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Oxygen optical sensing by doping a rhenium complex into a silica matrix: Design, characterization and performance

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ABSTRACT

The present paper synthesized a diamine ligand having an oxadiazole group and its Re(I) complex to investigate their potential for oxygen sensing. Conjugation chain in this ligand was increased so that collision probability between excited state electrons and O_2 molecules could be increased, favoring oxygen sensing. This Re(I) complex was confirmed and analyzed by single crystal structure, density functional theory calculation and photophysical measurement. It showed an emission peaking at 552 nm with two long-lived emissive components. Using a silica matrix of MCM-41, oxygen sensing performance of the resulting composite samples was analyzed and compared in detail. An optimal sample gave the highest sensitivity of 5.65 with short response time of 8 s.

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1. Introduction

Composite materials combine and hold features of their each component, and thus are gaining more research interests [1,2]. For a representative sample with organic–inorganic hybrid structure, its organic component usually focuses on sensing function since organic probes can be conveniently modified, while its inorganic component is usually designed as supporting matrix in virtue of its high mechanical strength and stability [2,3]. Some hybrid structures have been suggested so that each component, as well as its feature, can be well preserved [3,4].

Molecular O₂ is a life-supporting gas and thus considered as an important target in chemical industry, food processing and environmental protection [5,6]. Optical sensing systems for O₂ quantification have thus been intensively focused owing to their virtues of no analyte consumption, simple operation procedure and needing no sophisticated apparatuses [7,8]. Aiming at desired sensing performance, some criteria should be considered. For example, supporting matrix is responsible for dispersing probe molecules and allowing smooth analyte diffusion. Thus, an ideal one should has high diffusion coefficient, good photostability and compatibility with probe [9–12]. A silica based supporting matrix MCM-41 has been usually suggested among the numerous candidates [11,12].

For an ideal oxygen sensing probe, long lifetime and large distribution of excited electrons are desired since they increase sensing collision probability with analyte. Emissive metal complexes, Theoretical analysis on them suggests that their occupied frontier molecular orbitals (FMOs) have metal character, while their unoccupied FMOs are essentially ligand π^* [13–16]. Large distribution of excited electrons can be achieved by increasing ligand conjugation plane. What's more, electron-pulling group in conjugation plane may decrease non-radiative decay probability, increasing emission lifetime. Enlightened by above consideration, we intent to design a dia-

especially Re(I)-based ones, have been proved attractive [13-16].

mine ligand with a large conjugation plane and an electron-pulling group, as shown by Scheme 1. Its corresponding Re(I) complex is anticipated to be a promising probe for oxygen sensing. By doping this Re(I) complex into a silica matrix MCM-41, oxygen sensing composites are constructed. Corresponding sensing performance, along with sensing mechanism, is investigated.

2. Experimental

2.1. General information for reagents and apparatus

General reagents for ligand and complex synthesis are summarized as follows. Starting chemical 2-(2H-tetrazol-5-yl)pyridine (TPD) was synthesized following a reported method [17]. Other compounds, such as Re(CO)₅Br, 4-methylbenzoyl chloride, zinc bromide, sodium azide and MCM-41, were commercially provided by Yiquan Chemical Co. (Hangzhou) and used without further purifications. Organic solvents were purified through standard procedures before usage.







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Scheme 1. Synthesis and construction method for ligand POD, Re(I) complex Re(CO)₃(POD)Br and Re(CO)₃(POD)Br doped MCM-41.

Elemental analysis was taken on a Vario Element Analyzer. NMR, MS, UV-Vis absorption and emission spectra were measured using 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, respectively. Single crystal data were collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector, using graphite-monochromated Mo Ka radiation (50 kV, 30 A, 298 K). All hydrogen atoms were calculated. Emission lifetimes were recorded by a two-channel TEKTRONIX TDS-3052 oscilloscope, with pulsed Nd:YAG laser as excitation source (λ = 355 nm). Small-angle X-ray diffraction (SAXRD) was finished by a Rigaku-Dmax 2500 diffractometer ($\lambda = 0.154$ nm, scanning step = 0.02°). Theoretical calculation was carried out using GAMESS software at RB3LYP1/SBKJC level with Re(CO)₃ (POD)Br single crystal as initial geometry. Graphical presentation for FMOs was plotted by wxMacMolPlt with contour value of 0.025.

2.2. Synthesis of diamine ligand POD

Diamine ligand POD was synthesized following a reported procedure [17]. The mixture of TPD (10 mmol), 4-methylbenzoyl chloride (11 mmol) and anhydrous pyridine was stirred under ice bath for 30 min. Then this solution was heated to reflux and kept for 3 days. After cooling, plenty of water was added. The resulting crude product was collected and purified on a silica gel column (*n*-hexane: ethyl acetate = 50:1). ¹H NMR (CDCl₃): δ 2.42 (3H, s), 7.28 (2H, d, *J* = 6.0), 7.44 (1H, t), 7.90 (1H, t), 8.12 (2H, d, *J* = 6.0), 8.33 (1H, d, *J* = 6.0), 8.80 (1H, d, *J* = 3.6). *Anal.* Calc. For C₁₄H₁₁N₃O: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.93; H, 4.77; N, 17.54%. MS *m*/*z*: [m]⁺ calc. for C₁₄H₁₁N₃O, 237.1; found, 237.0.

2.3. Synthesis of complex Re(CO)₃(POD)Br

Complex Re(CO)₃(POD)Br was synthesized following a reported procedure [15]. The mixture of POD (5 mmol), Re(CO)₅Br (5 mmol) and toluene (25 mL) was heated to reflux under N₂ protection and kept for 12 h. Solvent toluene was extracted by rotary evaporation. The resulting crude product was purified on a silica gel column. ¹H NMR (300 MHz, CDCl₃): δ 2.56 (3H, s), 7.62 (1H, m), 7.73 (2H, m), 7.90 (1H, m), 8.31 (1H, t), 8.39 (1H, t), 8.42 (1H, d, *J* = 6.0), 8.95

(1H, d, *J* = 4.0). *Anal.* Calc. for $C_{17}H_{11}BrN_3O_4Re$: C, 34.76, H, 1.89, N, 7.15. Found: C, 34.67, H, 1.69, N, 7.31%. MS *m*/*z*: [m]⁺ calc. for $C_{17}H_{11}BrN_3O_4Re$, 586.9; found, 587.0. Its single crystal (CCDC 1096376) XRD analysis will be discussed in detail later.

2.4. Construction of composite Re(CO)₃(POD)Br doped MCM-41

Sensing composites were constructed by doping $\text{Re}(\text{CO})_3(\text{POD})$ Br into MCM-41 matrix with various doping concentrations, following below procedure [11,12]. Different amounts of $\text{Re}(\text{CO})_3$ (POD)Br were weighed and separately dissolved into CH_2Cl_2 (5 mL) solutions under stirring. MCM-41 matrix (1 g per portion) was added and stirred at room temperature for 30 min. Solid sample was then filtered off and washed with CH_2Cl_2 (10 mL × 3) to give sensing composite as light yellow powder.

3. Results and discussion

3.1. Single crystal structure of Re(CO)₃(POD)Br

 $Re(CO)_3(POD)Br$ is firstly investigated by its single crystal structure. As shown in Fig. 1A, $Re(CO)_3(POD)Br$ takes an octahedral coordination mode, which is consistent with literatures [13–15]. Selected geometric parameters listed in Table 1 suggest that this coordination field is a distorted one owing to the heterogeneous ligands in $Re(CO)_3(POD)Br$. It is noticed that the three Re–C bonds are slightly different from each other even though they have the same CO ligand. The two Re–N are slightly different from each other. Most bite angles in Table 1 are close to 90°, which are similar to literature values [13–15]. N–Re–N bite angle, however, is smaller than those in tetrahedral field [13–16]. These ligands try to achieve an optimal coordination with Re(I) center by adjusting their geometry. There is roomy space in Re(CO)_3(POD)Br coordination sphere, favoring oxygen attack.

A large conjugation plane is formed by a pyridine ring, an oxadiazole ring and a phenyl ring in POD ligand. Π - π attraction between POD planes makes Re(CO)₃(POD)Br molecules align in a highly ordered mode, as shown in Fig. 1B. POD planes of these molecules are nearly parallel to each other with minimal distance of 3.338 Å, which confirms the face-to-face π - π attraction between them. Zhang and coworkers have confirmed that such π -stacking is



Fig. 1A. Molecular structure of Re(CO)₃(POD)Br obtained from its single crystal.



Fig. 1B. Crystal packing mode of Re(CO)₃(POD)Br.

Table 1

Selected geometric parameters of Re(CO)₃(POD)Br single crystal.

Bond length	Å	Bond angle	٥
Re(01)-C(1)	1.890	N(11)-Re(01)-N(12)	73.20
Re(01)-C(2)	1.911	N(11)-Re(01)-C(3)	91.65
Re(01)-C(3)	1.903	N(12)-Re(01)-C(3)	95.78
Re(01)-Br(25)	2.615	N(11)-Re(01)-Br(25)	86.25
Re(01)-N(11)	2.239	N(12)-Re(01)-Br(25)	84.69
Re(01)-N(12)	2.169	C(1)-Re(01)-Br(25)	92.81
		C(2)-Re(01)-Br(25)	89.82
		C(1)-Re(01)-C(2)	88.54

a rigid structure which decreases structural distortion that happens in excited state, showing emission blue shift, long lifetime and high emission yield [16,18,19]. For sensing application, however, such π -stacking should be eliminated since this highly ordered array may block O₂ diffusion and thus compromise sensing procedure.

3.2. Electronic transitions of Re(CO)₃(POD)Br

Considering that oxygen sensing procedure is finished through an energy transfer collision between probe excited state and O_2 molecules, it would be necessary to get a clear understanding on the electronic nature of Re(CO)₃(POD)Br [11,12]. Density functional theory calculation is used here to explore its electronic transition [13–16]. Tables 2 and 3 give percentage composition of the first ten singlet excitations and their FMOs. Clearly, these onset electronic excitations are composed of transitions from occupied FMOs to unoccupied ones. These occupied FMOs are Re d orbitals in nature, admixed with contributions from other ligands. On the other hand, unoccupied FMOs are mainly composed of POD π^* , with slim contributions from other ligands and Re center. Electronic transitions between occupied and unoccupied FMOs are thus assigned as a mixed nature of metal-to-ligand-charge-transfer (MLCT) and ligand-to-ligand-charge-transfer (LLCT), as shown in Fig. 2 [13]. In its first excited state, electrons are localized at POD π^* with lifetime as long as a few microseconds owing to heavy metal turbulence effect. These long-lived excited electrons are vulnerable to O₂ attack, giving sensing signal.

3.3. Photophysical evaluation on probe Re(CO)₃(POD)Br

3.3.1. Absorption and excitation spectra

Fig. 3 gives Re(CO)₃(POD)Br UV–Vis absorption and excitation spectra in CH₂Cl₂ (10 μ M). Four absorption bands are observed, peaking at 237 nm, 290 nm, 329 nm and ~390 nm, respectively. The former three bands are similar to POD absorption shown in Fig. 3. They are thus attributed to ligand $\pi \rightarrow \pi^*$ (ILCT) transition. The last absorption band is a weak and broad one. No similar band is observed in POD absorption. Bearing above theoretical analysis result in mind, this new absorption band is assigned to MLCT/LLCT absorption [13–15]. Conjugation chain in POD is much longer than that in Phen, and Re(CO)₃(POD)Br optical edge is supposed to be moved to a long wavelength. Optical edge of Re(CO)₃(PDD)Br is determined as ~475 nm which is similar to that of Re(CO)₃(Phen)

Table 2	2
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Percentage composition of the first ten singlet excitations calculated at RB3LYP1/ SBKJC level.

Transitions	Energy (eV)	Composition
$S_0 \rightarrow S_1$	1.7748	70-71 (98.6%)
$S_0 \rightarrow S_2$	2.0040	69-71 (98.0%)
$S_0 \to S_3$	2.6563	68-71 (98.6%)
$S_0 \rightarrow S_4$	2.7338	70–72 (96.2%)
$S_0 \rightarrow S_5$	2.8541	69-72 (97.6%)
$S_0 \rightarrow S_6$	3.0450	67-71 (86.0%)/66-71 (11.6%)
$S_0 \rightarrow S_7$	3.1814	70-73 (93.5%)
$S_0 \rightarrow S_8$	3.2799	66-71 (56.4%)/69-73 (29.2%)/70-73 (3.9%)
$S_0 \rightarrow S_9$	3.3152	69-73 (68.8%)/66-71 (24.6%)
$S_0 \to S_{10}$	3.6321	68-72 (97.7%)

 Table 3

 Percentage composition of selected frontier molecular orbitals calculated at RB3LYP1/SBKJC level.

MOs	Energy (eV)	Contribution			
		Re	Br	СО	POD
73	-1.845	0.6	0.3	1.1	98.0
72	-2.253	1.3	0.4	1.6	96.7
71 (LUMO)	-3.099	5.3	2.0	3.9	88.8
70 (HOMO)	-5.627	35.5	41.8	18.2	4.4
69	-5.747	29.0	48.0	14.2	8.9
68	-6.566	61.4	0.7	27.6	10.2
67	-6.876	33.3	32.0	14.3	20.4
66	-6.993	36.8	34.0	16.4	12.0

Br, where Phen = 1,10-phenanthroline. We attribute the restricted optical edge of $Re(CO)_3(POD)Br$ to its electron-pulling group of oxadiazole [16].

Despite of their high absorption coefficients, the former three absorption bands are ineffective on exciting Re(CO)₃(POD)Br emissive center, as shown in Fig. 3. The last weak absorption band, however, is an effective excitation. This fact can be explained as follows. As above mentioned, the former three absorption bands are ligand $\pi \rightarrow \pi^*$ transitions whose molar distinction coefficients are much higher than that of MLCT transition [19]. These ligand $\pi \rightarrow \pi^*$ transitions, however, have to experience a series of system crossing procedures before transferring their energy to the emissive center, leading to their poor excitation efficiency. On the other hand, MLCT state can directly transfer its energy to the emissive center since the emissive center is derived from this MLCT state, showing a high coefficient.



Fig. 3. UV-Vis absorption (abs.) and excitation (ex.) spectra of $Re(CO)_3(POD)Br$ and POD in CH_2Cl_2 (10 μ M).

3.3.2. Emission spectra and lifetime

 $Re(CO)_3(POD)Br$ emission spectrum in CH_2Cl_2 (10 $\mu M)$ has a maximum at 552 nm with FWHM of 76 nm, as shown in Fig. 4, where FWHM means full width at half maximum. There are no vibronic progressions. Stokes shift between absorption edge (475 nm) and emission maximum (552 nm) is 77 nm. These factors suggest that $Re(CO)_3(POD)Br$ emissive center is a charge-transferderived one, which is consistent with our theoretical calculation



Fig. 2. FMOs of Re(CO)₃(POD)Br (up, HOMO; down, LUMO).



Fig. 4. Emission spectrum of Re(CO)₃(POD)Br in CH₂Cl₂ (10 μ M) and POD at 77 K (λ_{ex} = 355 nm). Inset: emission decay dynamics of Re(CO)₃(POD)Br in CH₂Cl₂ (10 μ M).

result [13]. Emission maximum and FWHM of a reference complex $Re(CO)_3$ (Phen)Br have been reported as 554 nm and 90 nm by Si and coworkers, respectively [15]. It is observed that the structural relaxation that happens in $Re(CO)_3$ (POD)Br excited state is limited. We attribute its causation to the roomy coordination sphere in Re (CO)_3(POD)Br and the electron-pulling group in POD ligand. To be more specific, for a crowded environment, the strong steric hindrance between ligands leads to distortion and tension. Many vibration levels are thus generated, which facilitates non-radiative decay. In a roomy coordination sphere, ligands are freely extended, their vibration levels are thus decreased, favoring radiative decay of emissive center.

Re(CO)₃(POD)Br excited state is analyzed by its emission decay dynamics, as shown by the inset of Fig. 4. Clearly, this emission follows a biexponential decay pattern with $\tau_1 = 0.409 \ \mu s (A_1 = 0.293)$ and $\tau_2 = 0.0797 \ \mu s (A_2 = 1.974)$, respectively. These two components are consistent with the MLCT/LLCT transition nature of Re (CO)₃(POD)Br. Phosphorescent nature of Re(CO)₃(POD)Br emission is thus confirmed by these long-lived decay components. According to the statement by Si and coworkers, the observation of an obvious absorption in $\pi \rightarrow \pi^*$ region and a short-lived decay component means a potential surface crossing procedure from $\pi \rightarrow \pi^*$ state to MLCT state [15]. The long-lived component τ_1 is thus recognized as radiative decay of MLCT state, while the short-lived one is attributed to radiative decay of $\pi \rightarrow \pi^*$ state. Such assignment agrees with electronic nature of each component.

Emission quantum yield of Re(CO)₃(POD)Br in CH₂Cl₂ (10 μ M) is determined by a literature method and obtained as 0.030 [19]. Compared to those of superior emitters, this emission yield is not satisfactory enough [13-16]. For a better understanding on our probe, its radiative probability (K_r) and non-radiative probability $(K_{\rm nr})$ are calculated as $0.135 \times 10^6 \, {\rm s}^{-1}$ and $4.370 \times 10^6 \, {\rm s}^{-1}$, respectively, by Formulas (1)–(3). It is observed that Re(CO)₃(POD)Br emissive state is dominated by its non-radiative decay path, leading to its poor emission yield. Geometric relaxation that happens in excited state has been proved as a major non-radiative decay path for MLCT excited state. There is, however, another possible path to be considered, namely the electronic configuration transition between ³MLCT state to ³LC (ligand centered) state. As reported by Zhang and coworkers, a large conjugation plane in ligand can lead to such electronic configuration transition, even though there is an electron-pulling group in it [16]. POD ³LC energy is determined as 394 nm by its low temperature phosphorescence spectrum, as shown in Fig. 4. This ³LC level is much higher than ³MLCT state, which denies the possibility of electronic configuration transition between ³MLCT state to ³LC state. As a consequence, geometric relaxation of MLCT excited state should be claimed as the major reason leading to $Re(CO)_3(POD)Br$'s unsatisfactory emission yield. To improve emission yield, complex geometric relaxation should be limited through ligands having large steric hindrance. Our first guess is to explore multidentate ligands so that geometric relaxation can be restrained without compromising O_2 diffusion.

$$\Phi = \frac{K_{\rm r}}{K_{\rm r} + K_{\rm nr}} \tag{1}$$

$$\frac{1}{\tau} = K_{\rm r} + K_{\rm nr} \tag{2}$$

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{3}$$

3.4. Morphology and characterization of Re(CO)₃(POD)Br doped MCM-41

Aiming at fluent and smooth analyte diffusion, probe is usually immobilized in supporting matrix. Meanwhile, self-quenching between probe molecules can be minimized [11,12]. MCM-41 has been proved as a promising supporting matrix for oxygen sensing purpose owing to its highly ordered tunnels [11,12]. In this initial effort, we choose MCM-41 as supporting matrix to explore oxygen sensing performance of Re(CO)₃(POD)Br. Three doping concentrations, 50 mg/g, 60 mg/g and 70 mg/g, are tried for performance comparison. These Re(CO)₃(POD)Br doped MCM-41 samples are firstly analyzed by their small angle X-ray diffraction (SAXRD) patterns shown in Fig. 5. There are three well-resolved Bragg reflection peaks in each curve, indexed as d_{100} , d_{110} , and d_{200} , respectively. Despite of their different intensity values, their 20° are nearly identical to corresponding ones of blank MCM-41 sample [11,12]. We thus tentatively come to a conclusion that the highly ordered tunnels in MCM-41 supporting matrix have been perfectly preserved after probe loading procedure.

To confirm that $\text{Re}(\text{CO})_3(\text{POD})\text{Br}$ has been successfully doped into MCM-41, absorption and solid state diffuse reflection spectra of blank MCM-41 and a representative sample (60 mg/g doped) are shown in Fig. 6. Blank MCM-41 is essentially silica and thus



Fig. 5. SAXRD curves of Re(CO)_3(POD)Br doped MCM-41 (50 mg/g, 60 mg/g and 70 mg/g) and blank MCM-41.



Fig. 6. Absorption (abs.) and solid state diffuse reflection (Ref.) spectra of blank MCM-41 and a representative sample (60 mg/g doped).

has slim absorption in the whole UV-Vis region. Correspondingly, its solid state reflection spectrum shows strong reflection from 200 nm to 600 nm. Absorption spectrum of 60 mg/g doped sample is consistent with that of Re(CO)₃(POP)Br in CH₂Cl₂, showing absorption bands peaking at 238 nm, 276 nm and 366 nm, respectively. It is thus confirmed that Re(CO)₃(POP)Br has been successfully loaded into MCM-41 matrix. Correspondingly, its solid state reflection spectrum has two minima peaking at 263 nm and 360 nm, respectively, which is consistent with its absorption bands. There are no new absorption or reflection bands, suggesting that dopant molecules are simply immobilized in MCM-41 tunnels with no strong interaction with them. We thus come to a conclusion that Re(CO)₃(POD)Br molecules are simply immobilized in MCM-41 tunnels with no strong interaction with them. The interaction between dopant and matrix exerts slim effect on sensing performance. In other words, sensing performance is dominated by dopant itself, which is consistent with literature reports [11,12,17,18].

3.5. Sensing performance of Re(CO)₃(POD)Br doped MCM-41

3.5.1. Sensitivity

Emission spectra of Re(CO)₃(POD)Br doped MCM-41 samples towards various O₂ concentrations are recorded to evaluate their oxygen sensing performance. As shown in Fig. 7, the presence of O₂ quenches sample emission effectively, giving sensing signals. For comparison, maximum sensitivity of each sample is defined as its ratio of I_0/I_{100} , where I_0 and I_{100} are emission intensity values in pure N₂ atmosphere and in pure O₂ atmosphere, respectively. Sensitivity values and other key sensing parameters of Re(CO)₃ (POD)Br doped MCM-41 samples are listed in Table 4. Our sensitivity values are found comparable to or even higher than literature values [11,12,13-18]. For similar sensing systems with Re(CO)₃ (IPD-Et)Br [IPD-Et = 4-(1-ethyl-1H-imidazo[4,5-f]][1,10]phenanthrolin-2-yl)-N,N-diphenylaniline] as dopant, their sensitivity is 3.99 with a long excited state lifetime of 4.68 µs [20]. Sensitivity of our samples is found higher (5.65) even though our excited state lifetime is only 0.222 µs. The positive effect of large conjugation chain on sensing performance can be confirmed. As a consequence, the following factors should be responsible for our improve sensing performance. First, collision probability between probe and O₂ is increased by the large conjugation plane in POD and the long-lived phosphorescent emissive center. Second, there is roomy space in Re(CO)₃(POD)Br coordination sphere, which favors oxygen



Fig. 7A. Emission spectra of $Re(CO)_3(POD)Br$ doped MCM-41 sample (50 mg/g) towards various O_2 concentrations from 0% to 100% (interval = 10%).



Fig. 7B. Emission spectra of $Re(CO)_3(POD)Br$ doped MCM-41 sample (60 mg/g) towards various O₂ concentrations from 0% to 100% (interval = 10%).



Fig. 7C. Emission spectra of $Re(CO)_3(POD)Br$ doped MCM-41 sample (70 mg/g) towards various O₂ concentrations from 0% to 100% (interval = 10%).

Table 4	
Key sensing parameters of Re(CO) ₃ (POD)Br doped MCM-	-41 samples.

Sample	λ (nm)	I_0/I_{100}	$K_{SV1} (O_2 \%^{-1})$	$K_{SV2} (O_2 \%^{-1})$	f_{01}	f_{02}	R^2	$T_{\rm res}(s)$	$T_{\rm rec}(s)$
50 mg/g	545	5.34	0.2004	0.0004	0.847	0.153	0.9990	9	21
60 mg/g	548	5.65	0.1943	0.0024	0.831	0.169	0.9994	8	17
70 mg/g	548	5.03	0.2019	0.0031	0.792	0.208	0.9991	9	22

attack. Third, MCM-41 matrix guarantees efficient O_2 transportation and diffusion, which is positive for O_2 sensing.

Never the less, our sensitivity (5.65) is still underdeveloped compared to literature values [11,12]. After a careful comparison between our result and literatures, we come to a conclusion that probe structure difference between our system and literature ones should be the major factor leading to our underdeveloped sensitivity. For a Ru(II)-based probe, all diamine ligands (sensing area) are open for oxygen attack, showing high sensitivity values [11,12]. For our Re(I)-based probe, its diamine ligand (sensing area) is covered by other ligands (CO, Br). O₂ molecules thus have to find a way to attack the excited electrons in diamine ligand, compromising sensitivity.

Compared to Re(CO)₃(POD)Br emission in CH₂Cl₂ (552 nm), Re (CO)₃(POD)Br emission in MCM-41 matrix shows a slight blue shift, which is attributed to rigidochromism [11,12]. FWHM values of these composite samples (~88 nm) are found larger than that of Re(CO)₃(POD)Br in CH₂Cl₂ (76 nm). We thus come to a conclusion that Re(CO)₃(POD)Br molecules have been trapped in MCM-41 matrix, depressing geometric relaxation.

It seems that 60 mg/g is the optimal doping concentration, while both a higher one (70 mg/g) and a lower one (50 mg/g) compromise sensitivity. Assuming that there are two opposite factors affecting sensitivity. One should be probe amount, the other should be self-quenching between probe molecules. Probe emission is rather weak when doping concentration is low, showing poor sensitivity. On the other hand, if probe molecules are more than enough, probe emission may be compromised by their self-quenching effect, leading to a decreased sensitivity [14–18]. There may be both enough probe molecules and limited self-quenching effect in the 60 mg/g doped sample, showing the highest sensitivity value.

3.5.2. Stern–Volmer working curves

To identify the sensing mechanism in Re(CO)₃(POD)Br doped MCM-41 samples, emission decay dynamics of a representative sample (60 mg/g) are recorded under pure N_2 , air and pure O_2 conditions, as shown by the inset of Fig. 8. Unlike the case in CH₂Cl₂ solution, Re(CO)₃(POD)Br emission in MCM-41 matrix follows single exponential decay mode with lifetimes of 7.79 μ s in pure N₂, 0.57 μ s in air and 0.43 μ s in pure O₂ conditions. These long-lived lifetimes clearly come from Re(CO)₃(POD)Br dopant, indicating its successful loading in MCM-41 matrix. This single exponential decay pattern suggests that all probe molecules are uniformly distributed in matrix [11,12]. These lifetime values are much longer than that in CH₂Cl₂ solution, which has been attributed to rigidochromism as above mentioned. It appears that probe excited state is vulnerable to O₂ molecules, suggesting a dynamic sensing mechanism described as Formula (4), where "*" means excited state.

$$Probe^* + {}^3O_2 \rightarrow Probe + {}^1O_2^* \tag{4}$$

Considering that (1) probe molecules are homogeneously distributed in matrix; (2) their emission follows single exponential decay mode; (3) sensing mechanism is a dynamic one, emission spectral response can be analyzed by Stern–Volmer equation [11,12,17]. As shown by Formula (5), an ideal Stern–Volmer work-



Fig. 8. Stern–Volmer curves of $Re(CO)_3(POD)Br$ doped MCM-41 (50 mg/g, 60 mg/g and 70 mg/g). Sensing error for each point is presented in cap. Inset: emission decay dynamics of a representative sample (60 mg/g) under pure N₂, pure O₂ and air conditions.



Fig. 9. Emission monitoring of $Re(CO)_3(POD)Br$ doped MCM-41 (50 mg/g, 60 mg/g and 70 mg/g) when atmosphere is periodically switched between 100% N_2 and 100% O_2 .

ing curve should be a linear one with slope of K_{SV} , where I and I_0 are emission intensity and maximum emission intensity under pure N₂ condition, respectively, K_{SV} and $[O_2]$ are Stern–Volmer constant and O₂ concentration, respectively [11,12]. Our Stern–Volmer working curves shown in Fig. 8, however, are not linear ones, which means that the sensing procedure in Re(CO)₃(POD)Br doped MCM-41 samples is a complicated one (Fig. 9).

$$I_0/I = 1 + K_{\rm SV}[O_2] \tag{5}$$

We tentatively assume that there are two kinds of sensing sites in these samples: only one of them is guenchable by O_2 molecules while the other is not. Given this hypothesis, Stern-Volmer equation should be modified with contribution of each sensing site taken into account. This modified equation is described as Formula (6), where f_{1} , f_{2} , K_{SV1} and K_{SV2} stand for fractional contributions and corresponding Stern-Volmer constants of sensing sites, respectively [11,12]. From fitting parameters listed in Table 4, it is observed that this modified formula fits well with our working curves. For all samples, K_{SV2} value is smaller than K_{SV1} value by two orders of magnitude, which means that sensing site-2 is highly insensitive to O₂ molecules. Non-linearity of our working curves and compromised sensitivity values are caused by this sensing site-2. This site is tentatively attributed to the "far-corner" in composite samples which is impenetrable by O₂ diffusion. For further improvement, composite structure should be modified to eliminate or decrease the amount of such "far-corner".

$$\frac{I_0}{I} = \frac{1}{\frac{f_1}{1 + K_{SV1}pO_2} + \frac{f_2}{1 + K_{SV2}pO_2}}$$
(6)

3.5.3. Response/recovery character and photostability

For a further confirmation on the correlation between sample emission and O2 existence, emission of Re(CO)3(POD)Br doped MCM-41 samples is monitored when atmosphere is periodically switched between 100% N₂ and 100% O₂. Clearly, sample emission is dependent on O_2 existence. Under pure N_2 condition, sample emission is maintained well, suffering from no photobleaching or photodecomposition. When atmosphere is switched to pure O_2 condition, sample emission is quenched to minimal level instantly. Such cycle can be fully repeated with no hysteresis. For comparison convenience, response $(T_{res})/recovery (T_{rec})$ time is defined as the time taken by a sample to decrease/increase to 95% of its initial emission intensity when atmosphere is periodically switched [11,12]. As shown in Table 4, T_{res} and T_{rec} values are found comparable to or even smaller than literature values, which can be attributed to the following factors [11,12]. First, the large POD conjugation chain and the long-lived MLCT excited state increase sensing collision probability between probe and O₂ molecules. Second, steric hindrance for O₂ attack around Re(CO)₃(POD)Br is limited owing to its small ligands. Third, the highly ordered MCM-41 tunnels guarantee efficient O₂ transportation and diffusion. As shown in Table 4, recovery time values are obviously longer than response time values, which can be explained by diffusion-controlled dynamic response and recovery behavior [21]. This observation is consistent with literature reports on similar systems [11,12,17].

4. Conclusion

As a conclusion, this paper developed $Re(CO)_3(POD)Br$ as a probe for oxygen sensing. An electron-pulling oxadiazole group

was incorporated into POD ligand to increase its conjugation chain. As a consequence, distribution and lifetime of excited electrons were increased to meet oxygen sensing collision. Our hypothesis was confirmed by single crystal analysis, theoretical calculation and photophysical measurement. By doping Re(CO)₃(POD)Br into MCM-41 matrix, oxygen sensing performance was carefully discussed. It was found that oxygen sensing was finished through a dynamic mechanism, showing the highest sensitivity of 5.65 and the shortest response time of 8 s. This promising performance was attributed to the following factors. First, the large conjugation chain in POD and the long-lived MLCT excited state increased collision probability between probe and O₂ molecules. Second, steric hindrance for O₂ attack around Re(CO)₃(POD)Br was limited owing to its small ligands. Third, the highly ordered tunnels of MCM-41 matrix guaranteed efficient O₂ transportation and diffusion. For further improvement, composite structure should be modified. hoping to eliminate or decrease the amount of "far-corner".

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.09.024.

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