Journal of Luminescence 194 (2018) 467–473

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Doping a phosphorescent rhenium complex into a silica matrix: Construction, characterization and oxygen emission sensing behavior

Fengjun Zhang*, Xiaosheng Cheng, Haihua Cui, Huayu Jia, Zhaojie Li

College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

ARTICLE INFO

Keywords:
Re(I) complex
Oxygen-sensing
Photophysical features
MCM-41
Theoretical analysis

ABSTRACT

In this paper, a Re(I) complex whose diamine ligand had an oxadiazole ring and a F atom was synthesized and explored for oxygen optical sensing. This Re(I) complex was identified and analyzed with single crystal analysis, density functional theory calculation and photophysical measurement. Its oxadiazole ring increased conjugation plane so that sensing collision probability between excited electrons and O_2 molecules could be increased. In addition, its electron-pulling effect, along with that of F atom, decreased non-radiative decay probability of our Re(I) complex, offering a long-lived emissive center for O_2 attack. After being doped into a silica matrix of MCM-41, its oxygen sensing performance was tentatively discussed. A dynamic sensing mechanism towards O_2 was observed with sensitivity as high as 7.74 and response time of 10 s.

1. Introduction

Owing to a capability of combining and holding features of their components, composites materials are convenient to be multi-functionalized and thus have harvested much research attention [1,2]. In a representative example of composite materials, an organic-inorganic hybrid structure is usually used. In this case, its organic component is designed for functional purpose since an organic component shall be easily modified, while its inorganic component serves as supporting matrix due to its good mechanical strength and stability [2,3]. These composite materials have been tried for various applications, such as catalysis, solar cells, light emitting and sensing [3,4].

Among the above mentioned applications, optical oxygen sensing has been intensively focused. As an important life-supporting gas, molecular O_2 has always been recognized as a key target in chemical industry, food processing and environmental protection [5,6]. Compared to traditional O_2 quantification techniques, optical oxygen sensing has shown advantages of no analyte consumption, easy-to-go operation procedure and needing no complicated apparatuses [7,8]. Some criteria should be met aiming at desired sensing performance in an ideal optical sensing composite. For instance, high diffusion coefficient, good stability and compatibility with probe are demanded from supporting matrix since it is responsible for probe dispersing and analyte diffusion [9–12]. A silica based supporting matrix, MCM-41, have been proved promising among the numerous candidates since it satisfies above factors well [11,12].

As for sensing probe, an ideal one should have long decay lifetime and broad distribution of excited electrons which increase sensing collision probability with analyte. Luminescent metal complexes, especially Re(I)-based ones, have been highly recommended owing to their promising performance [13–16]. Theoretical study on representative Re(I) complexes suggests that their occupied frontier molecular orbitals (FMOs) have dominant metal character, while their unoccupied FMOs are ligand π* in nature [13–16]. Thus, broad electronic distribution can be easily accomplished by increasing conjugation planes in Re(I) complex ligands. By introducing electron-pulling groups into these conjugation planes, non-radiative probability shall be decreased so that emission decay lifetime can be increased [13–16].

Instructed by the above consideration, a diamine ligand with a large conjugation plane and its Re(I) complex are designed in this paper, as shown in Scheme 1 (see Supporting information for a detailed explanation on our design strategy). A typical electron-pulling group, F atom, is connected to this ligand, hoping to increase decay lifetime and electronic distribution of excited electrons, favoring oxygen sensing. By immobilizing this Re(I) complex into a silica supporting matrix MCM-41, oxygen sensing performance of the resulting composite is analyzed and reported.

2. Experimental details

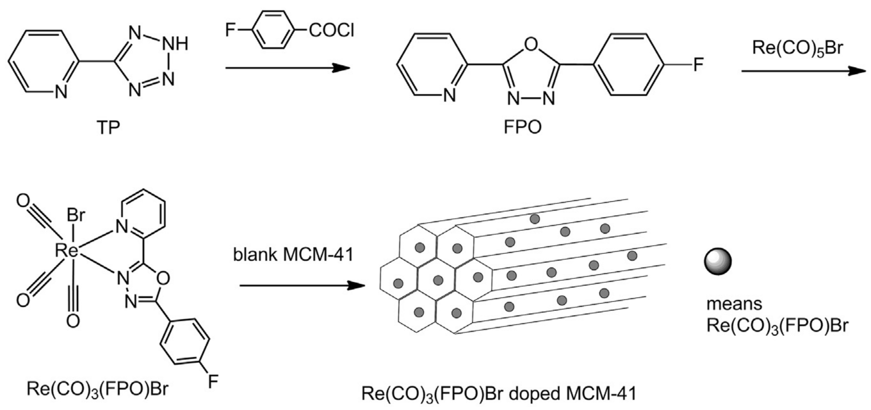
2.1. Reagents and apparatuses

Reagents for ligand and complex synthesis are listed below. Starting chemical TP (2-(2H-tetrazol-5-yl)pyridine) was firstly synthesized

---

* Corresponding author.
E-mail address: jszhangfengjun@126.com (F. Zhang).

http://dx.doi.org/10.1016/j.jlumin.2017.10.071
Received 22 June 2017; Received in revised form 19 October 2017; Accepted 25 October 2017



Scheme 1. Synthesis route for ligand FPO, Re(CO)$_3$(FPO)Br and Re(CO)$_3$(FPO)Br doped MCM-41 composites.

according to a literature method [17]. Other chemicals, including Re(CO)$_5$Br, sodium azide, 4-fluorobenzoyl chloride, zinc bromide and blank MCM-41, were purchased from Lida Chemical Co. (Hangzhou) and used as received. Organic solvents were purified following standard procedures.

Apparatuses for sample characterization are listed below. A Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector was applied to perform single crystal analysis, using graphite-monochromated Mo Kα radiation (50 kV, 30 A, 298 K). All hydrogen atoms were calculated. A Vario Element Analyzer was used to record elemental analysis data. A Varian INOVA 300 spectrometer, a Agilent 1100 MS series/AXIMA CFR MALDI/TOF MS spectrometer, a Shimadzu UV-3101PC spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer were responsible for NMR, MS, absorption and emission spectra, respectively. A two-channel TEKTRONIX TDS-3052 oscilloscope was used to record emission decay lifetime, with pulsed Nd:YAG laser as excitation source (λ = 355 nm). A Rigaku-Dmax 2500 diffractometer was used for small-angle X-ray diffraction (SAXRD) analysis (λ = 0.154 nm, scanning step = 0.02°). Theoretical calculation was performed by GAMESS software at RB3LYP/SBKJC level, using single crystal as initial geometry. Graphical presentation for FMOs was generated by wxMacMolPlt with contour value of 0.025.

2.2. Synthesis of ligand FPO

Ligand FPO (2-(4-fluorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole) was synthesized following a literature method [17]. 4-fluorobenzoyl chloride (11 mmol), TP (10 mmol) and anhydrous pyridine (0 °C, 20 mL) were mixed in a flask, stirred at room temperature for 30 min and at 110 °C for two days under N_2 protection. After cooling, this solution was poured into crushed ice. Solid product was collected and purified on a silica gel column (*n*-hexane:ethyl acetate = 30:1). Yield: 45%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.43 (1H, m), 7.64 (2H, m), 7.99 (1H, m), 8.26 (1H, t), 8.31 (1H, t), 8.44 (1H, d, J = 6.0), 8.89 (1H, d, J = 3.6). Anal. Calcd. For $C_{13}H_8N_3OF$: C, 64.73; H, 3.34; N, 17.42. Found: C, 64.61; H, 3.22; N, 17.63. ESI-MS *m/e*: calc. for $C_{13}H_8N_3OF$, 241.0; found, 241.7 [m]$^+$.

2.3. Synthesis of complex Re(CO)$_3$(FPO)Br

Complex Re(CO)$_3$(FPO)Br was synthesized following a literature method [15]. The mixture of FPO (1 mmol), Re(CO)$_5$Br (1 mmol) and anhydrous toluene (25 mL) was heated at 120 °C for 12 h under N_2 protection. Solvent was extracted by thermal evaporation under reduced pressure. Solid product was collected and purified on a silica gel column (*n*-hexane:ethyl acetate = 30:1). Yield: 37%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.50 (1H, m), 7.66 (2H, m), 7.82 (1H, m), 8.34 (1H, t), 8.46 (1H, t), 8.51 (1H, d, J = 6.0), 8.82 (1H, d, J = 3.6). Anal. Calcd. for $C_{16}H_8BrN_3O_4FRe$: C, 32.50, H, 1.36, N, 7.11. Found: C, 32.67, H, 1.49, N, 7.01. ESI-MS *m/e*: calc. for $C_{13}H_8N_3OF$, 590.9; found, 591.1 [m]$^+$. Its single crystal (CCDC 1063952) will be discussed below.

2.4. Construction of Re(CO)$_3$(FPO)Br doped MCM-41 composite samples

Oxygen sensing composite samples were constructed by doping Re(CO)$_3$(FPO)Br into MCM-41 matrix with various doping contents [11,12]. A typical run is described as follows. Controlled amount of Re(CO)$_3$(FPO)Br was carefully weighted and dissolved in CH_2Cl_2 (5 mL) solution under stirring. MCM-41 matrix (1 g) was then added into this solution. This mixture was stirred at room temperature for half an hour. Solid product was collected and washed with CH_2Cl_2 (10 mL × 3). Our sensing composite samples were obtained as light yellow powder.

3. Results and discussion

3.1. Single crystal structure of Re(CO)$_3$(FPO)Br

Single crystal structure of Re(CO)$_3$(FPO)Br is fortunately obtained which confirms its molecular identity. As shown in Fig. S1A (Supporting information), the central Re atom is coordinated by two N atoms from FPO, three C atoms from CO and a Br atom, showing a typical octahedral coordination environment, which is consistent with literature reports [13–15]. Key structural parameters of Re(CO)$_3$(FPO)Br are listed in Table S1 (Supporting information). It is observed that this octahedral coordination field is distorted by its heterogeneous ligands, including N-based FPO, C-based CO and Br atom. The three Re–C bonds are slightly different from each other owing the interference from FPO and Br. Similarly, the two Re–N bond length values are different from each other. Coordination attraction between Re and N(19) is stronger than that between Re and N(11) owing to the shorter Re–N(11) bond. This result can be explained by the fact that there are a short conjugation chain and electron-donating atoms in oxadiazole ring which increase electron donating ability of its N atom, compared to a pyridine ring. Most bond angles in Table S1 (Supporting information) are close to 90°, except for N-Re-N bite angle. This N-Re-N bite angle in Re(CO)$_3$(FPO)Br is smaller than those in complexes of tetrahedral coordination field, suggesting that FPO ligand is trying to minimize steric hindrance around Re center [13–16]. The resulting roomy space in Re(CO)$_3$(FPO)Br may favor oxygen sensing since O_2 molecules can easily access this emissive center, leading to fluent and efficient quenching on Re(CO)$_3$(FPO)Br emissive center.

Our desired large conjugation plane is observed in Re(CO)$_3$(FPO)Br, formed by a pyridine ring, an oxadiazole ring and a phenyl ring. Π-π attraction between FPO planes makes Re(CO)$_3$(FPO)Br molecules take a highly ordered arrangement, as shown in Fig. S1B (Supporting information). FPO planes align nearly parallel to each other with minimal face-to-face distance of 3.233 Å and intersection angle of 3.18°, confirming the π-π attraction between them. This highly ordered