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Spectroscopic Study of the Photophysical Properties of Rare Earth Ions Encapsulated: Water Soluble Functional Calixresorcin[4]Arene

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**SPECTROSCOPIC STUDY OF THE PHOTOPHYSICAL
PROPERTIES OF RARE EARTH IONS ENCAPSULATED:
WATER SOLUBLE FUNCTIONAL
CALIXRESORCIN[4]ARENE**

Key Words: Spectroscopy, Tetra *para* sulfo–phenylmethyl –calixresorcin[4]arene, Photophysical properties, Encapsulated terbium and europium ion

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ABSTRACT

A novel macrocyclic compound—water soluble functional calixresorcin[4]arenes—tetra *para* sulfo–phenylmethyl–calixresorcin[4]arenes was synthesized for the first time. The photophysical properties of terbium and europium ions encapsulated in the macrocyclic ligand were studied in detail. The triplet state energy of the calixresorcin[4]arene was

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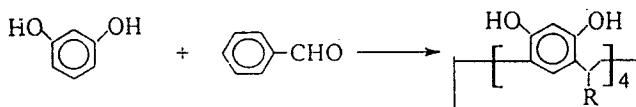
** Corresponding author

determined to be 24400 cm⁻¹ by the low temperature phosphorescence spectrum and it was found that it can sensitize both terbium ion and europium ion. The possible energy transfer process between the functional calixresorcin[4]arene and the encapsulated Tb³⁺ and Eu³⁺ was discussed. The luminescence quantum efficiency of Tb³⁺- calixresorcin[4]arene was calculated.

INTRODUCTION

In recent years, the interesting photophysical properties of rare earth with calixarenes have been reported [7-10]. It was found that some calixarene ligands can form photoactive complexes with rare earth ions. But all this research has been focused on the complexes with ligands containing phenolic cycle [11-15]. In the context, one novel macrocyclic water soluble functional calixarenes are a class of hydrophobic macrocyclic receptors composed of phenolic units linked by methylene bridges [1]. The versatility of these compounds has been demonstrated by a variety of functionalizations at the lower rim (phenolic hydroxyl groups), such as: ester, keto, amide, and sulfo derivatives [2-4]. It can encapsulate metal ions so as to form complexes with interesting properties.

The luminescence properties of rare earth ions have been of much interest because of their potential use as probes and labels for a variety of chemical and biological applications [5, 6, 7]. To design a good emitting system one has to take two prerequisites into consideration: one is that rare earth ions must be shielded from solvent molecules through encapsulation into the ligand, the other is that the ligand must have the lowest excited state sufficiently high for the energy transfer to rare earth ions. Current research has demonstrated that some macrocyclic compounds such as: crown ether derivatives, 2,2'-bipyridine-containing tripode and tetrapode ligands, and 2,2'-bipyridine based cryptands are useful as potential ligands for the encapsulation of rare earth ions. In the recent ixresorcin[4]arenes which have resorcin groups—tetra *para*sulfo-phenylmethyl-calixresorcin[4]arene with pendent sulfonate-group is synthesized and the photophysical properties of the ligand encapsulating the terbium and europium ions are studied. The energy transfer mechanism between ligand and encapsulated rare earth ions is discussed in detail.



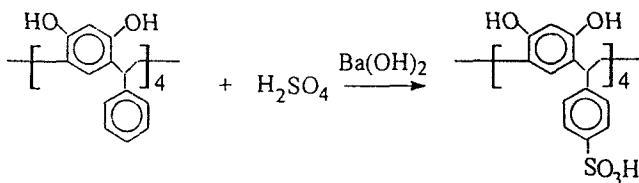
Scheme 1

EXPERIMENTAL DETAILS

The synthesis of tetra phenylmethyl-calixresorcin[4]arene (abbreviated as C[4]AL): 1.1g (10 mmol) resorcin was dissolved in 16 ml absolute ethanol. Then 16 ml water and 8 ml concentrated hydrochloric acid were added into the solution under a nitrogen atmosphere. For the next step, 1.2 ml (10 mmol) of benzaldehyde was dipped slowly for 30 minutes under nitrogen protection. The reaction was carried out for one hour at 50 °C and was cooled to 25 °C. After 48 hours of reaction, the precipitate was filtered and recrystallized from methanol, dried first at room temperature, and was stored over a silica-gel drier: yield 70%, m.p. 350-352 °C (Elemental analysis, found: C, 78.70 ; H, 5.06. $C_{52}H_{44}O_8$ requires C, 78.37; H, 5.56). IR, ν_{max} (KBr) benzoyl cycle (1619, 1404, 703 cm^{-1}). 1H (ppm) 8H (90 MHz; $CDCl_3$; 25 °C, $SiMe_4$) 8.688 (8 H), 6.247 (4 H), 6.847 (4 H), 5.748 (4 H), 7.088 (8 H), 7.077 (8 H), 6.866 (4 H). Scheme 1 gives the formula for the reaction.

The synthesis of water soluble tetra para sulfo-phenylmethyl-calixresorcin[4]arene (abbreviated as C[4]SAL): 2.2 mmol calixresorcinarenes was added into 20 ml concentrated sulfuric acid, and was heated to 80-90 °C. After 4 hours the mixture was cooled. A hot solution of $Ba(OH)_2$ was added into the above solution. Yield was 70%, m.p. >360 °C (Elemental analysis, found: C, 52.47; H, 3.29; S, 10.13. $C_{52}H_{44}O_{20}S_4$ requires C, 52.05; H, 3.70; S, 10.48). IR, ν_{max} (KBr) SO_3H (1171.9, 1077.6 and 1033.9 cm^{-1}); Benzoyl cycyle (1618, 1405 and 701 cm^{-1}). 1H (ppm) 8H (90 MHz; $CDCl_3$; 25 °C, $SiMe_4$) 7.583 (8 H), 7.213 (4 H), 7.341 (4 H), 7.085 (4 H). Scheme 2 gives the formula for the reaction.

The elemental analysis of these complexes were measured with a CARIO-ERBA 1106 elemental analyzer. Infrared (IR) spectra in the regions 4000-400 cm^{-1} were recorded on a



Scheme 2

BIO-RAD infrared spectrophotometer (Model FTS-7) with KBr pellet technique. UV-visible spectra were measured with a UV-300 spectrophotometer. The fluorescence spectra were obtained on a SPEX FL-2T2 spectrofluorometer with excitation and emission slit at 0.6 mm. The fluorescence lifetimes were performed on a SPEX 1934D spectrophotometer using a 450 W xenon lamp as the excitation source. The phosphorescence spectra and lifetimes measurements at 77 K were carried out on rigid-glass samples in a 12 mm square quartz cube, placed within a glass Dewar with quartz windows using the same instrument as above. Luminescence quantum yields were determined by using aqueous ions of Tb^{3+} ($\phi=0.08$ for 376 nm excitation) and Eu^{3+} ($\phi=0.0074$ for 394 nm excitation) as standards.

RESULTS AND DISCUSSION

The macrocyclic ligand—C[4]AL and C[4]SAL were synthesized according to Scheme 1 and Scheme 2, respectively. The compositions of these ligands were confirmed on the basis of elemental analysis, IR spectra, and NMR spectra (as shown in the experimental section).

In order to study the photophysical properties of rare earth ions (Tb^{3+} and Eu^{3+}) encapsulated in C[4]SAL ligand, luminescence spectra of C[4]SAL with terbium and europium salts ($\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$) in a water solution were measured. We measured the luminescence spectra by changing the molecular ratios of $\text{Eu}(\text{NO}_3)_3$ (and $\text{Tb}(\text{NO}_3)_3$) to C[4]SAL. It was found all terbium ion salts with C[4]SAL can show strong luminescence, while it was contrary to europium ion salts with C[4]SAL. The mixed solution of $\text{Eu}(\text{NO}_3)_3$ with C[4]SAL showed very weak characteristic luminescence of

TABLE 1

The Luminescence Properties of Tb^{3+} -C[4]SAL

Tb^{3+} -C[4]SAL	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$			Luminescence quantum efficiencies / %
1×10^{-5} - 5×10^{-6}	273.6	490,	542,	584,	621
2×10^{-5} - 5×10^{-6}	274.0	490,	543,	585,	620
5×10^{-5} - 5×10^{-6}	273.6	489,	544,	585,	621
1×10^{-4} - 5×10^{-6}	274.4	490,	544,	584,	620
1×10^{-4} - 1×10^{-5}	274.4	490,	544,	583,	620
1×10^{-4} - 2×10^{-5}	274.0	491,	544,	585,	620
1×10^{-4} - 5×10^{-5}	275.8	491,	544,	585,	620
1×10^{-4} - 1×10^{-4}	274.4	490,	544,	585,	620

Eu^{3+} ion. Table 1 show the luminescence properties of different mixed solutions of $\text{Tb}(\text{NO}_3)_3$ with C[4]SAL. Among these species, luminescence intensity is strongest when the molecular ratio of $\text{Tb}(\text{NO}_3)_3$ to C[4]SAL is 5 ($\text{Tb}(\text{NO}_3)_3 = 1.0 \times 10^{-4}$ mol/L, C[4]SAL= 2.0×10^{-5} mol/L) (as shown in Fig. 1). From Fig. 1, it can be seen the emission of Tb^{3+} -C[4]SAL at 491 nm, 544 nm, 585 nm and 620 nm originated from $5\text{D}_4 \rightarrow 7\text{F}_6$, $5\text{D}_4 \rightarrow 7\text{F}_5$, $5\text{D}_4 \rightarrow 7\text{F}_4$ and $5\text{D}_4 \rightarrow 7\text{F}_3$ transitions respectively, and $5\text{D}_4 \rightarrow 7\text{F}_5$ transition is the strongest. Different ratios between Tb^{3+} and C[4]SAL only change the emission intensity, whereas the emission position changes hardly. Simultaneously, the fluorescence spectrum of $\text{Tb}(\text{NO}_3)_3$ with the same concentration was measured.

The results show that the spectra exhibit the same emission, but the emission intensity of corresponding transitions were weaker than that of Tb^{3+} -C[4]SAL. The characteristic luminescence was quenched by C[4]SAL. All these phenomena proved that Tb^{3+} may coordinate with C[4]SAL and Tb^{3+} may be encapsulated into the cavity of C[4]SAL. So, the luminescence of the terbium ion is sensitized by the effective energy transfer from the macrocyclic ligand—C[4]SAL.

To further verify the coordination between Tb^{3+} and C[4]SAL, the IR and NMR spectrum of free ligand-C[4]SAL and Tb^{3+} -C[4]SAL were measured. At first, some amount of chloroform solution of C[4]SAL was used to extract Tb^{3+} salt solution. $\text{NH}_3\text{-NH}_4\text{Cl}$ acts as shock solution, whose pH value was adjusted to be 9 ~ 10. After

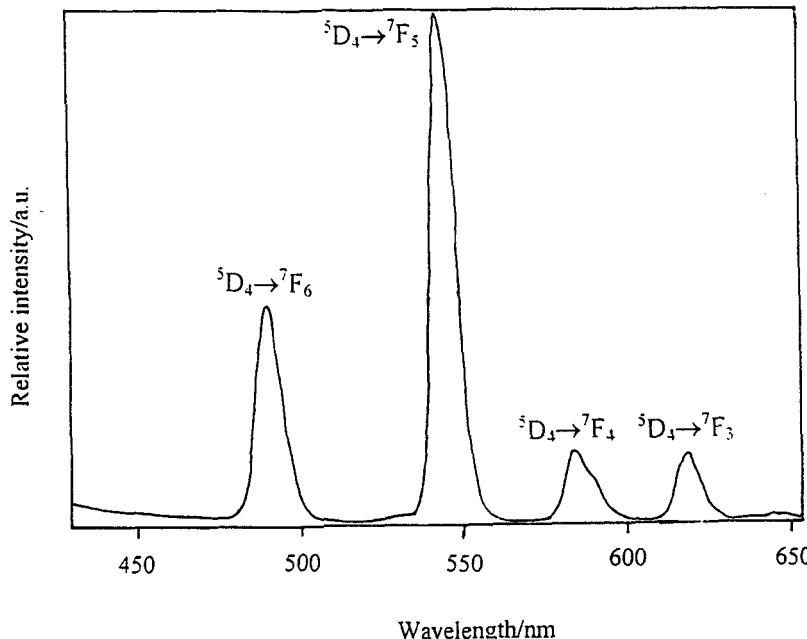


FIG. 1 The fluorescence spectrum of Tb^{3+} -C[4]SAL (—) ($\text{Tb}(\text{NO}_3)_3 = 1.0 \times 10^{-4}$ mol/L, C[4]SAL = 1.0×10^{-4} mol/L)

vibrating for one half hour, the solution was centrifugally treated with a rotational speed under 2000 rpm. Some solid sample was obtained and dried; and its IR spectrum was measured. Fig. 2 shows the IR spectra of C[4]SAL (A), and Tb^{3+} -C[4]SAL (B). From Fig. 2, it can be seen that the characteristic absorption band ($1614\text{--}1616\text{ cm}^{-1}$) belonging to the aromatic cycle in the IR spectrum of Tb^{3+} -C[4]SAL shows a weaker intensity compared with that of the free ligand C[4]SAL. But the characteristic absorption peak of the hydroxyl group hardly changes, which suggested that Tb^{3+} had entered the cavity of C[4]SAL, i.e., the ligand had encapsulated the Tb^{3+} ion.

Fig. 3 gives the NMR spectrum of C[4]SAL (A), and Tb^{3+} -C[4]SAL (B), respectively. From the figure, it can be seen that the chemical shift belonging to the aromatic cycle shift

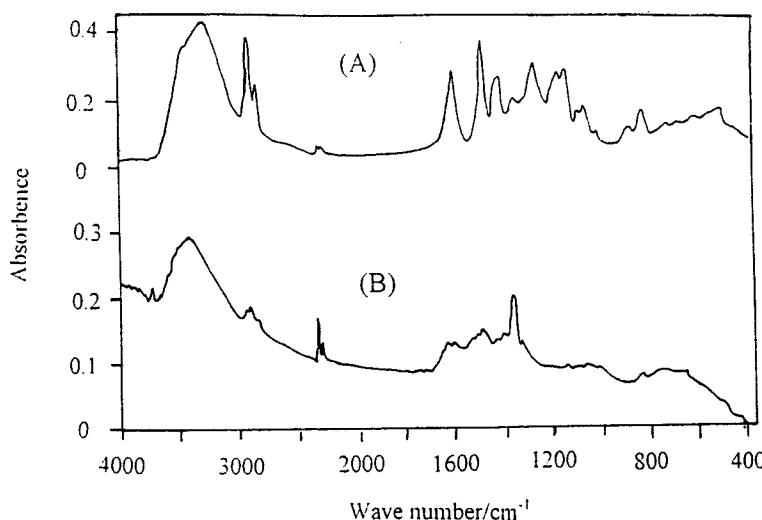


FIG. 2 The IR spectra of Tb^{3+} -C[4]SAL (A) and C[4]SAL (B)

from the lower field of free ligand (6.840-6.725, 7.898-7.871) to the higher field of complex Tb^{3+} -C[4]SAL (6.233-6.118, 7.291-7.264), confirms that there exists a weak interaction between the π electron conjugated system of aromatic (phenolic cycle of resorcin) groups and the Tb^{3+} ion. So the complex of Tb^{3+} and C[4]SAL has indeed formed, and Tb^{3+} has entered the cavity of C[4]SAL. The same results can be obtained for the Eu^{3+} -C[4]SAL complex.

Fig 4 shows the absorption and excitation spectra of Tb^{3+} -C[4]SAL. Obviously, the absorption spectrum of Tb^{3+} -C[4]SAL is similar to the excitation spectrum of Tb^{3+} -C[4]SAL. The maximum absorption peak is 284 nm and the maximum excitation peak is at 288 nm. It can be well explained that the energy donor is the phenolic cycle of resorcin belonging to the C[4]SAL. The C[4]SAL absorbs energy and transfers it effectively to Tb^{3+} .

In order to elucidate the energy transfer mechanism of the Tb complex with C[4]SAL, the low temperature phosphorescence spectrum of C[4]SAL was measured at 77°K. The Gd^{3+}

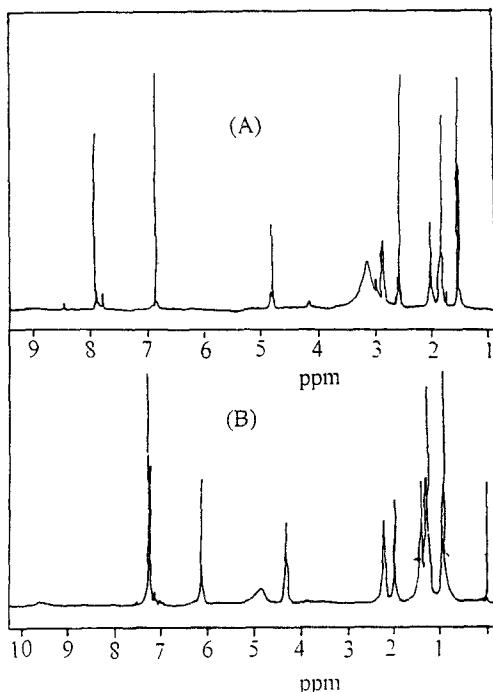


FIG. 3 The NMR spectra of Tb^{3+} -C[4]SAL (A) and C[4]SAL (B)

ion was introduced to the water solution of C[4]SAL for the reason that its coordination with C[4]SAL can enhance the phosphorescence of the ligand greatly. Fig. 5 gives the phosphorescence spectrum of C[4]SAL. The maximum phosphorescence emission peak is about at 410 nm ($\sim 24390 \text{ cm}^{-1}$), and the triplet state energy is determined to be about 24400 cm^{-1} .

The energy difference between the triplet of the ligands and the resonance energy levels of Eu^{3+} ($^5\text{D}_0$) (17400 cm^{-1}) and Tb^{3+} ($^5\text{D}_4$) (20500 cm^{-1}) were calculated to be 7000 cm^{-1} and 3900 cm^{-1} , separately. From the data of the energy difference [$\Delta E(\text{Tr}-^5\text{D}_j)$, $j=1$ or 4], it can be seen that the macrocyclic ligand can both sensitize the europium and terbium ions effectively, but the triplet energy position of C[4]SAL is more suitable for the excited

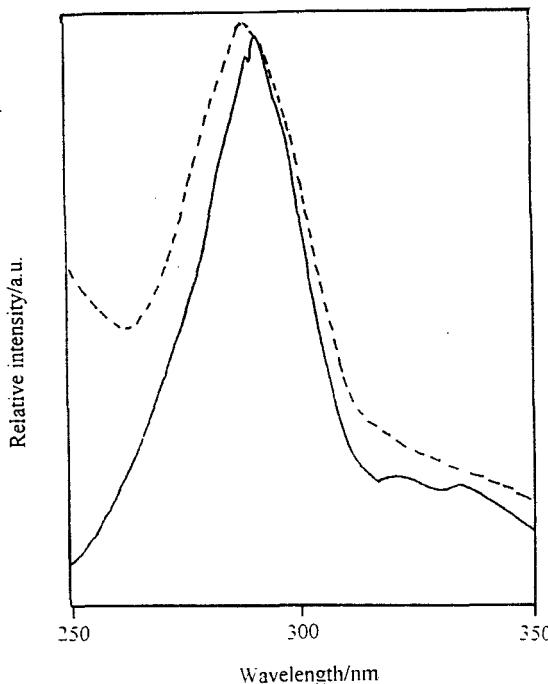


FIG. 4 The absorption spectrum (—) and excitation spectrum (—) of Tb^{3+} -C[4]SAL

energy level of Tb^{3+} , so it can be predicted that the fluorescence intensity of Tb^{3+} complexes would be stronger. According to the general luminescence principle of rare earth complexes with organic ligands, the intramolecular energy transfer (IMET) efficiency depends chiefly on two energy transfer processes: [15] the first is from lowest triplet level of ligands to the emissive energy level of Ln^{3+} ion by the Dexter's resonant exchange interaction; the second is an inverse energy transfer via a thermal de-activation mechanism. Both energy transfer rate constants are dependent on the energy difference between the lowest triplet energy level of ligands and the resonant emissive energy of Ln^{3+} .

The very weak emission intensity of Eu^{3+} -C[4]SAL is due to two reasons: one is the triplet state energy of C[4]SAL is not suitable for the resonant energy level of the Eu^{3+} ion; the other, and more important, reason is rationalized by the C=O-to- Eu^{3+} charge-transfer

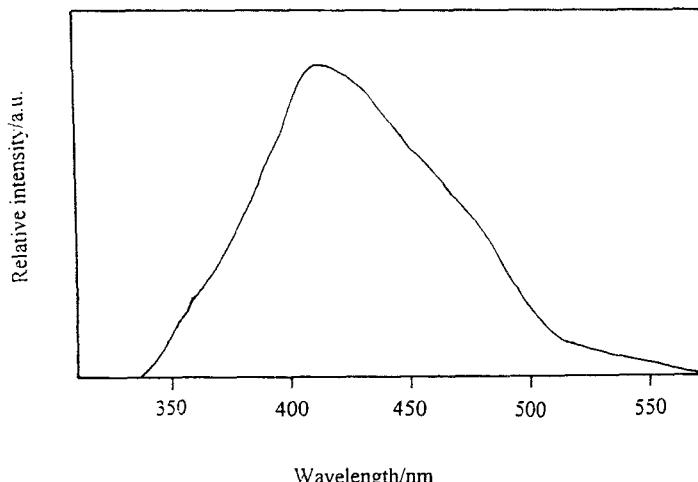


FIG. 5 The low temperature phosphorescence spectrum of Gd^{3+} -C[4]SAL at 77° K

band (abbreviated as CT Band) which appears PhO ($^3\pi\pi^*$) (about 26400 cm^{-1}) [11]. The charge-transfer state level efficiently deactivates the excited singlet state of the phenol unit ($^1\pi\pi^*$) (about at 34800 cm^{-1}) to the ground state and the energy of the excited singlet state can not be transferred to the triplet state energy ($^3\pi\pi^*$) by intersystem crossing (abbreviated as ISC) efficiently. So the energy transferred to the triplet state energy is too little to sensitize an emissive energy level of europium ion effectively.

Table 1 gives the fluorescence quantum efficiency of Tb^{3+} -C[4]SAL complex in water solution. From Table 1, it can be seen that the quantum efficiency of the Tb^{3+} -C[4]SAL complex is relatively large, which indicates that the macrocycle ligand—C[4]SAL is an ideal sensitizer for the luminescence of Tb^{3+} ion. The maximum quantum efficiency of Tb^{3+} ion is up to 0.18 when the component concentration is $\text{Tb}(\text{NO}_3)_3 = 1.0 \times 10^{-4}\text{ mol/L}$ and $\text{C}[4]\text{SAL} = 2.0 \times 10^{-5}\text{ mol/L}$.

CONCLUSIONS

A novel water soluble functional calixresorcin[4]arene-C[4]SAL is synthesized and the photophysical properties are discussed in detail. Compared to the NMR and IR spectra of

Tb^{3+} -C[4]SAL and C[4]SAL, it is found that both the terbium and europium ion can be encapsulated into the cavity of a macrocyclic ligand and then form coordination compounds between C[4]SAL and Tb^{3+} in a solution system. The triplet state energy of C[4]SAL is more suitable for the sensitized luminescence of Tb^{3+} than for that of Eu^{3+} . An effective intramolecular energy transfer process can take place from the triplet state energy of C[4]SAL to the resonant emissive level of Tb^{3+} effectively. Because of the existence of the charge-transfer band of C=O-to- Eu^{3+} and an unsuitable energy match, Eu^{3+} -C[4]SAL only shows very weak characteristic luminescence of Eu^{3+} .

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