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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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



# Composite nanofibers doped with a phosphorescent Re(I) complex having restricted conjugation plane in its diamine ligand: Preparation, characterization, photophysical property and oxygen-sensing performance



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#### HIGHLIGHTS

- An oxadiazole-containing diamine ligand and its Re(I) complex were studied.
- Crystal structure, photophysical property and electronic nature were studied.
- It owned a large conjugation plane favoring oxygen sensing.
- It was doped into a polymer matrix to construct composite fibers.
- A maximum sensitivity of 7.88 with short response time of 11 s was realized.

#### ARTICLE INFO

Article history: Received 5 April 2013 Received in revised form 19 May 2013 Accepted 24 May 2013 Available online 4 June 2013

Keywords: Re(1) complex Single crystal Photophysical performance Oxygen sensing

#### Introduction

# The detection of oxygen concentration has always been an important consideration in various branches of medical analysis, analytical chemistry, environmental monitoring and chemistry industry [1,2]. Consequently, various approaches have been

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#### GRAPHICAL ABSTRACT



#### ABSTRACT

In this paper, we report a Re(I) complex of Re(CO)<sub>3</sub>(Cl-PYO)Br, where Cl-PYO stands for 2-(4-chlorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole, including its synthesis, identification, molecular structure, theoretical calculation and photophysical character. Re(CO)<sub>3</sub>(Cl-PYO)Br is found to be a yellow emitter with long excited state lifetime in pure N<sub>2</sub> atmosphere. Theoretical calculation result suggests that this emission comes from a triplet metal-to-ligand-charge-transfer excited state. By doping Re(CO)<sub>3</sub>(Cl-PYO)Br into a polymer supporting matrix of poly(vinylpyrrolidone), the emission of the resulted composite materials is found to be sensitive towards various oxygen concentrations. The maximum sensitivity is obtained to be 7.88. Owing to the porous structure of fibrous poly(vinylpyrrolidone) matrix, a short response time of 11 s towards molecular oxygen is also realized with high photostability. © 2013 Elsevier B.V. All rights reserved.

developed for actual oxygen detection [3–6]. Compared with traditional methods for oxygen determination, such as Clark electrode and the Winkler titration approaches which suffer from disadvantages of long response time, oxygen consumption during detection, fragile electrodes and high requirement for instrumentations [3,4], optical sensors have attracted many research efforts. By showing advantages of non-destructive, fast and rapid detection characteristic, optical sensors for oxygen determination have been intensively constructed and reported [7,2].

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A typical optical sensing system is composed of sensing probes which are responsible for analyte detection and supporting matrix whose purpose is: (1) to dilute the sensing probes and decrease the self-quenching between sensing probes, and (2) to allow analyte transportation from surrounding. To achieve desired performance, there are also some requirements for both sensing probe and supporting matrix to meet. Besides proper emission intensity and energy, long excited state lifetime and large unoccupied frontier molecular orbitals (MOs) are desired from sensing probe to achieve effective quenching on the excited state of sensing probe. In addition, high photostability is also needed for stable quenching signal output. As for supporting matrix, porous structure and high surface-area-to-volume ratio are necessary for short response time. Some common matrixes such as silica-based molecular sieves and polymers have been proved to be excellent ones in optical sensing systems [7,8]. Thus, the key factor for developing promising optical sensors localizes on the exploration of sensing probes with proper emission intensity/energy, long excited state lifetime, large unoccupied frontier molecular orbitals (MOs) and high photostability.

Phosphorescent Re(I) complexes of Re(CO)<sub>3</sub>(N–N)X, where N–N and X stand for diamine ligand and halogen atom, respectively, are believed to be promising candidates for the sensing probes. According to literature reports [9–11], the occupied frontier MOs of Re(CO)<sub>3</sub>(N–N)X are composed of Re ion, CO and X ligands, while the unoccupied frontier MOs are essentially  $\pi^*$  orbital of N–N ligand. Further research suggests that large conjugation system in N–N ligand can increase excited state lifetime, which means that the conjugation plane of N–N ligand in Re(CO)<sub>3</sub>(N–N)X should be extended to favor effective quenching requirement mentioned above [10]. However, an oversized conjugation plane causes innerligand triplet decay of N–N ligand which suppresses the radiative decay of Re(CO)<sub>3</sub>(N–N)X, leading to emission absence [11]. In other words, the scale of conjugation plane should be restricted to satisfy both improved desired performance (long excited state lifetime and large unoccupied frontier MOs) and limited negative effects (emission absence).

Enlightened by above consideration, in this work, we design a diamine ligand with an oxadiazole moiety in its structure. The scale of conjugation plane is expected to be restricted by the electron-withdrawing effect of the oxadiazole moiety, so that the innerligand triplet decay can be eliminated. The photophysical performance of the corresponding Re(I) complex is also investigated, as well as its oxygen sensing behavior.

#### **Experimental section**

#### Synthesis

The synthetic procedure for the diamine ligand of 2-(4-chlorophenyl)-5-(pyridin-2-yl)-1,3,4-oxadiazole (referred as Cl-PYO), its Re(I) complex of Re(CO)<sub>3</sub>(Cl-PYO)Br and the corresponding composite nanofibers of Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP is shown in Scheme 1. 2-(2H-tetrazol-5-yl)-pyridine (referred as TP) was synthesized according to the literature procedure [12]. The other compounds including 4-chlorobenzoyl chloride, NaN<sub>3</sub>, poly(vinyl-pyrrolidone) (PVP, K30), ZnBr<sub>2</sub> and Re(CO)<sub>5</sub>Br were purchased from Aldrich Chemical Co. and used as received. All organic solvents were purified using standard procedures.

Cl-PYO. The synthetic route for Cl-PYO can be described as follows. The solution of 10 mmol of TP, 11 mmol of 4-chlorobenzoyl chloride and 25 mL of pyridine was heated to 120 °C under N<sub>2</sub> protection for 3 days. After cooling, the solution was poured into 500 mL of cold water to result solid. The obtained crude product was further purified on a silica column. Yield: 45%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (1H, m), 7.53 (2H, m), 7.92 (1H, m),



Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP composite nanofibers

Scheme 1. The synthetic procedure for Cl-PYO, Re(CO)<sub>3</sub>(Cl-PYO)Br and Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP.

8.22 (1H, t), 8.24 (1H, t), 8.31 (1H, d, J = 6.0), 8.83 (1H, d, J = 3.6). Anal. Calcd. For C<sub>13</sub>H<sub>8</sub>N<sub>3</sub>OCl: C, 60.60; H, 3.13; N, 16.31. Found: C, 60.39; H, 3.27; N, 16.17.

Re(CO)<sub>3</sub>(Cl-PYO)Br. The synthetic route for Re(CO)<sub>3</sub>(Cl-PYO)Br can be described as follows. The solution of 20 mmol of Cl-PYO, 20 mmol of Re(CO)<sub>5</sub>Br and 25 mL of toluene was heated to 120 °C under N<sub>2</sub> protection for 12 h. After cooling, the solution was dried by rotary evaporation. The residue was firstly purified by recrystal-lization from mixed solvent of *n*-hexane:CH<sub>3</sub>Cl = 1:1 (*V*:*V*) and then further purified on a silica column to obtained pure Re(CO)<sub>3</sub> (Cl-PYO)Br as yellow blocks. Yield 57%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.71 (1H, m), 7.79 (2H, m), 8.02 (1H, m), 8.41 (1H, t), 8.46 (1H, t), 8.54 (1H, d, *J* = 6.0), 8.99 (1H, d, *J* = 4.0). Anal. Calcd. for C<sub>16</sub>H<sub>8</sub>. BrClN<sub>3</sub>O<sub>4</sub>Re: C, 31.62, H, 1.33, N, 6.91. Found: C, 31.48, H, 1.39, N, 6.78. Its molecular identity was further confirmed by single crystal XRD analysis (CCDC 878325 which can be obtained free of charge from The Cambridge Crystallographic Data Center via <www.ccdc.cam.ac.uk/data\_request/cif>).

#### Electrospinning of Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP composite nanofibers

The composite nanofibers of 7.0 wt% doped Re(CO)<sub>3</sub>(Cl-PYO)Br/ PVP were obtained following the procedure described as follows [8]. First, PVP was dissolved in 10 mL of N,N'-dimethyl formamide (DMF) to give 20 wt% homogeneous solution. Then controlled amount of Re(CO)<sub>3</sub>(Cl-PYO)Br was added into the solution to form 7.0 wt% solution (compared with PVP weight). The obtained homogeneous solution was poured into a 5-mL glass syringe equipped with a plastic needle (inner diameter = 0.6 mm) at the opening end. A copper wire was connected to the anode terminal of a high-voltage generator with the other end inserted into the 5-mL glass syringe. An Al foil was placed in front of the 5-mL glass syringe with tip-to-target distance of 25 cm and connected to the grounding electrode to serve as the collecting plate. The driving voltage was 18 kV. Similar procedures were used to obtain 7.4 wt% doped Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP and 7.8 wt% doped Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP samples.

#### Methods and measurements

Theoretical calculation was performed on Re(CO)<sub>3</sub>(Cl-PYO)Br at RB3LYP/SBKJC level in vacuum. The initial structure was obtained from its single crystal. All calculations were finished by GAMESS with time-dependent density functional theory (TD-DFT). The pictures of LUMO (the lowest unoccupied molecular orbital), LUMO + 1 and LUMO + 2 were generated by wxMacMolPlt with contour value of 0.025. <sup>1</sup>H NMR spectra were recorded on a Varian INOVA 300 spectrometer. Element analysis data were performed using a Vario Element Analyzer. Single crystal XRD data were collected by Siemens P4 single-crystal X-ray diffractometer with Smart CCD-1000 detector and graphite-monochromated Mo Ka radiation, operating at 50 kV and 30 A at 298 K. All hydrogen atoms were calculated. UV-Vis absorption spectra were recorded by a HP 8453 UV-Vis-NIR diode array spectrophotometer. Photoluminescence (PL) spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. Luminescence decay data were collected on a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a tunable laser as the excitation source (Continuum Sunlite OPO). Scanning electron microscopy (SEM) and fluorescence microscopy images were generated by a Hitachi S-4800 microscope and a Nikon TE2000-U fluorescence microscopy (using mercury lamp as power supply), respectively. Oxygen sensing behavior of Re(CO)3(Cl-PYO)Br/PVP composite nanofibers was discussed on the basis of steady emission intensity quenching. In the measurement of Stern–Volmer plots, O<sub>2</sub> and N<sub>2</sub> were mixed with different concentrations via gas flow controls and injected directly



Fig. 1A. Molecular structure of  $\text{Re}(\text{CO})_3(\text{CI-PYO})\text{Br}$  obtained from single crystal analysis.

into a sealed glass chamber. All measurements were carried out in the air at room temperature without being specified.

#### **Results and discussion**

#### Single crystal structure of Re(CO)<sub>3</sub>(Cl-PYO)Br

The molecular structure obtained from its single crystal analysis data is shown in Fig. 1A. It can be seen that Re(I) ion is surrounded by three CO ligands, two N atoms from Cl-PYO ligand and one Br moiety, forming a distorted octahedral coordination sphere. The pyridine ring and the Cl-substituted phenyl ring are connected by the oxadiazole ring, showing a large conjugation plane. This large conjugation plane is expected to increase the population of  $Re(CO)_3(Cl-PYO)Br$  excited state electrons, offering more collision chances for analyte attack. On the other hand, the electron-with-drawing nature of the oxadiazole moiety is believed to limit the conjugation to eliminate the possibility of innerligand triplet decay [11].

Some key structural parameters of  $Re(CO)_3(CI-PYO)Br$  are listed in Table 1. It can be seen that Re–N, Re–C and Re–Br bond length values are comparable to literature values due to their similar coordination nature [9]. The three Re–C bond length values are nearly the same with each other. There is, however, a slightly difference between Re–N(1) and Re–N(2) bonds, which means that attraction between Re(I) ion and the N atom of pyridine is stronger than that between Re(I) ion and the N atom from oxadiazole ring. It is thus expected that the electron-withdrawing

 Table 1

 Key structural parameters of Re(CO)<sub>3</sub>(CI-PYO)Br obtained from single crystal.

Bond length	Å	Bond angle	0
Re-C(1)	1.887	N(1)-Re-N(2)	73.38
Re-C(2)	1.924	N(1)-Re-C(2)	92.15
Re-C(3)	1.889	N(2)-Re-C(2)	95.86
Re-Br(1)	2.614	N(1)-Re-Br(1)	86.27
Re-N(1)	2.229	N(2)-Re-Br(1)	84.69
Re-N(2)	2.166	C(1)-Re-Br(1)	92.70
		C(3)-Re-Br(1)	90.35

nature of oxadiazole may decrease the coordination ability of its N atoms. The

N–Re–N bite angle is measured to be 73.38° and this value is found to be much smaller than the bite angles in tetrahedral coordination spheres ( $\sim$ 80°) [10,12], which means that the coordination sphere around Re(I) ion is less crowded owing to the small steric hindrance of CO and Br moieties. This decreased may also help to suppress the geometric distortion that happens in Re(CO)<sub>3</sub>(Cl-PYO)Br excited state, leading to a stable emissive center [11].

We mentioned that Cl-PYO owns a large conjugation plane in Re(CO)<sub>3</sub>(Cl-PYO)Br and this large conjugation plane makes every two Cl-PYO planes from Re(CO)<sub>3</sub>(Cl-PYO)Br molecules align exactly parallel to each other, as shown by Fig. 1B. The face-to-face distance between the two Cl-PYO planes is 3.25 Å, which confirms the existence of  $\pi$ - $\pi$  attraction. The  $\pi$ -stacking in Re(CO)<sub>3</sub>(Cl-PYO)Br crystal makes all molecules take a more organized alignment, forming a rigid structure. Similar case have been reported by Zhang and coworkers [11], where such rigid structure has been proved to be effective on depressing the geometric distortion in complex excited state, leading to PL performance improvement.

#### Theoretical calculation on Re(CO)<sub>3</sub>(Cl-PYO)Br

The composition of frontier MOs and electronic transitions are then analyzed by TD-DFT calculation, which has been reported to be a useful tool to reveal the electronic nature of transition metal complexes [9,11,10]. As shown in Table 2, the occupied frontier MOs of HOMO, HOMO-1, HOMO-2, HOMO-3 and HOMO-4 all have predominant metal character, admixed with contributions from Br or CO moieties. As for the unoccupied ones of LUMO, LUMO + 1 and LUMO + 2, they are essentially  $\pi^*$  orbitals of Cl-PYO ligand, with very little contribution from the other moieties. Above result is consistent with Vlcek's report about the excited states of transition metal complexes [13-15]. The first three onset electronic excitations correspond to transitions from HOMO. HOMO-1 and HOMO-2 to LUMO, respectively, suggesting that these transitions own mixed character of metal-to-ligand-charge-transfer and ligand-to-ligand-charge-transfer (MLCT&LLCT). This conclusion is consistent with literature reports [9,10].

In order to get a clear view on the population of excited state electrons, the graphic presentations for the frontier MOs are shown in Figs. 2A and B. It can be seen that the electron clouds of LUMO, LUMO + 1 and LUMO + 2 are distributed on the whole conjugation plane of Cl-PYO. The excited state electrons localizing on these orbitals can thus be more completely quenched by oxygen molecules, favoring sensitivity improvement.



**Fig. 1B.** Face-to-face  $\pi$ -stacking in Re(CO)<sub>3</sub>(Cl-PYO)Br crystal.

Composition of front	ier MOs and first	ten singlet excitations

MO/transition	Energy (eV)	Contribution (%)				Character
		Re	Cl-PYO	CO	Br	
LUMO + 2(73)	-1.981	0.4	98.3	1.0	0.2	Cl-PYO
LUMO + 1(72)	-2.357	1.4	96.4	1.7	0.5	Cl-PYO
LUMO(71)	-3.246	5.2	88.9	3.9	2.0	Cl-PYO
HOMO(70)	-5.714	35.1	4.5	18.1	42.4	Br/Re
HOMO-1(69)	-5.831	28.9	8.8	14.0	48.3	Br/Re
HOMO-2(68)	-6.664	61.2	10.1	27.9	0.8	Re/CO
HOMO-3(67)	-6.950	31.0	25.6	13.5	29.8	Re/Br
HOMO-4(66)	-7.070	37.0	13.3	16.4	33.3	Re/Br
$S_0 \rightarrow S_1$	1.7152	70 → 2	71(98.4)			ML/LLCT
$S_0 \rightarrow S_2$	1.9437	$69 \rightarrow 7$	71(97.8)			ML/LLCT
$S_0 \rightarrow S_3$	2.6088	68 → 2	71(98.7)			ML/LLCT
$S_0 \rightarrow S_4$	2.7286	70 → 2	72(95.3)			ML/LLCT
$S_0 \rightarrow S_5$	2.8463	$69 \rightarrow 7$	72(96.6)			ML/LLCT
$S_0 \rightarrow S_6$	2.9822	$67 \rightarrow 7$	71(81.5) &	$66 \rightarrow 71$	(15.3)	ML/LLCT
$S_0 \rightarrow S_7$	3.1243	70 → 1	73(89.2) &	$66 \rightarrow 71$	(5.6)	ML/LLCT
$S_0 \rightarrow S_8$	3.2226	$66 \rightarrow 3$	71(48.9) &	69 → 73	(32.7)	ML/LLCT
$S_0 \rightarrow S_9$	3.2581	69 → T	73(64.5) &	66 → 71	(25.6)	ML/LLCT
$S_0 \rightarrow S_{10}$	3.6425	68 → <sup>2</sup>	72(96.2)			ML/LLCT

#### Photophysical property of Re(CO)<sub>3</sub>(Cl-PYO)Br UV–Vis absorption and excitation spectra

Fig. 3 shows the absorption and the excitation spectra of  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$  in CHCl<sub>3</sub> solution (10  $\mu$ M). The absorption spectrum of Cl-PYO shows a single peak at 293 nm, ending at 348 nm. As for  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$ , its absorption spectrum owns two peaks of 283 nm and 377 nm, extending to visible region of 508 nm [9]. Compared with the absorption spectrum of  $\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})\text{Br}$  whose optical edge is reported to be 502 nm, it can be seen that the large conjugation plane has little effect on decreasing the energy gap of metal complexes. This observation is conflicting with Zhang's report which states that the enlarged conjugation plane in diamine ligand leads to largely decreased energy gaps [10]. We believe that the electron-withdrawing effect of the oxadiazole moiety should be the main causation.

The high-energy absorption peak of Re(CO)<sub>3</sub>(Cl-PYO)Br is quite similar to the absorption spectrum of free Cl-PYO ligand shown in Fig. 3. Thus, the high-energy absorption peak at 283 nm is attributed to the  $\pi \rightarrow \pi^*$  transitions of Cl-PYO ligand. The spectral shift could be caused by electron-delocalization in Cl-PYO ligand when coordinated with Re(I) ion. The low-energy absorption peak at 377 nm is a newly-generated one with no vibronic progressions, suggesting the charge-transfer character of its transition. With the TD-DFT calculation result on hands, we assign the low-energy absorption to the electronic transitions of MLCT and LLCT.

There is an obvious difference between the absorption and the excitation spectra of Re(CO)<sub>3</sub>(Cl-PYO)Br. Interestingly, the weak absorption from 350 nm to 508 nm is highly effective on exciting the emissive center. On the other hand, the strong absorption from 250 nm to 345 nm is nearly unable to excite the emissive center. A possible explanation is given as follows. As revealed by TD-DFT calculation result, the low-energy absorption features are assigned to the electronic transitions of MLCT and LLCT, while the high-energy ones are attributed to ligand  $\pi \rightarrow \pi^*$  transitions. The molar distinction coefficients of MLCT and LLCT transitions are reported to be much lower than those of ligand  $\pi \to \pi^*$  transitions [9,13]. However, (MLCT&LLCT) excited state is highly effective on exciting the emissive center since the emissive center is derived from (MLCT&LLCT) excited state. The ligand  $\pi \rightarrow \pi^*$  excited state suffers badly from energy loss caused by intersystem crossing and internal transitions, leading to its low efficiency of exciting the emissive center. Thus, the spectral difference between the absorption and the excitation spectra is reasonable.



**Fig. 2A.** The graphic presentation for LUMO (upper), LUMO + 1 (middle) and LUMO + 2 (down) of Re(CO)<sub>3</sub>(CI-PYO)Br.

PL spectra and emission decay characteristic

Fig. 4 gives the PL spectrum of Re(CO)<sub>3</sub>(Cl-PYO)Br in CHCl<sub>3</sub> solution (10 µM). Similar to its absorption spectrum, the emission spectrum peaking at 560 nm shows no vibronic progressions, which is consistent with the charge transfer nature of (MLCT&LLCT) excited state. The full-width-at-half-maximum of this broad emission is 77 nm, with Stokes shift between absorption edge (508 nm) and emission peak (560 nm) of 52 nm. Compared with the emission spectrum of Re(CO)<sub>3</sub>(1,10-phenanthroline)Br whose emission band peaks at 554 nm with Stokes shift of 90 nm [9], it can be seen that the conjugation enlargement in diamine ligand moves the emission energy to low energy region. The presence of electron-withdrawing moiety of the oxadiazole moiety seems to be able to restrict the geometric distortion that happens in Re(CO)<sub>3</sub>(Cl-PYO)Br excited state. This observation is consistent with the conclusion in Section 'Single crystal structure of Re(CO)<sub>3</sub> (Cl-PYO)Br' discussion part.

To further confirm the electron-withdrawing effect of the oxadiazole moiety, the triplet state energy of Cl-PYO is analyzed by its low temperature phosphorescence spectrum as shown in Fig. 4. The phosphorescence localizes mainly in blue region from 400 nm to 500 nm, extending to 630 nm. Literature report on similar conjugation ring suggests a low triplet state energy of 650 nm



Fig. 2B. The graphic presentation for HOMO (upper), HOMO-1 (middle) and HOMO-2 (down) of  $Re(CO)_3(CI-PYO)Br$ .

[10]. Thus, we can conclude that the triplet state energy of Cl-PYO ligand is greatly enhanced by the oxadiazole moiety. Correspondingly, the higher triplet state Cl-PYO can transfer its excited state energy to the lower emissive state of  $Re(CO)_3(Cl-PYO)Br$ . With the elimination of low energy ligand triplet state, the negative effects (emission absence) caused by enlarged conjugation plane can be eliminated.

Under pure N<sub>2</sub> atmosphere, the emission of Re(CO)<sub>3</sub>(Cl-PYO)Br in solid state exhibits biexponential decay behavior with  $\tau_1$  = 1.415 µs ( $A_1$  = 0.274) and  $\tau_2$  = 0.277 µs ( $A_2$  = 1.187). These long-lived components identify the triplet nature of both



Fig. 3. UV–Vis absorption spectra of  $Re(CO)_3(CI-PYO)Br$  and free CI-PYO, as well as the excitation spectrum of  $Re(CO)_3(CI-PYO)Br$ .

components. As suggested by TD-DFT calculation result, the emissive center owns a mixed nature of MLCT and LLCT. Thus, the emissive center should be described as a <sup>3</sup>(MLCT&LLCT) one. Both decay components donate their contributions to the radiative decay of Re(CO)<sub>3</sub>(CI-PYO)Br center. Upon pure O<sub>2</sub> atmosphere, the decay lifetime greatly decreases to only 0.073  $\mu$ s with single exponential decay pattern, which means that there is only one dominant decay process remaining. It is thus reasonable to expect that the other radiative process is quenched by O<sub>2</sub>, and their further identification will be later discussed. In addition, since O<sub>2</sub> quenches one of the two radiative processes, the quenching mechanism can thus be assigned as a dynamic one [7,12].

#### Characterization on Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP composite nanofibers

TD-DFT calculation result and emission decay comparison under  $N_2/O_2$  have confirmed that the excited state of  $Re(CO)_3$ (Cl-PYO)Br is vulnerable to  $O_2$  attack, which means that  $Re(CO)_3$ (Cl-PYO)Br can be developed as a sensing probe for oxygen sensing. In order to avoid the self-quenching between  $Re(CO)_3$ (Cl-PYO)Br molecules at high concentrations and to accelerate  $O_2$  transportation, we decide to construct composite nanofibers by electrospinning which has been proved to be a promising sensing system for optical sensors. The obtained nanofibers process a large surface-to-volume-ratio which is two orders of magnitude bigger than those of bulk materials and continuous films [8]. To start with, PVP is selected to be the supporting matrix with three dopant concentrations of 7 wt%, 7.4 wt% and 7.8 wt%.



**Fig. 4.** Emission spectrum of  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$  and low temperature phosphorescence (77 K) of Cl-PYO. Inset: emission decay character of  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$  upon pure N<sub>2</sub> and pure O<sub>2</sub> atmospheres.

Fig. 5 shows the solid state absorption spectra of the three composite samples, pure PVP and Re(CO)<sub>3</sub>(Cl-PYO)Br. The absorption spectrum of Re(CO)<sub>3</sub>(Cl-PYO)Br in solid state is similar with that of Re(CO)<sub>3</sub>(Cl-PYO)Br in CHCl<sub>3</sub> solution. However, the two peaks blue shift to 259 nm and 353 nm, compared with the corresponding ones in solution of 283 nm and 377 nm. This blue shift may be caused by the aggregation state difference. In other words, the solution absorption indicates the monomolecular absorption, while the solid absorption presents both monomolecular and intermolecular actions, as suggested by Section 'Single crystal structure of Re(CO)<sub>3</sub>(Cl-PYO)Br' part. As for pure PVP, its absorption spectrum exhibits two characteristic peaks at 259 nm and 309 nm. The absorption spectra of the three composite samples can nearly be considered as the simple adducts of the absorption spectra from PVP and Re(CO)<sub>3</sub>(Cl-PYO)Br. The characteristics of both PVP and Re(CO)<sub>3</sub>(Cl-PYO)Br are well preserved. which means that there is no strong interaction between PVP matrix and dopant molecules.

Fig. 6 shows the SEM images of the three composite samples. All fibers are randomly distributed on the substrate without branch structure, giving a uniform and smooth morphology. The mean diameters of the three composite samples are measured to be  $\sim$ 1.5 µm, with very slight variations, which may be attributed to the identical dominant supporting matrix and the low dopant concentration. The porous structure of these fibrous samples provides a high surface-to-volume-ratio as above mentioned, favoring quick response and sensitivity improvement. Under mercury lamp excitation, the composite fibers exhibit yellow emission which comes from Re(CO)<sub>3</sub>(Cl-PYO)Br dopant. The uniform emission confirms that Re(CO)<sub>3</sub>(Cl-PYO)Br has been successfully doped into PVP matrix homogenously. We have mentioned that there is pi-pi stacking in Re(CO)<sub>3</sub>(Cl-PYO)Br crystal, which may affect its PL performance [11]. However, when doped into PVP matrix, Re(CO)<sub>3</sub>(Cl-PYO)Br molecules are diluted and immobilized by the matrix. Thus, such pi-pi stacking can be eliminated in those composite samples, without affecting the sensing performance.

#### Sensing behavior of Re(CO)<sub>3</sub>(Cl-PYO)Br/PVP composite nanofibers

#### Spectral response

The emissions of the three composite samples are all quenchable by  $O_2$  and the emission intensity decreases largely with increasing  $O_2$  concentrations. Fig. 7 shows the emission spectra of the 7.4 wt% doped sample under various  $O_2$  concentrations. Clearly, the emission intensity at 544 nm decreases largely under pure  $O_2$  atmosphere, which evidentially confirms that the 7.4 wt% doped sample is an oxygen-sensitive material. Compared



Fig. 5. Solid state UV–Vis spectra of pure PVP, pure  $Re(CO)_3(CI-PYO)Br$  and the three composite nanofibers.



Fig. 6. SEM images of the 7.0 wt% doped sample (up left), the 7.4 wt% doped sample (up right), the 7.8 wt% doped sample (down left) and a preventative fluorescence microscopy image of the 7.4 wt% doped sample (down right).

with the emission spectrum of pure  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$  peaking at 560 nm, the doped sample exhibits blue shift tendency. We attribute the causation to rigidochromism as below. It has been pointed out that the geometric distortion that happens in complex excited state is mainly responsible for the energy loss of emissive center [11]. When doped into the polymer matrix of PVP, the geometric distortion can be suppressed by the rigid surrounding, leading to decreased Stokes shift and thus the spectral blue shift. Such blue shift has also been reported by literatures [8,14].

For comparison convenience, here we define a relative sensitivity as  $I_0/I_{100}$ , where  $I_0$  is the emission intensity under pure N<sub>2</sub> atmosphere and  $I_{100}$  is that under pure O<sub>2</sub> atmosphere. The sensitivity values of the three samples are listed in Table 3. It can be seen that the 7.4 wt% doped sample shows the highest sensitivity, which means that 7.4 wt% should be the optimal dopant concentration. Both higher dopant concentration and lower concentration can compromise the sensitivity, and we are giving an explanation as follows. There should be two factors that dominate the sensitivity [7,12,14,15]. One is the emission intensity from the sensing probes, the other is the self-quenching and self-absorption between the sensing probes. When the dopant concentration is low, the emission intensity is distinctly weak. leading to unsatisfied sensitivity. On the other hand, a much higher dopant concentration leads to severe self-quenching and self-absorption between the sensing probes which lead to emission intensity decrease, compromising the sensitivity. These two factors may get a balance in the 7.4 wt% doped sample, offering the maximum sensitivity of 7.88. This sensitivity value is found to be comparable with or even higher than literature values of similar sensing systems based on metal complexes, even though the excited state lifetime of Re(CO)<sub>3</sub>(Cl-PYO)Br is much shorter than theirs [12,14,15]. It is thus concluded that the enlarged conjugation plane in Cl-PYO is positive to improve sensitivity, as expected.

#### Stern-Volmer plots

If a sensing probe follows monoexponential decay pattern and localizes in homogenous medium, the intensity form of Stern–Volmer formula can then be presented as Formula 1, where  $I_0$  is the emission intensity under pure N<sub>2</sub> atmosphere, *I* stands for emission intensity,  $K_{SV}$  is Stern–Volmer constant and  $[O_2]$  is  $O_2$  concentration.

$$I_0/I = 1 + K_{SV}[O_2]$$
(1)



Fig. 7. The emission spectra of the 7.4 wt% doped sample under various  ${\rm O}_2$  concentrations.

According to Formula (1), the Stern–Volmer curve should be a linear one. However, the Stern–Volmer curves of the three composite samples are all nonlinear ones as shown in Fig. 8, which means that the sensing mechanism cannot be simply explained by Formula (1).

As mentioned above, the emission of  $\text{Re}(\text{CO})_3(\text{Cl-PYO})\text{Br}$  exhibits biexponential decay behavior with two components. It is thus expected that there should be at least two kinds of sensing sites within the composite samples. In this case, a two-site model of Formula (2) should be applied to describe the quenching mechanism, where  $f_1$  and  $f_2$  are the fractional contributions from each sensing site ( $f_1 + f_2 = 1$ ),  $K_{SV1}$  and  $K_{SV2}$  are the associated Stern–Volmer constants for each sensing site [7,14,15].

$$\frac{I_0}{I} = \frac{1}{\frac{f_1}{1 + K_{SV1}pO_2} + \frac{f_2}{1 + K_{SV2}pO_2}}$$
(2)

The fitting parameters are listed in Table 3. It is obvious to see that the quenching mechanism of the three composite samples can be well explained by Formula (2), which means that there are indeed at least two sensing sites within those samples. All  $K_{SV1}$  values are quite small, which means that site 1 is nearly immune to O<sub>2</sub> attack, compromising the linearity of Stern–Volmer curve and sensitivity improvement. We attribute this insensitive site to the short-lived component of  $\tau_2$  (0.277 µs) since its excited state lifetime is too

 Table 3

 Sensitivity values and nonlinear fitting results of the three composite samples.

Sample	I <sub>0</sub> / I <sub>100</sub>	$K_{SV1}$ ( $O_2\%^{-1}$ )	$K_{SV2}$ (0 <sub>2</sub> % <sup>-1</sup> )	$f_1$	$f_2$	R <sup>2</sup>
7.0 wt% doped	6.20	0.00663	0.18506	0.1982	0.8018	0.99957
7.4 wt% doped	7.88	0.00079	0.25665	0.1014	0.8986	0.99984
7.8 wt% doped	7.27	0.00261	0.27205	0.1341	0.8659	0.99931

short for O<sub>2</sub> to finish an effective quenching. This hypothesis is then confirmed by the emission decay character of Re(CO)<sub>3</sub>(Cl-PYO)Br under pure O<sub>2</sub> atmosphere mentioned above. Upon pure O<sub>2</sub> atmosphere, the decay lifetime greatly decreases to only 0.073 µs with single exponential decay pattern, which means that there is only one dominant decay process remaining. It is reasonable to say that the long-lived component has already been fully quenched, with the short-lived component left behind. Actually, the excited state lifetime of the short-lived component also decreases from 0.277 µs to 0.073 µs. It can thus be concluded that the insensitive site should be the short-lived component of Re(CO)<sub>3</sub>(Cl-PYO)Br. Compared with literature report based on phosphorescent Cu(I) complex and polymer matrix owing linear Stern-Volmer curve [8], the Stern-Volmer plots of Re(CO)<sub>3</sub>(Cl-PYO)Br based sensing systems are found to be underdeveloped. For future studies, the contribution from the short-lived component to emissive center should be minimized to achieve linear Stern-Volmer curve as well as high sensitivity.

#### Time scan spectrum

Fig. 9 shows the time scan spectrum of the 7.4 wt% doped sample under periodically varied atmospheres (pure  $O_2$  pure  $N_2$  pure  $O_2$  cycle). Upon pure  $O_2$  atmosphere, the emission intensity decreases largely. When changed to pure N<sub>2</sub> atmosphere, the emission intensity can always restore to its initial intensity, without showing photobleaching. PVP matrix is believed to be the cover for Re(CO)<sub>3</sub>(Cl-PYO)Br, which can protect the excited molecules from photodeconstruction. For compassion convenience, here, we define response time  $(T_{res})$  as the time taken for the sample to lose 95% of its initial emission intensity when the atmosphere changes from pure N<sub>2</sub> to pure O<sub>2</sub>. Similarly, the recovery time ( $T_{rec}$ ) as the time taken to recover 95% if its final emission intensity when the atmosphere changes from pure  $O_2$  to pure  $N_2$  [12]. The response time for the 7.4 wt% doped sample is obtained to be 11 s and the recovery time is as long as 19 s. Those values are comparable or even shorter than literature ones based on phosphorescent Cu(I)



Fig. 8. Stern–Volmer curves of the composite samples at various oxygen concentrations.



Fig. 9. The time scan spectrum of the 7.4 wt% doped sample under periodically varied atmospheres.

and Ru(II) complexes [7,8,14], suggesting that the 7.4 wt% doped sample is highly sensitive towards O<sub>2</sub>, and we attribute this rapid response to the large surface-area-to-volume ratio and porous channels which favor oxygen transportation. Another interesting phenomenon is that the recovery time is longer than the response time, which may be explained by the diffusion-controlled dynamic response and recovery behavior of a hyperbolic-type sensor reported by Mills and coworkers [16–19].

#### Conclusion

In this paper, we report the synthesis, single crystal structure, theoretical calculation and photophysical performance of a phosphorescent Re(I) complex of Re(CO)<sub>3</sub>(Cl-PYO)Br. The emission of Re(CO)<sub>3</sub>(Cl-PYO)Br owns a long-lived excited state lifetime of  $\tau_1$  = 1.415 µs ( $A_1$  = 0.274) and  $\tau_2$  = 0.277 µs ( $A_2$  = 1.187). Theoretical calculation on Re(CO)<sub>3</sub>(Cl-PYO)Br suggests that the emission at 560 nm comes from a triplet metal-to-ligand-charge-transfer character. By doping Re(CO)<sub>3</sub>(Cl-PYO)Br into a polymer supporting matrix of PVP, the emission of the corresponding composite materials is found to be sensitive towards various oxygen concentrations, with a maximum sensitivity of 7.88. We attribute this high sensitivity to the enlarged conjugation plane which could increase the population of excited state electrons and favor the oxygen attack on Re(CO)<sub>3</sub>(Cl-PYO)Br excited state. Owing to the porous structure of fibrous PVP matrix. a short response time of 11 s is also observed with good photostability. All these results suggest that phosphorescent Re(I) complexes doped fibrous membranes are promising candidates for low-cost and quick-response oxygen sensing materials. Further efforts are now being devoted to minimize the contribution from the short-lived component to the emissive center to achieve linear Stern-Volmer curve as well as high sensitivity.

#### Acknowledgement

This work was supported by the National Science Foundation, Beijing, China, under Grant 51274120.

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