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Synthesis, characterization and oxygen-sensing performance of a rhenium complex having an enlarged sensing area

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ABSTRACT

In this paper, we reported a Re(I) complex $Re(CO)_3$(IPD-Et)Br having an enlarged conjugation chain for oxygen sensing purpose, where IPD-Et=4-(1-ethyl-1 *H*-imidazo [4,5-f][1,10] phenanthrolin-2-yl)-*N*,*N*-diphenylaniline. Its conjugation chain was composed of triphenylamine group and imidazole group. In addition, an alkyl chain was connected with this N–N ligand to breach π–π attraction between ligand planes. It was assumed that above two factors could improve oxygen sensing sensitivity. Theoretical calculation and analysis firstly confirmed this hypothesis. Then photophysical measurement on $Re(CO)_3$(IPD-Et)Br suggested that its emission was a lon-lived one peaking at 545 nm and thus vulnerable to molecular O_2. Composite systems were constructed for oxygen sensing, using $Re(CO)_3$(IPD-Et)Br as probe and mesoporous silicate MCM-41 as supporting matrix, respectively. Linear Stern–Volmer curves, short response time of ~13 s and high sensitivity of 3.99 were finally obtained.

1. Introduction

As an important issue in various branches of chemical analysis and engineering, food processing, medical treatment and environmental protection, techniques for oxygen concentration determination have always been developing [1,2]. Some classic techniques can usually provide precise and reliable results, including Winkler titration and Clark electrode approach [3,4]. Nevertheless, there are also some problems to be solved, such as analyte consumption, complicated operation procedures and the necessity of professional equipments. Thus, efforts should be devoted to the exploration for novel oxygen sensing techniques.

Optical sensing technique is now drawing much attention owing to their advantages in terms of fast response, simple sensing operation and limited requirement for equipments [5,6]. A typical sensing system consists of a probe and its supporting matrix [5–8]. The probe is responsible for analyte recognition, while the supporting matrix allows smooth analyte diffusion and minimizes probe self-quenching. There are criteria for an ideal supporting matrix: (1) high diffusion coefficient, allowing fast response; (2) good compatibility, eliminating phase separation between probe and supporting matrix; (3) high photostability, giving reliable sensing results. To meet above requirements, many candidates have been tried and reported. As a promising one, mesoporous silica molecular sieve MCM-41 has been proved promising owing to its high O_2 diffusion coefficient, highly ordered mesoporous structure, high photostability and good compatibility with various probes [7,8].

To increase collision probability with O_2 molecules, long excited state lifetime is desired from sensing probes [7–10]. Transition metal complexes usually have long-lived emissive centers at microsecond scale and thus can well satisfy this requirement. As a class of representative phosphorescent emitters, rhenium (I) complexes with molecular formula of $Re(CO)_3$(N–N)X have been intensively studied, where N–N and X stand for a diamine ligand and a halogen atom, respectively [11,12]. It has been reported that ground state electrons localize at metal center, while excited state electrons migrate to complex LUMO which is essentially π^* ortbial of diamine ligand [9,11]. Photo-active excitations correspond to the electronic transitions between metal center and N–N π^* ortbial. If excited electrons transfer their energy to surrounding energy acceptors, complex emission will be quenched, showing sensing behavior.

It is thus reasonable to assume that a large conjugation plane in N–N ligand can increase O_2 collision probability and thus improve sensing performance. Zhang and coworkers have suggested that π–π stacking between ligand conjugation planes makes complex molecules take a bonded structure, barricading quencher attack. In addition, oversized conjugation chain in N–N ligand can quench MLCT emissive center through a thermally activated electronic transition from ^{3}MLCT state to ^{3}LC state, where LC and MLCT are ligand-centered and metal-to-ligand–charge–transfer, respectively [12,13]. As a consequence, conjugation chain in N–N ligand should

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be finely adjusted aiming at large enough sensing area, limited π–π stacking and no electronic transition from ^{3}MLCT state to ^{3}LC state.

In this report, we decide to synthesize a N–N ligand with triphenylamine and imidazole groups to meet above requirement. Its conjugation chain is enlarged by triphenylamine group but also limited by imidazole group. In addition, an alkyl chain is connected with this N–N ligand to breach π–π attraction between ligand planes. Photophysical feature and oxygen sensing performance of its corresponding Re(I) complex are analyzed to confirm our hypothesis. Molecular structures of our N–N ligand and corresponding Re (I) complex are shown in Scheme 1.

2. Experimental details

2.1. General information

Starting chemicals and materials used in this work, including 1,10-phenanthroline, triphenylamine, Re(CO)$_5$Br, EtBr and blank MCM-41, were purchased from Aldrich Chemical Co. and used as received. Inorganic salts and organic solvents were bought from Shanghai Chemical Cooperation. Organic solvents were redistilled before usage. Sample characterization was finished by the following equipments. A Varian INOVA 300 spectrometer was used to record NMR spectra. A Vario Element Analyzer was responsible for elemental analysis. A Hitachi F-4500 fluorescence spectrophotometer and a Shimadzu UV-3101PC spectrophotometer were applied for phtophysical measurement. Excited state decay data were collected by a two-channel TEKTRONIX TDS-3052 oscilloscope, using pulsed Nd:YAG laser as excitation source ($\lambda = 266$ nm). A Rigaku-Dmax 2500 diffracrtometer ($\lambda = 0.154$ nm, scanning step$=0.02°$) was used to measure small-angle X-ray diffraction (SAXRD) patterns. Above operations were taken in the air at room temperature without specific notifications. Structural optimization was performed by MOPAC 2006 with PM7 Hamiltonian. Density functional theory calculation was finished by GAMESS using function of RB3PW91 and an effective core potential (ECP) basis set of SBKJC. Graphical presentation for frontier molecular orbitals was plotted by wxMacMolPlt, with contour value of 0.025.

2.2. Synthesis of IPD-Et

4-(1-ethyl-1*H*-imidazo [4,5-f] [1,10] phenanthrolin-2-yl)-*N*,*N*-diphenylaniline (IPD-Et) was synthesized following a two-step procedure which was described as follows. Starting compounds of 1,10-phenanthroline-5,6-dione and 4-(diphenylamino)benzaldehyde were firstly synthesized and purified following literature procedures [7,12]. Then, 1,10-phenanthroline-5,6-dione (10 mmol), 4-(diphenylamino)benzaldehyde (10 mmol), NH$_4$AC (15.4 g) and HAC (30 mL) were mixed together and heated to reflux under N$_2$ protection for 5 h. This solution was poured into crushed ice and extracted with CH$_2$Cl$_2$ (3×20 mL). After solvent evaporation, crude product was obtained and recrystallized in petroleum ether to give 4-(1*H*-imidazo [4,5-f] [1,10] phenanthrolin-2-yl)-*N*,*N*-diphenylaniline (IPD) as light yellow solid. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.23 (t, 2*H*), 7.77 (m, 2*H*), 7.65 (d, 2*H*), 7.35-7.26 (m, 15*H*). Anal. Calcd for $C_{31}H_{21}N_5$: C, 80.32; H, 4.57; N, 15.11. Found: C, 80.21; H, 4.66; N, 15.20.

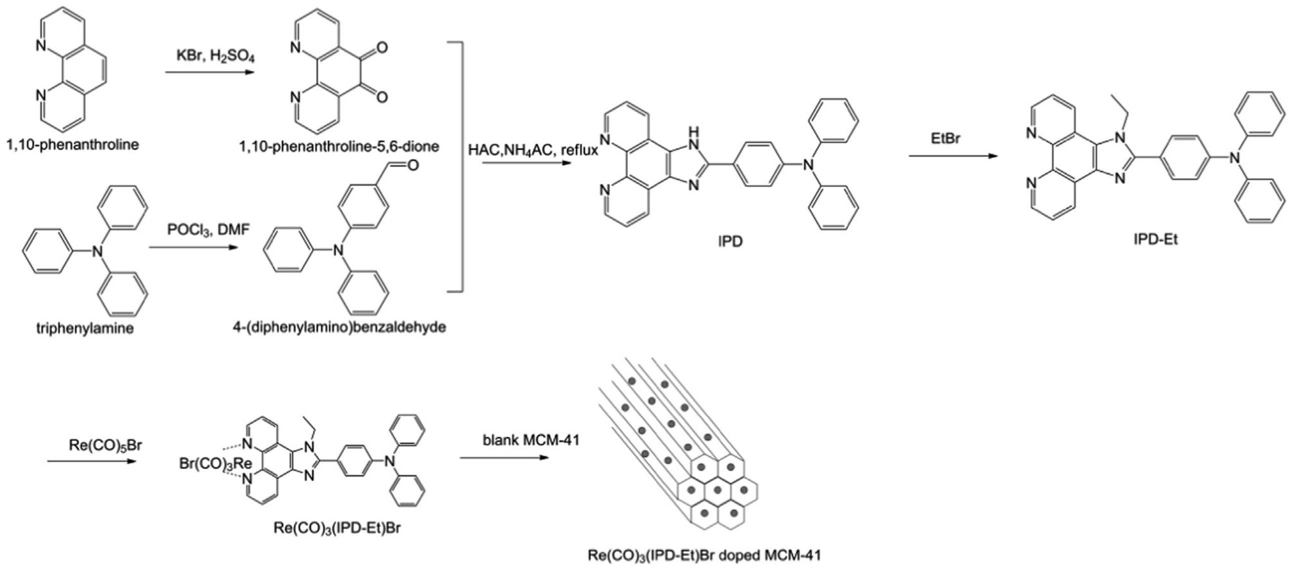
IPD (5 mmol) and NaH (50 mmol) were mixed in anhydrous *N*,*N*′-dimethyl formamide (15 mL), heated to reflux for 1 h under N$_2$ protection. EtBr (20 mL) was dropwise added into this solution and kept at 100 °C for another 24 h. The resulting solution was poured into crushed ice and filtered off. Crude product was collected and recrystallized in ethanol to give IPD-Et as yellow solid. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.21 (t, 2*H*), 7.74 (m, 2*H*), 7.63 (d, 2*H*), 7.33-7.24 (m, 14*H*), 4.66 (m, 2*H*), 1.65 (t, 3*H*). Anal. Calcd for $C_{33}H_{25}N_5$: C, 80.63; H, 5.13; N, 14.25. Found: C, 80.58; H, 5.20; N, 14.24.

2.3. Synthesis of Re(CO)$_3$(IPD-Et)Br

Re(CO)$_3$(IPD-Et)Br was synthesized following a classic procedure described as follows [11]. Re(CO)$_5$Br (0.2 mmol) and IPD-Et (0.2 mmol) were dissolved in toluene (15 mL) and then heated to reflux under N$_2$ protection for 10 h. After solvent evaporation, crude product was collected and purified on a silica column to give Re(CO)$_3$(IPD-Et)Br as light orange solid. ^{1}H NMR (acetone-d_6, 300 MHz): δ 9.26 (t, 2*H*), 7.78 (m, 2*H*), 7.67 (d, 2*H*), 7.36–7.28 (m, 14*H*), 4.69 (m, 2*H*), 1.68 (t, 3*H*). Anal. Calcd for $C_{36}H_{25}N_5O_3BrRe$: C, 51.37; H, 2.99; N, 8.32. Found: C, 51.28; H, 2.87; N, 8.24.

2.4. Construction of Re(CO)$_3$(IPD-Et)Br doped MCM-41

Re(CO)$_3$(IPD-Et)Br doped MCM-41 was constructed following a literature procedure described as follows [14,15]. Re(CO)$_3$(IPD-Et) Br was finelly quantified and added into CH$_2$Cl$_2$ (5 mL) under stirring. After the mixture became transparent, MCM-41 (1 g) was added and stirred for half an hour. Crude product was filtered and



Scheme 1. Construction route of Re(CO)$_3$(IPD-Et)Br and Re(CO)$_3$(IPD-Et)Br doped MCM-41.