Dyes and Pigments 97 (2013) 26–31

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

An optical anion chemosensor based on a europium complex and its molecular logic behavior

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ARTICLE INFO

Article history:
Received 27 August 2012
Received in revised form
16 October 2012
Accepted 22 November 2012
Available online 29 November 2012

Keywords:
Europium complex
AcO^- ion
Optical sensor
Oxygen
Energy backtransfer
Logic gate

ABSTRACT

In this paper, synthesis and photophysical properties of an organoeuropium complex, $Eu(DBM)_3DPPZ$ (DBM = dibenzoylmethane, DPPZ = dipyrido [3,2-a:2′,3′-c]phenazine), are described and discussed. The europium complex sensor can efficiently recognize AcO^- ion over other anions by the increase of luminescence intensity, which is applicable to naked eye detection for AcO^- ion. The sensing mechanism is ascribed to the replacement of DPPZ by AcO^- ion. Moreover, the Eu^{3+} emission is also found to be sensitive to molecular oxygen through a back-energy transfer mechanism. Based on these characters, this "off–on"-type luminescent sensor could successfully mimic an IMP (IMPLICATION) gate at molecular level with AcO^- ion and oxygen as inputs. The output of a sharp characteristic Eu^{3+} emission is read as "*0*" only in the absence of AcO^- ion under oxygen atmosphere. As far as we know, this is the first example of a logic gate corresponding to a two-input IMP function obtained from a europium complex.

1. Introduction

Anions play fundamental roles in biological, security and environmental science [1] and thus have attracted considerable interests for their detection. Several approaches aiming at selective optical indicators for anions (such as F^- or AcO^-), which provide extraordinary signal changes in absorption or luminescence spectra, have been presented in recent decades [2–9]. Among these numerous indicators, organic lanthanide complexes have been proved to be excellent candidates owing to their advantageous photophysical properties such as large stokes shift, narrow emission bands and long excited state lifetimes [10–14]. Furthermore, the emission color depends only on the lanthanide ion and is independent of the environment of a given lanthanide ion. Among the lanthanides of interest, those enabling a simple and sensitive fluorimetric detection, such as Eu^{3+} and Tb^{3+}, are particularly relevant [15–18].

It has been known for some time that counter ions can coordinate to lanthanide ions in coordinating unsaturated ligands to fulfill the coordination requirements of the lanthanides ions. Furthermore, it is also known that weakly-coordinated ligands can be displaced by stronger ones [14]. Generally, there are two ways of modulating the emission property of lanthanide complexes by anions. Firstly, water molecules bound to the lanthanide center could be displaced by anions, leading to enhanced luminescent intensity; the other one is the displacement of ligands by anions resulting in the increase or decrease of luminescent intensity [4]. Li and coworkers [16] have nicely demonstrated a terbium complex for detecting anions by luminescence modulation through back-energy transfer mechanism. Upon addition of F^- ion, the terbium emission greatly increased and this change became saturated when F^- reached about three equivalents of the terbium complex. However, further addition of a large excess of F^- ion caused emission decrease. Similar emission modulation behavior of the terbium complex was also observed for AcO^- ion.

Besides being used as chemosensors for detecting anions, lanthanide complexes can also be applied in sensing other analytes, such as cations and oxygen, as well as mimicking a molecular level logic gate [19–24]. Optical oxygen sensors based on [$Eu(TTA)_3$(-phencarz)]/PS composite nanofibrous membranes were prepared in our previous work [20]. Gunnlaugsson and coworkers [22,23] reported terbium macrocyclic quinolyl conjugates as luminescent molecular switches and logic gate functions using H^+/OH^- and O_2 as inputs. Pischel and coworkers [24] designed a molecular logic gate based on phthamide-sensitized Tb^{3+} luminescence with Cl^-, O_2, and triethylamine as inputs. However, to the best of our knowledge, no

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http://dx.doi.org/10.1016/j.dyepig.2012.11.021

molecule logic device based on europium complexes has been reported although they have similar remarkable luminescent property as well as terbium complexes.

On the basis of the above opinions, we attempt to develop a luminescence probe based on an organic europium complex of $Eu(DBM)_3DPPZ$ (DBM = dibenzoylmethane, DPPZ = dipyrido[3,2-a:2′,3′-c]phenazine) [25], which could be applicable to detect AcO^- with naked eyes. Moreover, the Eu^{3+} emission is also found to be sensitive to molecular oxygen. According to these properties, a molecular level IMP (IMPLICATION) gate based on this "off–on"-type luminescence sensor could be successfully mimicked with AcO^- and oxygen as the two inputs where the output, a sharp characteristic Eu^{3+} emission, is read as "*0*" only in the absence AcO^- under oxygen atmosphere.

2. Experimental details

2.1. Materials and reagents

DBM and Eu_2O_3 (99.99%) were purchased from Aldrich Chemical Company and Sinopharm Chemical Reagent Company. $EuCl_3 \cdot 6H_2O$ was prepared by dissolving Eu_2O_3 in concentrated hydrochloric acid. All reagents and chemicals were used without further purification.

2.2. Instruments and methods

^1H NMR spectra were recorded using a mercury-300BB spectrometer (Varian, USA) operated at 300 MHz with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. The UV/Visible (UV/Vis) absorption spectra were obtained on a Shi-madzu-UV-3101 scanning spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer with the excitation and the emission wavelength bandpasses were set at 2.5 nm and 1.0 nm, respectively. The luminescence lifetimes were obtained with 355 nm light generated from a third-harmonic-generator pump, using a pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of 1.0 cm^{-1}, a pulse duration of 10 ns, and a repetition frequency of 10 Hz. The quantum yield was measured by comparing fluorescence intensity (integrated areas) of a standard sample (Rhodamine 6G) and the unknown sample according to the following equation:

$$\Phi_{unk} = \frac{n_{unk}^2 A_{ref} I_{unk}}{n_{ref}^2 A_{unk} I_{ref}} \Phi_{ref} \quad (1)$$

where Φ_{unk} is the luminescence quantum yield of sample; $\Phi_{ref} = 0.92$ is the luminescence quantum yield of Rhodamine 6G (ethanol, 10^{-6} M) [16], I_{unk} and I_{ref} are the integrated fluorescence intensities of unknown sample and Rhodamine 6G, respectively; A_{unk} and A_{ref} are the absorbance of unknown sample and Rhodamine 6G at the wavelength of excitation. n_{unk} and n_{ref} are the refractive indexes of corresponding solvents (pure solvents were assumed). All spectrophotometric spectra were carried out in CH_3CN solutions at room temperature. For the sensitivity experiment toward dissolved oxygen, the solvent was bubbled by N_2 and O_2 alternately for *ca.* 20 min. with a degassing device.

2.3. Synthesis of $Eu(DBM)_3DPPZ$

DPPZ was synthesized according to our previously reported procedure [26]. DPPZ: ^1H NMR (300 Hz, $CDCl_3$): δ (ppm) 9.65 (d, J = 8.1 Hz, 2H), 9.28 (d, J = 3.3 Hz, 2H), 8.37 (dd, J = 6.6 Hz, 6.3 Hz, 2H), 7.94 (dd, J = 6.3 Hz, 6.6 Hz, 2H), 7.82 (dd, J = 8.1 Hz, 8.1 Hz, 2H). $Eu(DBM)_3DPPZ$ (Scheme 1) was obtained according to the conventional method with minor modifications as follows. DBM (0.067 g, 0.3 mmol) and DPPZ (0.028 g, 0.1 mmol) were dissolved in ethanol (10 mL) under stirring. Sodium hydroxide was added until the pH value of the solution approached 7. Then $EuCl_36H_2O$ (0.037 g, 0.1 mmol) in water (2 mL) was added to the mixture solution. The mixture was stirred for 12 h under reflux. The product was collected by filtration and recrystallized from ethanol. Elemental analysis (%) calcd for $C_{63}H_{46}EuN_4O_6$: C, 68.35; H, 4.19; N, 5.06. Found: C, 68.11; H, 4.06; N, 5.17.

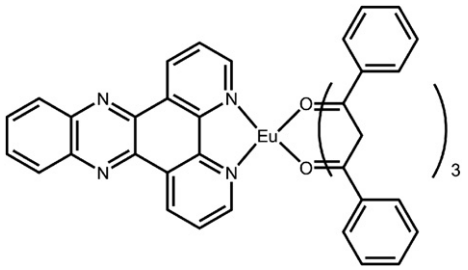
3. Results and discussion

3.1. Photophysical property of $Eu(DBM)_3DPPZ$

Fig. 1 shows the UV–Vis absorption spectra of $Eu(DBM)_3DPPZ$ (5 μM) and the free ligands (5 μM) in CH_3CN solutions, as well as the photoluminescence (PL) spectrum of the europium complex. The absorption maximum of free DBM at 348 nm is attributed to the π–π* enol absorption of the β-diketonate [27]. The π–π* electronic absorption of ligand DPPZ are located at 270 nm, 359 nm, and 375 nm [28]. As for $Eu(DBM)_3DPPZ$, the absorption are located at 266 nm and 353 nm. It is observed that a red shift of the major π–π* electronic transition occurs compared with the absorption spectrum of free DBM and a blue shift after further coordinating with DPPZ, which may be attributed to the coordinative interactions between Eu^{3+} ion and the ligands. The sharp characteristic emission at 610 nm of the Eu^{3+} ion from $^5D_0$–$^7F_2$ transition is observed, accompanied by the weak emissions corresponding to $^5D_0$–^7F_J (J = 0, 1, 3, 4) transitions as shown in Fig. 1. In addition, a weak emission band at ~415 nm, which attributes to the emission from DPPZ ligand, is also observed in the CH_3CN solution. This observation suggests that the excited state energy of DPPZ is not completely transferred to the emissive center, which will be later discussed.

To further investigate the luminescence property of $Eu(DBM)_3DPPZ$, we selectively determined the emission quantum efficiencies and the lifetimes of the $^5D_0$ excited state for $Eu(DBM)_3DPPZ$ and a reference complex of $Eu(DBM)_3(H_2O)_2$. As shown in Table 1, the quantum yield and the lifetime of $Eu(DBM)_3DPPZ$ is 0.65% and 53 μs, respectively, which are greatly lower than those of $Eu(DBM)_3(H_2O)_2$, revealing that introducing DPPZ as the second ligand actually reduces the quantum yield and shortens the lifetime of Eu^{3+} ion. In fact, the lifetime is dominated by total radiative transition rate k_{rad} and nonradiative decay rate k_{nr}, which can be written as

$$\tau = \frac{1}{k_{rad} + k_{nr}} \quad (2)$$



Scheme 1. Molecular structure of $Eu(DBM)_3DPPZ$.

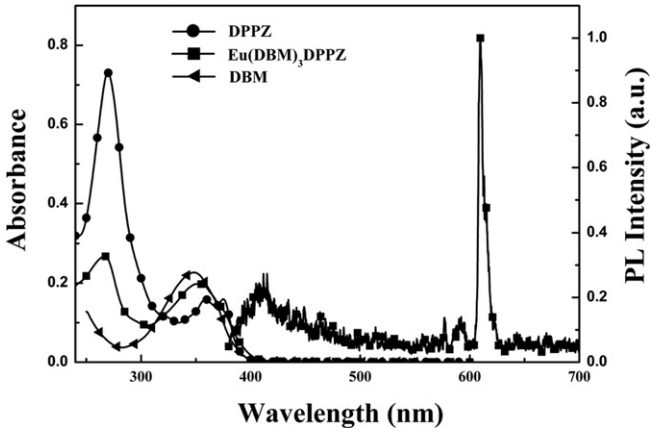


Fig. 1. Absorption and PL spectra of $Eu(DBM)_3DPPZ$ (5 μM) and absorption spectra of the ligands (5 μM) in CH_3CN solutions.

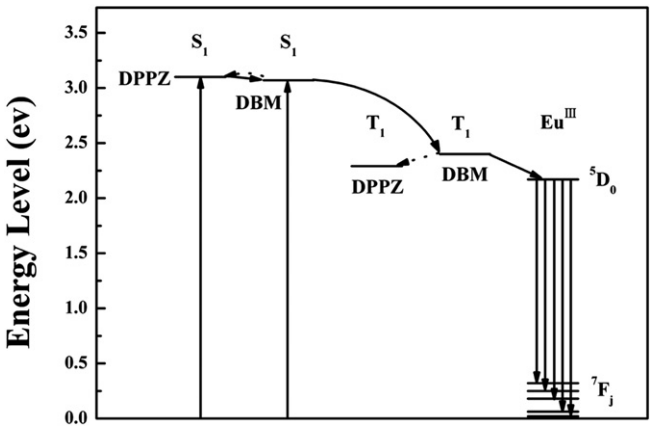


Fig. 2. Schematic energy-level diagram and energy-transfer process. S_1: first excited singlet state; T_1: first excited triplet state.

$$\tau = \frac{\Phi}{k_{rad}} \quad (3)$$

The corresponding radiative and nonradiative decay rates are calculated and summarized in Table 1. It is found that the radiative transition rate of $Eu(DBM)_3DPPZ$ is lower than that of $Eu(DBM)_3(H_2O)_2$.

The luminescence property of $Eu(DBM)_3DPPZ$ could be explained by the energy transfer between ligands and central metal ion [20,27]. Generally, sensitization pathway in luminescent Eu^{3+} complexes consists of an initial strong absorption of UV energy that excites the ligands to excited S_1 and subsequent intersystem crossing of the ligands to their T_1 states. Finally, the energy is nonradiatively transferred to a resonance state of coordinated Eu^{3+} ion, which in turn, undergoes a multiphoton relaxation and subsequent emission in visible region. The singlet-state energy levels of DPPZ and DBM are estimated by referencing their absorption edges, which are calculated to be 3.10 eV (400 nm) and 3.07 eV (405 nm), respectively. The singlet- and triplet-state energy levels are illustrated in Fig. 2. The energy gaps ΔE ($^1\pi\pi^*-^3\pi\pi^*$) between $^1\pi\pi^*$ and $^3\pi\pi^*$ levels are 6533 and 5404 cm^{-1} for DPPZ and DBM, respectively, which shows that the intersystem crossing processes are effective for the two ligands [29]. The triplet energy levels of DPPZ and DBM are 2.29 eV (540 nm) and 2.4 eV (517 nm), respectively, as reported in our before works [27,30]. For $Eu(DBM)_3DPPZ$, since the energy gap between Eu^{3+} $^5D_0$ level (17,500 cm^{-1}) [29] and the triplet energy of DPPZ is about 970 cm^{-1}, which is less than the critical value of 1500 cm^{-1}, the thermally activated energy backtransfer could occur [3], resulting the decrease of quantum efficiency and lifetime, as well as above mentioned inefficient energy transfer from excited state DPPZ to the emissive center.

3.2. PL spectral responses of $Eu(DBM)_3DPPZ$ toward anions

In order to evaluate the sensitivity of the europium complex toward anions, PL spectral response profiles at 610 nm of the complex (5 μM) with different anions are recorded in CH_3CN solutions, as shown in Fig. 3. Interestingly, different PL spectral responses are observed when different anions are added. Insignificant changes are detected upon addition of weakly-coordinative Cl^-, Br^-, and non-coordinative ClO_4^-, whereas the addition of F^-

Table 1
Photophysical parameters for $Eu(DBM)_3(H_2O)_2$ and $Eu(DBM)_3DPPZ$.

Complex	Abs. (nm)	Ex. (nm)	Em. (nm)	τ (μs)	Φ (%)	k_{rad} (s^{-1})	k_{nr} (s^{-1})
$Eu(DBM)_3(H_2O)_2$	352	357	610	175	4.73	270	5.43×10^3
$Eu(DBM)_3DPPZ$	266, 353	364	610	53	0.65	123	1.87×10^4

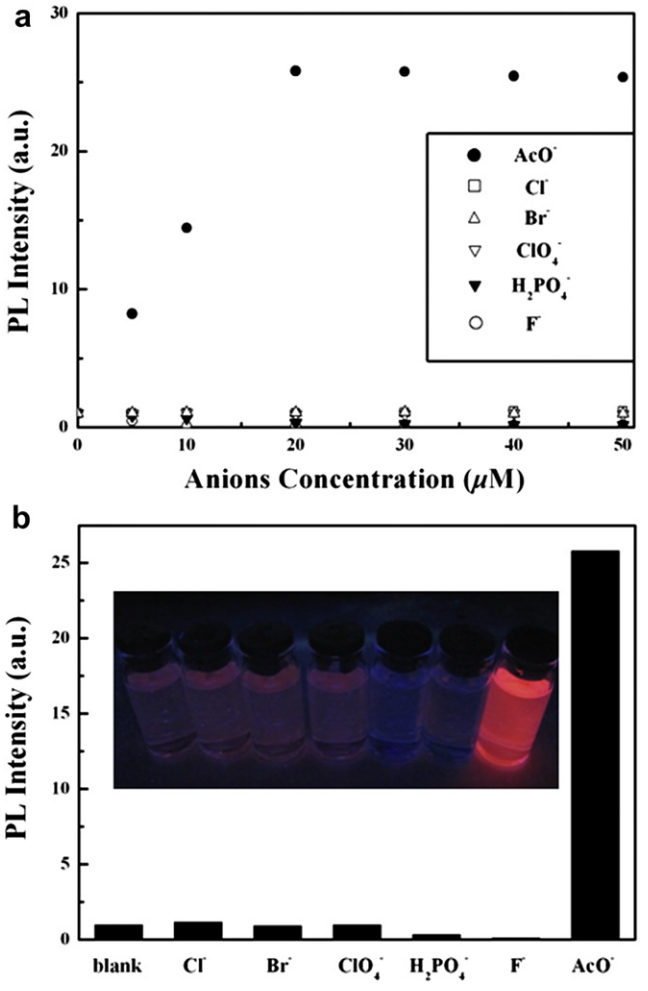


Fig. 3. (a) Normalized PL titrations of $Eu(DBM)_3DPPZ$ (5 μM) in CH_3CN upon addition of F^-, Cl^-, Br^-, ClO_4^-, $H_2PO_4^-$, AcO^-. (b) Normalized PL responses of $Eu(DBM)_3DPPZ$ in the presence of various anions (Cl^-, Br^- and ClO_4^-: 50 μM; $H_2PO_4^-$, F^-, and AcO^-: 20 μM). Inset: photographs of solutions of the complex in the presence of different anions from left to right in the same sequence as exhibited above, taken under UV illumination. $\lambda_{em} = 610$ nm, $\lambda_{ex} = 364$ nm.

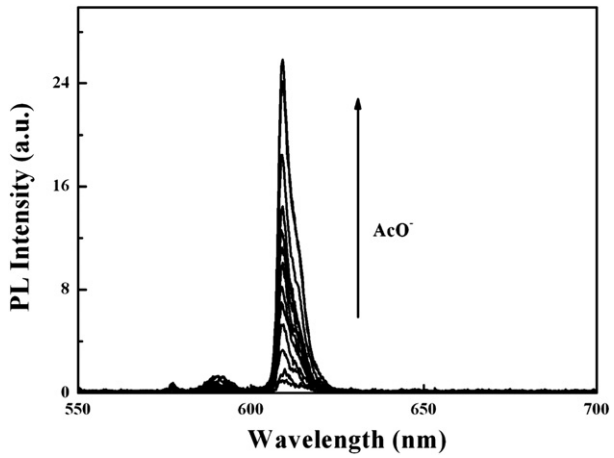


Fig. 4. PL spectra variation of Eu(DBM)$_3$DPPZ (5 μM) in the presence of increasing concentration of AcO^- in CH_3CN solution. $\lambda_{ex} = 364$ nm.

and $H_2PO_4^-$ anions decomposes the europium complex, leading to luminescence quenching of the complex. In contrast, the PL intensity sharply increases upon the addition of AcO^-, and this change becomes saturated and exhibits a *ca.* 25.8-fold enhancement when AcO^- reaches about four equivalents of Eu(DBM)$_3$DPPZ, which is applicable to naked-eye detection (Fig. 3b). Because of its strong bonding ability, AcO^- is able to substitute DPPZ which is weakly coordinated to Eu^{3+} complex [16], consequently the back-energy transfer from $^5D_0$ of Eu^{3+} and the triplet state of DBM to the triplet state of DPPZ is restrained. Taken together, these properties render this complex a suitable candidate for the detection of ACO^- with good selectivity.

To further test the recognition ability of Eu(DBM)$_3$DPPZ toward AcO^-, the PL intensity variation of Eu(DBM)$_3$DPPZ (5 μM) upon gradual addition of AcO^- ion is monitored under 364 nm excitation. Fig. 4 illustrates the detailed PL spectral response of Eu(DBM)$_3$DPPZ toward AcO^- concentration ranging from 0 to 20 μM. In the absence of AcO^-, the PL intensity is very weak. Upon increasing concentration of AcO^-, the solution of the complex shows an enhancing luminescence emission at 610 nm (Fig. 4). Meanwhile, the plot of PL intensity of Eu^{3+} emission against the concentration of added AcO^- ion is depicted in Fig. 5. A good linearity between I/I_0 and concentration of AcO^- ion in the range of 0–10 μM is obtained with a linearly dependent coefficient $R^2 = 0.991$. Correspondingly, the

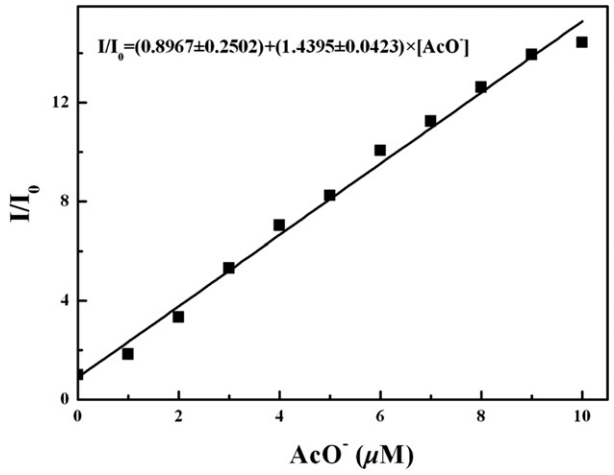


Fig. 5. The plot of normalized PL response I/I_0 of Eu(DBM)$_3$DPPZ (5 μM) upon additions of AcO^- from 0 to 10 μM in CH_3CN solution. $\lambda_{ex} = 364$ nm.

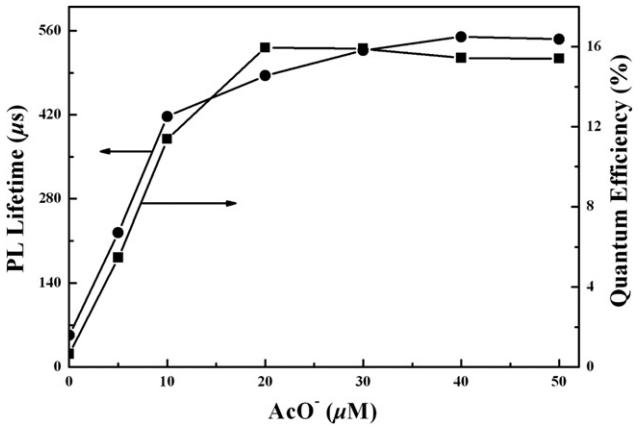


Fig. 6. The plot of PL lifetime and quantum efficiency variations of Eu(DBM)$_3$DPPZ (5 μM) in the presence of increasing concentration of AcO^- in CH_3CN solution.

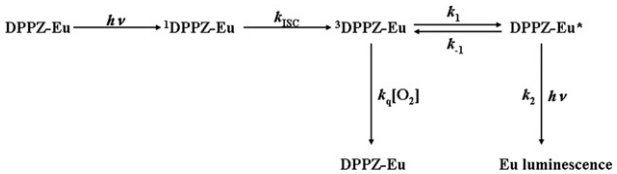
observable sensitivity of the complex is about 1 μM. Moreover, both the luminescence quantum efficiency and the lifetime of the complex are improved upon gradually addition of AcO^-, which is consistent with the luminescence intensity variation tendency (Fig. 6). Above results indicate that Eu(DBM)$_3$DPPZ possesses high sensitivity for AcO^- and can be used as a luminescent sensor for this anion through naked-eye detection.

3.3. Oxygen sensitivity of Eu(DBM)$_3$DPPZ

Generally, the luminescence of most lanthanide complexes is not perturbed by oxygen variations. However, as mentioned above, competitive thermally activated back-energy transfer will occur between the $^5D_0$ level of the Eu^{3+} ion and the triplet energy of DPPZ ligand. As a consequence, the luminescence of the Eu^{3+} ion becomes sensitive to the presence of oxygen [31]. The mechanism can be tentatively explained by Scheme 2 [20]. Fig. 7 shows the PL spectra of Eu(DBM)$_3$DPPZ in the CH_3CN solution (5 μM) under nitrogen, air and oxygen atmospheres. The PL intensity under nitrogen increases *ca.* 4.9-fold compared with that under oxygen. The quantum efficiencies with different dissolved oxygen content are also calculated shown as the inset of Fig. 7 and decreases with enhancement of oxygen content, as consistent with the variation of the PL intensity. On the basis of above results, it can be concluded that Eu(DBM)$_3$DPPZ may be employed for practical applications in the oxygen sensing systems by incorporating the complex into a solid matrix serving as a supporting one which allows oxygen transport from surroundings [20].

3.4. Logic gate express of the luminescence results of Eu(DBM)$_3$DPPZ

We have demonstrated that Eu(DBM)$_3$DPPZ could be used in AcO^- sensing and meanwhile, it is sensitive to the presence of oxygen, which enables the europium complex to be fabricated as a more advanced and functional molecular device, such as a logic



Scheme 2. Kinetic scheme of the luminescence of Eu(DBM)$_3$DPPZ quenched by oxygen molecules.

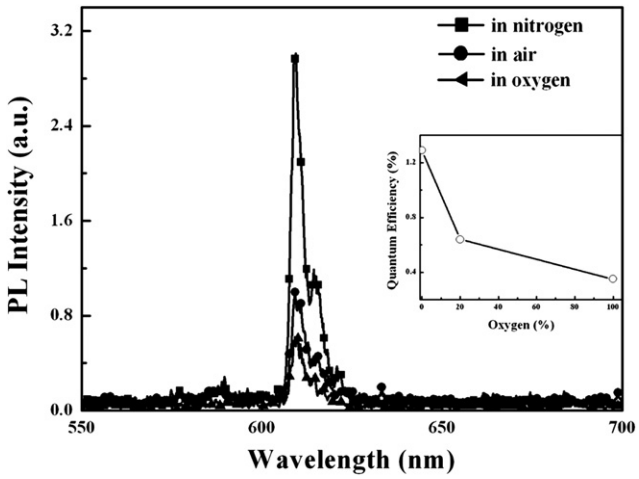
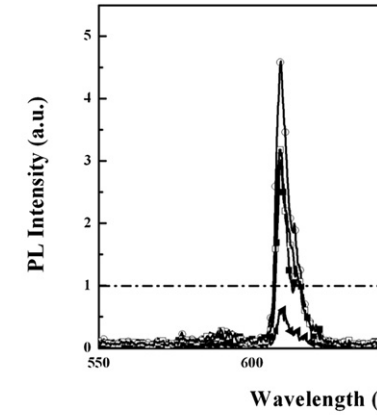
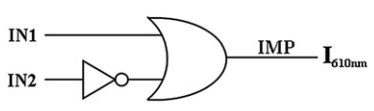


Fig. 7. PL spectra of $Eu(DBM)_3DPPZ$ under nitrogen, air, and oxygen in CH_3CN solution (5 μM). λ_{ex} = 364 nm.

gate. Here, the Eu^{3+} emission of $Eu(DBM)_3DPPZ$ can be defined as the logic gate output, which provides an entry for developing a molecular logic gate using AcO^- (IN1) and O_2 (IN2) as two inputs. For inputs, the presence and the absence of AcO^- (2 μM) and O_2 are defined as *1* and *0*, respectively. For output, we define the normalize PL intensity of the complex greater than that under air as *1* (>1) and lower than that under air as *0* (≤1). Based on the above definitions, the luminescence decrease of the complex is observed only in the absence of AcO^- under oxygen atmosphere, where the reverse energy transfer occurs, leading to effective luminescence quenching by molecular oxygen, so that the output is read as "*0*". Under other circumstances the luminescence of the complex is enhanced, thus leading to output "*1*". The PL spectra, the respective symbolic representation of the IMP function and the corresponding truth table are illustrations in Fig. 8. As far as we know, this is the first example of a europium complex logic gate corresponding to a two-input IMP function.





Input		Output
AcO^-	O_2	I_{610nm}
0	0	1 (3.01)
0	1	0 (0.62)
1	0	1 (4.60)
1	1	1 (3.17)

Fig. 8. Top: Normalized PL spectra of $Eu(DBM)_3DPPZ$ (5 μM) in presence or absence of AcO^- (2 μM) with O_2 or N_2 in CH_3CN solution. Bottom: molecular scale implementation and truth table for IMP logic function using the europium complex.

4. Conclusions

In summary, a novel luminescence chemosensor based on a europium complex, $Eu(DBM)_3DPPZ$, is designed and synthesized for detection AcO^- in a CH_3CN solution. The europium complex sensor shows a high selectivity for AcO^- ion over other anions and a good linearity between the PL intensity of the complex and the concentration of AcO^- ion, which is applicable to naked-eye detection for AcO^-. The sensing mechanism could be ascribed to the displacement of DPPZ by AcO^-. Moreover, the Eu^{3+} emission is also found to be sensitive to molecular oxygen through a back-energy transfer mechanism. Based on these results, this "off–on"-type luminescence sensor could successfully mimic a molecular level IMP gate with AcO^- and oxygen as the two inputs where the output, a sharp characteristic Eu^{3+} emission, is read as "*0*" only in the absence AcO^- under oxygen atmosphere. As far as we know, this is the first example of a europium complex logic gate corresponding to a two-input IMP function. We believe that the present system will provide useful information to the range of optical devices that can operate at molecular level.

Acknowledgments

The authors gratefully thank the financial supports of the NSFC (Grant Nos. 51172224 and 51103145) and the Science and Technology Developing Project of Jilin Province (Grant Nos. 20100533 and 201201009).

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