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A new Tb^{3+}-selective fluorescent sensor based on 2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-henylhydrazinecarbothioamide

M.R. Ganjali[a,b,*], B. Veismohammadi[a], M. Hosseini[c], P. Norouzi[a,b]

[a] *Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran*
[b] *Endocrinology & Metabolism Research Center, Medical Sciences/University of Tehran, Tehran, Iran*
[c] *Department of Chemistry, Islamic Azad University, Savadkooh Branch & Young Researcher Club, Savadkooh, Iran*

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ABSTRACT

A novel fluorescent chemosensor 2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide (L) has been synthesized, which revealed an emission of 530 nm and when excited at 360 nm. The fluorescent probe undergoes a fluorescent emission intensity quenching upon binding to terbium ions in MeCN solution. The fluorescence quenching of L is attributed to the 1:1 complex formation between L and Tb(III) which has been utilized as the basis for the selective detection of Tb(III). The linear response range covers a concentration range of Tb(III) from 4.0×10^{-7} to 1.0×10^{-5} M and the detection limit is 1.4×10^{-7} M. The association constant of the 1:1 complex formation for L–Tb^{+3} was calculated to be $6.01 \times 10^{6}\ M^{-1}$, and the fluorescent probe exhibits high selectivity over other common metal ions mono-, di-, and trivalent cations indicate good selectivity for Tb(III) ions over a large number of interfering cations.

1. Introduction

Difficulties in the quantity of determination of lanthanides result from the great chemical similarity of their ions [1,2]. Available instrumental methods for this purpose including, flame photometry, atomic absorption spectrometry, electron microscope analysis and neutron activation analysis often suffer from such parameters as high cost, need for large size samples and inability for continuous monitoring.

In the past two decades, an increasing interest has been focused on the development of fluorescent sensors, which offer distinct advantages in terms of sensitivity, selectivity, response time and remote sensing [3–9]. The key point in development of such fluorescence sensors is the design of a fluorescence sensing element, which usually consists of a fluorophore (signaling moiety) linked to an ionophore (recognition moiety), called as a fluoroionophore. Here, the recognition process by the ionophore part is converted to a change in the fluorophore's fluorescence signal, brought about by the perturbation of such photoinduced processes as energy transfer, charge transfer, electron transfer, formation or disappearance of excimers and exciplexes. Obviously, the topology, size and nature of donating atoms of the recognition moiety play the most important role in selectivity behavior and binding efficiency of the sensor [10].

Terbium oxide is used in green phosphors in fluorescent lamps and color TV tubes. Sodium terbium borate is used in solid state devices. The brilliant fluorescence allows terbium to be used as a probe in biochemistry, where it somewhat resembles calcium in its behavior. Terbium "green" phosphors (which fluorescence a brilliant lemon-yellow) are combined with divalent Europium blue phosphors and trivalent europium red phosphors to provide the "trichromatic" lighting technology, which is by far the largest consumer of the world's terbium supply. Trichromatic lighting provides much higher light output for a given amount of electrical energy than incandescent lighting [11]. They have long fluorescence lifetime and their excited states have strong fluorescence emission, thus europium(III) and terbium(III) have extensive applications in biological medicine, especially in the fluorescence imagery cancer radiation treatment [12], fluorescence mark [13], and fluorescence analysis [14].

On the other hand, dansyl groups are one of the most attractive fluorophores [15–17] due to its strong fluorescence, relatively long emission wavelength and easy derivation. Commonly a typical fluorescent cation sensor consists of a fluorophore and a binding unit.

In this paper, a novel and simple fluorescent cation receptor was obtained by incorporating phenylhydrazinecarbothioamide moieties (binding sites) into dansyle group (fluorophore). As expected, the receptor L, Scheme 1, (5×10^{-6} M) exhibited a quenching in the

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[*] Corresponding author at: Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran. Tel.: +98 21 61112788; fax: +98 21 66495291.

E-mail address: ganjali@khayam.ut.ac.ir (M.R. Ganjali).

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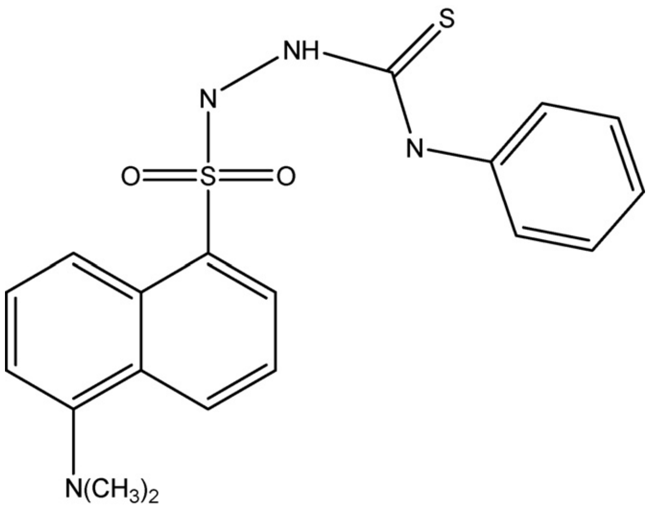

Scheme 1. Chemical structure of compound L.

fluorescent emission intensity upon addition of cations tested in MeCN when excited at $\lambda_{ex} = 360$ nm.

2. Experimental

2.1. Reagents

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

The fluorogenic reagent L was prepared as follows: A mixture of phenyliosthiocyanate (2 mmol, 0.27 gr) and 5-(dimethylamino)-1-naphthalene sulfonohydrazide) (2 mmol, 0.53 gr) in dichloromethane (35 ml) was stirred at ambient temperature for 5 h. The precipitate was filtered and washed with dichloromethane (5 ml) [18]. The solid was recrystallized from 1:1 acetone–ethanol and the product was obtained as yellow crystals. H NMR (100 MHZ, $CDCl_3$):

2.99 (6H, S, NMe_2), 7.35 (1H, t, $J = 7.5$ Hz, CH), 7.38 (1H, d, $J = 6.5$ Hz, CH), 7.43 (1H, dd, $J = 8.9$ Hz, $J = 6.0$ Hz) CH, 7.64 (1H, dd, $J = 8.5$ Hz, $J = 6.3$ Hz CH), 7.70–7.75 (4H, M, 4CH), 8.22 (1H, d, $J = 6.3$ Hz, CH), 8.30 (1H, d, $J = 8.5$ Hz, CH), 8.35 (1H, d, $J = 8.9$ Hz, CH), 8.9 (1H, br, NH), 10.05 (1H, S, NH) 45.20 (NMe_2), 112.25, 114.39, 119.65, 126.69 (4CH), 126.95, 127.43 (2CH), 128.33, 129.05 (2CH), 129.61 (Cl, 130.15, 133.64 (2CH), 133.17 (C), 135 (CH) 153.72 (C), 190.39 C = S.

2.2. Apparatus

All fluorescence measurements were carried out on a PerkinElmer LS50 luminescence spectrometer.

3. Result and discussion

The cation binding properties were investigated by UV–vis absorption and fluorescence spectroscopy. The titration experiments were carried out in CH_3CN solution by adding aliquots of Tb(III). As shown in Fig. 1, this ligand possessed three intensive absorption bands centred at 240 ($\varepsilon = 18680$) and 330 ($\varepsilon = 10640$) which can be contributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. Notably, the titration of L against Tb^{3+} led to a pronounced and red-shifted shoulder in the UV spectra ($\Delta\lambda_{max} = 40$ nm shift) with two well defined isosbestic point at 266 nm and 314 nm (Fig. 1).

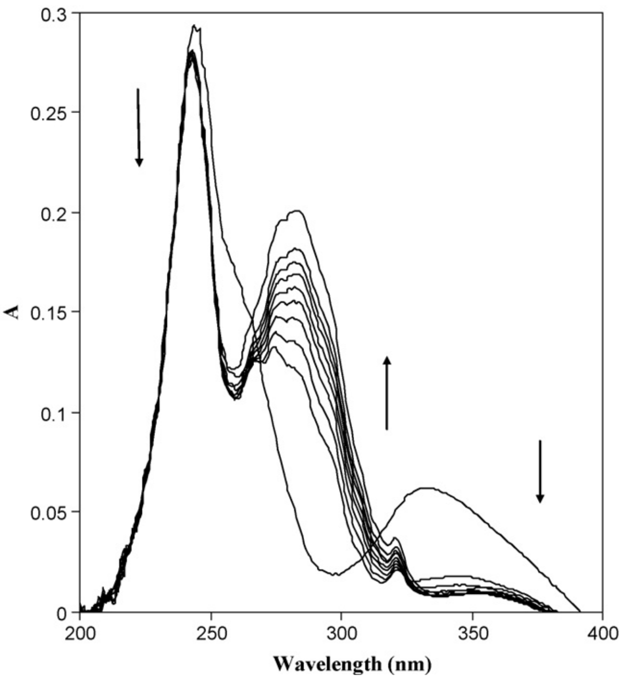

Fig. 1. Changes in the UV–vis spectra of L (5×10^{-5} M) upon addition of Tb^{+3} (1×10^{-3} M) in MeCN solution.

All of the fluorescence titration experimental was performed in MeCN solution and maximum excitation wavelength was selected at 360 nm. As illustrated in Fig. 2, compound L showed a typical emission band of the dansyl group around 530 nm, which was considerably quenched in the presence of Tb^{3+}. This phenomenon may occur by electron transfer from the exited dansyl moiety to the proximate terbium ions [19]. When the concentration of Tb^{3+} ions was increased up to 2.6×10^{-6} M, more than 80% quenching of the initial fluorescence of L was observed (Fig. 2). The shape and position of the fluorescence excitation and emission bands does not change in the presence of terbium ions compared to those of the free ligand. Both the excitation and emission intensities sharply decreased as a function of Tb^{3+}. It is noteworthy that because of very short fluorescence lifetimes and low concentration conditions used, the effect of the concentration quencher should be negligible.

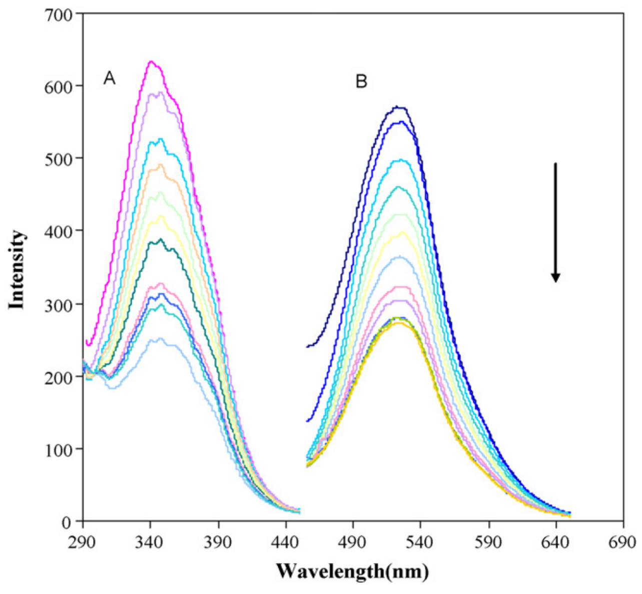

Fig. 2. Fluorescence titration of L with Tb^{+3} in MeCN solution, $[L] = 5 \times 10^{-6}$ M, $[Tb^{+3}] = 5 \times 10^{-4}$ M, $\lambda_{ex} = 360$ nm.

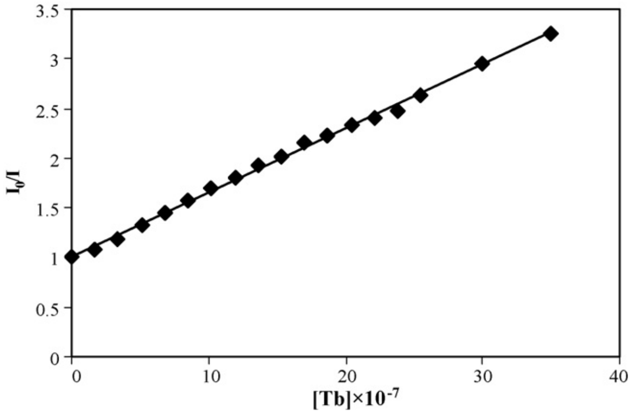

Fig. 3. Stern–Volmer plot of titration of L with Tb^{3+}.

From the fluorescence titration experiments, the association constant (K_a) of the 1:1 complex formation for L–Tb^{3+} was calculated to be $(6.22 \pm 0.02)10^6\,M^{-1}$ by the Stern–Volmer equation [20]. Furthermore, the detection limit of L as a fluorescent sensor for the analysis of Tb^{3+} was also determined from the plot of the fluorescence intensity as a function of the concentration of added metal ions (Fig. 3). It was found that L has a detection limit of 1.4×10^{-7} M for Tb^{3+} ions [21], which is quite low for the detection of the Tb^{3+} ions found in many chemical and biological systems.

To obtain more information about the conformational changes of L upon complexation to the lanthanide ion, the molecular structures of the uncomplexed compound L and its complex with the lanthanide ion were build using the molecular mechanics calculations. It is worth mentioning that, in many cases, large molecular systems can be modeled successfully by molecular mechanics, whilst avoiding quantum mechanical calculations entirely [22]. The calculations carried out in this study were based on the use of MM$^+$ Molecular Mechanics force field, with a Polak-Ribiere algorithm having a convergence limit 0.01 kcal mol^{-1}, performed on a Pentium IV personal computer with Hyperchem version 7.0 [23]. The structure of the free ligand was optimized using the 6-31G* basis set at the restricted Hartree-Fock (RHF) level of theory. The optimized structure of the ligand was then used to find out the initial structure of its lanthanide complex. Finally, the structure of the resulting 1:1 complex was optimized at the semiempirical PM3 [24] level of theory employing the restricted Hartree-Fock (RHF). The optimized structures are shown in Fig. 4.

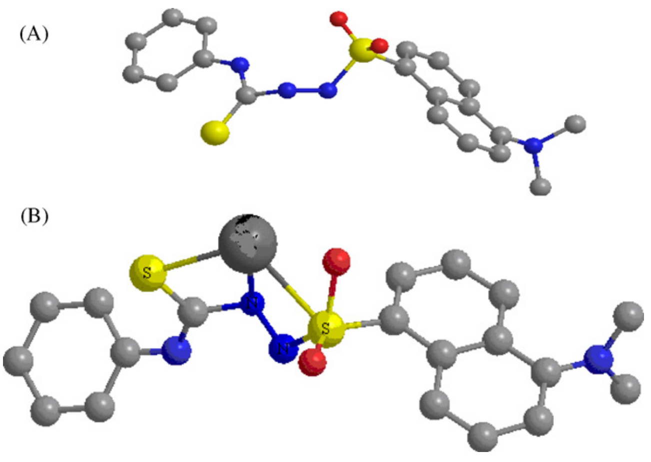

Fig. 4. Optimized structures of free L (A) and its 1:1 complex with Tb^{3+} ion.

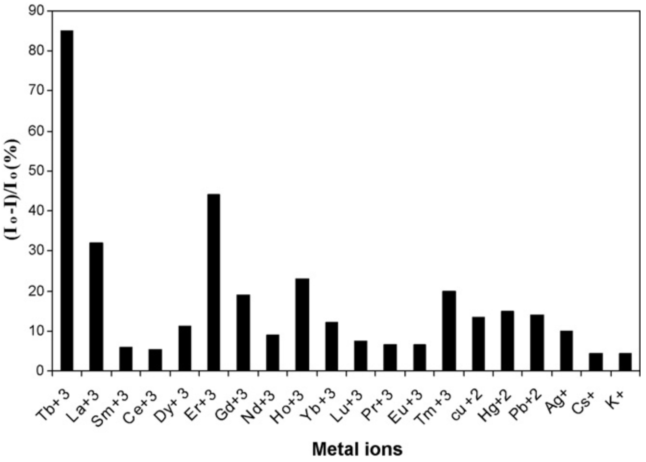

Fig. 5. Quench ratio $(I_o - I)/I_o$ of fluorescence intensity of L (5×10^{-6} M) upon the addition of two equiv metal ions in MeCN solution.

As shown is Fig. 4, the case of free ligand, the benzo ring and the dibenzo dansyl groups in the ligand are located in a more or less planar situation whilst in the case of the complex, the structure is somewhat folded to result in the lowest conformational energy. In the optimized complex structure, compound L is a tri dentate ligand and establishes coordination bonds with the lanthanide ion over its two sulfurs and one nitrogen donating groups.

Under the same conditions as above, we also tested the fluorescent response of L to other metal ions besides Tb^{3+}. As shown in Fig. 5, though the fluorescence of L at 520 nm was strongly quenched by Tb^{3+}, no significant spectral changes of L occurred in the presence of two equiv Nd^{3+}, Sm^{3+}, Yb^{3+}, Er^{3+}, La^{3+}, Ce^{3+}, Lu^{3+}, Eu^{3+}, Gd^{3+}, Ho^{3+}, Tm^{3+}, Pr^{3+}, Dy^{3+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}, Cs^{+} and K^{+} respectively, in MeCN solution. Furthermore, the K_a values of 1:1 complexes L–M^{n+} for other metal ions were calculated from the fluorescence titration experiments, and summarized in Table 1. The selectivity towards Tb^{3+} with respect to other metal ions (expressed as the ratio of the stability constants) was found to be around 55-fold or more. These results implied that L showed high selectivity towards Tb^{3+} over other metal ions tested in a neutral aqueous solution.

To test the practical applicability of L as a Tb^{3+}-selective fluorescence chemosensor, competition experiments were carried. Thus, L (5×10^{-6} mol L^{-1}) was treated with Tb^{3+} (5×10^{-5} mol L^{-1}) in the presence of background metal ions (5×10^{-4} mol L^{-1}), respectively, which resulted in diverse fluorescence behaviors. As shown in Fig. 6, except for La^{3+}, Er^{3+}, and Ho^{3+} ions, other background metal ions had little or no obvious interference with the detection of Tb^{3+} ions. These results suggested that compound L could be used as a potential Tb^{3+}-selective fluorescent chemosensor.

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

Cation	log K_f
Tm^{3+}	2.15 ± 0.15
Ce^{3+}	2.15 ± 0.11
Nd^{3+}	<2.0
Sm^{3+}	2.25 ± 0.11
La^{3+}	3.46 ± 0.17
Er^{3+}	3.86 ± 0.17
Tb^{3+}	6.22 ± 0.17
Dy3^{+}	2.78 ± 0.17
Ho^{3+}	3.88 ± 0.17
Eu^{3+}	<2.0
Yb^{3+}	2.45 ± 0.15
Lu^{3+}	<2.0

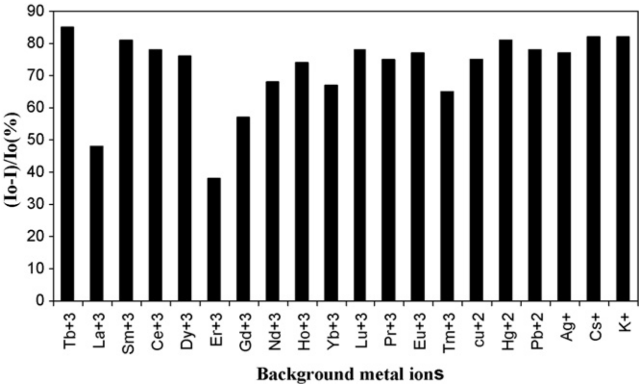

Fig. 6. Quench ration $(I_o - I)/I_o$ of fluorescence intensity of L (5×10^{-6} M) upon the addition of Tb^{+3} (5×10^{-5} mol L^{-1}) in the presence of background metal ions (5×10^{-4} mol L^{-1}), in MeCN.

4. Conclusion

In summary, we have presented a new fluorescent sensor based on a dansyl 2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide, which showed high sensitivity and selectivity towards Tb^{3+} ions over a wide range of metal ions in MeCN solution. The detection limit for $Tb^{3+}$was found to be 1.4×10^{-7} M. Thus, L may be considered as a potentially practical Tb^{3+}-selective fluorescent.

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