# Near-infrared Luminescence from Ytterbium(III) Ternary Complexes by Visible-light Excitation of Attached Chlorophyll Derivatives

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Ytterbium complex of 1,4,7-tris(carboxymethyl)-1,4,7,10-tetraazacyclododecane was assembled with several chlorophyll derivatives bearing a carboxy group in organic solvents. Visible-light sensitization of specific chlorophylls caused a rise of near-infrared emission from $Yb^{3+}$, due to triplet excited energy transfer in a supramolecule.

Near infrared (NIR) emitting lanthanide complexes have been objects of considerable interest in biomedical analysis in terms of their potential for cellular imaging. In contrast to common commercially available fluorescent dyes and recently emerging quantum dots, lanthanide complexes equipped with suitable organic sensitizers are attractive because of their long luminescence lifetimes, large Stokes shifts, and relatively high quantum yields.[1]

There have been numerous works devoted to designing ligands that transfer their photoexcited energy efficiently to a lanthanide center giving unique luminescence. While much of the effort has been focused on improvement of transfer efficiencies to visible emitters including $Eu^{3+}$ and $Tb^{3+}$, current research has concentrated on investigating ligands for sensitization of NIR emitting lanthanide ions. Porphyrins are a group of promising ligands for migrating energy to lanthanide ions, which have been recently reported by Parker et al.[2] and Wong et al.[3] However, there are no published results concerning dihydroporphyrin (chlorin) sensitizers. Chlorophylls are naturally occurring chlorin pigments and the principle light-absorbing components in natural photosynthesis. They have intense Soret bands with high absorption cross sections and their low-energy triplet states ($10400$–$11700\,cm^{-1}$)[4] render them possibly suitable for sensitization of the relatively low-lying excited states of Yb ions ($10200\,cm^{-1}$).

Preparation of ligands covalently linked with a porphyrin moiety and lanthanoid-metallation of free base porphyrins require troublesome synthetic procedures.[2,3] Enlightened by the latest studies of Faulkner et al. concerning supramolecular assembly of lanthanoid complexes with carboxylated sensitizers,[5] we describe here the synthesis and photophysical properties of a class of ytterbium-based ternary complexes containing chlorophyllous pigments. In contrast to such usual ligands as bipyridine and phenanthroline, the highly $\pi$-conjugated chlorophyll derivatives have intense absorbance at wavelengths longer than 400 nm. The photoluminescence of ytterbium complex Yb-DO3A (Figure 1) in organic solvents was investigated by visible excitation of added chlorophyll sensitizers and the effect of the chlorophyllous structures on the NIR luminescence will be discussed.

The detailed synthesis of carboxylated chlorophyll derivatives **1**–**9** is described in Supporting Information.[6] Their electronic absorption spectra are shown in Figure S1 and their absorption maxima are summarized in Table S1.[6] All pigments showed strong Soret bands at around 400 nm and exhibited characteristic $Q_y$ peaks at longer wavelengths from 640 to 680 nm. Because ytterbium ion has a lower-lying excited state at around $10200\,cm^{-1}$, use of the above synthetic sensitizers might be possible to transfer their excited energy to $Yb^{3+}$.

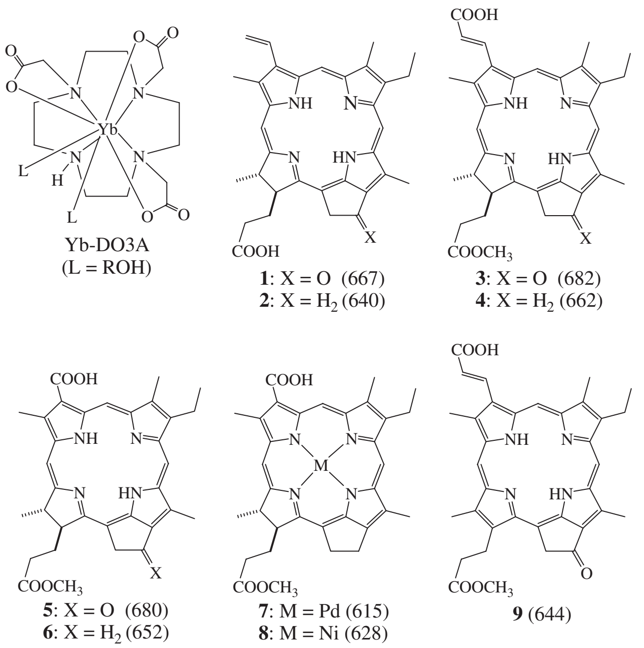

**Figure 1.** Ytterbium(III) complex Yb-DO3A and sensitizing chlorophyllous chromophores **1**–**9**. Values in parentheses indicate $Q_y$ maxima (nm) in THF/MeOH = 1/10.

To examine the photosensitizing ability of carboxylated chlorophyll pigments, photoluminescence from Yb-DO3A at 980 nm was measured in THF and MeOH (1:10): [Yb-DO3A] = [sensitizer] = 0.1 mM with excitation at 410 nm at room temperature.

First, pyropheophorbide-*a* (**1**) with a carboxy group at the $17^2$-position was used due to its easy accessibility (prepared by simple hydrolysis of the easily available corresponding methyl ester),[6] but no emission was observed from Yb ions. Addition of $13^1$-deoxo-compound **2** with a higher energy level excited state (a 27-nm blue shift of $Q_y$ peak by removal of the $13^1{=}O$ presented in Figure 1; see Figure S2[6]) gave no luminescence from the Yb center. The carboxy groups in both the compounds are not conjugated by a chlorin $\pi$-system in a molecule; thus a carboxy group was introduced at the 3-vinyl group as in **3** and **4**. No emission from ytterbium ions was observed with excitation of such chlorins conjugated with COOH through CH=CH.

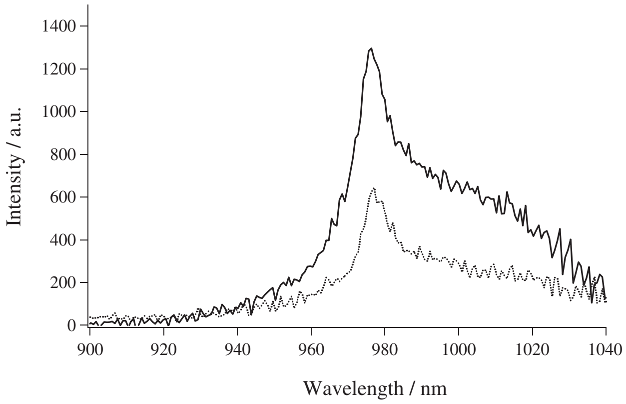

**Figure 2.** Emission spectra of a 1:1 mixture of Yb-DO3A (ca. 0.1 mM) with **6** (solid) or **9** (dotted) in THF/MeOH = 1/10 at room temperature (410 nm excitation).

Finally, we designed chlorin sensitizers directly conjugated at the 3-position. In compound **5**, no luminescence from ytterbium ions was detected, but **6** lacking the $13^1$-oxo group showed the desired energy-transfer phenomenon with emission of ytterbium at 980 nm (Figure 2). The above results proved that excited energy levels of sensitizers ($\lambda_{\max}$ of $Q_y$ band <660 nm) as well as the conjugation between chlorin $\pi$-system and COOH moiety play significant roles in the sensitizing emission. To further confirm the two points, porphyrin **9** with a higher excited energy and a conjugated COOH was prepared, and the same $Yb^{3+}$ emission was observed by excitation of **9** (Figure 2). Compounds **6** and **9** complexed with Yb-DO3A through coordination of their $COO^-$ with $Yb^{III}$ as shown in the graphical abstract. In the resulting supramolecules, photoexcited energy of the chlorophyll pigments was transferred to the $Yb^{III}$ center. At room temperature, the excited $Yb^{III}$ center displayed a typical luminescence band around 980 nm which was assigned to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Since the ternary complexation of Yb-DO3A with **6** and **9** would be less efficient under the present conditions, the observed quantum yields were low: 1% for **6** and 0.7% for **9** (Table S2).[6]

To the best of our knowledge, **6** is the first example of a chlorin chromophore that has sensitized ytterbium ions. For near-IR emitters, the excitation by relatively long wavelength light is useful for any system in which avoidance of UV irradiation to the tissue in vivo is important. Instead of excitation of **6** at its Soret band (410 nm), irradiation of a solution of Yb-DO3A and **6** with its $Q_x$ peak (507 nm) gave a similar Yb-emission at 980 nm as mentioned above (Figure S3).[6,7] Such a visible-light excitation leads to a quite promising biological application.

The energy transfer from a photoexcited sensitizer to a lanthanide complex is predominant through triplet states and sometimes by way of singlet states.[8] To exclude the possibility of singlet energy transfer, a palladium complex of **6** as in **7** was prepared, and its photosensitization was examined. Photoexcitation of **7** easily generated its triplet state: the emission band was located at 811 nm in a glassy solvent of 2-methyltetrahydrofuran at 77 K (Figure S4).[6] Visible-light excitation of **7** effectively sensitized ytterbium ions emitting the NIR light (Figure S5).[6] The results prove that the main energy-transfer route would follow the triplet energy state as accepted by most researchers. This is confirmed by the observation that the nonfluorescent nickel complex of **6** as in **8** also sensitized ytterbium ions. Thus, photosensitizers for Yb-DO3A should have a higher triplet energy than that of the ytterbium as well as a carboxy group at a position close to the light-absorbing moiety in a molecule.

In this work, we reported NIR-luminescence from $Yb^{3+}$ by irradiation of some carboxylated chlorophyll derivatives **6–9** with visible light. The carboxylate moiety coordinated to $Yb^{3+}$ in Yb-DO3A to form the ternary complex and the triplet excited energy of **6–9** would be transferred to the $Yb^{3+}$ center in the supramolecule to afford the emission peak at 980 nm.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

7 Unfortunately, we were unable to observe ytterbium emission by excitation at the $Q_y$ band; the detailed reason for this is still under investigation.

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