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Phosphorescent rhenium emitters based on two electron-withdrawing diamine ligands: Structure, characterization and electroluminescent performance

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ABSTRACT

In this paper, two diamine ligands having electron-withdrawing oxadiazole group and their corresponding Re(I) complexes were synthesized. Their geometric structure, electronic transition, photophysical property, thermal stability and electrochemical property were discussed in detail. Experimental data suggested that both complexes were promising yellow emitters with suited energy levels and good thermal stability for electroluminescent application. The correlation between emission performance and electron-withdrawing group was analyzed. It was found that electron-withdrawing group favored emission performance improvement. Their electroluminescence performance was also explored. Yellow electroluminescence was observed with maximum brightness of 1743 cd/m².

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1. Introduction

Luminescent transition metal complexes are gaining more and more research attention due to their potential application in optoelectronic devices such as solar cells, optical sensors and electroluminescence (EL) devices [1–3]. By showing virtues of controllable emission wavelength, high quantum yield, good stability, short excited state lifetime and suitable energy levels, phosphorescent iridium complexes have been intensively studied [1–4]. There are, however, some issues to be solved, such as the concentration-triggered self-quenching, multiple emission bands, expensive source and complicated synthesis. The requirement for superior emitting dopants with easy synthesis, single emission band and low self-quenching has sparked the exploration for novel phosphorescent metal complexes.

Phosphorescent Re(I) complexes have recently drawn increasing attention as they offer a new path to efficient emitting dopants [5,6]. Some precursive efforts have demonstrated EL application from Re(I) complexes [7–10]. Literatures have reported some promising Re(I) complexes with general molecular formula of Re(CO)₃(diamine ligand)X, where X stands for a halogen atom [5,6,11,12]. The correlation between emissive performance and diamine ligand structure has been systematically discussed by introducing a series of electron-donor/acceptor groups into diamine ligand [5,6,11–13]. It is

concluded that large conjugation chain with electron-withdrawing group in diamine ligand favors the improvement of emissive performance. Particularly, Grushin and coworkers have suggested that fluorine atom in diamine ligand may improve both photoluminescence (PL) and EL performance of corresponding Re(I) complexes by improving thermal stability and film-forming ability which are crucial for device construction [13].

Then Zhang and coworkers suggest that oversized conjugation chain in diamine ligand may compromise emissive center through a thermally-activated potential surface crossing from emissive center to ligand triplet state, leading to emission quenching [14]. In other words, the conjugation length in diamine ligand should be limited to avoid above negative effect.

Guided by above consideration, in this paper, two diamine ligands having electron-withdrawing oxadiazole and fluorine atom in their molecular structures are designed. The conjugation length in both ligands is limited, hoping to realize promising emissive performance from their corresponding Re(I) complexes.

2. Experimental details

2.1. General information

The molecular structures of the two diamine ligands and their Re(I) complexes are shown as Scheme 1. The starting reagents,

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including benzoyl chloride, 4-fluorobenzoyl chloride, NaN_3 , ZnBr_2 and some common organic solvents were bought from Shanghai Chemical Company (Shanghai, China) and used for synthesis directly. 2-cyanopyridine 4,4',4''-tris[3-methylphenylphenylamino] triphenylamine (*m*-MTDATA), 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-hydroxyquinoline)aluminum (Alq_3) and $\text{Re}(\text{CO})_5\text{Cl}$ were purchased from Aldrich Chemical Co. and used without further purifications.

NMR spectra and elemental analysis were performed by a Varian INOVA 300 spectrometer and a Carlo Erba 1106 elemental analyzer, respectively. IR spectra were taken on a Bruker Vertex 70 FTIR (400–4000 cm^{-1}) (KBr pellet technique). Single crystal analysis was finished on a Siemens P4 single-crystal X-ray diffractometer at 298 K, using graphite-monochromated Mo $K\alpha$ radiation and a Smart CCD-1000 detector. All hydrogen atoms were calculated. Density functional theory (DFT) and singlet excitation calculation were run at RB3LYP/SBKJ level in vacuum, using single crystal structures as the initial structures for calculation. Graphical presentation for frontier molecular orbitals (MOs) was finished by wxMacMolPlt software package, with contour value of 0.020. UV–vis absorption and PL spectra were measured on a HP 8453 UV–vis–NIR diode array spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer. PL quantum yields were determined following a literature procedure [15]. PL decay dynamics were recorded by a two-channel TEKTRONIX TDS-3052 oscilloscope using pulsed Nd:yttrium aluminium garnet (YAG) laser (355 nm) as the excitation source, with line width of 1.0 cm^{-1} , pulse duration of 10 ns and repetition frequency of 10 Hz. Thermal property was studied on a SDT2960 thermogravimeter (TA Instruments, New Castle, DE) with heating rate of $10^\circ \text{C}/\text{min}$. Electrochemical feature was analyzed 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, respectively. The whole operation was performed in CH_3CN solution ($\sim 10^{-3} \text{ M}$) with tetrabutylammonium hexafluorophosphate as supporting electrolyte (0.1 M). Dissolved O_2 was removed by N_2 stream.

2.2. Synthesis of ligands

2-(2*H*-tetrazol-5-yl)-pyridine. The starting reagent 2-(2*H*-tetrazol-5-yl)-pyridine was obtained following a literature procedure [16]. The solution of 10 mmol of picolinonitrile, 20 mmol of NaN_3 and 1 g of ZnCl_2 in 50 mL of redistilled *N,N*-dimethylformamide was stirred at room temperature for half an hour and then heated to 80°C for 10 h under N_2 atmosphere. After cooling, plenty of

crushed ice was added into the solution. The resulting crude product was purified on a silica gel column (*n*-hexane: $\text{CH}_2\text{Cl}_2=50:1$). ^1H NMR (300 MHz, CDCl_3 , 25°C): δ 7.86 (1*H*, m), 8.16 (1*H*, m), 8.34 (1*H*, d, $J=6.0$), 8.87 (1*H*, m). Anal. Calcd for $\text{C}_6\text{H}_5\text{N}_5$: C, 48.98; H, 3.43; N, 47.60. Found: C, 48.85, H, 3.53; N, 47.52.

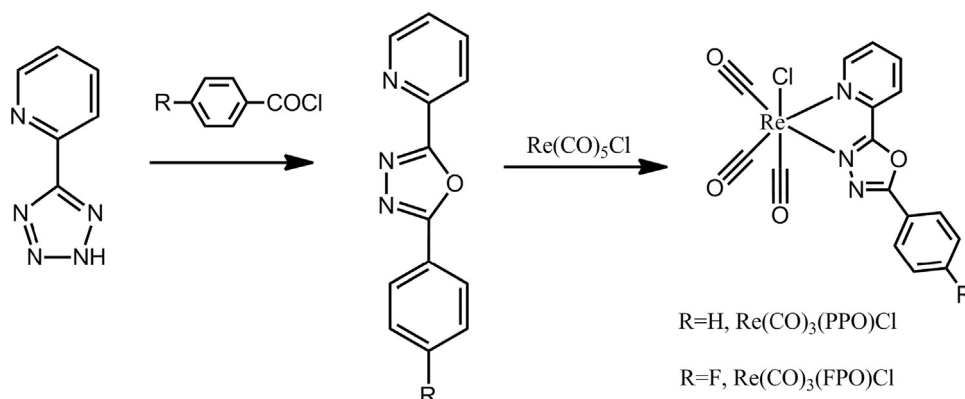
2-phenyl-5-(pyridin-2-yl)-1,3,4-oxadiazole (PPO). The mixture of 20 mmol of 2-(2*H*-tetrazol-5-yl)-pyridine, 20 mmol of benzoyl chloride and 30 mL of anhydrous pyridine was heated to reflux for 2 days under N_2 protection. After cooling, plenty of crushed ice was added into the solution. The resulting crude product was purified on a silica gel column (*n*-hexane: $\text{CH}_2\text{Cl}_2=30:1$). ^1H NMR (CDCl_3): δ 7.45 (1*H*, m), 7.57 (3*H*, m), 7.94 (1*H*, m), 8.26 (1*H*, t), 8.22 (1*H*, t), 8.35 (1*H*, d, $J=6.0$), 8.86 (1*H*, d, $J=3.6$). Anal. Calcd. For $\text{C}_{13}\text{H}_9\text{N}_3\text{O}$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.85; H, 4.16; N, 18.74.

2-(4-fluorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (FPO). FPO was obtained following the synthetic procedure for PPO except that benzoyl chloride was replaced by 4-fluorobenzoyl chloride. ^1H NMR (300 MHz, CDCl_3): δ 7.43 (1*H*, m), 7.56 (2*H*, m), 7.94 (1*H*, m), 8.23 (1*H*, t), 8.26 (1*H*, t), 8.32 (1*H*, d, $J=6.0$), 8.84 (1*H*, d, $J=3.6$). Anal. Calcd. For $\text{C}_{13}\text{H}_8\text{N}_3\text{OF}$: C, 64.73; H, 3.34; N, 17.42. Found: C, 64.64; H, 3.25; N, 17.61.

2.3. Synthesis of complexes

$\text{Re}(\text{CO})_3(\text{PPO})\text{Cl}$. 0.2 mmol of PPO and 0.2 mmol of $\text{Re}(\text{CO})_5\text{Cl}$ were dissolved in 20 mL of toluene which was heated to reflux for 8 h under N_2 protection. Then the solvent was removed by rotary evaporation. The crude product was purified on a silica gel column (*n*-hexane: $\text{CH}_2\text{Cl}_2=10:1$). ^1H NMR (300 MHz, CDCl_3): δ 7.65 (1*H*, m), 7.77 (3*H*, m), 7.95 (1*H*, m), 8.33 (1*H*, t), 8.37 (1*H*, t), 8.46 (1*H*, d, $J=6.0$), 8.96 (1*H*, d, $J=4.0$). ^{13}C NMR (CDCl_3): δ 123.83, 124.12, 127.78, 128.64, 129.32, 134.09, 137.35, 149.43, 157.79, 164.88, 182.73. IR (KBr, cm^{-1}): 723, 799, 1039, 1080, 1165, 1365, 1459, 1497, 1566, 1622, 1935, 2031, 3061. Anal. Calcd. for $\text{C}_{16}\text{H}_9\text{ClN}_3\text{O}_4\text{Re}$: C, 36.33, H, 1.72, N, 7.94. Found: C, 36.51, H, 1.66, N, 7.78. This composition was further confirmed by single crystal XRD analysis.

$\text{Re}(\text{CO})_3(\text{FPO})\text{Cl}$. $\text{Re}(\text{CO})_3(\text{FPO})\text{Cl}$ was obtained following the synthetic procedure for $\text{Re}(\text{CO})_3(\text{PPO})\text{Cl}$ except that PPO was replaced by FPO. ^1H NMR (300 MHz, CDCl_3): δ 7.62 (1*H*, m), 7.75 (2*H*, m), 7.87 (1*H*, m), 8.34 (1*H*, t), 8.39 (1*H*, t), 8.47 (1*H*, d, $J=6.0$), 8.92 (1*H*, d, $J=3.6$). ^{13}C NMR (CDCl_3): δ 116.12, 121.84, 123.81, 124.25, 129.26, 137.38, 149.35, 157.77, 163.04, 164.63, 182.75. IR (KBr, cm^{-1}): 743, 787, 1032, 1088, 1142, 1327, 1465, 1547, 1608, 1942, 2035, 2912, 3058. Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{ClN}_3\text{O}_4\text{FR}$: C, 35.14, H, 1.47, N, 7.68. Found: C, 35.27, H, 1.36, N, 7.53. This composition was further confirmed by single crystal XRD analysis.



Scheme 1. The synthetic route for $\text{Re}(\text{CO})_3(\text{PPO})\text{Cl}$ and $\text{Re}(\text{CO})_3(\text{FPO})\text{Cl}$.

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