Europium complexes with large conjugation plane in diamine ligands: Synthesis, characterization, photophysical features and oxygen sensing performance

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A B S T R A C T

In this paper, two europium complexes with large conjugation planes and proper triplet levels in their diamine ligands, $Eu(DBM)_3IPD$ and $Eu_3(DBM)_9TBB$, were synthesized and explored for oxygen sensing purpose, where DBM = 1,3-diphenyl-propane-1,3-dione, IPD = 4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)-N,N-diphenylaniline, TBB = 1,3,5-tris((2-(pyridin-2-yl)-1H-benzo[d]imidazol-1-yl)methyl)benzene. It was anticipated that large conjugation planes and proper triplet levels could improve oxygen sensing performance by increasing collision probability with O_2 molecules. The two europium complexes were firstly characterized through single crystal analysis, UV–Vis absorption spectra, emission spectra and excited state lifetimes. Then, by doping them into a polymer matrix of poly(vinylpyrrolidone) with electrospinning technique, oxygen sensing parameters of the resulting composite fibers were studied and compared. Maximum sensitivity of 3.38 and short response time of 12 s were obtained. Linear Stern–Volmer plots were observed.

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1. Introduction

As an important analytical problem in various fields, such as chemical industry, food processing, analytical and environmental chemistry, oxygen quantification is always of importance [1,2]. Clark electrode and Winkler titration approach are classical techniques which give precise and reliable readings. On the other hand, they generally need sophisticated equipments and complicated sample pretreatment. In addition, some drawbacks such as oxygen consumption, long response time and electrode contamination are usually encountered [3,4]. It is thus concluded that novel oxygen sensing systems with simple operation procedure, low need for equipments and fast response should be explored.

It seems that optical sensors can well satisfy above requirements owing to their simple, easy and non-destructive characters. Optical oxygen sensors usually provide advantages in terms of small size, low cost, electrical safety, needing no reference elements and the fact that sensing signals are free of electromagnetic interference [5,6]. To allow fluent analyte transportation and diffusion, probe molecules are usually doped into supporting matrixes such as polymers, silicates and Langmuir–Blodgett films

[7,8]. Some criteria should be met aiming at desired performance. For instance, high diffusion coefficient is desired from supporting matrixes to achieve fast response; efficient quenching around probe molecules is critical for high sensitivity; high photostability is needed to obtain reliable sensing signals. Among the numerous candidates for supporting matrix, polymer fibers prepared by electrospinning method have been proved promising owing to its good mechanical strength and high diffusion coefficient [7,8]. As for sensing probe, stable emission, long excited state lifetime and high compatibility with supporting matrix are usually desired.

Rare-earth (RE) based materials are anticipated to meet above requirements. Due to their unique antenna excitation mechanism and *f–f* radiation, RE-based emitters can emit sharp and narrow bands without being affected by surrounding environment and co-existing matters [9,10]. Their excited state lifetime is usually microsecond-scaled, offering more chances to meet O_2 molecules. What's more, they can be easily loaded into supporting matrix owing to their good solubility in common solvents. Above characters make RE-based materials promising candidates for oxygen sensing application.

Some precursive efforts have been devoted to RE-based oxygen sensing systems. Their sensitivity, however, is yet to be improved [9,10]. It is reported that oxygen sensing is finished through a thermally activated energy roll-off from excited RE center to ligand

triplet state. With this hypothesis, a diamine ligand with suitable triplet level and large conjugation plane may increase collision probability with oxygen and thus improve sensitivity.

Guided by above consideration, in this work, two diamine ligands with large conjugation plane and proper triplet level were designed and synthesized. Their synthetic route could be found in Scheme 1. Detailed analysis on their corresponding europium complexes were performed, including molecular structure, absorption spectra, excited state lifetimes and emission spectra. By doping these europium complexes into a polymer matrix, their emission response toward molecular oxygen was explored and analyzed.

2. Experimental details

2.1. General information

Starting materials of triphenylamine, 1,10-phenanthroline (Phen), 1,3-diphenyl-propane-1,3-dione (DBM), poly(vinylpyrrolidone) (PVP), mesitylene, N-bromosuccinimide (NBS), benzoylperoxide (BPO) and 2-(pyridin-2-yl)-1H-benzo[d]imidazole (PBI) were purchased from Aldrich Chemical Company and used with no further purifications. Inorganic chemicals including NH_4Ac, HAc, $EuCl_3$, NaOH and NaH were bought from Shanghai Chemical Company (Shanghai, China) and used as received. Organic solvents used in this work were purified with standard procedures and redistilled before usage.

Equipments for sample characterization are listed below. A Varian INOVA 300 spectrometer and a Agilent 1100 MS spectrometer (COMPACT) were used to record NMR and mass spectra, respectively. A Vario Element analyzer was used to finish elemental analysis. UV–Vis absorption and emission spectra were obtained from a Shimadzu UV-3101PC spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Oxygen-sensing performance was measured on the basis of steady emission intensity quenching with this F-4500 fluorescence spectrophotometer. Emission decay dynamics were measured on a two-channel TEKTRONIX

TDS-3052 oscilloscope with pulsed Nd:YAG laser as excitation source (355 nm). Single crystal data were collected on a Bruker Smart Apex CCD single-crystal diffractometer ($\lambda = 0.7107$ Å) at 273 K. Single crystal structure was solved with SHELXL-97 program. All hydrogen atoms were calculated. Scanning electron microscopy (SEM) and fluorescence microscopy images were recorded by a Spot Maqn microscope and a Nikon TE2000-U fluorescence microscopy (powered by a mercury lamp), respectively. All operations were carried out in the air at room temperature without further notifications.

2.2. Synthesis of IPD

4-(1H-imidazo [4,5-f][1,10]phenanthrolin-2-yl)-N,N-diphenylaniline (IPD) was synthesized with 4-(diphenylamino)benzaldehyde (TPA-CHO) and 1,10-phenanthroline-5,6-dione (Phen-O) as starting chemicals which were firstly synthesized following literature procedures [7,11,12]. Then TPA-CHO (2.5 g), Phen-O (2.0 g), NH_4Ac (15.4 g) and HAc (50 mL) were heated to reflux under N_2 protection for 5 h. After cooling, the solution was added into cold water (500 mL) and extracted with $CHCl_3$. After solvent evaporation, crude product was recrystallized in ethanol. ^1H NMR (300 Hz, $CDCl_3$): δ 9.09 (t, 2 H), 7.68 (m, 2 H), 7.55 (m, 2 H), 7.30–7.25 (m, 14 H). MS m/z: $[m]^+$ calc. for $C_{31}H_{21}N_5$, 463.2; found, 463.2. Anal. Calcd. for $C_{31}H_{21}N_5$: C, 80.32, H, 4.57, N, 15.11. Found: C, 80.28, H, 4.59, N, 15.07.

2.3. Synthesis of TBB

1,3,5-tris((2-(pyridin-2-yl)-1H-benzo[d]imidazol-1-yl)methyl)benzene (TBB) was synthesized with 1,3,5-tris(bromomethyl)benzene and PBI as starting chemicals. 1,3,5-tris(bromomethyl)benzene was firstly prepared by the following procedure. Mesitylene (100 mmol), NBS (300 mmol), BPO (5 mmol) and CCl_4 (50 mL) were mixed together and heated to reflux for 20 h under N_2 protection. After cooling, the solution was added into cold water
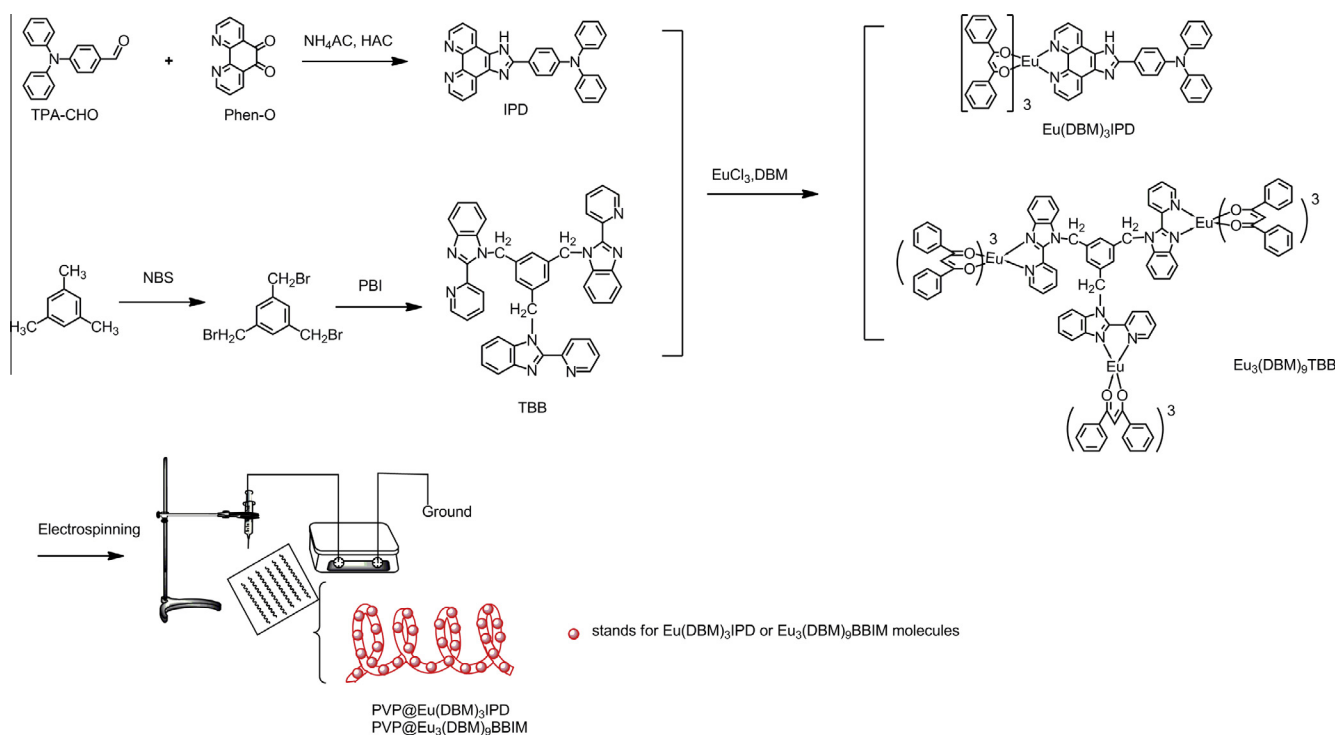
Scheme 1. Synthetic route for two diamine ligands (IPD, TBB), their Eu(III) complexes (Eu(DBM)₃IPD, Eu₃(DBM)₉TBB) and composite fibers (PVP@Eu(DBM)₃IPD, PVP@Eu₃(DBM)₉TBB).