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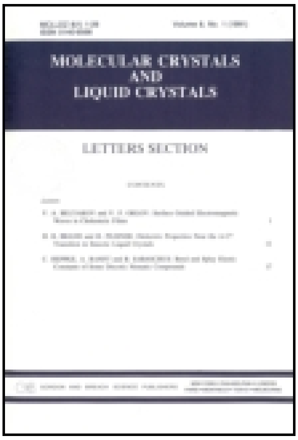

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Synthesis and Optical Properties of Dendritic Porphyrin-Erbium Complexes

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Synthesis and Optical Properties of Dendritic Porphyrin-Erbium Complexes

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Organic compound with lanthanide complexes have been greatly researched for the advance of optical property and processibility to apply on optical amplifiers. We studied on lanthanide metal-dendritic porphyrin complex in solution state. Peripherally substituted carboxylic groups on G_1 and G_2 dendritic porphyrins were gradually occurred to form the precipitation with increasing Er^{3+} ions in solution state. With increasing the amount of Er^{3+} ions resulting complexes begin to form loosely cross-linked complexes causing precipitation in THF solution. No optical change of G_2-Er complex was observed in the presence of large excess (10eq-100eq) of strong chelating ligand such as EDTA in THF solution, which is indicative that G_2-Er is chemically very stable because of so-called dendritic chelating effect.

Keywords Energy transfer; Erbium-porphyrin complex; near-infrared emission; optical amplifier; precipitaion

Introduction

Organic lanthanide complex materials were actively researched because of their high potentials for various kinds of applications such as optical amplifiers, plastic lasers and light-emitting diodes. The original property for the use of the optical amplifier is a near IR emission of lanthanide ions due to the intra-4f transition of them such as Er^{3+} (1.55 μm), Nd^{3+} (1.3 μm) and Yb^{3+} (0.98 μm) [1–5]. However, low-solubility and high-cost of the inorganic rare atoms cause the demand for advanced materials and many lanthanide organic complexes were introduced. The complexes which used hydroxyquinoline as a ligand were introduced and they gave the prosed candidates for active components in NIR-luminescent devices [6,7]. Perfluorinated Er^{3+} complex [8], Xerogel-bonded lanthanide [9] were also introduced in order to overcome these problems.

Lanthanide ions are usually coordinated to organic chromophores such as porphyrin and phthalocyanine. These chromophores have large molar absorption coefficient in visible area for the excitation of valence bands and the energy transfer via triplet excited state occurred towards lanthanide ions to augment the near-IR emission [10–12]. Herein, we discussed synthesis and optical properties of the light-harvesting porphyrin-erbium complexes in

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which porphyrin ligands containing carboxylic acid-terminated dendritic wedges have been prepared as novel ligands for lanthanide ions.

Experimental

Synthesis

Synthesis of G_1-Er complex. The mixture of G_1 (52 mg, 0.022 mmol), Na_2CO_3 (11 mg, 0.11 mmol) in 10 ml of THF were stirred in rt for 1 hr. $ErCl_3$ hexahydrate (31 mg, 0.12 mmol) was added and stirred again for 2 hrs. The resulting precipitate was filtered and washed by distilled water and ethanol. The cake was dried *in vacuo*. The red-brownish compound, G_1-Er 76 mg was obtained.

Synthesis of G_2-Er complex. The mixture of G_2 (120 mg, 0.028 mmol), Na_2CO_3 (28 mg, 0.28 mmol) in 15 ml of THF were stirred in room temperature for 1 hr. $ErCl_3$ hexahydrate (43 mg, 0.12 mmol) was added and stirred again for 2 hrs. The resulting precipitate was filtered and washed by distilled water and ethanol. The cake was dried *in vacuo*. Finally, 100 mg of G_2-Er was obtained as red-brownish solid.

Results and Discussion

Dendrimeric porphyrins containing peripherally carboxylic acid units were prepared by following previous literature [13]. The Porphyrin-Er complexes were prepared by coordination of porphyrins with excess amounts of $ErCl_3$ under basic condition as shown in Fig. 1. The complexes begin to form loosely cross-linked complexes as time went on and caused precipitation during the reaction.

A THF solution of G_2 was prepared to know the binding ratio by titrating with Er^{3+} ions. UV-Vis absorption maximum (λ_{max}) at 429 nm of G_2 was regularly decreased in compliance with increasing Er^{3+} ions (1eq→7eq) and absorption intensity at 435–455 nm was increased as shown in Fig. 2. No spectral change of spectra was observed when added Er^{3+} ions exceed 4 equivalents. Excitation energy transfer from porphyrin to Er^{3+} ion can be evaluated by decreasing PL intensity of porphyrin. As shown in Fig. 3, PL intensity of G_2 was consistently decreased until 4eq of Er^{3+} ions. From these results, G_2 combines with at most 4eq Er^{3+} ions to form metal-ligand complexes in solution state. Large excess of Er^{3+} ions(>7eq) produces the precipitate of G_2-Er. We assumed that loosely cross-linked complexes were precipitated.

The stability of G_2-Er complexes was analyzed by absorption spectral change with adding EDTA(10eq–100eq) after formation of G_2-Er in THF solution, as shown in Fig. 4. As a result, no spectral changes were clearly observed after adding 100eq of EDTA on porphyrin. Along this result, formation of G_2-Er complex was initiated via strong coordinative interactions by dendritic chelating effect.

The Porphyrin ligand formed the cross-linked complex quickly at room temperature, however the solubility in organic solvent such as THF and chloroform get lower than lanthanide-free ligands. We approached another analytical method which can be measured from solid state samples such as FT-IT and TGA analysis. The C=O peak in caroboxilic acid of porphyrin ligands show their IR absorption due to the stretching vibration moiety at 1689 cm^{-1} as shown in Fig. 5, and the absorption peak was disappeared in the spectra of fully cross-linked G_2-Er complex. In addition, TGA data shows the heat stability of Erbium complexes are better than ligands as shown in Fig. 6. The porphyrin ligand show the starting

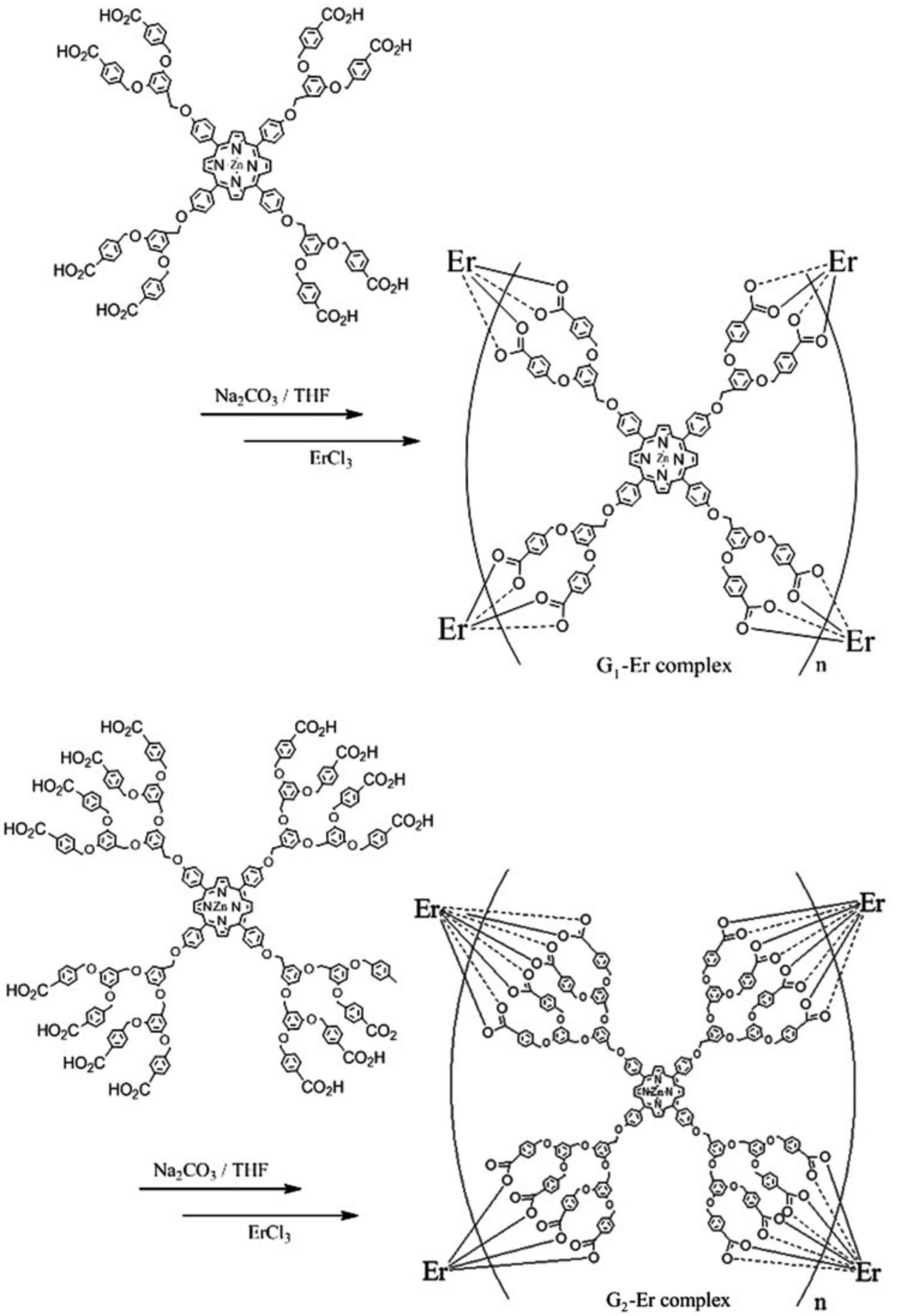

Figure 1. Structure of porphyrin-Er complexes.

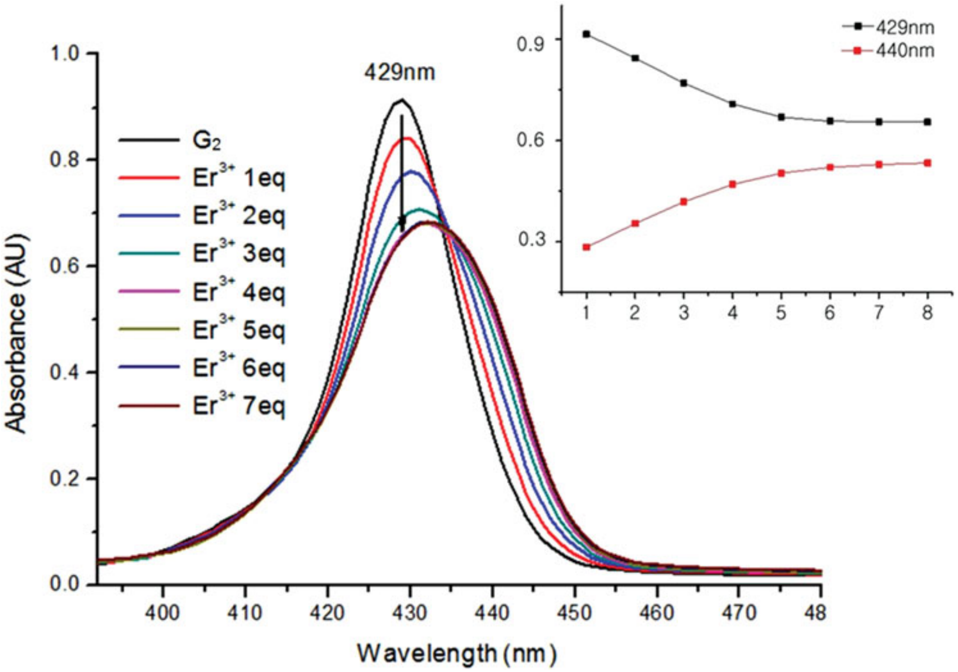

Figure 2. Absorption spectral change of G_2 with Er^{3+} ions (1eq–7eq).

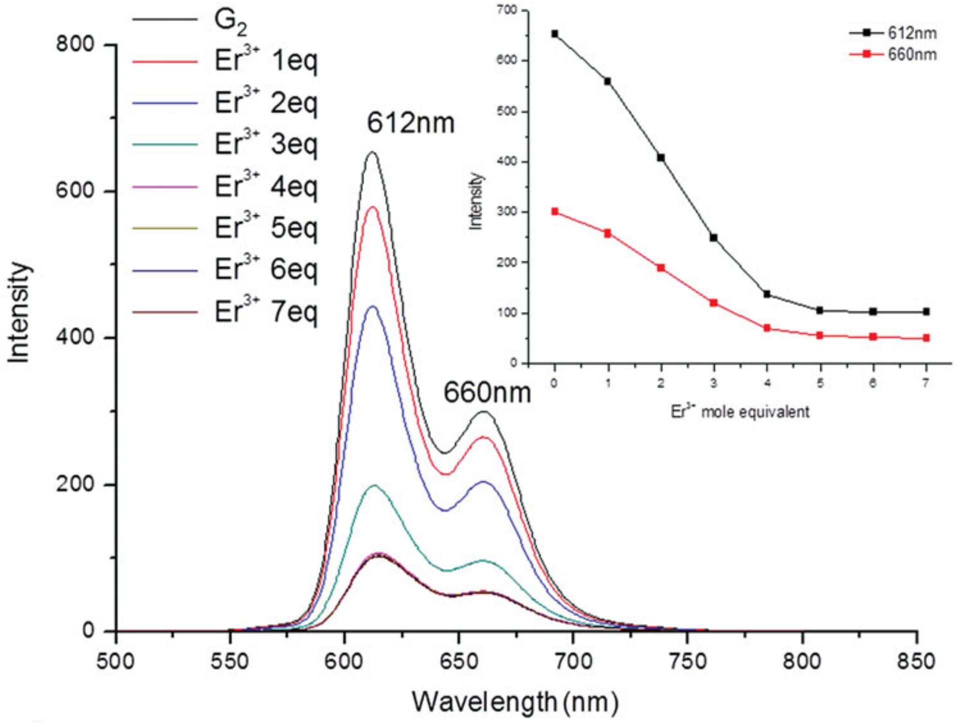

Figure 3. PL spectral change of G_2 with Er^{3+} ions (1eq ∼ 7eq).

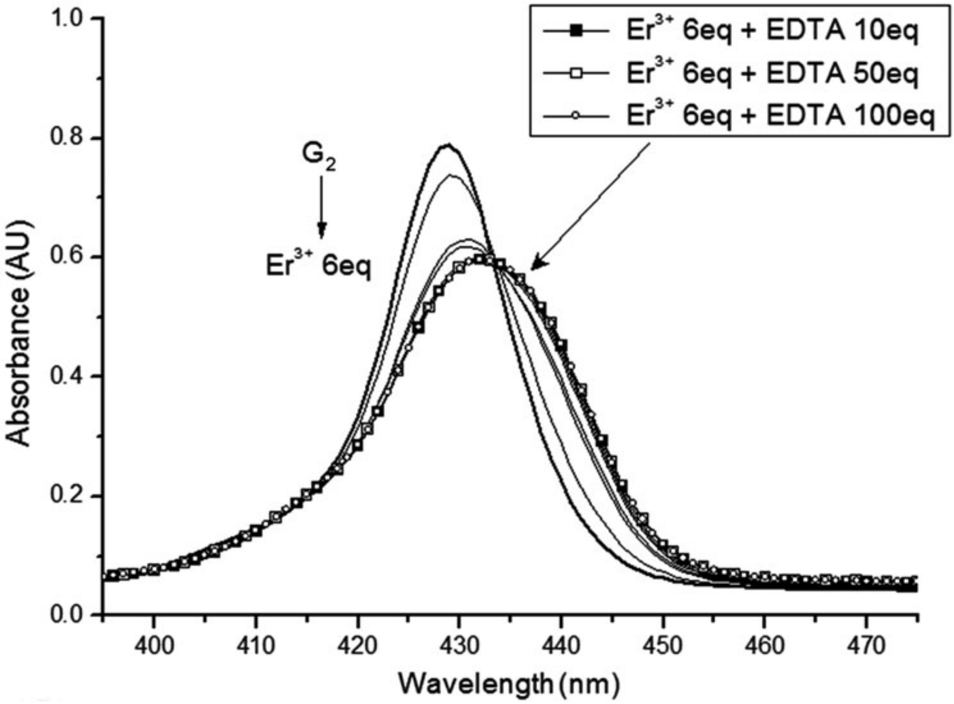

Figure 4. Absorption spectral change of G_2 by adding Er^{3+} and EDTA.

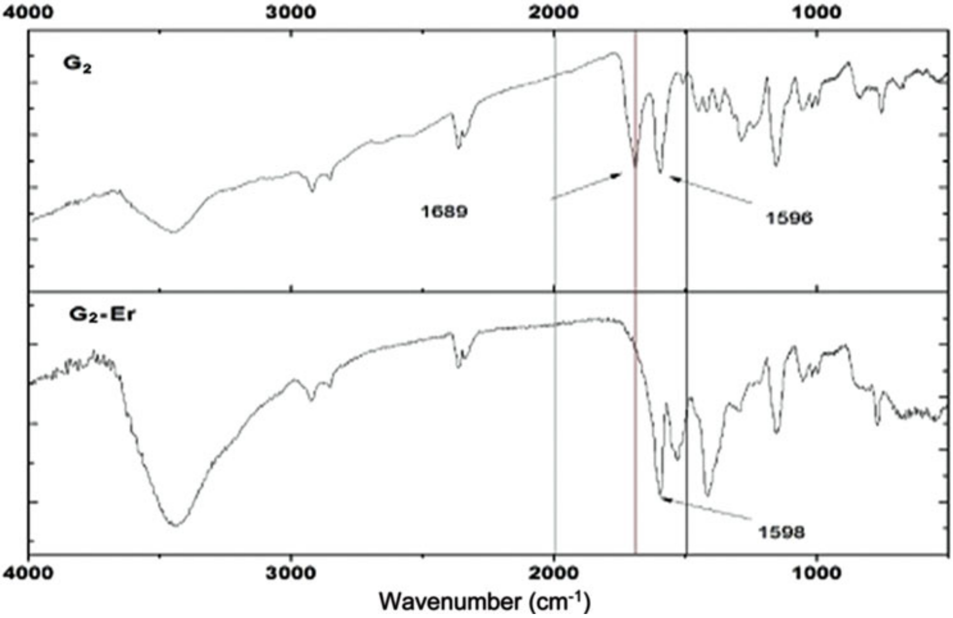

Figure 5. FT-IR spectra of G_2 porphyrin ligand and Er complex.

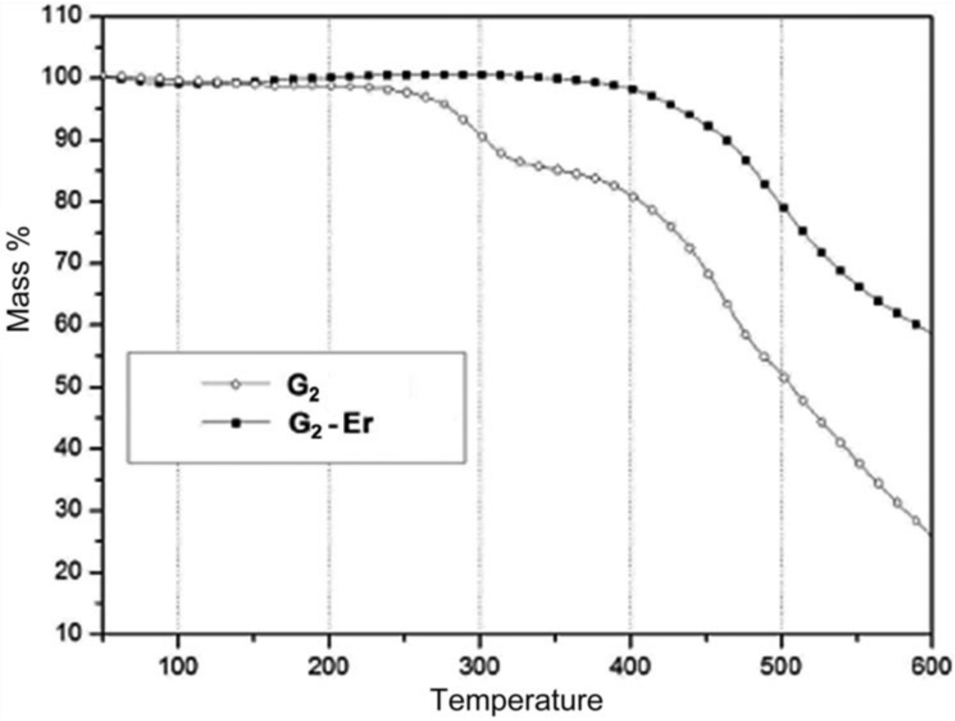

Figure 6. Thermogravimetric data of G_2 porphyrin ligand and Er complex.

temperature of dissociation around 300°, while the G_2-Er show higher temperature around 400°.

Conclusions

Dendritic porphyrin-Er complex was successfully synthesized. According to the results of absorption and PL spectral changes, porphyrin ligand G_2 was coordinated with 4eq of Er^{3+} ions. Interestingly, a significant PL quenching of porphyrin was observed by adding Er^{3+} ions in THF solution, which is indicative of efficient transfer of excitation energy from porphyrin moiety to Er moiety in complex. The mild synthetic process of the porphyrin-Er complex is expected to be applied for manufacturing Er optical amplifier materials. Further research progress including near-IR emission of these materials will be reported elsewhere.

Acknowledgment

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