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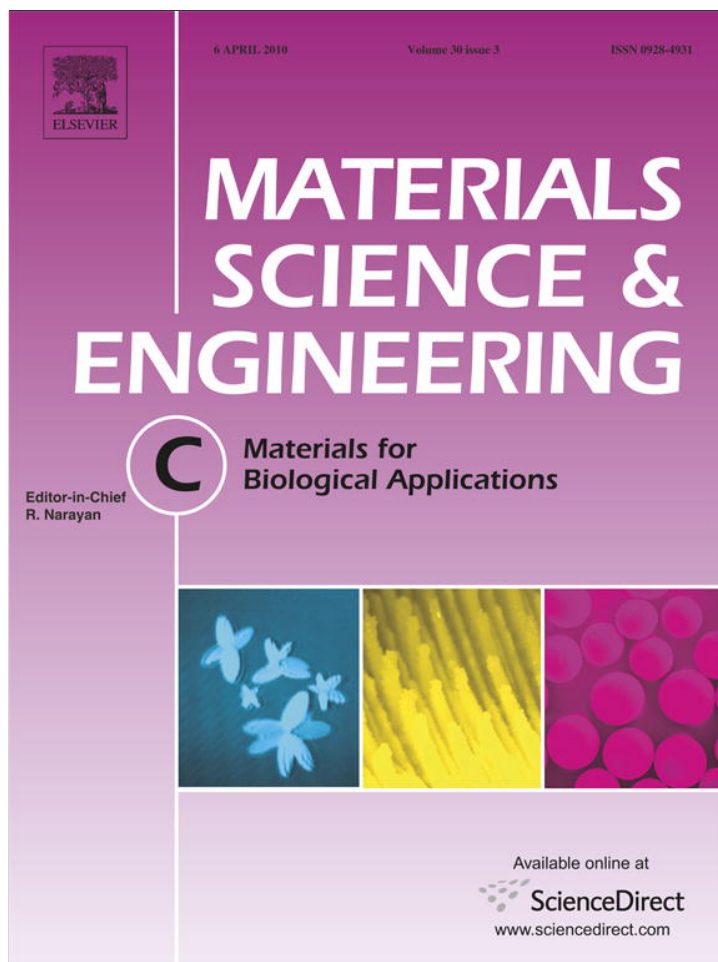


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A novel ratiometric fluorescent Yb^{3+} sensor based on a N'-(1-oxoacenaphthylen-2(1H)-ylidene)furan-2-carbohydrazide as a suitable fluorophore

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ABSTRACT

N'-(1-oxoacenaphthylen-2(1H)-ylidene)furan-2-carbohydrazide (**L**) was synthesized for the first time and used as a ratiometric fluorescent chemosensor for high selective recognition of Yb^{3+} ions in acetonitrile (MeCN) solution. The **L**– Yb^{3+} complexation quench the fluorescence of **L** at 420 nm and induces new fluorescent enhancement at 516 nm. Due to the formation of a 2:1 metal ligand complex in acetonitrile solution, the red shift of fluorescent emission spectrum occurred. The sensor shows a linear response toward Yb^{3+} ion concentration in the range of 3.3×10^{-7} M to 1.0×10^{-4} M with detection limit of 1.2×10^{-7} M. The fluorescent probe exhibits high selectivity for Yb^{3+} ion over the other common mono-, di-, and trivalent cations.

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1. Introduction

Ytterbium is found with other rare earth elements in several rare minerals. It is most often commercially recovered from monazite sand (~0.03% ytterbium). Ytterbium is applied to numerous fiber amplifier and fiber optic technologies and in various lasing applications. It illustrates a single dominant absorption band at 985 in the infra-red region, making it useful in silicon photocells to directly convert radiant energy to electricity. Ytterbium metal increases its electrical resistance when subjected to very high stresses. This property is used in stress gauges for monitoring ground deformations from earthquakes and nuclear explosions. It is also used in thermal barrier system bond coatings on nickel, iron and other transitional metal alloy substrates [1].

Despite the fact that ytterbium is fairly stable, it should be stored in closed containers to protect it from air and moisture. All ytterbium compounds should be treated as highly toxic, although initial studies appear to indicate that the danger is limited. Ytterbium compounds are, however, known to cause skin and eye irritation and may be teratogenic. Moreover, metallic ytterbium dust poses a fire and explosion hazard [2].

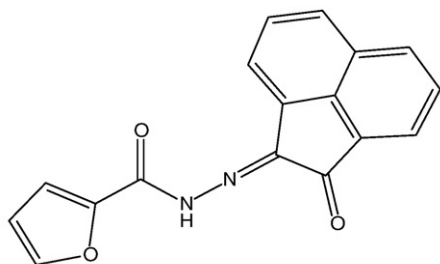
The available methods for the low-level determination of rare-earth ions in solutions include spectrophotometry, Inductively coupled

plasma mass spectrometry (ICPMS), Inductively coupled plasma atomic emission spectroscopy (ICP-AES), isotope dilution mass spectrometry, neutron activation analysis and X-ray fluorescence spectrometry. These methods are either time consuming, involving multiple sample manipulation or too expensive for the most analytical laboratories.

Among the various detection techniques, potentiometric sensors, colorimetric and fluorescent chemosensors have been developed quickly for their simplicity and high sensitivity [3–21]. Recently, ratiometric fluorescent probes allow the measurement of emission intensities at two different wavelengths. This should provide a built-in correction for environmental effects (i.e., revoking artifacts as a result of probe concentration variations) and can also increase the dynamic range of fluorescence measurements [22]. As the sensitivity as well as dynamic range of a ratiometric probe are controlled by the ratio of emission intensities at two wavelengths [23,24]. It is highly desirable to obtain a large ratiometric fluorescence response at two wavelengths. However, the design for ratiometric fluorescent probes with a great ratiometric signal remains very challenging [25–28].

There have been many studies on different chemosensors for transition and heavy metal ions. Among these metal ions, a little attention has been paid to the development of lanthanide chemosensors [25–36]. However, to the best of our knowledge, ratiometric fluorescent sensors for Yb^{3+} , especially with fluorescence enhancement technique, have not been reported yet. Thus, development of a new ratiometric receptor capable of recognizing Yb^{3+} ions has attracted our interest.

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N'-(1-oxoacenaphthylen-2(1*H*)-ylidene)furan-2-carbohydrazide

Scheme 1. Structure of compound **L**.

Herein, we present compound *N'*-(1-oxoacenaphthylen-2(1*H*)-ylidene)furan-2-carbohydrazide (**L**) as a novel ratiometric fluorescent Yb^{3+} sensor. This compound is a suitable ionophore for lanthanide ions recognition and a good fluorophore for fluorescent analysis. Due to naphthylenic part of this ionophore, it can easily emit fluorescence emission. Also, due to the existence of donating nitrogen atoms in the **L** structure in order to causing a semi-cavity and formation of wrap-around complexes, the concept of soft-hard acid–base, the charge density, and the size of the ytterbium ion was expected to increase both the stability and selectivity of its complexes with ytterbium ion more than other transition metal ions.

2. Experimental

2.1. Reagents

All chemicals were of the reagent-grade from Fluka and Merck chemical companies.

The procedure for the preparation of fluorophore **L** is as follow:

A mixture of furan-2-carbohydrazide (2 mmol) and acenaphthylene-1,2-dione (2 mmol) and catalytic amount of acetic acid was refluxed in ethanol for 1.5 h. Then the residue was crystallized with 95% ethanol. ^1H NMR (250 MHz, Acetone- d_6): δ 6.61 (dd, 1H, $J = 4.5, 7.0$ Hz, CH), 7.00 (s, 1H, NH), 7.23 (d, 1H, $J = 7.0$ Hz, CH), 7.72 (d, 1H, $J = 4.5$ Hz, CH), 7.42–8.19 (m, 6H, 6CH). ^{13}C NMR (77 MHz, Acetone- d_6): δ 11.7 and 113.5 (2CH), 121.4 and 126.8 (2C), 127.4, 127.5 and 129.6 (3CH), 132.3 (C), 134.2, 134.3 and 134.4 (3CH), 137.6 (C), 146.0 (CH), 147.1 (C), 155 (C=N), 167 and 190 (2C=O).

2.2. Apparatus

All fluorescence measurements were carried out on a Perkin-Elmer LS50 luminescence spectrometer.

2.3. Fluorescence measurements

A fluorimetric cell was filled with 3.0 ml fluorophore **L** (5×10^{-5} M in acetonitrile solution). Then, emission spectrum of the solution was taken. This solution was titrated with standardized ytterbium ion solution and the fluorescence intensity of the system was measured. All emission spectrum was taken at an excitation wavelength of 367 nm.

3. Results and discussion

Due to the radii of lanthanide ions (from Ce^{3+} to Lu^{3+} with the range of 1.02–.80 Å, respectively), these elements have different properties such as charge densities and size and hydration energy (from Ce^{3+} to Lu^{3+} with the range of 3370–3760 kJ mol^{-1}) [37]. Thus, by using a suitable ionophore having the semi-cavity and relatively high flexibility, it is possible to construct a highly selective lanthanide ion sensor. The existence of donating nitrogen atoms in the **L** structure in order to cause a



Fig. 1. Color response of the receptor **L** in MeCN (4.0×10^{-5} M) to the addition of anions (4.0×10^{-4} M in MeCN) from the right to the left: **L** only; **L** + Pr, **L** + Nd, **L** + Eu, **L** + Er, **L** + Tb, **L** + Ce, **L** + Lu, **L** + Gd, **L** + Sm, **L** + Yb.

semi-cavity and formation of wrap-around complexes, the concept of soft-hard acid–base, the charge density, and the size of the ytterbium ion was expected to increase both the stability and selectivity of its complexes with ytterbium more than the other transition metal ions. Thus, UV–Vis absorption study in the acetonitrile solution was carried out as a primary test.

3.1. Preliminary studies

The analytes recognition could be easily followed by monitoring of the changes in the UV–Vis absorption spectrum of the receptor **L**. Initially, the qualitative estimation of the affinity of the sensor **L** towards various lanthanide ions was performed visually (see Fig. 1). Instantaneous color changes were observed from lightless to light yellow upon addition of Yb^{3+} ion solutions to **L** (4.0×10^{-5} M). Conversely, no detectable color changes were observed even in addition of a large excess of other lanthanide ions to the sensor **L**. The result indicated that the color changes were most probably owing to the formation of a new complex, with different electronic properties, between the receptor **L** and Yb^{3+} ions which cause a new color (yellow) was observed.

Fig. 2 shows the family spectra recorded on titration of a 5.0×10^{-5} M solution of **L** in acetonitrile (MeCN) with a standard ytterbium MeCN solution (5.0×10^{-3} M). Obviously seen from Fig. 2, compound **L** is characterized by a broad strong absorption band centered at 321 nm ($\epsilon = 18,680$), which can be contributed to $\pi \rightarrow \pi^*$ transition [38]. Notably, as the concentration of Yb^{3+} increased stepwise, the absorption intensity at the λ_{max} of 321 nm decrease and a new band at 473 nm appeared, which is intramolecular charge transfer (ICT) band [39]. In addition, there are two well-defined isosbestic points at 269 and 340 nm, respectively,

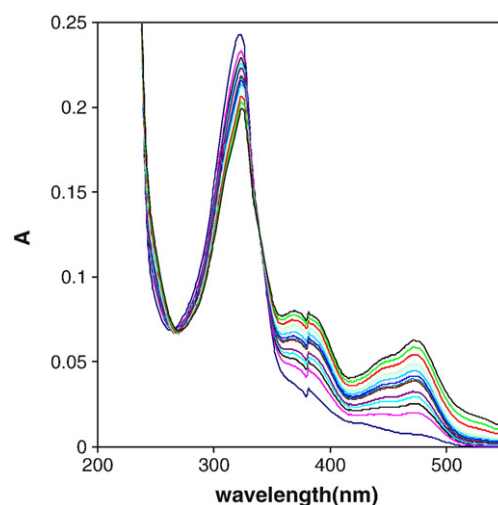


Fig. 2. Changes in the UV–vis spectra of **L** (5×10^{-5} M) upon addition of Yb^{3+} (5×10^{-3} M) in CH_3CN .

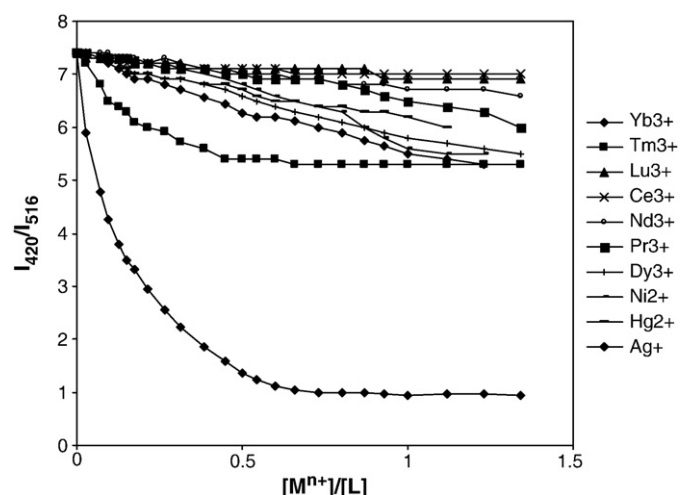


Fig. 3. Fluorescence intensity vs. $[M^{n+}]/[L]$ mole ratio plots in MeCN solution for different metal ions.

indicating that the stable complex having a certain stoichiometric ratio between the receptor **L** and Yb^{3+} form.

3.2. Fluorescence titration

In order to evaluate whether **L** could be used as a selective fluorescent chemosensor for ytterbium ion, in preliminary experiments the complexation of **L** with a number of metal ions was investigated spectrofluorometrically in acetonitrile solution at 25.0 ± 0.1 °C. A 5.0×10^{-5} M solution of **L** in acetonitrile was titrated with microliter amounts of 1.0×10^{-3} M solutions of metal ions spectrofluorometrically (at $\lambda_{ex} = 367$ nm), at a constant ionic strength of 0.01 M ammonium nitrate in 25.0 ± 0.1 °C. The resulting mole ratio plots are shown in Fig. 3. As it is obvious, in all cases, the ligand forms a 1:2 complex with metal ions in acetonitrile solution. For the evaluation of formation constants of the resulting 1:2 complexes from fluorescence intensity vs. mole ratio data, a non-linear least-squares curve fitting program KINFIT was used

Table 1
The formation constants of **L**– M^{n+} complexes.

Cation	$\log K_f$
Lu ³⁺	<2.0
Ce ³⁺	2.35 ± 0.11
Nd ³⁺	<2.0
Sm ³⁺	2.95 ± 0.11
Tb ³⁺	<2.0
Pr ³⁺	<2.0
La ³⁺	2.96 ± 0.17
Eu ³⁺	2.86 ± 0.17
Yb ³⁺	6.85 ± 0.15
Dy ³⁺	2.68 ± 0.17
Hg ²⁺	2.88 ± 0.17
Ni ²⁺	<2.0
Zn ²⁺	3.35 ± 0.15
Ag ⁺	<2.0

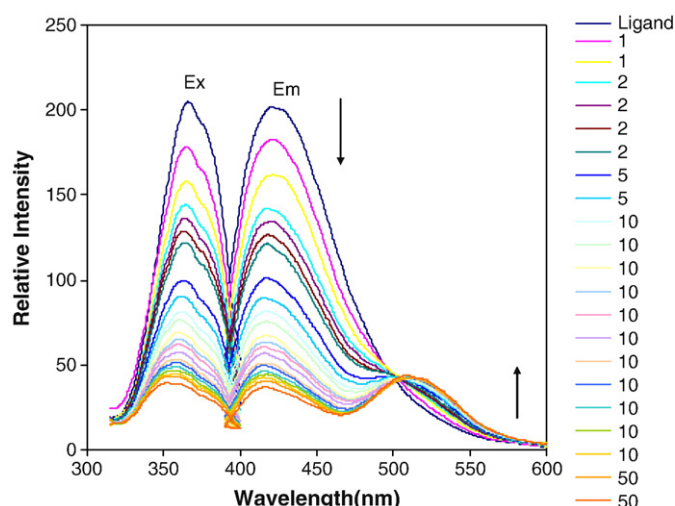


Fig. 4. Excitation (Ex) and emission (Em) spectra of **L** (5.0×10^{-5} M) in MeCN in the presence of increasing concentration of Yb^{3+} (1.0×10^{-3} M).

[40] and the results are given in Table 1. From Table 1, it was concluded that **L** was appropriate for the Yb^{3+} fluorescent sensor design.

To more evaluation whether **L** can be used as a selective fluorescent receptor for Yb^{3+} ion, excitation and emission fluorescence spectra variations were recorded which occurred upon addition of increasing amount of the Yb^{3+} ion to a MeCN solution of the **L** (5.0×10^{-5} M) at 25.0 ± 0.1 °C. Compared with the changes in absorption spectra, the response of **L** to Yb^{3+} was more remarkable in its fluorescence emission spectra.

As shown in Fig. 4, upon complexation with Yb^{3+} , the characteristic strong fluorescence excitation and emission band of **L** at 367 and 420 nm was greatly decreased, and a new band centered at 516 nm was increased. About 96 nm red shift in emission spectra occurred with this cation binding event, and an isoemission point at 503 nm was found for **L**. The structural rigidity of metal complex and metal binding close to the fluorophore might be the factors that cooperate to induce the emission band shift [41–44]. The sensor is effective for detection of 3.3×10^{-7} M to 1.0×10^{-4} M of Yb^{3+} , and the detection limit was calculated as 1.2×10^{-7} M based on 3σ of the blank as definition by IUPAC [44].

3.3. Selectivity

The selectivity behavior is obviously one of the most important characteristics of a chemosensor that is the relative sensor response for

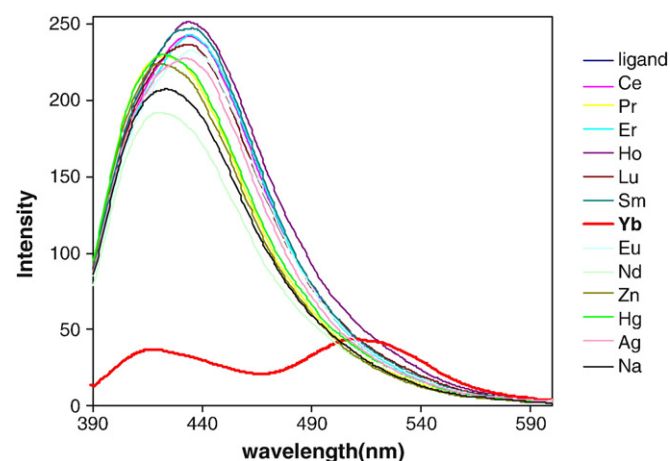


Fig. 5. Fluorescence ratiometric responses of **L** (3 ml 5.0×10^{-5} M) upon addition of cations (50 μM) (5.0×10^{-3} M) (λ_{ex} : 367 nm).

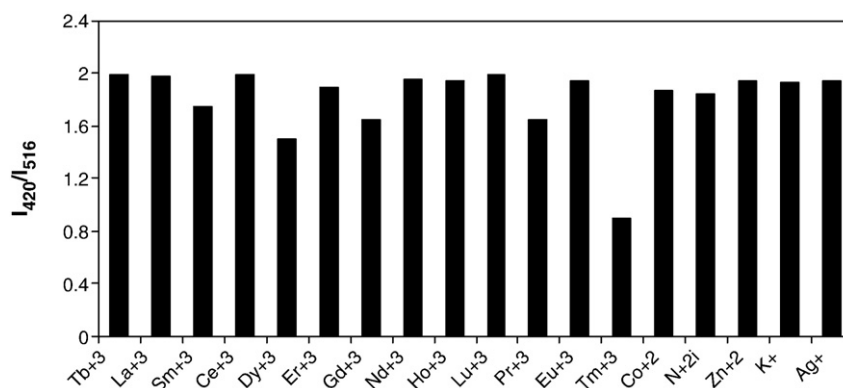


Fig. 6. Fluorescence ratiometric responses of **L** (3 ml 5.0×10^{-5} M) containing $30 \mu\text{M}$ Yb^{3+} and the background cations ($120 \mu\text{M}$) (λ_{ex} : 367 nm).

the primary ion over other ions present in solution. To examine the selectivity of **L**, we investigated its affinity for other metal cations. The influence of various metal cations on the fluorescence behaviour of **L** was shown in Fig. 5. No obvious changes in the fluorescence intensity ratio were observed, even though double equivalents of other lanthanides or other metal ions.

By contrast, the addition of Yb^{3+} ion to the solution of sensor resulted in a drastic fluorescence emission change. The fluorescence peak at 420 nm is red-shifted to 516 nm with a marked fluorescence intensity enhancement. Interestingly, sensor **L** shows excellent selectivity to Yb^{3+} in comparison to other cations.

To explore practical applicability of **L** as a Yb-selective fluorescent chemosensor, competition experiments were also performed in the presence of Yb^{3+} at $30 \mu\text{M}$ mixed with $120 \mu\text{M}$ background metal cations such as Co(II) , Ni(II) , Zn(II) , K^+ , Ag(I) and other lanthanide. The fluorescence intensity ratios (I_{420}/I_{516}) of solutions containing both background of other cations and Yb^{3+} are shown in Fig. 6. As it can be seen, other background metal ions had small or no obvious interference with the detection of Yb^{3+} . All these results indicated that **L** could be used as a potential candidate of fluorescent chemosensor for Yb^{3+} ions with very high selectivity.

4. Conclusion

In this paper, for the first time a novel ratiometric fluorescent chemosensor **L** was synthesized and its complexation with some metal ions was investigated. It showed selective and sensitive ratiometric fluorescence response to Yb^{3+} ions in MeCN solution. Upon the addition of Yb^{3+} ion, the fluorescence of **L** underwent a red shift from 420 to 516 nm gradually. A stable complex of **L**– Yb^{3+} with a stoichiometry of 2:1 was formed. Receptor **L** exhibits ratiometric fluorescent probe along a wide concentration range of Yb^{3+} ions with no interferences of background metal ions.

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