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Hot bands of (f, f*) emission from ytterbium(III) porphyrins in solution

Motoko Asano-Someda*, Youkoh Kaizu

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

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Abstract

Temperature dependence of (f, f*) emission spectra from two ytterbium(III) porphyrins was investigated upon photoexcitation of the porphyrin macrocycle. The observed emission spectra consist of an intense sharp band at 975 nm and broad side-bands. The latter features are almost independent of porphyrin peripheral substituents, but sensitively depend on temperature. The bands in the higher energy side fade with decreasing temperature and disappear at 77 K. Analysis of the temperature dependence on the higher energy bands gives activation energies, which reasonably match with an energy difference from the main intense band. The higher energy bands are hot bands, of which structure is attributable to the crystal field splitting in the excited $^2F_{5/2}$ state. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Temperature dependence; Excited states; Crystal field; Band feature; Photosensitization

1. Introduction

Photosensitization of emission from rare-earth ions has been studied extensively with a relevance of numbers of current applications [1–3]. Luminescence spectra from rare-earth ions usually exhibit sharp bands due to high shielding of f-orbitals from the surroundings. This narrow band feature in condensed phases and even under fluid conditions, is advantageous for their applications, e.g. laser source materials and biological probes. However, the (f, f*) transition itself is principally forbidden, and thus, photosensitization by using chromophores is required for efficient excitations.

While the electronic structure of the Yb^{3+} ion is relatively simple because of its f^{13} configuration (only one hole in the seven f-orbitals), the properties of Yb^{3+} emission remain rather unexplored compared with Nd^{3+} and other lanthanides which exhibit visible emission [4–8]. The first excited state, $^2F_{5/2}$, locates in near-IR region, and there is no other electronic excited state below the UV energy region. This is quite unique among lanthanide ions, because usually a multi-f-electron system splits into numbers of electronic states by strong spin-orbit coupling, thus, yielding many energy levels which cover from the UV to IR energy regions [9]. In Yb^{3+} ions, the excited $^2F_{5/2}$ state exhibits emission around 10,000 cm^{-1} directly to the ground $^2F_{7/2}$ state. This low-energy emission can be a benefit in utilizing Yb^{3+} as probes for several reasons: for instance, energy transfer to other species rarely occurs, and the low energy level for the emitting state provides a wide choice of photosensitizers, which absorb visible light.

Porphyrin is one of the strong candidates for photosensitization because it has very intense absorption bands in the visible region. Scheme 1 shows an energy diagram of Yb^{3+} porphyrin system. Upon photoexcitation of visible light, fluorescence is observed from the S_1 and S_2 states of the porphyrin π-system but also emission from Yb^{3+} (f, f*) state is observed [10–12]. However, near-IR (f, f*) emission from the Yb(III) porphyrins has been reported only by a few groups [10–12]. The two spectra reported on different porphyrin substituents exhibit different band features, although it is unexpected that (f, f*) emission would be very sensitive to the ligand peripheral substituents. It has not been clear how (f, f*) emission is influenced by the ligand substituents and other environments. Here, we report temperature dependence of (f, f*) emission from two kinds of Yb(III) porphyrins upon excitation of the porphyrin ligand, in order to understand band features of Yb^{3+} emission in such coordinated complexes in condensed phases. Our results clearly show that contribution of hot bands remarkably changes emission spectral features.

2. Experimental

Ytterbium(III) porphyrins were prepared as described previously [13]. Anal. TPPYb(III)OH, Calcd. for $C_{44} H_{33} N_4 O_3$ Yb ($TPPYbOH\ 2H_2O$) (molecular weight 838.81): C,

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* Corresponding author. Tel.: +81-3-5734-2604; fax: +81-3-5734-2655.
E-mail address: motoko@chem.titech.ac.jp (M. Asano-Someda).

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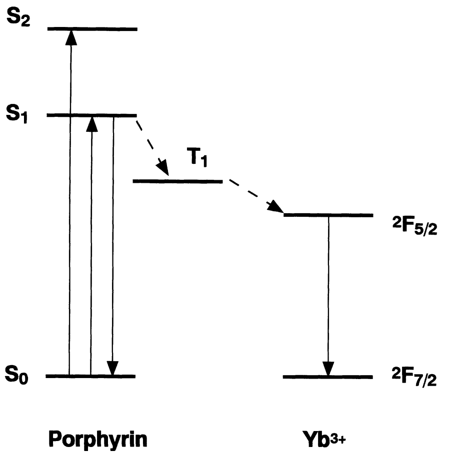

Scheme 1. Energy diagram of Yb(III) porphyrin.

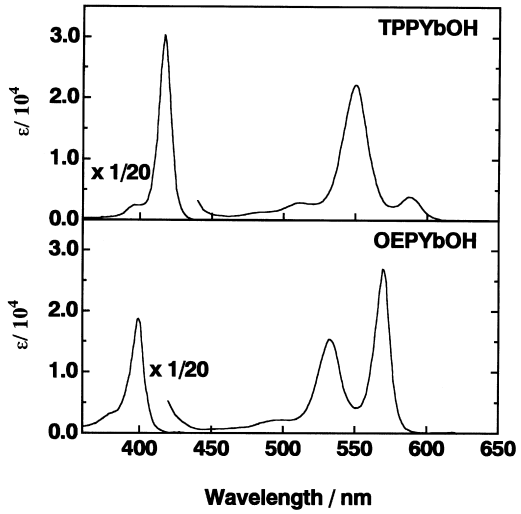

Fig. 1. Absorption spectra of Yb(III) porphyrin in methanol at room temperature.

63.00; H, 3.97; N, 6.68. Found: C, 63.09; H, 3.53; N, 6.48.

OEPYb(III)OH, Calcd. for $C_{36}H_{47}N_4O_2Yb$ (OEPYbOH H_2O) (molecular weight 740.84): C, 58.37; H, 6.40; N, 7.57. Found: C, 58.42; H, 6.23; N, 7.62.

Near IR emission spectra were measured by using a single-photon-counting method [14]. Porphyrins were pumped by a CW Ar ion laser (model NEC GLC 3300) at 514.5 nm. After dispersing through a Nikon P-250 monochrometer, emission was detected by a Hamamatsu photonics model C737 photoncounter equipped with a Hamamatusu R316 photomultiplier and a preamplifier model C1556. To obtain better *S/N* ratios, a light chopper (33 Hz) was placed between the sample and the laser, and dark counts acquired with the chopper closed were subtracted from counts under the laser irradiation. The resolution of the spectrometer was set to approximately 5 nm. Emission spectra, thus, obtained are shown without intensity calibration.

For the lifetime measurements, excitation was done by using the second harmonic of a nanosecond Nd:YAG laser (Spectron SL 401). Emission was detected by a Hamamatsu R316 photomultiplier and other details were described previously [14].

The temperature of the sample solution was controlled by an Oxford cryostat Model DN 704. Absorption spectra were taken with a conventional spectrophotometer (Hitachi 330).

3. Results and discussion

3.1. Basic properties of (f, f) emission in Yb^{3+} porphyrins*

Absorption spectra of the two Yb^{3+} porphyrins are very similar to those of the corresponding typical diamagnetic matalloporphyirns, e.g. zinc(II) porphyrin versions. As shown in Fig. 1, no remarkable deviations from the zinc versions could be observed. Both Yb^{3+} porphyrins exhibit strong absorption bands in near-UV and VIS region due to (π,π^*) transitions of the porphyrin ring, although the two

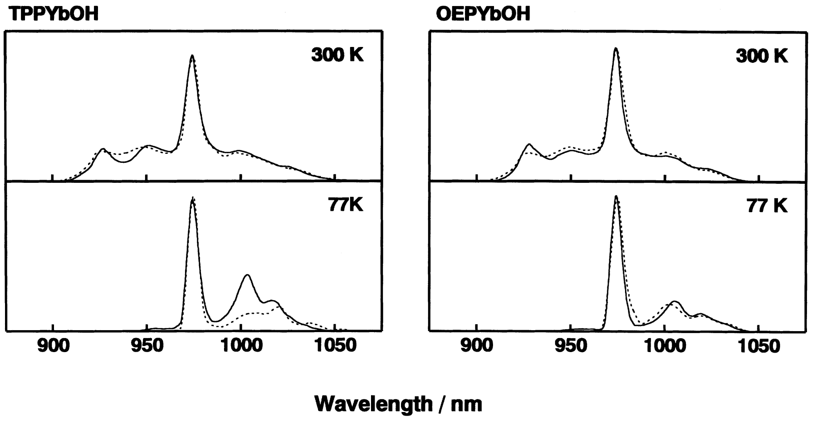

Fig. 2. Emission spectra in near IR region of Yb(III) porphyrins. Solid line stands for emission measured in methanol:ethanol = 3:7 whereas dotted line stands for that in toluene.

spectra show some differences, which are induced by the different peripheral substituents.

Fig. 2 shows near-IR emission spectra of two Yb^{3+} porphyrins measured at 300 and 77 K upon excitation at 514.5 nm, where we can excite porphyrin ring efficiently. The solid line stands for emission spectra in methanol:ethanol = 3:7 whereas the broken line stands for those in toluene. Unlike the VIS-absoption spectra in Fig. 1, two porphyrins exhibit quite similar near-IR-emission spectra under the same environmental condition. In all spectra, a sharp, prominent band is observed at 975 nm. This band can be assigned to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} ion due to energy transfer from the porphyrin ligand since the triplet state of porphyrin π-system is much higher in energy and the peak position is in quite good agreement with the calculated and observed (f, f*) transition energy in Yb^{3+} ion [9–12].

However, the observed band is accompanied by broad wings not only in the lower energy region (>975 nm) but also in the higher energy region (<975 nm). In these features, the relative intensities and band shape do not largely depend on the porphyrin peripheral substituents and solvents, but are very sensitive to temperature. In particular, the broad bands with <975 nm disappear at 77 K in both TPPYbOH and OEPYbOH.

It is noted that the spectra at 300 K are principally the same as that in [10] whereas the spectra at 77 K are rather close to that in [12]. It is found that spectral differences between the two literatures are due to a difference of temperature but not due differences in porphyrin substituents.

In contrast, emission lifetimes measured at 975 nm are rather less sensitive to temperature; for TPPYbOH, 1.9 μs at 300 K and 1.6 μs at 77 K; for OEPYbOH, 1.7 μs at 300 K and 2.0 μs at 300 K in methanol:ethanol = 3:7. These values are close to that found for Yb(III) tetratolyl porphyrin, 5 μs in ethanol [10]. There are only slight differences in the lifetimes between the two porphyrins.

3.2. Temperature dependence of (f, f*) emission

To understand the change of the spectra between 300 and 77 K and also the origin of the broad features, temperature dependence was examined in detail. Figs. 3a and b show (f, f*) emission spectra of TPPYbOH and OEPYbOH in methanol–ethanol as a function of temperature, respectively. The intensity in the shorter wavelength region (<975 nm) decreases as temperature goes down. On the contrary, the band in the longer region (>975 nm) becomes relatively intense in lower temperatures.

Ratios of the emission intensities at 927 versus 975 nm, ln (I_{927}/I_{975}) were plotted against $1/T$ in Fig. 4. The plots were made in the temperature range before the solvent makes a glass, in order not to involve drastic changes of environments such as phase transition of the matrices. In both of the porphyrins, the plots were on a straight line, which suggest that emission in higher energy region arises from a thermal process. From the slope of the line, activation energies were estimated as 410 and 430 cm^{-1} for TPPYbOH and OEPYbOH, respectively. These numbers well match the energy difference of the two wavelengths, 927 and 975 nm, i.e. 530 cm^{-1}. This fact supports the contention that the bands at <975 nm is ascribed to emission from the excited (sub) states thermally populated.

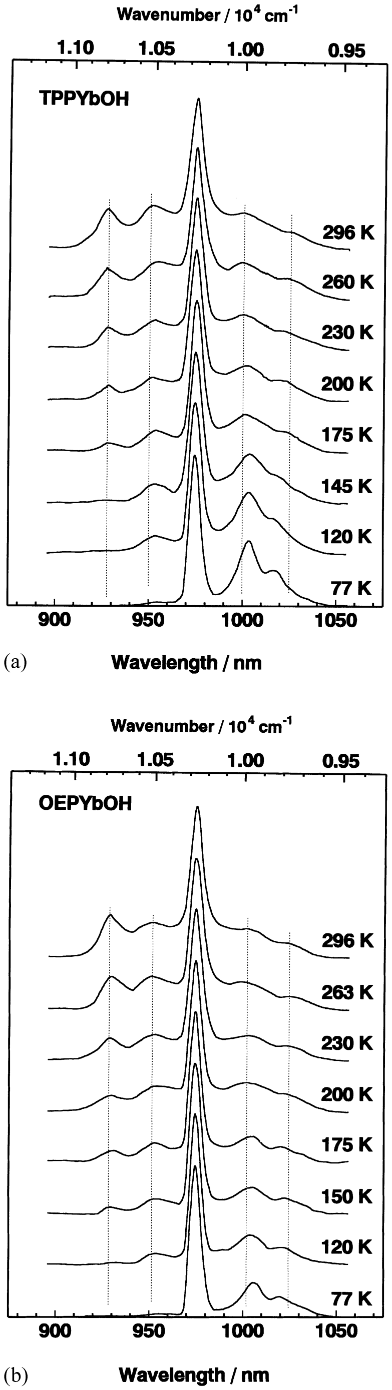

Fig. 3. Temperature dependence of emission spectra of (a) TPPYbOH and (b) OEPYbOH in methanol:ethanol = 3:7. Emission intensities are normalized as the band at 975 nm has the same intensity. The other bands slightly shift with temperatures (see detail in text, Section 3.3).

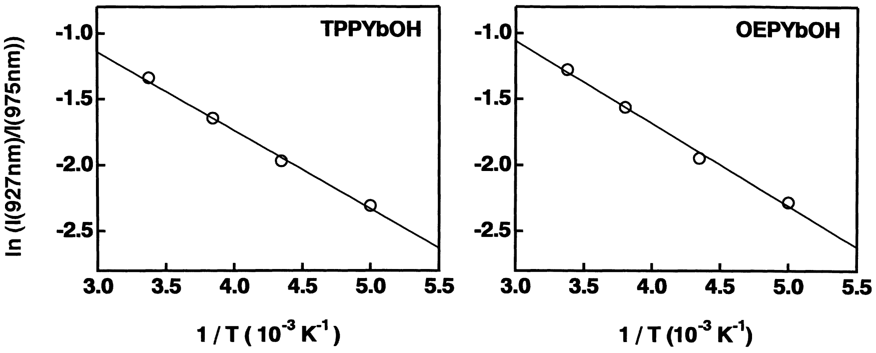

Fig. 4. Semilogarithmic plots of emission relative intensities (I_{927}/I_{975}) vs. reciprocal temperature for TPPYbOH and OEPYbOH. Plots were made in the temperature range between 300 and 200 K. The slopes give activation energies, 410 and 430 cm^{-1} for TPPYbOH and OEPYbOH, respectively.

3.3. Possible origins of the broad band features

Temperature dependence of the emission intensity concludes that the bands at <975 nm are hot bands. Since there is no other electronic transition in this energy region, those hot bands are attributable to the substructure in the excited $^2F_{5/2}$ state. As can be seen in Figs. 2 and 3, two peaks at <975 nm appear when the temperature increases. The two peaks are separated from the main intense band approximately by 530 and 270 cm^{-1}, respectively. With similar energy gaps, band structures are also observed at >975 nm. This suggests that the ground state is also split into substates. Fig. 5 summarizes a schematic energy diagram of Yb^{3+} ion and relation with the observed emission spectra. Since the energy splitting in the ground state is the same magnitude as that in the excited state, these splitting must be caused by the same origin.

In the previous section, we saw that there is a slight difference between the activation energy estimated from the temperature dependence (410–430 cm^{-1}) and the optical energy gap of the two wavelengths (530 cm^{-1}). Although the difference is not large, this can be rationalized by considering that each emission spectrum from the excited substates has progression bands. As seen in Fig. 5, the observed emission spectrum at each temperature is a superposition of three emission spectra, of which two are emitted from thermally populated states. Thus, the emission intensity at 975 nm consists of the three emission bands, i.e. ($^2F_{5/2}, 0 \rightarrow {}^2F_{7/2}, 0$), ($^2F_{5/2}, 1 \rightarrow {}^2F_{7/2}, 1$), and ($^2F_{5/2}, 2 \rightarrow {}^2F_{7/2}, 2$) bands, and the intensities of the latter two bands are temperature dependent. In contrast, the band at 927 nm consists of only the ($^2F_{5/2}, 2 \rightarrow {}^2F_{7/2}, 0$) transition. As temperature goes up, the contribution of the ($^2F_{5/2}, 0 \rightarrow {}^2F_{7/2}, 0$) band becomes smaller in the total intensity of the band at 975 nm. With this situation, the intensity ratio $I\,(^2F_{5/2}, 2 \rightarrow {}^2F_{7/2}, 2)/I\,(^2F_{5/2}, 0 \rightarrow {}^2F_{7/2}, 0)$ becomes larger than that of I_{925}/I_{975} with increasing temperature. This implies that the intensity ratio $I\,(^2F_{5/2}, 2 \rightarrow {}^2F_{7/2}, 2)/I\,(^2F_{5/2}, 0 \rightarrow {}^2F_{7/2}, 0)$ should show a larger temperature dependence, which will give a larger activation energy than that estimated in the previous section. The larger energy gap would be more consistent with the optical energy gap obtained above. This argument not only well explains the fact that smaller activation energies could be estimated without such consideration, but also provides a strong support for the contention that the excited state is split into substates which exhibit hot emission bands.

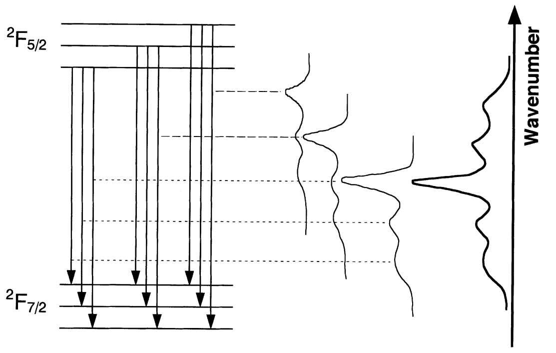

Fig. 5. Relation between the observed emission spectra and energy levels of Yb(III) ion. The observed spectrum in the left are composed of three spectra, and two spectra in the right are ascribed to emission from the excited substates thermally populated.

Although several lanthanide ions exhibit emission to the electronic states lying upper the ground state, it is equivocal that the broad feature at >975 nm is ascribed to substructures in the ground state. This is because Yb^{3+} has f^{13} electronic configuration that can be split into only two electronic states by spin-orbit coupling. In systems involving Yb ions, similar broad features have been also observed in the red of the intense sharp emission band. Early spectroscopic studies for β-diketonate Yb compounds suggested that crystal field splitting is the origin of the structure of emission spectra and that the splitting is calculated as in the order of hundreds of cm^{-1} [15,16]. In the case of Yb^{3+} doped crystals, the strong three emission bands separated by hundreds of cm^{-1} to each other were assigned to the bands split due to the crystal filed, whereas the other weak bands were ascribed to vibronic bands [17]. Certainly, in many metalloporphyrins metal-nitrogen vibrational modes have been observed in the low frequency region of the resonance Raman spectra (e.g. the ν_8 (A_{1g}) mode is observed around 400 cm^{-1}) [18]. However, f-orbitals are highly shielded from the surroundings by the outer 5p orbitals, and usually the intensities of vibronic bands are considerably weak. In our case, the observed side features are appreciably intense in the emission spectra, thus, suggesting that the crystal field is more likely.

In addition, a careful inspection of Fig. 3 reveals that the side bands are shifted upon the temperature change. It is noted that the direction and size of the shifts depend on the bands. If the observed progression bands were of vibrational origin, then the two bands at >975 nm should shift to the same direction. However, these shift oppositely: the band around 1000 nm shifts to longer wavelength whereas the band around 1025 nm shifts to shorter upon cooling. It is unlikely that the vibrational frequencies change differently between one and two quanta. In contrast, it is feasible that the crystal field gives different temperature behaviors for the splittings in terms of energy. Consequently, it is highly likely that the crystal field splitting leads to the substructure in the excited and ground states.

4. Conclusions

In the present work, we have shown how emission spectra of Yb^{3+} ions are influenced by the environmental conditions. With two different Yb^{3+} porphyrins, very similar (f, f*) emission spectra were observed at each temperature. However, features of the emission spectra largely depends on temperature but does not depend on solvents and porphyrin macrocycle. From temperature dependence, contribution of the hot bands considerably changes band features of the emission spectra. These hot bands are ascribed to the substructure in the excited states, due to crystal field splitting within the $^2F_{5/2}$ state.

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