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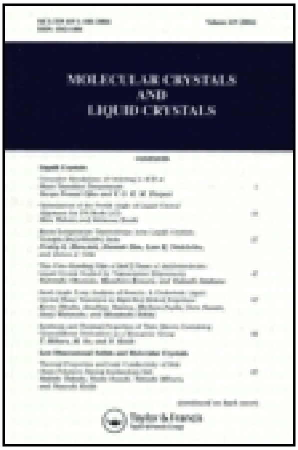

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# Synthesis and Luminescent Properties of Lanthanide-Cored Supramolecular Complexes Based on Porphyrins for Optical Amplification

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# Synthesis and Luminescent Properties of Lanthanide-Cored Supramolecular Complexes Based on Porphyrins for Optical Amplification

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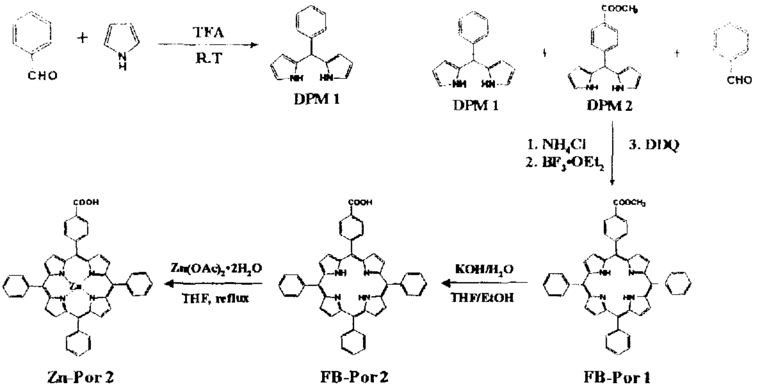
Abstract We have investigated the development of lanthanide-cored supramolecular complexes containing porphyrins to circumvent the solubility problem and maximize the optical amplification properties. Their chemical structures were identified by FT-IR, $^1$H-NMR, UV-Vis absorption and emission spectroscopies. FB-Por 1 and 2 show a very intense UV-visible absorption band at 419 nm, which is attributed to the Soret band. In addition, the relatively weak bands at 516, 551, 591 and 647 nm are assigned to the Q bands. Upon a photoexcitation wavelength with 430 nm, the PL spectra of FB-Por 1 and 2 exhibit a strong band at 653 nm and a weak peak at 715 nm. Zn-Por 1 and 2 show a very intense band at 420 nm for B-band $\pi$~$\pi^*$ transitions. In addition, the weak bands at 547 and 585 nm were assigned to the Q bands. With an excitation wavelength of 430 nm, the PL spectra of Zn-Por 1 and 2 show a moderate band at 596 nm and a strong band at 646 nm.

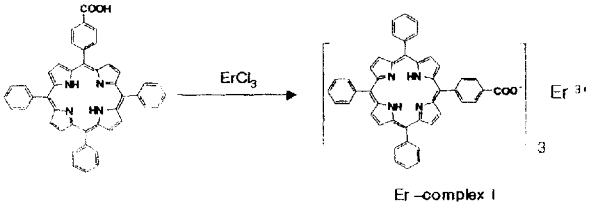
Keywords Lanthanide-cored supramolecular complex; Porphyrins, Ligand-exchange reaction, Optical amplification, Photoluminescence

## INTRODUCTION

To achieve the superhigh speed telecommunication systems, the development of integrated planar waveguide optical amplifiers is extremely essential. At present, erbium-doped silica amplifiers are widely used. But, the poor solubility of lanthanide cations ($Ln^{3+}$) in conventional inorganic/organic media leads to the low amplification property. When the higher doping concentration of lanthanide cations was introduced, clustered $Ln^{3+}$ species can be formed, which in turn has limited the amplification property. It is ascribed to the cooperative energy-transfer processes (i.e., self-quenching process) between the clustered $Ln^{3+}$ species. Their processes reduced the intensity of luminescence. To circumvent the solubility problem and maximize the optical amplification property, we have investigated the development of lanthanide-cored supramolecular complexes containing porphyrins. In this paper, we describe the synthesis and luminescent properties of lanthanide-cored supramolecular complexes containing porphyrins.



SCHEME 1 Synthetic routes to the dipyrromethane and the porphyrins.



SCHEME 2 Synthetic routes to the lanthanide-cored supramolecular complex based on porphyrin.

## RESULTS AND DISCUSSION

### Preparation of lanthanide-cored supramolecular complexes based on porphyrins

The dipyrromethane and porphyrins were synthesized according to a procedure described by Lindsey et al. [1]. The synthetic routes to the dipyrromethane and porphyrins were shown in SCHEME 1. Their chemical structures were identified by FT-IR, $^1$H-NMR, UV-Vis absorption and emission spectroscopics. A $^1$H-NMR spectrum of FB-Por 1 showed two characteristic peaks of 4.1 and

–2.85 ppm assigned to the methoxycarbonyl and the pyrrole N-H groups, respectively. Those peaks disappeared in the Zn-Por 2, after the insertion of Zn(II) ion into a pre-hydrolyzed porphyrin [3]. In the UV-visible spectrum, FB-Por 1 and 2 showed a very intense band at 419 nm, which was attributed to the Soret band. In addition, the relatively weak bands at 516, 551, 591 and 647 nm were assigned to the Q bands. Upon a photoexcitation wavelength with 430 nm, the PL spectra of FB-Por 1 and 2 exhibited a strong band at 653 nm and a weak peak at 715 nm (see FIGURE 1).

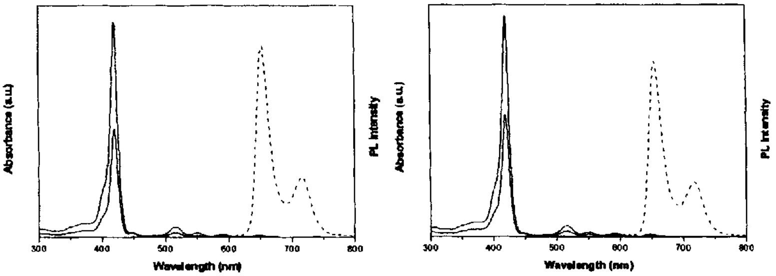


FIGURE 1 UV-Vis absorption and PL spectra of FB-Por ($COOCH_3$) (left) and FB-Por (COOH) (right) in chloroform solution

Also, Zn-Por 1 and 2 showed a very intense band at 420 nm for B-band $\pi$~$\pi^*$ transitions. In addition, the weak bands at 547 and 585 nm were assigned to the Q bands. Generally, metalloporphyrins were more symmetrical macrocycles than free based porphyrins, so that their Q band spectra consisted of only two bands. With an excitation wavelength of 430 nm, the PL spectra of Zn-Por 1 and 2 showed a moderate band at 596 nm and a strong peak at 646 nm (see FIGURE 2).

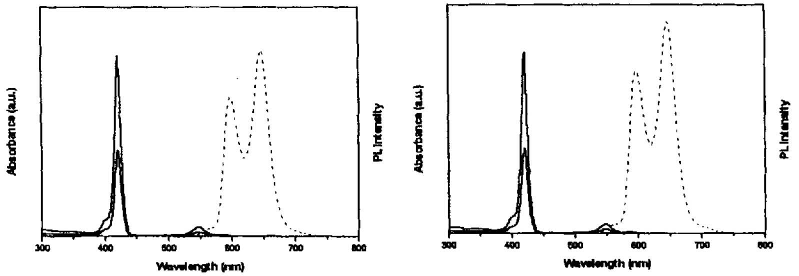


FIGURE 2 UV-Vis absorption and emission spectra of Zn-Por ($COOCH_3$) (left) and Zn-Por (COOH) (right) in chloroform solution.

As shown in SCHEME 2, lanthanide-cored supramolecular complexes based on porphyrin were synthesized using the ligand-exchange reaction. First, we synthesized an Er-cored supramolecular complex using the Er(III) Acetate, according to the previous Frechet's method [2]. But, the reaction did not proceed because of the chemical stability of Er(III) Acetate and steric hinderance of porphyrin. So, we achieved successfully the synthesis of Er-cored supramolecular complexes based on porphyrins using $ErCl_3$ in a different synthetic method. Their chemical structures were identified by FT-IR, $^1$H-NMR, UV-Vis absorption and emission spectroscopies. In progress, their luminescent and optical amplification properties are being investigated.

## ACKNOWLEDGMENT

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