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Synthesis, photophysical and oxygen-sensing properties of a novel Eu^{3+} complex incorporated in mesoporous MCM-41

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ABSTRACT

A novel Eu^{3+} complex of $Eu(DPIQ)(TTA)_3$ (DPIQ=10H-dipyrido [*f*,*h*] indolo [3,2-*b*] quinoxaline, TTA=2-thenoyltrifluoroacetonate) was synthesized and encapsulated in the mesoporous MCM-41, hoping to explore an oxygen-sensing system based on the long-lived Eu^{3+} emitter. The $Eu(DPIQ)(TTA)_3$/MCM-41 composites were characterized by infrared spectra (IR), ultraviolet-visible (UV–vis) absorption spectra, small-angle X-ray diffraction (SAXRD), luminescence intensity quenching upon various oxygen concentrations, and fluorescence decay analysis. The results indicated that the composites exhibited the characteristic emission of the Eu^{3+} ion and the fluorescence intensity of $^5D_0$–$^7F_2$ obviously decreased with increasing oxygen concentrations. The oxygen sensing properties of the composites with different loading levels of $Eu(DPIQ)(TTA)_3$ complex were investigated. A sensitivity of 3.04, a short response time of 7 s, and good linearity were obtained for the composites with a loading level of 20 mg/g. These results are the best reported values for optical oxygen-sensing materials based on Eu^{3+} complexes so far.

1. Introduction

Oxygen is one of the most important chemical species for life. The determination of molecular oxygen is required in various fields of biochemical and clinical analyses as well as environmental monitoring. To date, the Clark electrode (CE) which is based on the electrochemical-reduction of oxygen on a polarized cathode has become the most traditionally used oxygen sensors [1]. However, the CE suffers some drawbacks, such as oxygen consumption during sensing process, relatively long response time, and the tendency of electrode to be poisoned by sample constituents (e.g., H_2S, proteins, and certain anesthetics) [2]. Given these limitations, researchers have expended substantial efforts to develop new techniques for oxygen detection. Among these techniques, optical oxygen sensors based on luminescence quenching are much more attractive due to the advantages of low cost, miniaturization, easy utilization, and not suffering from electrical interference or oxygen consumption [3].

Optical oxygen sensors are composed of organic dyes immobilized in oxygen permeable matrices. Many luminescent dyes have been developed as oxygen-sensing probes [4–7]. Probe molecules with high luminescence quantum yield, long fluorescence lifetime, and good photostability are desirable for optical oxygen sensors. Additionally, the properties of optical oxygen sensors depend on the structures of supporting matrices to a great extent. For example, a high gas diffusion coefficient is necessary for rapid response; a high locally quenching around the complex molecule is necessary for good sensitivity [6–8].

Eu^{3+} complexes, as important luminescent materials, have been widely applied in optical amplifications, light-conversion molecular devices (LCMD), organic light-emitting diodes (OLEDs), and other fields [9,10]. Recently, the luminescence properties of Eu^{3+} complexes supported on a stable matrix have been studied extensively because their photophysical properties could be modified by interaction with host structures [11–15]. Generally, several Eu^{3+} complexes display extremely sharp emission lines, intense luminescence with high quantum yields, and long fluorescence lifetimes [16]. Therefore, they are expected to be promising candidates as novel optical oxygen-sensing materials. However, only a few attempts have been made to use Eu^{3+} complexes as optical oxygen-sensing materials so far [17,18].

In this paper, we firstly synthesize a novel Eu^{3+} complex $Eu(DPIQ)(TTA)_3$, and encapsulate the Eu^{3+} complex into MCM-41. MCM-41 may provide a better support for the Eu^{3+} complex because of their large surface area, highly ordered and nearly parallel channel, which is necessary for higher sensitivity and

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faster response time [19,20]. The oxygen sensing properties of the composites are investigated and the obtained values are found to be much better than those of other oxygen-sensing materials based on Eu^{3+} complexes.

2. Material and methods

2.1. Materials and reagents

Analytical grade solvents and compounds were used for preparation. Tetraethoxysilane (TEOS, Tianjin Chemicals Co.), cetyltrimethylammonium (CTAB, Aldrich), and ethanol (Tianjin Chemicals Co.) were used as received. The water used in our work was deionized. 1, 10-Phenanthroline monohydrate was obtained from Beijing Fine Chemical Company (Beijing, China). Concentrated HCl was obtained from Shanghai Chemical Company (Shanghai, China).

2.2. Synthesis procedures

2.2.1. Synthesis of DPIQ ligand

DPIQ was synthesized by modification according to the literatures [21,22]. Isatin (1 mmol, 0.147 g) was refluxed with 1, 10-phenanthroline-5, 6-diamine (1 mmol, 0.21 g) in 20 mL ethanol for more than 8 h until a suspension was formed. The mixture was hot filtered off to recuperate a pale yellow powder. The crude product subsequently was purified by recrystallization from methanol to give the desired product. ^{1}H NMR($CDCl_3$, 500 MHz): δ 10.07 (d, 1H, J=8.5 Hz), 9.22 (d, 1H, 2.5 Hz), 9.13 (d, 1H, 2.0 Hz), 9.05 (d, 1H, 5.5 Hz), 8.52 (d, 1H, 5.5 Hz), 7.62–7.72 (m, 2H), 7.57 (d, 1H, 8.5 Hz), 7.33 (m, 3H). IR (KBr pellets): 3414, 3048, 2986, 2812, 2754, 1720, 1601, 1566, 1375, 737 cm^{-1}. Anal. Calcd for $C_{20}H_{11}N_5$: C, 74.76; H, 3.43; N, 21.80. Found: C, 74.61; H, 3.21; N, 21.69.

2.2.2. Synthesis of Eu(DPIQ)(TTA)$_3$ complex

$Eu(DPIQ)(TTA)_3$ was synthesized according to a literature procedure [23]. (0.3 mmol, 0.067 g) HTTA and (0.1 mmol, 0.032 g) DPIQ was dissolved in 5 mL ethanol solution under stirring. Sodium hydroxide was added until pH value of the solution approached 7. Then (0.1 mmol, 0.037 g) $EuCl_3 \cdot 6H_2O$ in 2 mL water was added to the mixed solution. The mixture was stirred for 1 h at 60 °C. The product was collected by filtration and recrystallized from ethanol. IR (KBr pellets): 3425, 1714, 1600, 1537, 1407, 1351, 730, 501 cm^{-1}. Anal. Calcd. for $C_{44}H_{23}N_5F_9O_6S_3Eu$: C, 46.48; H, 2.04; N, 6.16. Found: C, 46.64; H, 1.86; N, 6.32.

2.2.3. Synthesis of Eu(DPIQ)(TTA)$_3$/MCM-41 composites

$Eu(DPIQ)(TTA)_3$/MCM-41 composites were prepared by a similar route as the literature [24]. In typical preparation, 10 mg $Eu(DPIQ)(TTA)_3$ was dissolved in 5 mL dichloromethane solution to form a light yellow transparent solution, then 1 g MCM-41 was added. The mixture was stirred for 5 h and filtered to give a yellowish power. The yellowish power was washed by dichloromethane for several times until the filtered dichloromethane solution was colorless under UV illumination, and dried in the air. 10 mg $Eu(DPIQ)(TTA)_3$/g MCM-41 was obtained. The composites with different loading levels of $Eu(DPIQ)(TTA)_3$ (20 and 30 mg $Eu(DPIQ)(TTA)_3$/g MCM-41) were prepared by altering the concentration of the starting solution of $Eu(DPIQ)(TTA)_3$.

2.3. Characterization

The ^{1}H NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer. The infrared spectra were measured using a Magna560 FT-IR spectrophotometer. The elemental analysis was obtained using a Vario Element Analyzer. The SAXRD spectra were reported on a Siemens D5005 diffractometer. The UV–vis absorption spectra were obtained using a Cary 500 Scan UV–vis-NIR Spectrophotometer. The fluorescence decay analysis was carried out using a Nd:YAG (neodymium yttrium aluminum garnet) laser system (Spectra Physics). Luminescence spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer. For the Stern–Volmer plot measurements, oxygen and nitrogen were mixed at different concentration via gas flow controls and passed directly to the sealed gas chamber.

3. Results and discussion

3.1. Synthesis and characterization

The DPIQ and $Eu(DPIQ)(TTA)_3$ were synthesized as the literature methods [21–23]. Their composition and purity were confirmed by ^{1}H NMR, IR spectroscopy and elemental analysis. The structure of $Eu(DPIQ)(TTA)_3$ was depicted in Fig. 1.

Infrared spectra of DPIQ, TTA, $Eu(DPIQ)(TTA)_3$, and $Eu(DPIQ)(TTA)_3$/MCM-41 composites with different loading levels of Eu^{3+} complexes are shown in Fig. 2a and b. As shown in Fig. 2a, the IR spectra show a displacement of stretching vibration of C=O from 1654 cm^{-1} in free HTTA to 1600 cm^{-1} in the Eu^{3+} complex, and a displacement of stretching vibration of C=N from 1375 cm^{-1} in the free DPIQ to 1351 cm^{-1} in the Eu^{3+} complex, indicating that the Eu^{3+} ion is coordinated through oxygen and nitrogen atoms [25]. In Fig. 2b, the symmetric vibration peak of Si–O–Si is moved from 814 (pure MCM-41) to 808 cm^{-1} (samples A, B, and C), revealing that $Eu(DPIQ)(TTA)_3$ complexes have been contained in MCM-41 [26]. In addition, a number of sharp vibration peaks appear in the range of 560–840 and 1000–1750 cm^{-1} for the $Eu(DPIQ)(TTA)_3$/MCM-41 complexes, whereas they do not appear in the $Eu(DPIQ)(TTA)_3$/MCM-41 composites, which suggests the pure complexes were actually incorporated into MCM-41 channels but not physically absorbed outside [11].

3.2. UV–vis absorption spectra and fluorescence properties

The UV–vis absorption spectra of TTA, DPIQ, $Eu(DPIQ)(TTA)_3$, and $Eu(DPIQ)(TTA)_3$/MCM-41 composites with different loading levels of Eu^{3+} complexes in dichloromethane solution are drawn in Fig. 3. As for pure $Eu(DPIQ)(TTA)_3$, two absorption bands located around 225 and 279 nm are observed, corresponding to the π–π^* electronic transitions of DPIQ [27,28]. The band at 336 nm is assigned to the absorption of TTA electronic transitions. The absorption feature of $Eu(DPIQ)(TTA)_3$/MCM-41 composites is consistent with that of the pure $Eu(DPIQ)(TTA)_3$ dissolved in dichloromethane solution, indicating that $Eu(DPIQ)(TTA)_3$ has been dispersed in the channels of MCM-41. For the composite with a loading level of 10 mg/g, the absorption bands are very weak because of the low concentration of Eu^{3+} complexes [12].

The emission spectra of $Eu(DPIQ)(TTA)_3$ in the air, pure nitrogen, and pure oxygen and amplified part of emission spectra are shown in Fig. 4a and b. As shown in Fig. 4a, $Eu(DPIQ)(TTA)_3$ exhibits characteristic emission of Eu^{3+} ion, and the hypersensitive ΔJ=2 transition gives rise to the greatest changes in the Eu^{3+} emissions in pure oxygen, compared to that in the air and pure nitrogen. Again, the Eu^{3+} emissions at 578,