A series of luminescent Re(I) complexes with electron-donor/acceptor moieties: Synthesis, characterization, and photoluminescence

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A B S T R A C T

In this paper, we synthesize three Re(I) complexes of Re(CO)$_3$(PPO)Br, Re(CO)$_3$(PTO)Br, and Re(CO)$_3$ (PBI)Br, where PPO=2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole, PTO=2-(pyridin-2-yl)-5-p-tolyl-1,3,4-oxadiazole, PBI=2-(pyridin-2-yl)-1H-benzo[d]imidazole. Their single crystals and photophysical properties are measured and discussed in detail. The correlation between ligand structure and corresponding PL characteristics of Re(I) complex has been investigated. It is found that a ligand with strong electron-donor can efficiently increase both absorption and emissive energy of Re(I) complex. In addition, electron-rich ligand can increase the electron density of the complex and thus enhance the oscillator strength of electronic transition, improving the photoluminescence performance.

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1. Introduction

The development of practical components for chemical sensors, display devices, biological probes, phototherapy, and solar-energy conversion has engaged a research interest in luminescent transition metal complexes, especially heavy metal complexes such as Ru(II) and Re(I) complexes [1–4]. Adachi and coworkers firstly report the organoelectronic application from Re(I) complexes, after which more and more attentions have been paid to phosphorescent Re(I) complexes [5]. Compared with other luminescent transition metal complexes, phosphorescent Re(I) complexes exhibit their unique advantages such as high photoluminescence (PL) efficiency, short excited state lifetime, and environmental harmony [6–8].

Some phosphorescent Re(I) complexes, which are superior emitters, have been reported and studied. But many of them are usually chloro ones and very expensive, which somewhat decelerates the practical application of Re(I) complexes. Therefore, the strong appeal of replacing the expensive compounds with cheap ones, as well as the need for a deeper understanding of the correlation between molecular structures and photophysical properties, has resulted in a continuous progress in the design and synthesis of luminescent Re(I) complexes. It is reported by Zhang and coworkers that the introduction of electron-donor/acceptor moieties into diamine ligands exerts an influence on the PL properties of their corresponding Re(I) complexes [6,7]. Particularly, electron-drawing moieties such as oxdiazole are positive to improve both PL and electroluminescence (EL) performances [8]. However, all the above mentioned

electron-donor/acceptor moieties were connected by an inert spacer of alkyl chain, blocking their electronic effect on the emissive center. Thus, the reported Re(I) complexes are all yellow-emitting ones.

In moving towards materials with the required color gamut for full color displays, many efforts have been devoted to adapt the emissive energy by introducing various electron-donor/acceptor moieties into ligands, and corresponding theoretical analyses have been done. Recently, Feng and Si published their theoretical calculation result on typical phosphorescent emitters [6,9]. As for a metal-related electronic transition complex such as [Cu(N–N)(P–P)] and Re(N–N)Br, where N–N and P–P stand for diamine and phosphorous ligands, it is found that the highest occupied molecular orbital (HOMO) is mainly composed of contributions from metal electrons and Br atom, while, the lowest unoccupied molecular orbital (LUMO) is usually ligand π^* in nature. The phosphorescence corresponds to an excited state from HOMO to LUMO and thus assigned as a metal-to-ligand-charge-transfer (MLCT) character. Zhang and coworkers then prove that electron-donor moieties located at ligand conjugation ring can efficiently heighten LUMO energy level, leading to a band gap increase and consequently an emission blue shift. On the other hand, electron-acceptor moieties may lower LUMO energy level, leading to a band gap decrease and consequently an emission red shift [10]. This elementary conclusion may be used to adapt the emissive energy.

Guided by the above research results, we intend to further investigate the correlation between band gap and electron-donor/acceptor moieties in ligand. In this paper, we synthesize three Re(III) complexes owing to electron-donor/acceptor moieties. The correlation between ligand structure and corresponding PL characteristics of Re(I) complex has been discussed in detail.

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2. Experimental section

The molecular structures of the three Re(I) complexes are shown in Scheme 1. Benzoyl chloride, 4-methylbenzoyl chloride, sodium azide, zinc bromide, Re(CO)$_5$Br, 2-cyanopyridine, and 2-(pyridin-2-yl)-1H-benzo[d]imidazole (referred as PBI) were purchased from Aldrich Chemical Co. and used as received without further purifications. All organic solvents were purified and degassed using standard procedures.

2.1. Synthesis of diamine ligands

The starting material of 2-(2H-tetrazol-5-yl)-pyridine (referred as TP) was synthesized according to the literature procedure [11]. A typical synthetic method for 2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole (PPO) and 2-(pyridin-2-yl)-5-p-tolyl-1,3,4-oxadiazole (PTO) is described as follows. The mixture of 10 mmol of TP, 11 mmol of benzoyl chloride or 4-methylbenzoyl chloride, and 20 mL of pyridine was brought to reflux under N$_2$ atmosphere for 3 days. The mixture was then poured into cold water and filtered. The obtained crude product was purified by column chromatography.

PPO. ^{1}H NMR (CDCl$_3$): δ 7.48 (1H, m), 7.54 (3H, m), 7.95 (1H, m), 8.22 (1H, t), 8.26 (1H, t), 8.33 (1H, d, $J=6.0$), 8.87 (1H, d, $J=3.6$). Anal. Calcd. for C$_{13}$H$_9$N$_3$O: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.83; H, 4.17; N, 18.76.

PTO. ^{1}H NMR (CDCl$_3$): δ 2.44 (3H, s), 7.36 (2H, d, $J=6.0$), 7.42 (1H, t), 7.98 (1H, t), 8.13 (2H, d, $J=6.0$), 8.35 (1H, d, $J=6.0$), 8.82 (1H, d, $J=3.6$). Anal. Calcd. for C$_{14}$H$_{11}$N$_3$O: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.94; H, 4.73; N, 17.56.

2.2. Synthesis of Re(I) complexes

Re(I) complexes were synthesized according to a synthetic method described as follows. The mixture of 0.21 mmol of diamine ligand, 0.20 mmol of Re(CO)$_5$Br, and 20 mL of toluene was brought to reflux under N$_2$ atmosphere for six hours. After cooling, the solvent was removed by evaporation. The crude product was purified by recrystallization from the mixed solvent of n-hexane:CH$_3$Cl$=1:1$ (V:V). The residue was further purified on a silica gel column to give the desired product.

Re(CO)$_3$(PPO)Br. ^{1}H NMR (CDCl$_3$): δ 7.66 (1H, m), 7.73 (3H, m), 7.93 (1H, m), 8.34 (1H, t), 8.34 (1H, t), 8.46 (1H, d, $J=6.0$), 8.98 (1H, d, $J=4.0$). Anal. Calcd. for C$_{16}$H$_9$BrN$_3$O$_4$Re: C, 33.52; H, 1.58;

N, 7.33. Found: C, 33.63; H, 1.63; N, 7.26. Its identity is further confirmed by single crystal XRD [12].

Re(CO)$_3$(PTO)Br. ^{1}H NMR (CDCl$_3$): δ 2.54 (3H, s), 7.42 (2H, d, $J=6.0$), 7.56 (1H, t), 8.04 (1H, t), 8.16 (2H, d, $J=6.0$), 8.32 (1H, d, $J=6.0$), 8.97 (1H, d, $J=4.0$). Anal. Calcd. for C$_{11}$H$_{11}$BrN$_3$O$_4$Re: C, 25.64; H, 2.15; N, 8.15. Found: C, 25.72; H, 2.23; N, 8.07. Its identity is further confirmed by single crystal XRD [13].

Re(CO)$_3$(PBI)Br. ^{1}H NMR (CDCl$_3$): δ 7.39 (4H, m), 7.86 (1H, s), 8.43 (1H, s), 8.65 (1H, s). Anal. Calcd. for C$_{15}$H$_9$BrN$_3$O$_3$Re: C, 33.04; H, 1.66; N, 7.71. Found: C, 33.14; H, 1.74; N, 7.44.

2.3. Methods and measurements

Density functional theory (DFT) calculation was performed on the three Re(I) complexes at RB3PW91/SBKJC level. Singlet excitation calculation on the three Re(I) complexes was performed by time dependent density functional theory (TD-DFT) at RB3PW91/SBKJC level. The initial structures were obtained from their single crystal structures. All computations were finished by GAMESS.

Single crystal data were collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 A at 298 K. All hydrogen atoms were calculated. Luminescence decay data were obtained under pure N$_2$ atmosphere 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. The Nd:YAG laser possesses a line width of 1.0 cm^{-1}, a pulse duration of 10 ns, and a repetition frequency of 10 Hz. All PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. UV–visible absorption spectra were recorded using a HP 8453 UV–vis–NIR diode array spectrophotometer. ^{1}H NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. All measurements were carried out in the air at room temperature without being specified.

3. Results and discussion

3.1. Geometric structures of the three Re(I) complexes

3.1.1. Re(CO)$_3$(PPO)Br and Re(CO)$_3$(PTO)Br crystals

Single crystal analysis can provide enough structural data to confirm molecular identity, as well as molecular geometry. However, single crystals were obtained for only Re(CO)$_3$(PPO)Br and Re(CO)$_3$(PTO)Br, not for Re(CO)$_3$(PBI)Br. After a comparison between the three diamine ligands, it is believed that the large
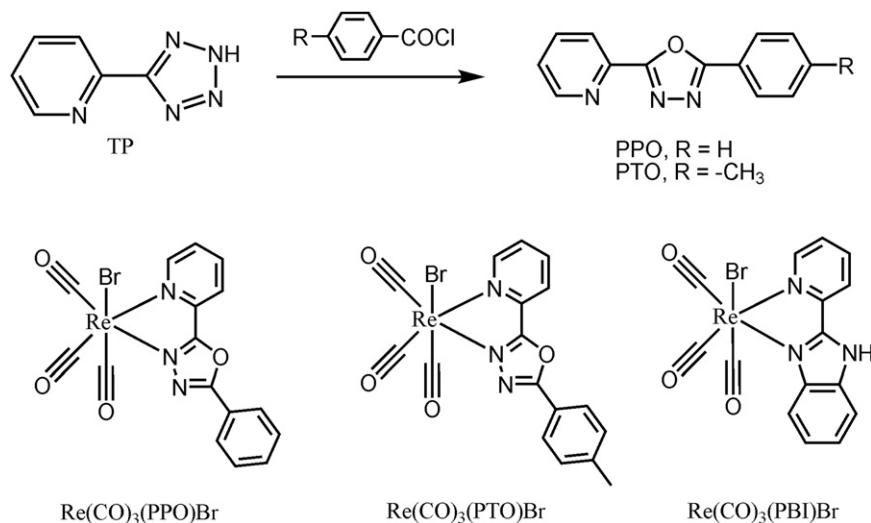
Scheme 1. The synthetic route for the three Re(I) complexes.