C_{27}H_{16}BrN_2O_3Re$. Calcd: C 47.51, H 2.36, N 4.10; Found: C 47.52, H 2.31, N 3.99.

2.2.5. Synthesis of Re-FPPhen

The procedure is similar to that of Re-PPhen. Yield: 42.7%. IR(KBr, cm^{-1}): 2023, 1917, 1894, 893; ^1H NMR (500 MHz, CD_2Cl_2): 9.57(s, 2H), 8.70(s, 2H), 8.13(s, 2H), 7.86–7.84(m, 4H), 7.35(dd, J = 8.55 Hz, 4H); Elemental analysis for $C_{27}H_{14}BrF_2N_2O_3Re$. Calcd: C 45.13, H 1.96, N 3.90; Found: C 45.72, H 1.91, N 3.85.

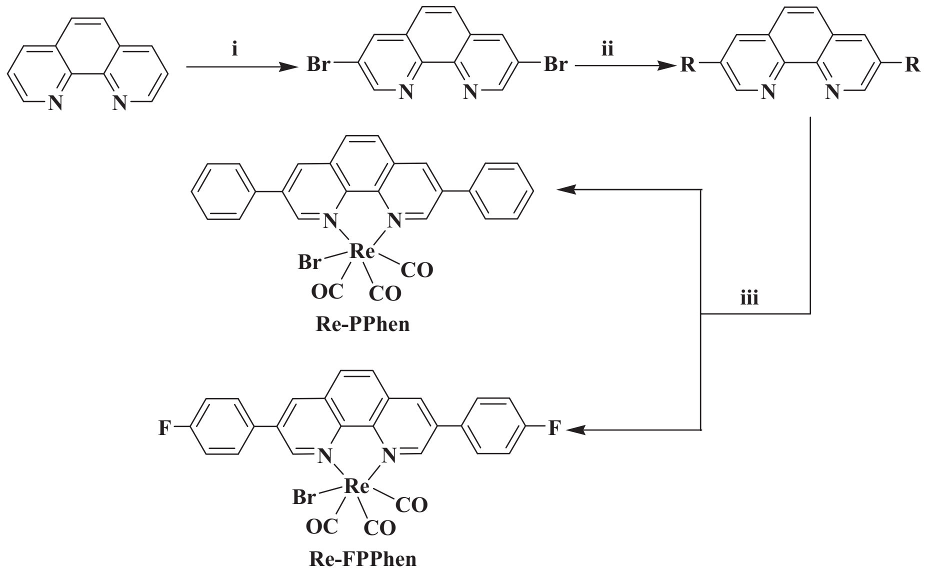
2.3. Device fabrication and EL measurements

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 solvents 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 conventional structures of ITO/m-MTDATA(10 nm)/NPB(20 nm)/CBP: x% Re-FPPhen(30 nm)/Bphen(10 nm)/Alq_3(20 nm)/LiF(1 nm)/Al(120 nm), in which m-MTDATA (4,4′,4″-tris[3-methylphenyl(phenyl) amino]triphenyl-amine), NPB (4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl), CBP (4,4′-N,N′-dicarbazolebiphenyl), Bphen (4,7-diphenyl-1,10-phenanthroline), and Alq_3 (tris(8-hydroxyquinoline)aluminum) were used as hole injection layer, hole transporting layer, host, 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. Thermal deposition rates for organic materials, LiF, and Al were ∼1, ∼1, and ∼10 Å s^{-1}, respectively. EL spectra were measured by a PR655 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 Keithley 2400 source meter. All measurements were carried out at RT under ambient conditions.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routines of two Re(I) complexes are outlined as shown in Scheme 1. 3,8-dibromo-1,10-phenanthroline was firstly synthesized via bromination of 1,10-phenanthroline [38]. It is worthy to note that there are more rich-electron in the 3,8-position of 1,10-phenanthroline by an AM1 Hamiltonian calculation [39], so the brominating substituent reaction should proceed smoothly in the 3,8-position of 1,10-phenanthroline. The bromination positions



Scheme 1. Synthetic routines of two Re(I) complexes. (i) Br_2, S_2Cl_2, pyridine, 1-chlorobutane, reflux 12 h; (ii) $Pd(PPh_3)_4$, $R\text{-}B(OH)_2$, PTC, $NaCO_3$, toluene/ethanol, N_2, reflux 24 h; (iii) $Re(CO)_5Br$, toluene, N_2, reflux 5 h.

agreed with the results of AM1 Hamiltonian calculation via the evidence of ^1H NMR. The yield of 3,8-dibromo-1,10-phenanthroline was moderate through elaborate separation technique of silica-gel column chromatography. Subsequently, PPhen and FPPhen could be received as light white solid powder by Suzuki cross-coupling reactions with 3,8-dibromo-1,10-phenanthroline and corresponding boronic acids. Finally, two Re(I) complexes were obtained by direct complexation of PPhen and FPPhen with $Re(CO)_5Br$ in refluxing toluene in moderate yield. All reactions were carried out under nitrogen atmosphere, especially for Suzuki cross-coupling reactions due to the vulnerable palladium (0) catalyst. All synthesized compounds exhibited good solubility in common solvents such as dichloromethane, chloroform and N,N-dimethylformamide. Thus the characterizations for them by ^1H NMR and MS were easily accomplished.

3.2. IR spectra characteristics

IR spectra of PPhen, FPPhen and their corresponding Re(I) complexes in KBr pellets are plotted in Fig. 1. Compared with free ligand PPhen, three CO stretching vibration bands of Re-PPhen complex are seen in Fig. 1(a), characteristic of monomeric pseudooctahedral *fac*-$Re(CO)_3^+$ [40]. The high energy peak was found at 2023 cm^{-1}. The two low energy peaks were poorly resolved and appeared as a broad band at ca. 1900 cm^{-1}. IR spectra from FPPhen and Re-FPPhen displayed similar behaviors in Fig. 1(b), which was slightly blue-shift compared with those of PPhen and Re-PPhen. All evidences indicated that two Re(I) complexes accorded with the proposed structures.

3.3. Photophysical properties

Absorption and PL spectra for the free ligands and corresponding Re(I) complexes were obtained in dichloromethane solution, and shown in Fig. 2. Absorption spectra of Re-PPhen and Re-FPPhen were very similar to those of analogous Re(I) tricarbonyl complexes [41], and the assignments had been made accordingly. By comparison to the absorption of the free ligand (PPhen), the absorption bands of Re-PPhen located at 287 and 342 nm could be assigned to spin-allowed $^1\pi$–π^* PPhen-centered electronic transitions. The moderately intense, poorly distinguished absorption bands extending into the visible region from ca. 380 to 550 nm were tentatively assigned to an admixture of metal-to-ligand charge transfer states, $d\pi(Re)\rightarrow\pi^*(PPhen)$ (^{1}MLCT and ^{3}MLCT). And absorption bands of Re-FPPhen exhibited the features similar to those of Re-PPhen except for more intense MLCT bands. These

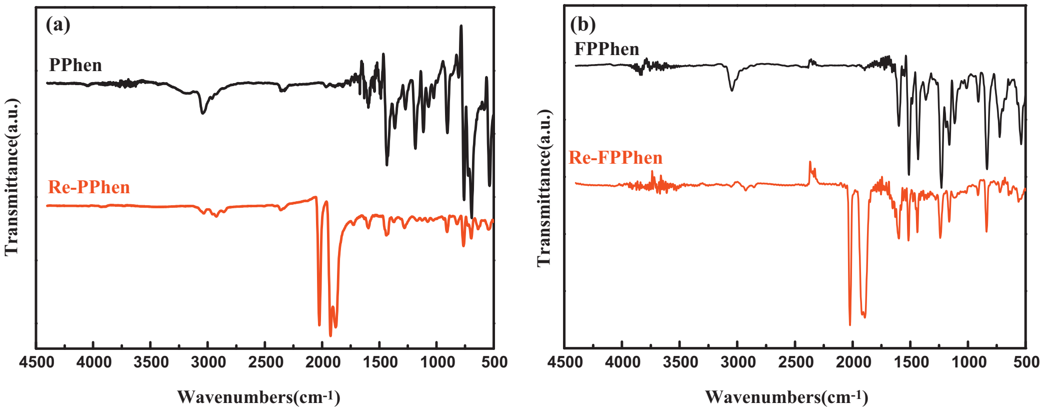


Fig. 1. IR spectra of PPhen, FPPhen and their corresponding Re(I) complexes in KBr pellets.

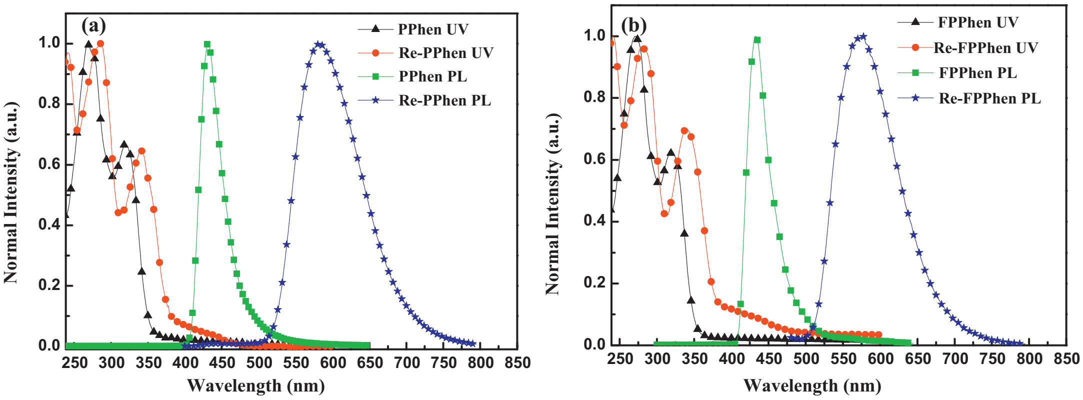


Fig. 2. Absorption and PL spectra of PPhen, FPPhen and their corresponding Re(I) complexes in dichloromethane.

assignments were supported by subsequent density functional theory (DFT) calculations on two Re(I) complexes.

When excited in dichloromethane solution at RT within maximum excitation wavelength or MLCT absorption bands, Re-PPhen exhibited maximum emission at 582 nm. The maximum emission spectrum of Re-FPPhen showed blue shift of ca. 7 nm owing to the introduction of electron-withdrawing fluorine group. The emission wavelengths of two Re(I) complexes were significantly red-shifted relative to the PL spectra of free ligands. Both of the complexes displayed broad emission spectra with the full width of half maximum (FWHM) of ca. 90 nm which had been assigned as MLCT-based luminescence, typical of this type of complex [28,34,42]. Such broad emission could be also very useful for constructing simple white OLEDs combined with a blue emitter.

As shown in Fig. 2, there was little overlap between the absorption and emission spectra of two Re(I) complexes. The Stokes shift for these complexes which was obtained between the maximum of the lowest energy absorption band and the maximum of the emission band was as large as about 240 nm. The large Stokes shift may be caused by significant structural differences between the ground state and excited state upon photo excitation. Such a large Stokes shift is especially valuable for light-emitting materials since the absence of self-absorption will definitely facilitate efficient light emission.

The PLQYs of two Re(I) complexes were also investigated in order to further explore their photophysical properties. The PLQYs are highly sensitive to subtle modification of organic ligand including diverse substitutes and the change of substitute's position. The PLQYs of Re-PPhen and Re-FPPhen measured in deaerated dichloromethane at ambient temperature by using quinine sulfate as a reference were 0.11 and 0.13, respectively, which were much higher than those of previous Re(I) complexes [32,34]. By comparing with the PLQYs, it indicated that the fluorine group could also enhance the compound's luminescent efficiency besides the well-known carbazole chromophore, which would be instructive for designing luminescent materials with high performances.

3.4. Density functional theory calculations on Re(I) complex

The ground state geometries and electronic structures of two Re(I) complexes were calculated according to DFT calculations using the GAUSSIAN-03 software package (Gaussian Inc.) at the B3LYP/LANL2DZ level since such investigations have been proven to be very helpful in understanding the photophysical properties of Re(I) complexes [43]. Therefore, it will be instructive to examine the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the complexes.

As can be seen from Fig. 3, the calculated results revealed that the ground state geometries of the two complexes displayed a distorted octahedral configuration of ligands around the metal center because two complexes had similar geometrical structures with the only differences being fluorine atom introduced in the para-position of substituted phenyl moiety. The HOMOs of Re-PPhen and Re-FPPhen were mainly composed of the π orbitals of the carbonyl group, the bromine, and the d orbitals of Re cation which was in antibonding coordination with the axial bromine group and bonding with the three carbonyl groups. While the LUMOs of Re-PPhen and Re-FPPhen were essentially π* orbital localized on

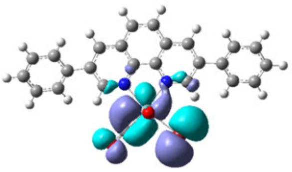
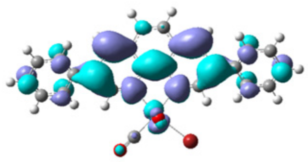
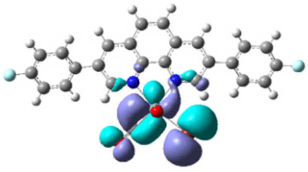
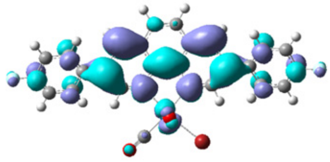
Complex	HOMO	LUMO
Re-PPhen		
Re-FPPhen		

Fig. 3. Contour plots of HOMOs and LUMOs for Re-PPhen and Re-FPPhen as determined by DFT calculations.

Table 1
The photophysical data of Re-PPhen and Re-FPPhen.

Compound	Abs (λ_{max}, nm)	PL (λ_{max}, nm)	T_{dec} (°C)[a]	PLQY	τ (μs)[b]	Δ_{st} (nm)[c]
Re-PPhen	287, 342, 442	582	350	0.11	0.21	240
Re-FPPhen	283, 340, 425	575	365	0.13	0.16	235

[a] Temperature values with 5% weight loss.
[b] Luminescence decay lifetime.
[c] Stokes shift.

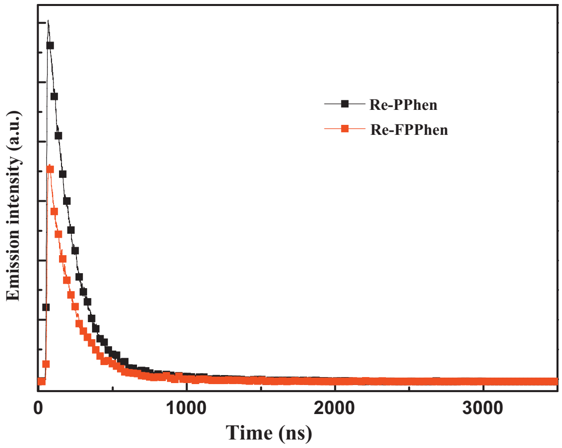


Fig. 4. The emission decay curves of Re-PPhen and Re-FPPhen in solid state powder.

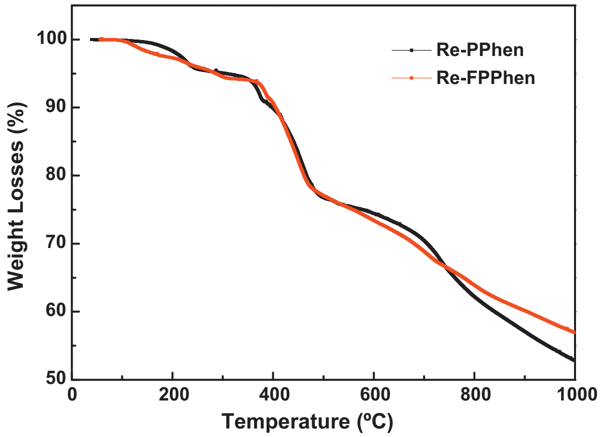


Fig. 5. TGA traces of Re-PPhen and Re-FPPhen in N_2 atmosphere at a heating rate of 10 °C min^{-1}.

almost the whole substituted 1,10-phenanthroline ligand (PPhen, FPPhen), with very slim contributions from Re atom. These results illuminated that the difference among the diimine ligands dramatically influenced the distribution of the unoccupied molecular orbitals in the corresponding Re(I) complexes, which should also result in the different electronic transition characters upon excitation. Our calculated results were well in agreement with previous reports [44,45].

3.5. Lifetime analysis

The lifetime measurements for the excited state of two Re(I) complexes were recorded under the excitation at 355 nm at RT. The emission decay curves of Re-PPhen and Re-FPPhen in solid state are shown in Fig. 4. Phosphorescence decay followed the single exponential equation: $y = A_1 \times \exp(-x/t_1) + y_0$, where A_1 was the initial intensity of luminescence decay, t_1 the luminescence decay lifetime and y_0 the random noise. Therefore, the lifetimes of two complexes with 0.21 and 0.16 μs, respectively, were obtained, which were more shorter than those of common Ir(III) complexes [46]. Such short lifetimes would be suitable to suppress the efficiency roll-off at high current density in the OLEDs.

3.6. Thermal analysis

TGA were performed on two complexes in nitrogen atmosphere in order to investigate their stable characteristics. The TGA traces of Re-PPhen and Re-FPPhen are presented in Fig. 5. Both of the Re(I) complexes showed that they had high thermal stability with 5% weight loss. Re-PPhen began to lose weight when it was heated up to 350 °C, which should be attributed to the loss of the bromide anion and carbonyl groups. Re-PPhen probably began to dramatically disassociate or sublimate at ca. 485 °C. Re-FPPhen showed the similar thermal characteristics like Re-PPhen and began to decompose at 365 °C. Therefore, two Re(I) complexes should be stable

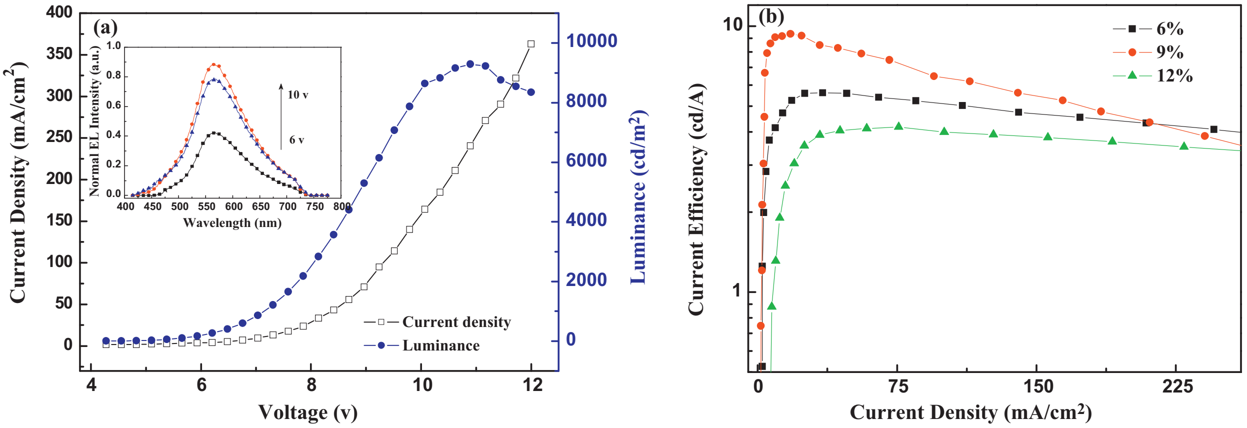


Fig. 6. (a) *L–I–V* characteristics of 9% Re-FPPhen doped device. Inset: EL spectra of 9% Re-FPPhen doped device under different voltages; (b) current efficiency–current density curves of different doped devices.

Table 2
Electroluminescent performances of OLEDs based on Re-FPPhen.

Ratio (%)	V_{on} [a] (V)	η_L [b] (cd A^{-1})	η_L [c] (cd A^{-1})	η_p [d] (lm W^{-1})	η_p [e] (lm W^{-1})	EQE[f] (%)
6	4.1	5.6	5.1	2.4	1.9	0.56
9	3.9	9.4	6.4	4.1	2.1	1.2
12	4.3	4.2	4.0	1.7	1.5	0.43

[a] Turn-on voltage.
[b] Maximum current efficiency.
[c] Current efficiency at 100 mA cm^{-2}.
[d] Maximum power efficiency.
[e] Power efficiency at 100 mA cm^{-2}.
[f] Maximum external quantum efficiency.

enough to be sublimated to construct OLEDs at ca. 300 °C. The photophysical data in detail are shown in Table 1.

3.7. Electroluminescent properties

We used Re-FPPhen complex as dopant in the emitting layer to fabricate electroluminescent devices. Fig. 6(a) depicts *L–I–V* characteristics of 9% Re-FPPhen doped device. It could be found that the luminance increased with increasing injection current as well as voltage in the device. The device exhibited a peak luminance of 9293 cd m^{-2} at 11 V, which, to our knowledge, was higher than those of any OLEDs based on Re(I) complexes [28,30–35]. The turn-on voltage was found to be less than 5 V. EL spectra of 9% Re-FPPhen doped device under different voltage were observed with the maximum emission of about 565 nm as shown in inset of Fig. 6(a), which was almost independent of voltages. The current efficiencies of Re-FPPhen complex as a function of current density are illustrated in Fig. 6(b). A maximum current efficiency of 9.4 cd A^{-1} was obtained at current density of 17.6 mA cm^{-2}, corresponding to maximum power efficiency of 4.1 lm W^{-1} and external quantum efficiency of 1.2%. All those devices witnessed slow efficiency decay with increasing current density, which was probably attributed to its short luminescent lifetime. The important EL performances of the devices based on different ratios of Re-FPPhen are summarized in Table 2. These encouraging results made it clear that two Re(I) complexes with adorning 1,10-phenanthroline ligand were promising for application in OLEDs.

4. Conclusions

In conclusion, two novel Re(I) complexes with substituted 1,10-phenanthroline, i.e., Re-PPhen and Re-FPPhen, were designed, synthesized and characterized by FTIR, ^{1}H NMR and elemental analysis. Both Re-PPhen and Re-FPPhen displayed predominant ^{3}MLCT emissions centered at 580 and 572 nm at room temperature. Interestingly, two complexes displayed a remarkably large Stokes shift up to about 240 nm, which was very favorable to light emission. Furthermore, Re-PPhen and Re-FPPhen exhibited high PLQYs of 0.11 and 0.13, short luminescent lifetimes of 0.21 and 0.16 μs as well as high decomposition temperatures at 350, 365 °C, respectively. The fabricated OLEDs with Re-FPPhen complex as dopant showed very high luminance of 9293 cd m^{-2} and reasonable luminance efficiency of 9.4 cd A^{-1}. All those indicated that two Re(I) complexes are good candidates for potential application in OLEDs.

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