

A promising Rhenium(I) complex with fluorine/oxadiazole-bifunctionalized diamine ligand: Synthesis, structure and photophysical property

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ABSTRACT

In this paper, a diamine ligand of 2-(4-fluorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (denoted as FPO) and its corresponding Re(I) complex of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ are synthesized. Full characterization on $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$, including NMR, elemental analysis and single crystal analysis, confirms its molecular identity. Upon photon excitation, the emission of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ owns a long excited state lifetime of 8.95 μs in pure N_2 atmosphere and shows a maximum intensity at 540 nm. Theoretical calculation on $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ single crystal suggests that the excited state has a triplet metal-to-ligand-charge-transfer character. By embedding $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ into a polymer supporting matrix of polystyrene, the emission signal is found to be sensitive towards varying oxygen concentrations, with a maximum sensitivity of 7.84. Due to the porous structure of nanofibrous polystyrene matrix, a short response time of 8 s towards molecular oxygen is also observed with stable quenching signal.

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1. Introduction

Owing to the attractive virtues of non-destructive, simple and quick detection character, optical sensors have harvested much research interest in the past few years [1–4]. Compared with traditional ones for sensing gases, ions and organic matters, optical sensors have shown their advantages of small size, electrical safety and low cost, without needing reference element. Optical sensors for oxygen detection have gained particularly attention due to the important role of oxygen concentration in different branches of chemistry industry, bio- and medical analysis, analytical chemistry and environmental monitoring [5,6].

To allow analyte transportation from environment and eliminate the self-quenching between sensing probes, sensing probes are usually grafted onto or doped into supporting matrixes such as silica-based molecular sieves and polymers [7]. There are also some requirements that should be met to achieve desired performance. For example, uniform and effective quenching on sensing probes is critical for high sensitivity with linear work plot, porous structure and high surface-area-to-volume ratio are necessary for quick response, finally high photostability is needed to give stable and reliable sensing signals. In other words, the exploration for sensing probes with suited emission wavelength and intensity, proper excited state lifetime, good photostability and compatibility with supporting matrixes is still waiting to be conquered.

It seems that luminescent Re(I) complexes can meet above requirements perfectly, considering their tunable emission energy, high photoluminescence (PL) quantum yield, and good photostability [8–10]. According to literature reports on luminescent Re(I) complexes with diamine ligands [11,12], the occupied frontier molecular orbitals (MOs) have metal character, while the unoccupied frontier MOs are essentially π^* orbital of diamine ligand. The emission owns a character of triplet metal-to-ligand-charge-transfer [3] MLCT [$d(\text{Re}) \rightarrow \pi^*(\text{diamine ligand})$]. The excited state electrons localized on π^* orbital of diamine ligand are then vulnerable to energy acceptors such as molecular oxygen, which makes them potential sensing probes. It is expected that the enlargement of conjugation system in diamine ligand can increase the population of excited state electrons [12], favoring oxygen attack. On the other hand, oversized conjugation plane leads to a low-energy triplet ligand-to-ligand-charge-transfer (LLCT) within diamine ligand and consequently emission quenching. This means that the conjugation plane should be properly enlarged without compromising the emission.

Guided by above results, we decide to design a bifunctional diamine ligand which can satisfy both large conjugation and restricted negative effects on emission. In this paper, we synthesize a diamine ligand of 2-(4-fluorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole which owns typical electron-withdrawing moieties of oxadiazole and fluorine atom in its molecular structure. They are expected to act as a bifunctional role: to enlarge conjugation plane in the diamine ligand and to prevent the emergence of low-energy triplet LLCT, resulting in a promising sensing probe for oxygen detection.

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2. Experimental details

Scheme 1 shows the preparation procedure for the bifunctional diamine ligand of 2-(4-fluorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (denoted as FPO), its Re(I) complex of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ and the corresponding composite nanofibers of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}/\text{PS}$. The starting compound of 2-(2H-tetrazol-5-yl)-pyridine (denoted as TP) was synthesized according to the literature procedure [13]. 4-fluorobenzoyl chloride, NaN_3 , polystyrene (denoted as PS, number-average molecular mass = 100,000), ZnBr_2 and $\text{Re}(\text{CO})_5\text{Br}$ were purchased from Aldrich Chemical Co., and used as received. All organic solvents were purified using standard procedures.

2.1. Synthesis of FPO diamine ligand

The preparation route for FPO ligand can be described as follows. The mixture of 10 mmol of TP, 11 mmol of 4-fluorobenzoyl chloride and 20 mL of pyridine was heated to reflux under N_2 atmosphere for 3 days. After cooling, the mixture was poured into cold water and filtered. The obtained crude product was purified by column chromatography. Yield: 37%. ^1H NMR (300 MHz, CDCl_3): δ 7.48 (1H, m), 7.57 (2H, m), 7.97 (1H, m), 8.24 (1H, t), 8.27 (1H, t), 8.38 (1H, d, $J = 6.0$), 8.87 (1H, d, $J = 3.5$). 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, 64.58; H, 3.19; N, 17.56.

2.2. Synthesis of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ complex

$\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ was synthesized according to a literature procedure described as follows [13]. The mixture of 20 mmol of FPO, 20 mmol of $\text{Re}(\text{CO})_5\text{Br}$ and 20 mL of toluene was heated to reflux under N_2 atmosphere for 10 h. After cooling, the solvent was removed by rotary evaporation. The crude product was purified by recrystallization from mixed solvent of *n*-hexane: $\text{CH}_2\text{Cl}_2 = 1:1$ (V:V). The residue was further purified on a silica gel column to give the desired product. ^1H NMR (300 MHz, CDCl_3): δ 7.65 (1H, m), 7.76 (2H, m), 7.99 (1H, m), 8.38 (1H, t), 8.38 (1H, t), 8.49 (1H, d, $J = 6.0$), 8.93 (1H, d, $J = 4.0$). Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{BrN}_3\text{O}_4\text{FRe}$: C,

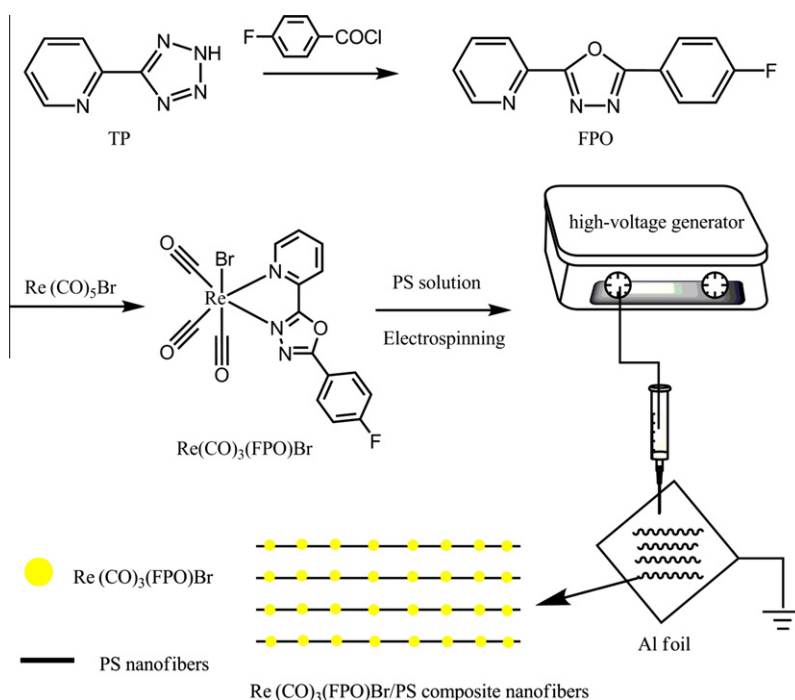
32.50, H, 1.36, N, 7.11. Found: C, 32.63, H, 1.43, N, 7.18. This molecular structure was further confirmed by single crystal XRD analysis.

2.3. Preparation of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}/\text{PS}$ composite nanofibers

The composite nanofibers of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}/\text{PS}$ was prepared according to a procedure described as follows [14]. First, PS was dissolved in *N,N'*-dimethyl formamide (DMF) to form several 22 wt.% homogeneous solutions. Then various amounts of $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ were added into the homogeneous solutions. The final solutions were individually placed in 5 mL glass syringes, with the opening ends connected to plastic needles (inner diameter = 0.6 mm) as the nozzle [14]. The anode terminal of a high-voltage generator was connected to a copper wire inserted into the polymer solutions in the glass syringes. Al foils were used as the collector plate and connected to the grounding electrode. The driving voltage was 18 kV, with the tip-to-target distance of 25 cm.

2.4. Calculation methods and equipment

Density functional theory (DFT) and singlet excitation calculations by time dependent density functional theory (TD-DFT) were performed on $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$. The initial geometry was obtained from its single crystal structure. All computations were finished by GAMESS at RB3LYP/SBKJC level in vacuum. Graphical presentations were plotted by wxMacMolPlt with contour value of 0.028. Single crystal analysis was performed on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo $K\alpha$ radiation, operating at 50 kV and 30 A at 298 K. All hydrogen atoms were calculated. Emission decay character was obtained with a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd: yttrium aluminium garnet (YAG) laser as the excitation source. All PL spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. UV-Vis absorption spectra were measured using a HP 8453 UV-Vis-NIR diode array spectrophotometer.



Scheme 1. The preparation procedure for FPO, $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}$ and $\text{Re}(\text{CO})_3(\text{FPO})\text{Br}/\text{PS}$.

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