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Near-IR luminescence and photophysics of Yb-porphyrinate complexes

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Abstract

Near-infrared photoluminescence of a series of Yb³⁺-porphyrinate complexes were studied. The complexes can be efficiently excited with visible light and give characteristic Yb³⁺ emission. The photoluminescence efficiency was greatly affected by the structure of complexes, especially the side moiety of the porphyrin ring. One of the complexes gives a well-split spectrum at room temperature, and the intensity shift of the split peaks as a function of temperature can be described by the Maxwell–Boltzmann law. The transitions were discussed and a proposed energy level diagram of Yb³⁺ is proposed. Good agreement was obtained between the experimental results and theory. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The trivalent rare earth or lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes. Most of the work on luminescent lanthanide complex has been concentrated on Eu³⁺, Tb³⁺, Dy³⁺ and Sm³⁺ complexes, which all show emission in the visible range of the spectrum. More specifically, chelates of Eu³⁺ and Tb³⁺ have drawn considerable interest because of their potential application as luminescent markers in fluoroimmuno assays and time-resolved microscopy [1]. In such applications, the complexes usually contain an organic chromophore which can

transfer excitation energy to the encapsulated lanthanide ion in order to overcome the ion's intrinsically low extinction coefficient. Recently, there has been a growing interest in complexes of the near-infrared (NIR) emitting lanthanide ions, such as Er³⁺, Yb³⁺ and Nd³⁺, for applications in fluoroimmuno assays [2–4], laser systems [5,6], and optical amplification [7]. However, only a few studies have been reported on the sensitized emission of Nd³⁺, Yb³⁺ and Er³⁺ [2–4,8,9].

In this Letter, we study the NIR luminescence properties of a series of novel Yb-porphyrinate complexes. NIR luminescence of Yb-porphyrinate complexes have been applied in in vivo luminescence localization of tumors using fiber-laser spectrofluorometry, in which the luminescence contrast ratio reaches 10–45, compared with 1.1–1.2 for classic technique, and the phototoxicity of porphyrin also decreases after Yb-porphyrinate

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complex was used [10]. However, knowledge on the relation between luminescence efficiency and structural information will help to develop a novel complex with more efficient emission, and thus further enhance the luminescence contrast. Thus a series of Yb-porphyrinate complexes in which the porphyrins ring were replaced with different moieties were synthesized. Experimental results on luminescence properties and X-ray crystal structure revealed that the side moiety of porphyrin greatly affects the luminescence efficiency of the Yb-porphyrinate complexes. Based on the Maxwell–Boltzmann law, the well-split spectrum of Yb^{3+} ions and its temperature dependence are also discussed.

2. Experiment

For NIR photoluminescence (PL) spectrum measurement, the samples were excited by the 512 nm line of an argon laser, with a typical power of 500 mW, or a Xenon 1000 W lamp dispersed by a monochromator for photoluminescence excitation spectrum (PLE) measurement. The excitation light was modulated at 20 Hz using a mechanical chopper. The emitted light was collected and separated by a double monochromator, with a slit width of 0.4 mm for both input and output slits, and a 800 nm long-pass filter was used to avoid any second-order light reaching the detector. A liquid nitrogen cooled InSb IR-detector converted the emitted light into an electric signal, which was detected using a lock-in amplifier and was recorded with a microcomputer. For low temperature measurement, the samples were mounted

in a closed-cycle cryostat, which can be adjusted from 10 to 300 K.

For lifetime measurement, the third harmonics, 355 nm line of a Nd:YAG laser was used as excitation light. Fluorescence from sample was detected at 975 nm with a photomultiplier tube model 77343 from Oriel corporation. A HP54522A 500 MHz oscilloscope was used to monitor the fluorescence decay curve, from which the lifetime was elucidated. The UV-Vis absorption spectrum was measured with a Cary-100 spectrophotometer.

3. Results and discussion

The Yb-porphyrinate complexes studied are listed in Table 1. They can be formulated as $[\text{Yb(III)(P)(3L)}]\text{Cl}_n$, where P is [5,10,15,20-tetrakis(*p*-(R)phenyl)porphyrin] (where R = H, OH, CH_3 or OCH_3), 3L is 1 to 3 other molecules directly coordinated to Yb^{3+} ions and $n = 0$ or 1. Single crystals of all these complexes were grown. Their X-ray crystal structures were determined and published elsewhere [11] except that of complex(V), whose structure is shown in Fig. 1.

All the Yb-porphyrinate complexes exhibit the typical Yb^{3+} emission upon excitation with visible light. As Yb^{3+} has a two-level-energy system, direct excitation of Yb^{3+} could only be achieved with a ~ 980 nm light. However, the experimental excitation spectra of these Yb-porphyrinate complexes are completely different. They all show broad band across the visible spectrum range, from 350 to 700 nm (Fig. 2 inset), and are very similar to their absorption spectra in concentrated

Table 1
Luminescence intensities of Yb-porphyrinate complex

Complex	Formula ^a	Peak intensity (a.u.)
I	$[\text{Yb(P}_2)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$	588
II	$[\text{Yb(P}_3)(\text{THF})(\text{H}_2\text{O})_2]\text{Cl}$	13104
III	$[\text{Yb(P}_1)(\text{THF})(\text{H}_2\text{O})\text{Cl}]$	21060
IV	$[\text{Yb(P}_4)(\text{H}_2\text{O})_3]\text{Cl}$	36270
V	$[\text{Yb(P}_4)(\text{CoP})]$	159588

^a P_1 = [5,10,15,20-tetrakis(phenyl)porphyrin]; P_2 = [5,10,15,20-tetrakis(*p*-hydroxylphenyl)porphyrin]; P_3 = [5,10,15,20-tetrakis(*p*-methylphenyl)porphyrin]; P_4 = [5,10,15,20-tetrakis(*p*-methoxyphenyl)-porphyrin]; THF = tetrahydrofuran; CoP = (cyclopentadienyl)tris(diethylphosphito)cobaltate(I) anion.

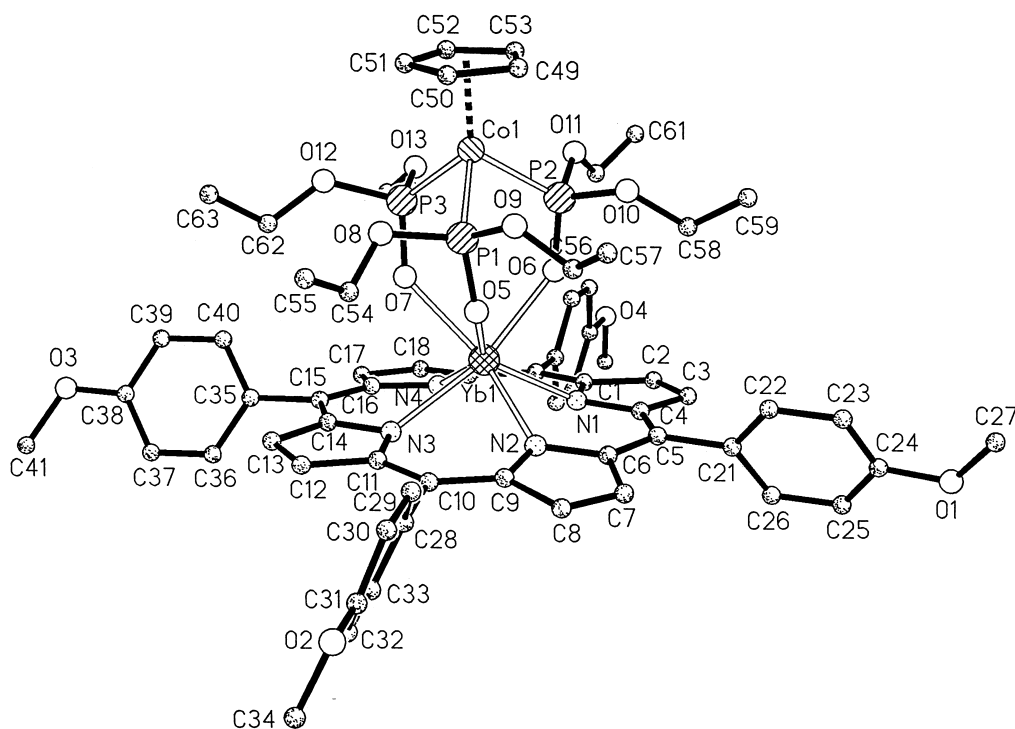


Fig. 1. X-ray crystal structure of complex (V), H atoms are omitted for clarity.

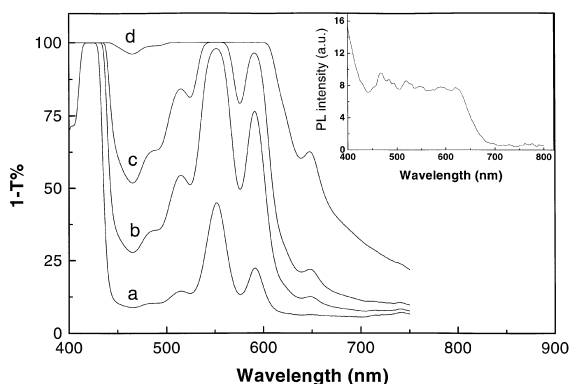


Fig. 2. Absorption spectrum of complex (V) in ethanol solution, solutions become more concentrated from a to d. Inset: PLE spectrum of complex (V), spectrum for all the Yb complexes similar to it in shape, but their intensities are weaker.

ethanol solutions (Fig. 2, curves c and d). The absorption spectra in concentrated solution are different from that in dilute solution, the latter show a strong peak at ~ 420 nm and several weak

peaks at 500–650 nm. These peaks have been taken as characteristic absorption of porphyrin ring. When comparing these spectra in solutions of different concentrations, it is easily concluded that the broad bands in Fig. 2 (curve c, d and inset) were caused by saturated absorption of porphyrin ring.

Fluorescence of Ln^{3+} ions in organic complexes is generally considered involving an energy transfer process. In this process, light was first absorbed by the organic ligand, the ligand then transfers energy through its triplet state to Ln^{3+} ions, which emit fluorescence. This mechanism has been very successful in explaining the fluorescence of complexes of many Ln^{3+} ions, especially for those of Tb^{3+} , Eu^{3+} , Dy^{3+} and Sm^{3+} [1]. Such a mechanism means that the excitation spectrum for the Ln^{3+} fluorescence should be similar to its absorption spectrum, and this is just what we observed in the present experiment. The present mechanism also implies that the ligand can dramatically affect the efficiency of light absorption and energy transfer,

and the intensities of Yb^{3+} emission. This was also observed for the present complexes, as shown in Table 1. Ligand will mainly affect Yb^{3+} fluorescence at two stages: light absorption and quenching of excited state. Since all the Yb^{3+} complexes give similar color and the light absorption is saturated, the present experiment should mainly reflect the quenching effect.

Luminescence quenching by high-frequency vibration mode of $-\text{OH}$ group has been well documented in studies of Tb^{3+} and Eu^{3+} complexes [1]. The quenching efficiency of $-\text{OH}$ vibration mode depends on the energy difference between the bottom of the excited state and the top of the ground state. Thus the quenching effect of $-\text{OH}$ group is more efficient for Yb^{3+} ions than for Tb^{3+} or Eu^{3+} ions. As can be seen from fluorescence of complex (IV) and (V), when the $-\text{OH}$ group directly attached to Yb^{3+} ions was replaced with a (CoP) group, the Yb^{3+} luminescence intensity is greatly enhanced. Similar effect was also found when $-\text{OH}$ was a side moiety of tetraphenylporphyrin ring in complex (I), the luminescence intensity slightly decreased compared to unreplaced complex (III). The type of side moiety on tetraphenylporphyrin ring was also found to greatly affect the luminescence intensity. When the side moiety is a methoxyl group, the Yb -porphyrinate complexes always give strong Yb^{3+} emissions, as could be seen for complex (IV) and complex (V) in Table 1. It is considered that methoxyl group, which is an electron donor, could share π electron with porphyrin ring, and thus enhance the degree of electron delocalization and absorbency of the molecule. However, although $-\text{OH}$ group is also an electron donor, quenching effect of $\text{O}-\text{H}$ high frequency vibration mode is more significant, and thus shows no luminescence enhancement.

The emission spectra for complex (V) and complex (IV) are shown in Fig. 3 (curve a and inset). Spectra for all the other complexes except complex (V) are similar to those of complex (IV). They consist of a strong and narrow peak at ~ 980 nm and some broad bands range from about 920–1080 nm. Similar shapes have also been reported in many papers, both for Yb^{3+} in complexes [2] and inorganic solids [12]. However, the

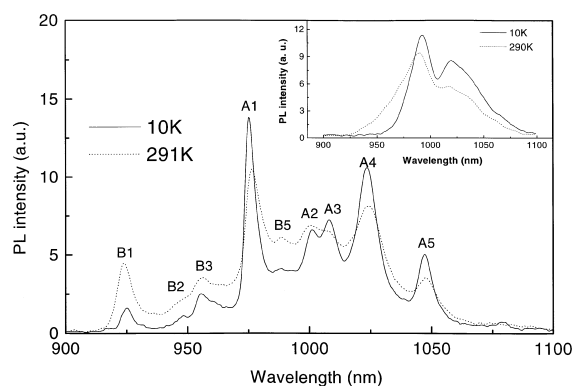


Fig. 3. PL spectrum of complex (V) at 10 K (solid line) and 291 K (dotted line); Inset: PL spectrum of complex (IV) at 10 K (solid line) and 291 K (dotted line), which is similar to the spectra of other complexes except complex (V) in shape.

spectrum shape for complex (V) is more interesting. It shows many well-split peaks in the range 920–1060 nm, and this is probably the most-split spectrum for Yb^{3+} complex at room temperature. To elucidate the mechanism of the peak splitting, experiment was done to study the luminescence at low temperature (Fig. 3, curve b).

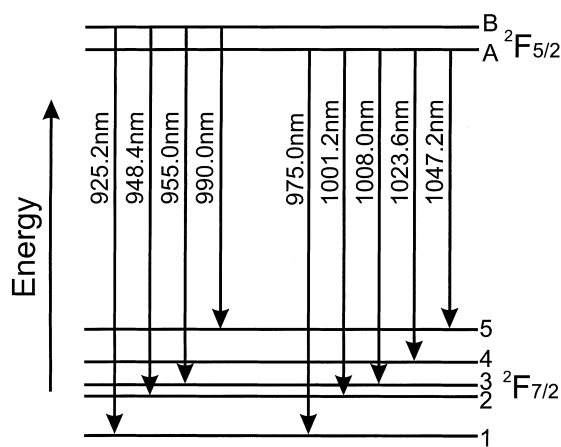
When the temperature was reduced from 291 to 10.3 K, there was no additional peak splitting and shift of peak positions was minimum, but the relative peak intensities changed dramatically. These peaks can be classified into two groups according to their intensity changing as shown in Fig. 3. Group (A) represented by the peak at 975 nm decreased with temperature, while group (B) represented by peak at 925.2 nm increased with temperature. A detailed examination of peak positions revealed that the difference between A_i and A_j is equal to that between B_i and B_j (where $i, j = 1$ to 5) within the experimental error, as shown in Table 2.

To deduce the mechanism of the well-split spectrum, an energy level diagram for Yb^{3+} ion in complex (V) was proposed as shown in Fig. 4. The electronic levels of Yb^{3+} , $^2F_{5/2}$ and $^2F_{7/2}$ were proposed to split into 2 and 5 degenerate levels, respectively. Peak $A_i(B_i)$ in Fig. 3 should correspond to the transition between degenerate level A (B) and i in Fig. 4, and the change in peak intensity is attributed to the shift of energy equilibrium between levels A and B at different temperatures.

Table 2

Peak position and their energy difference in complex (V)

<i>i</i>	Position of A _{<i>i</i>} (cm ⁻¹)	A ₁ –A _{<i>i</i>} (cm ⁻¹)	Position of B _{<i>i</i>} (cm ⁻¹)	B ₁ –B _{<i>i</i>} (cm ⁻¹)
1	10256	–	10808	–
2	9988	268	10544	264
3	9920	336	10471	336
4	9769	487	–	–
5	9549	707	10101	707

Fig. 4. Proposed transitions between degenerate levels of $^2F_{5/2}$ and $^2F_{7/2}$ of Yb^{3+} ion in complex (V).

According to the Maxwell–Boltzmann law, if the lifetime of an excited state is long enough, electrons in these degenerate levels will reach equilibrium before transition to the ground state. Thus the number of electrons in degenerated level *i*, n_i , can be written as:

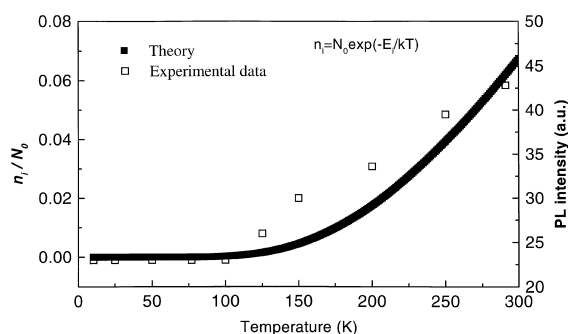
$$n_i = N_0 \exp(-E_i/kT), \quad (1)$$

where N_0 is the number of electrons in all the degenerate levels, k the Boltzmann constant, T the temperature in K, and E_i is the relative height of level *i*. It is obvious from Eq. (1) that there will be more electrons at a higher degenerated level at room temperature than at low temperature. Good agreement was found between this theoretical explanation and the experimental results, in which peaks corresponding to the transition from level B increased while those from level A decreased with rising temperature. If level A is taken as the lowest degenerate level of $^2F_{5/2}$, E_B can be easily determined as 552 cm^{-1} from the difference between A_1

and B_1 (Table 2). Then variation of n_i/N_0 with temperature could be calculated from Eq. (1) as shown in Fig. 5. The experimental intensities of B_1 at different temperatures, which are proportional to n_i , are also shown in Fig. 5, and the two curves give similar trends.

The Maxwell–Boltzmann law can also be applied to explain the spectral change of Eu^{3+} ions with temperature [13], but the equilibrium took place for degenerated levels of ground state in that case. For excitation state, the equilibrium could only be obtained when the lifetime is long enough. Report on lifetime of Yb^{3+} complex is very few. Klink [3] et al. have determined the lifetime of $18.6 \mu\text{s}$ for Yb^{3+} triphenylene complex at room temperature. However, a much longer lifetime of $40 \mu\text{s}$ was determined by us for complex (V) in the present study, which should be long enough for the system to reach an equilibrium.

Although the emission spectra for other Yb-porphyrinate complexes except complex (V) give a different shape, the low temperature experiments also show some evidence for the presence of energy

Fig. 5. Variation of n_i/N_0 in the Maxwell–Boltzmann equation for B_1 . The curve is theory and the data points are experimental. Their agreement is reasonably good.

equilibrium among excited states of Yb^{3+} (Fig. 2 inset): The short wavelength half of the broad band increased or remained constant with temperature, while the long half including the narrow peak at 975 nm reduced, similar to a peak-broadened spectrum of complex (V). The well-split spectrum of complex (V) possibly results from its rigid structure, since (CoP) group, which is a multi-dentate ligand forming a chelate with Yb^{3+} ions via the O donors, will coordinate much stronger than other small molecules do. These broad bands in other complexes have sometimes been taken as the vibronic peaks of A_1 , however, the present study suggests that contribution from peak splitting should be considered.

4. Conclusion

NIR luminescence of novel Yb-porphyrinate complex series has been studied. The fluorescence intensities of these complexes were determined and compared. The relation between the luminescence efficiency and the structure of the complexes was deduced. It was found that the addition of methoxyl group to the tetrabenzenporphyrin ring and replacement of OH group directly attached to the Yb^{3+} ions with (CoP) greatly enhanced the luminescence efficiency of the complex.

The excited spectrum of the Yb-porphyrinate complex shows a broad band across visible spectrum, and is very different from the directly excited spectrum of Yb^{3+} ions. This indicated that the energy transfer process contributes to the Yb^{3+} luminescence.

The emission spectrum of the complex (V) is well split, and is very different from the other complexes. The peak intensity change as a function of temperature can be explained from the proposed energy diagram using the Maxwell–Boltzmann law.

The Yb-porphyrinate complexes presented here can be considered as potential luminescent labels for fluoroimmuno assays and fluorescence imaging. Whereas Eu^{3+} - and Tb^{3+} -based labels need

ultraviolet radiation for excitation, which can harm the biological material and requires special attention, our Yb-porphyrinate complex can be excited with visible light. As an additional advantage, most biological materials are transparent to the narrow NIR emission. Further work is in hand to realize the luminescent label potential.

Acknowledgements

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