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Lanthanide-Cored Supramolecular Systems with Highly Efficient Light-Harvesting Dendritic Arrays towards Tomorrow's Information Technology

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Abstract: We have developed novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays for integrated planar waveguide-typed amplifiers. Er^{3+} ions were encapsulated by the supramolecular ligands, such as porphyrins and macrobicyclics. The supramolecular ligands have been designed and synthesized to provide enough coordination sites for the formation of stable $\text{Er}(\text{III})$ -chelated complexes. For getting a higher optical amplification gain, also, the energy levels of the supramolecular ligands were tailored to maintain the effective energy transfer process from supramolecular ligands to erbium(III) ions. Furthermore, to maximize the light-harvesting effect, new aryl ether-functionalized dendrons as photon antennas have been incorporated into lanthanide-cored supramolecular systems. In this paper, molecular design, synthesis and luminescent properties of novel lanthanide-cored integrated supramolecular systems with highly efficient light-harvesting dendritic arrays will be discussed.

Keywords: lanthanide-cored supramolecular systems, light-harvesting dendritic arrays, optical amplification gain, energy transfer process, new aryl ether-typed dendrons, photon antennas.

Introduction

In the era of new millennium, beginning with the current 21st century, advanced photonics technology for the information technology (IT) is being rapidly developed and considered to be the world leading technology among all IT-related industries. In line with this, advanced photonic devices based on semiconductors and inorganic materials

have continuously been pursued for the realization of super-high speed communication systems of large capacity optical communication, information storage, and processing. However, because of the currently existing limitations of these materials on the performance, extensive research on the development of new advanced materials is essential to overcome such limitations and to achieve photonic devices for the next generation superhigh speed communication. With regard to this, the organic polymeric materials have been considered as such future photonic materials and their main advantages, compared with semiconductors and inor-

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ganic materials, are as follows: ease of property control and synthetic feasibility through molecular chemistry, fast response time and large broad bandwidth, low cost, good processibility, and simple device manufacturing process at low temperatures, and ease of integrated device fabrication. However, their thermal instability in the optical property and high optical transmission loss in the practical use at wavelength of 1.3 or 1.55 μm are still limited in real device applications. High transmission loss has been attributed to the optical absorption by the inherent presence of C-H overtone band in organic polymers. To compensate for the above mentioned shortcomings, the development of integrated planar waveguide optical amplifiers utilizing the basic principle of optical amplification in optical fibers for telecommunication is extremely high in demand. In particular, integrated optical amplifier wavelength division multiplexing (WDM) devices are recognized to be essential for successfully realizing photonic devices in WDM technology, which has attracted much attention because of its paramount importance in superhigh speed communication systems. Despite such needs, the problem still remains in the materials for the use in the real optical amplifiers.¹

Up to now, silica-based optical fibers widely used for the optical telecommunication can maintain very low loss (below 0.18 dB/km) when operated at wavelength of 1.55 μm . However, even with such insignificant loss with silica-based materials, the transmission loss in intercontinental telecommunication networks requires compensation. For example, erbium (Er)-doped fiber amplifiers (EDFA) must be installed at every 30-40 km distance along the communication network for the successful transmission, in the order of several hundred to thousand kilometer ranges.² The development of EDFA was considered to be revolutionary in that it changed not only the basic concept of optical communication but also the primary wavelength of optical telecommunication from 1.3 to 1.55 μm . The amplification gain of current EDFA is not enough for amplifying the optical signals in small-sized photonic devices, while the amplification gain is not a problem for long distance of several to tens of meters. To get high gain of 30 dB in small-sized photonic devices, one solution must be to design the spiral-typed planar waveguide for making a device with long pathway. However, problems in design and fabrication of spiral-typed planar waveguides with small radius and high curvature-related loss make it difficult to produce miniature sized and more variety of photonic devices. In addition, Er³⁺-doped concentration on silica optic fiber is limited to 100-1,000 ppm. If higher than the limiting concentration is to be employed, Er³⁺ ion interaction between themselves would cause non-radiative process to occur, hence rapidly reducing the amplification gain. For these reasons, it is not possible to obtain the amplification gain of higher than 30 dB with Er³⁺-doped silica optical fibers for developing integrated planar waveguide amplifiers (IPWAs).^{1,2}

In order to solve the above mentioned problems, many research efforts have primarily focused on developing lanthanide ion-doped polymeric materials. At present time, the frontier research groups in USA, Europe, Japan and other industrializing nations are studying to develop polymeric materials for use in planar waveguide optical amplifiers, by way of doping lanthanide ion-chelated complexes into polymeric matrices. Polymer-based planar waveguide optical amplifier, based on PMMA optical fiber core doped with 1 ppm concentration of an organic dye, was first reported in 1993 at Keio University in Japan.³ Although it was 50 cm in length and the optical amplification (OA) was excellent with 30 dB, the amplification time was very short due to the amplification mechanism being the spontaneous emission process rather than the stimulated emission process. In the effort of overcoming such shortcomings, a graded-index polymeric optical amplifier using the same polymer fiber doped with lanthanide ions was developed by the same research group.⁴ It was reported that the optical loss was three times less than the earlier dye-doped system at 0.614 μm , due to the amplification gain by the lanthanide ions. More recently, Chen group at University of Texas (Austin) reported that the planar waveguide amplifier with a length of 2.2 cm based on Nd³⁺-doped photolime gel was fabricated by spin coating and the amplification gain at 1.06 μm was about 8.5 dB.⁵ Similarly, a short amplifier in the form of 1.5 cm length polymeric optical fiber doped with lanthanide metal ion (Eu³⁺) was developed by the Philip Company by polymerizing lauryl methacrylate monomer doped with Eu³⁺ in a teflon tube.⁶ The amplification gain was reported to be 4.1 dB. At the present time, host-guest systems via low temperature sol-gel chemistry have been extensively studied for developing OA materials containing lanthanide ions homogeneously dispersed into a silica matrix (SiO₂) by the frontier research groups like NTT in Japan, several universities and private laboratories in USA (e. g., Colorado U., Arizona U., Bellcore, Corning, etc), and McGill University in Canada.⁷⁻⁹ Of particular interest, the host-guest system was demonstrated to be employed in making the planar waveguide optical amplifiers and integrated WDM amplifiers. Very recently, Fréchet group at UC-Berkeley also reported the preparation of the Er-cored dendrimer complexes for OA materials. But, the chemical structure was characterized very poorly and the amplification property was not detected.¹⁰

Very recently, in order to solve the above mentioned problems and realize the development of IPWAs, we have developed novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays. Er³⁺ ions were encapsulated by supramolecular ligands such as porphyrins and macrobicyclic derivatives of azacryptands, macrobicyclic *N,N*-dioxides, macrobicyclic polypyridines, carcerands, bispherands, or cavitacryptands. The supramolecular ligands have been designed and synthesized such that they provide enough coordination sites to form stable

Er(III)-chelated complexes. For obtaining a higher optical amplification gain, also, the energy levels of the supramolecular ligands were tuned to maintain the effective energy transfer process from supramolecular ligands to Er(III) ions. Furthermore, to maximize the light-harvesting effect, we have incorporated new aryl ether-typed dendrons as photon antennas into integrated supramolecular systems. In this paper, molecular design, synthetic routes, and luminescent properties of novel lanthanide-cored integrated supramolecular systems with highly efficient light-harvesting dendritic arrays for integrated planar waveguide-typed amplifiers will be discussed.

Spectroscopic Properties and Optical Amplification Principle of Lanthanide Ions

The electronic configurations of trivalent lanthanide ions have $4f^n$ ($n = 1 \sim 14$) structures, which fill the $4f$ orbital according to the atomic numbers. The spectral structure arising from the $4f^n - 4f^n$ transitions characterizes solid state spectroscopy of trivalent lanthanide ions, and has made tremendous studies about the interactions between lanthanide ions and their environment. The sharp spectral lines are due to the fact that the f -electrons are shielded from the crystalline environment by the outer $5s$ and $5p$ electrons and are slightly perturbed by the effects of lattice phonons and static strain fields. Since the spin-orbit interaction is larger than the effect of the crystal field, the luminescence spectra consist of groups of lines which arise from crystal field splittings of J multiplets of the free ion in general.¹¹ Wybourne,¹² Dieke,¹³ and Hüfner¹⁴ studied the classical spectroscopy of lanthanide ions in crystals, including their energy levels and transition strengths.

With the development of tunable dye lasers, a variety of techniques for increasing spectral resolution and extracting information, which is masked by undesired effects, are possible. These techniques are generally classified as *nonlinear laser spectroscopy*. Many of these techniques have been applied in the field of lanthanide spectroscopy of solids. The major object is to overcome the resolution limit imposed by inhomogeneous broadening due to lattice strains and imperfections. By eliminating inhomogeneous broadening, the study of many new effects becomes possible. These include fundamental homogeneous dephasing processes, spectral diffusion, hyperfine and superhyperfine interactions, and Stark and Zeeman splittings which provide new insights into the structure and dynamics of solids.¹¹

Generally, the term *induced* or *forced* electric dipole is used to emphasize that electric dipole transitions require the initial and final states are in different parity states by the selection rule, whereas no parity change is involved in transitions within a configuration. Judd¹⁵ and Ofelt¹⁶ independently derived expressions for the oscillator strength of induced dipole transitions within the $4f^n - 4f^n$ configuration. Since their

results are similar and were published simultaneously, their results are known as the Judd-Ofelt theory. They summed over the intensities of the individual crystal field components of a given state. The fundamental mechanism of the Judd-Ofelt theory is the perturbation caused by mixing of the crystal field potentials between the orbitals with different parities and $4f^n$ orbitals.

The $4f^n - 4f^n$ transitions are forbidden because $4f^n$ of rare earth ions and energy levels of electron shells have equal parity. However, absorption spectra between $4f^n - 4f^n$ transition are experimentally observed. This is explained by assuming that a higher-lying opposite parity configuration is mixed into the $4f^n$ states via the potential due to the ligand field.¹² In contrary, $4f^n - 4f^{n-1}5d^1$ transitions or charge transfer transitions ($4f^n - 4f^{n-1}5L^1$, $L = \text{ligand}$) are partly allowed by mixing with the odd-parity wave functions via the potential due to the crystal field, as shown in Figure 1. The absorption and emission cross-sections are very small in solid phase and the corresponding fluorescence decay times are sufficiently long (as of the order of ms), compared with the rate at which it is populated in the excitation process. Also there is a Stark splitting between the degenerated $4f$ energy levels by the effect of electric field near lanthanide ions removing the degeneracy of the $4f$ level.

In analyzing the mechanisms of excited state relaxation of lanthanides in crystal hosts, two modes of relaxation are recognized: radiative and radiationless (or non-radiative) processes. Axe¹⁷ represented the radiative processes in quantitative terms using the Judd-Ofelt theory. Radiationless relaxation was formulated in terms of multiphonon relaxation processes.^{18,19} Such processes become less probable as the energy gap between an excited state and the next lower energy state increases. Since excited state relaxation is generally achieved prior to transitions to several lower-lying states, a total radiative relaxation rate can be defined as a summation over all states lower in energy than the fluorescing state. Figure 2 shows the principal fluorescing states of the

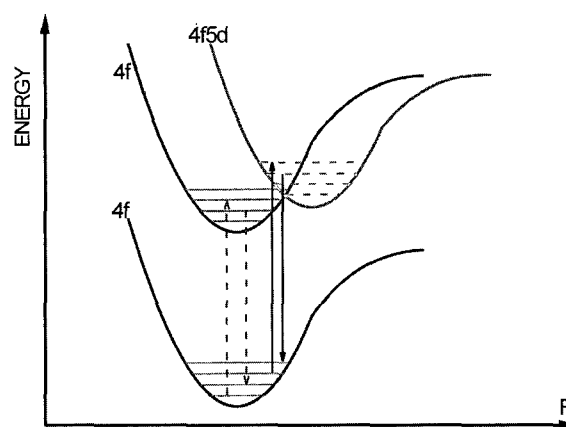


Figure 1. Forbidden $4f^n - 4f^n$ transitions and allowed $4f^n - 4f^{n-1}5d^1$ electron transitions in lanthanide ions.

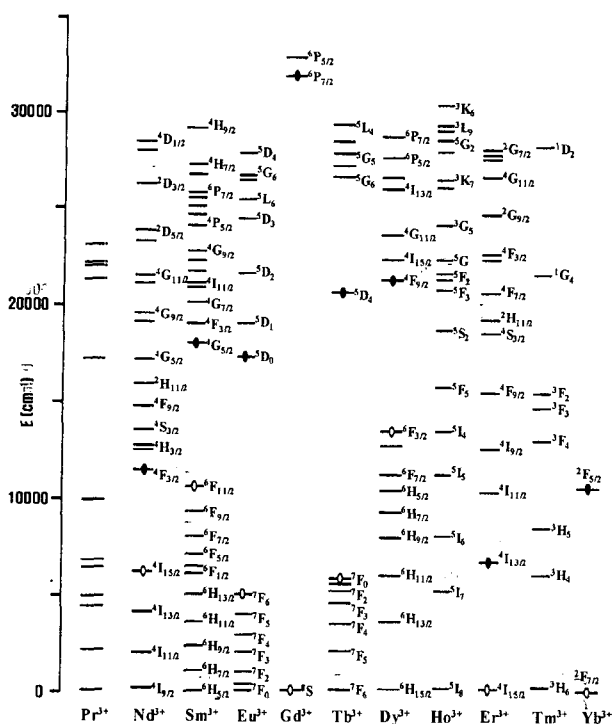


Figure 2. Energy levels of trivalent lanthanide ions.

lanthanides in crystal hosts.²⁰ Fluorescence from many of these levels is observed only at low temperatures since rapid relaxation of an excited state by radiationless processes compete strongly with the radiative mode unless the energy gap to the next lower level is large. As the gap increases, the process rapidly decreases in probability such that radiative decay can efficiently compete with a relaxation mechanism. Usually both radiative and radiationless processes operate to relax an excited state. The total fluorescence lifetime of the state is a sum of the radiative rate and the rates of the various radiationless processes.

Several lanthanide ions, such as Pr³⁺, Nd³⁺, Dy³⁺, Er³⁺, and Yb³⁺, show luminescence in the infrared region. The luminescence of wavelengths 1.54 μm from Er³⁺ ion and 1.34 μm from Pr³⁺ ion is used as standard wavelengths in optical communications, in which light is used to transport information between different users. Some of lanthanide ions, such as Sm³⁺, Tb³⁺, and Eu³⁺, exhibit the emission band in the visible region. Their luminescent complexes have been considered the potential candidates for light-emitting diodes.

Erbium-doped materials have attracted much attention because of their potential applications in photonics.^{1,21} When Er³⁺ is incorporated in a solid, the presence of the surrounding atoms slightly perturbs the 4f states.¹⁴ Due to the Stark effect, the degenerate levels split into manifolds. The principle of optical amplification of Er³⁺ ion is shown in Figure 3. The Er³⁺ ion is excited to upper states higher than ⁴I_{13/2} level by absorbing photons of pumping laser such as 488 or 980 nm, etc. And then, the transferred energy from the upper state

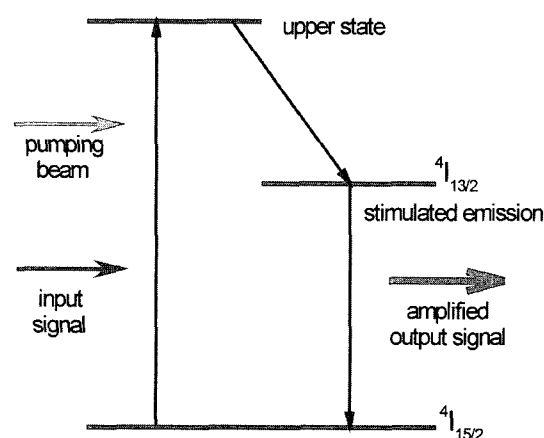


Figure 3. Optical amplification principle of Er³⁺ ions.

than ⁴I_{13/2} level makes transition to the metastable excited state by radiationless transition. When the same input signal with the metastable excited state is introduced at the same time, the excited state energy is emitted with the same polarization as the input signal, *i.e.*, stimulated emission, and electrons fell to the ground state. Consequently, the input signal and the stimulated emission beam are summed into the amplified output signal. The stimulated emission lifetime of the ⁴I_{13/2} → ⁴I_{15/2} radiative transition at 1.54 μm of Er³⁺ in a solid is of the order of 10 ms. The measured lifetime strongly depends on the presence of impurities and defects in the host.

Lanthanide-Cored Supramolecular Systems with Highly Efficient Light-Harvesting Dendritic Arrays

Recent Progress in Luminescent Lanthanide Complexes.

The development of integrated planar waveguide optical amplifiers is extremely essential.^{1,21} At present, erbium-doped silica amplifiers are widely used. But, the poor solubility of lanthanide cations (Ln³⁺) in conventional inorganic/organic media leads to low amplification property. When the higher doping concentration of lanthanide cations was introduced, clustered Ln³⁺ species can be formed, which in turn have limited amplification property. It is ascribed to the cooperative energy-transfer processes (*i.e.*, self-quenching process) between the clustered Ln³⁺ species. Their processes reduced the intensity of luminescence. Because of this reason, it is impossible to obtain high efficiency of optical amplification by doping Er³⁺ ions in silica optical fiber. Also it is difficult to expect optical amplification of 30 dB in planar waveguide form, since the amplified luminescence intensity in lanthanide ions by direct excitation is very low due to their low absorption and emission cross sections. In order to enhance the amplified luminescence intensity, the development of luminescent lanthanide complexes based on the energy transfer mechanisms by using the supramolecular complexes as organic ligands has been extensively studied.²²⁻⁴⁵ Luminescent lanthanide complexes consist of a lanthanide

ion and its chelating luminescent ligand, in which luminescent ligand can be tailored to contain built-in functionalities that give the desired properties to the overall complex. Also, the luminescent ligand affects photophysical properties of the complexes. In most cases, the luminescent ligand contains a light-absorbing group in the form of an organic (or antenna) chromophore and a tightly chelating organic molecule, as shown in Figure 4.²²

DTPA ligands having a high binding affinity with lanthanide ion are known to form stable complexes, which are soluble in aqueous or nonaqueous solution. Werts *et al.*²³ synthesized luminescent complexes such as AMFLU-DTPA and AMEO-DTPA with fluorescein and tetra-bromoeosin and observed luminescence in near infrared region (see Figure 5). Fluorescein indicates the extremely low triplet efficiency. In AMFLU-DTPA case, effective sensitization occurred because intersystem crossing (ISC) effect increased by the heavy lanthanide ions.

Moving the excitation wavelength to longer wavelength

region by introducing the antennas such as naphthalene, triphenylene,²⁴ and fluorescein²⁵ into calix[4]arene derivatives made possible the effective energy transfer from antenna to lanthanide ions. The quantum yield of ISC in antenna, the separation between antenna and the central ion, and the overlap of energy levels of donor and acceptor are important factors in energy transfer via antenna. The calix[4]arene involving the antenna coordinated to the lanthanide ions and their periodic arrays are important in increasing the energy transfer efficiency. The ISC efficiency from the singlet to triplet states and the luminescence intensity depend on the antennas and the separation between calix[4]arene and antenna. The environment of lanthanide ions affects the luminescence intensity and lifetime. However, the quantum yield still remains low in this calix[4]arene derivatives.

Reinhoudt *et al.*²⁶ studied near infrared luminescence of lanthanide complexes for optical amplification materials. They synthesized luminescent lanthanide complexes of polydentate hemispherand ligands, and observed luminescence of 1.54 μm

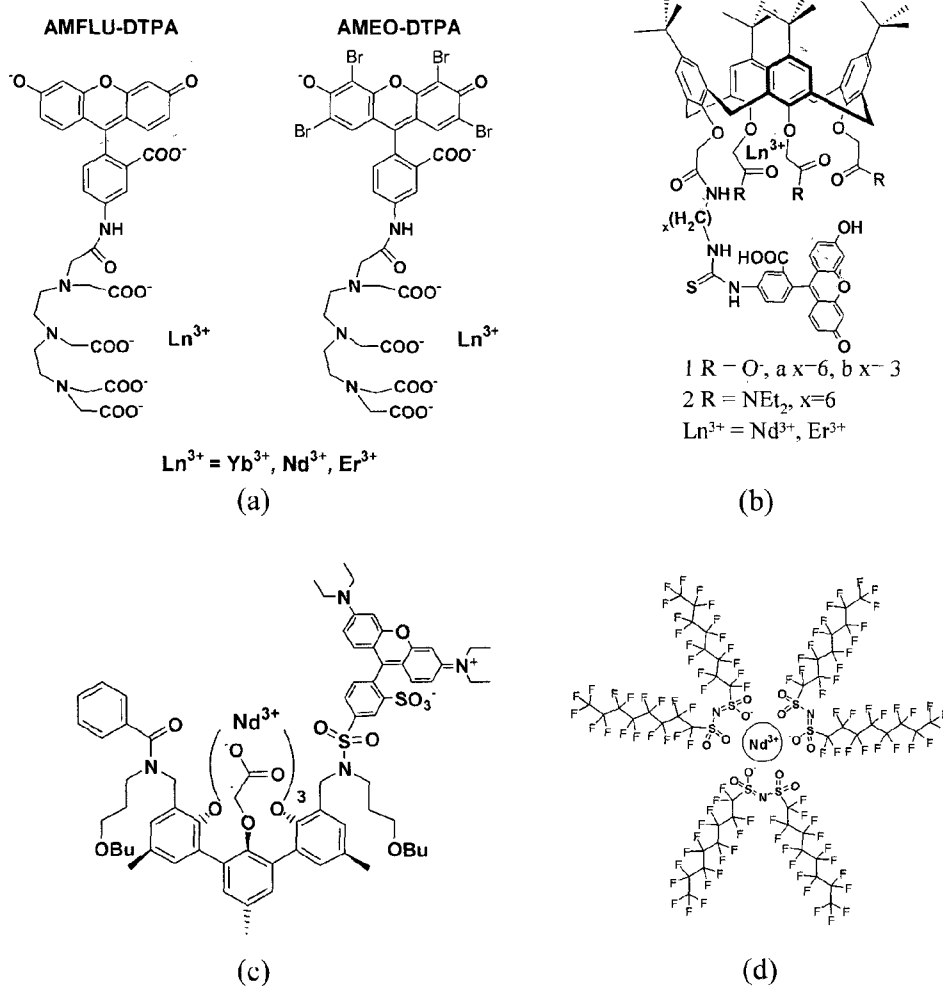


Figure 4. Chemical structures of some known luminescent lanthanide complexes based on (a) DTPA, (b) calix[4]arene, (c) hemispherand, and (d) dendritic ligands.

by direct excitation of Er^{3+} ions with Ar^+ laser. They also reported near infrared luminescence through energy transfer effects by exciting organic ligands, and reduction of luminescence intensity by decreasing absorption coefficients in lanthanide ions with temperature. Near infrared luminescence is observed in polydentate hemispherand complexes containing triphenylene^{27,28} or lissamine^{29,30} group, where triphenylene and lissamine act as antenna chromophores (see Figure 6). These show relatively high ISC quantum efficiency such that lanthanide ions are easily excited by the triplet state of chromophores.

Gillin and Curry^{31,32} studied near infrared luminescence in

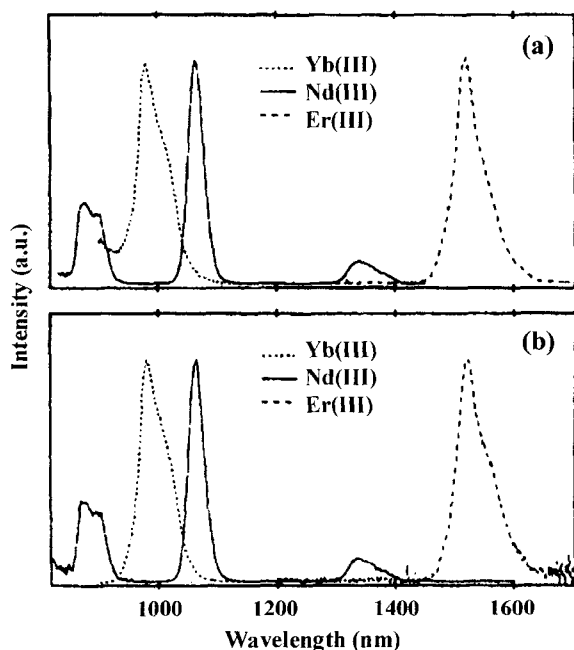


Figure 5. Near-infrared luminescence spectra. (a) Emission spectra of the AMFLU-DTPA/ Ln^{3+} complexes ($\lambda_{\text{exc}} = 488 \text{ nm}$); (b) Emission spectra of the AMEO-DTPA/ Ln^{3+} complexes ($\lambda_{\text{exc}} = 488 \text{ nm}$).

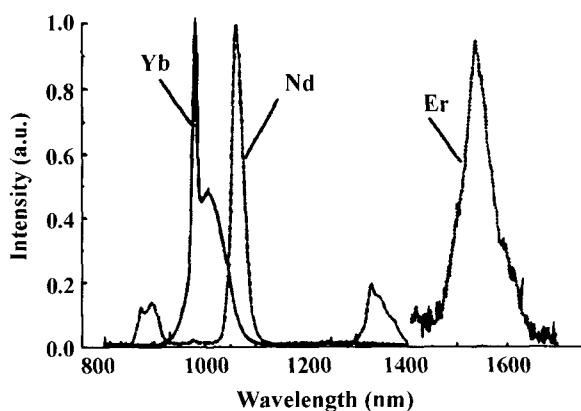


Figure 6. Photoluminescence spectra of triphenylene-based lanthanide complexes (351.1/363.8 nm lines of Ar ion pump laser).

the applications as optical amplification materials and light-emitting devices. They synthesized tris (8-hydroxyquinoline) series and observed luminescence and electroluminescence at $1.54 \mu\text{m}$ in organic device. Yanagita *et al.*^{33,34} synthesized lanthanide complex compounds with tris (dibenzoylmethano) ligand and observed near infrared luminescence by making organic monomer luminescence device.

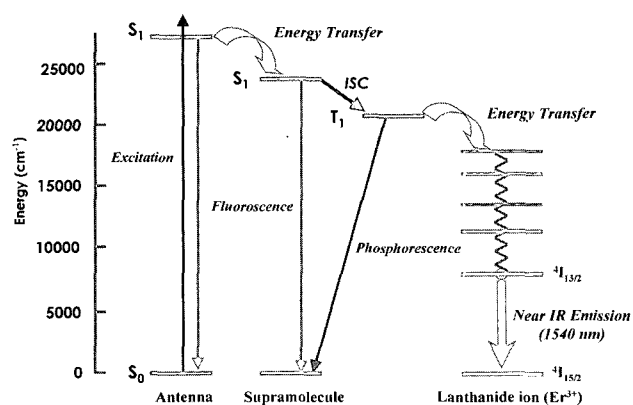
Since the ISC quantum yield of porphyrin is almost 100%, porphyrin acts as a sensitizer which easily excites lanthanide ions by the triplet state of chromophores. Harrison *et al.*³⁵ synthesized Er (TPP) acac complex by using porphyrin as a ligand, and showed the possibility of light-emitting material by doping in PPV series polymer materials.

Hasegawa *et al.*³⁶ reported luminescent lanthanide complex using supramolecular ligands of dendrimer type. It attains a high quantum yield of 3% in comparison with the low luminescence quantum yield of generally known lanthanide complexes, in which this reason is considered as results of completely exclusion of high-energy vibrations and solvents. Vögtle *et al.*^{37,38} synthesized dendrimer containing 21 amide groups in the interior and 24 chromophoric dansyl, which show an intense fluorescence band in the visible region. The results have been interpreted on the basis of the energy levels and redox potentials of dendrimer and metal ion.

Usui *et al.*³⁹ have triggered the research of polymer-based amplification device with PMMA. However, PMMA has large optical loss in near infrared region. Yoshimura *et al.*^{40,41} obtained low loss optical devices with deuterated PMMA and deuterated/perfluorinated PMMA. But, PMMA series are thermally unstable. Therefore, deuterated polysiloxanes⁴² and perfluorinated polyimides⁴³ with higher melting points are developed. Orignac *et al.*⁷ reported planar waveguide amplification device and integrated device of WDM using sol-gel chemistry. It is difficult to dope lanthanide ions into polymers. In this case, we use the host-guest system with lanthanide ion-chelated complexes. Very recently, Lindgren *et al.*⁴⁴ used fluorinated hyperbranched polymers and dendrimers as organic ligands coordinated to lanthanide trivalent ions to obtain NIR and IR regions. Also, Destri *et al.*⁴⁵ synthesized Er(III)-chleated complexes based on oligothiophene derivatives and observed near infrared luminescence via energy transfer process taking place between Er(III) ions and oligothiophene derivatives.

Lanthanide-Cored Supramolecular Systems with Highly Efficient Light-Harvesting Dendritic Arrays. Up to now, luminescent lanthanide complexes containing supramolecular ligands as antenna chromophores were not developed in specific reference to luminescent lanthanide complexes. They are simply supramolecular complexes containing well-known antenna chromophores to photoexcite the lanthanide ions via the energy transfer process. They were not satisfied with the quantum yield of energy transfer and the luminescence efficiency yet. Also, such efforts are just in the early stage and not only the basic concept not established, but also the

structure-property relationship is not yet clearly understood. Therefore, the dependence of lanthanide ion and ligand structure on amplification principles (such as the optical amplification lifetime, excited state dynamics, etc) need to be systematically established. Based on the relationship established, the design and synthesis of luminescent lanthanide

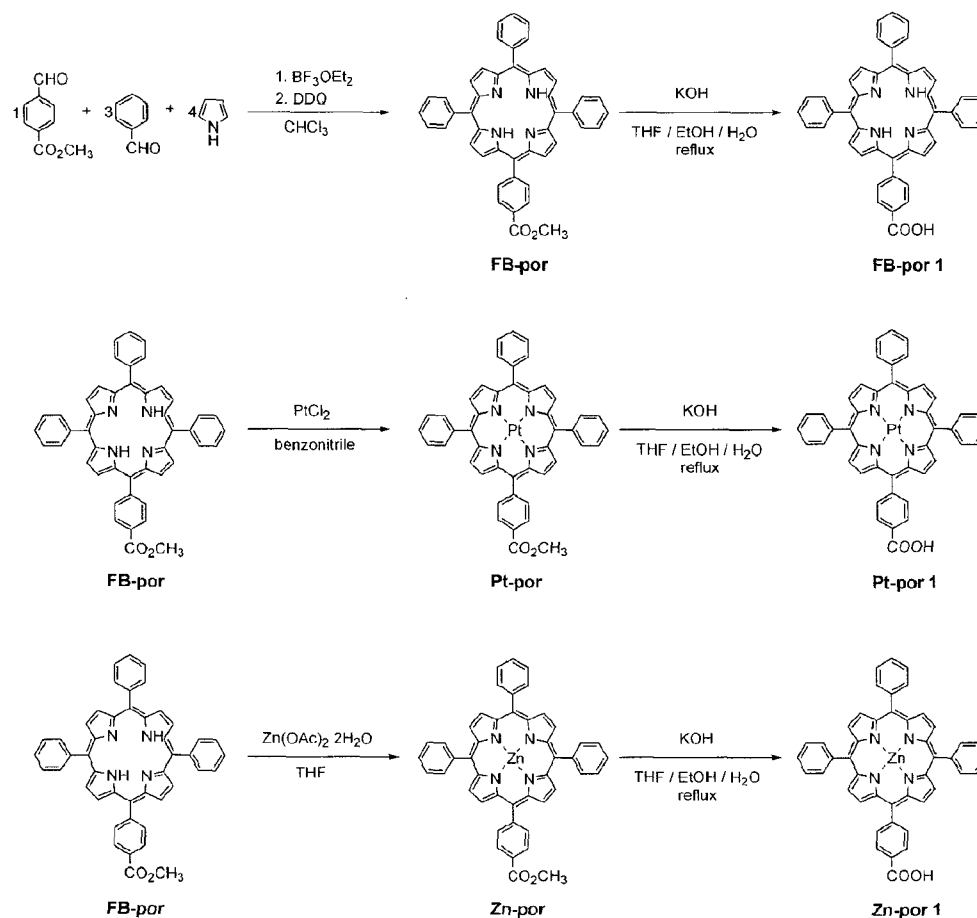


Scheme I. The basic concept of novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays.

complexes using molecular engineering approach need to be investigated.

Very recently, we have systematically designed and developed novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays. Er^{3+} ions were effectively encapsulated by supramolecular ligands, such as porphyrins and macrobicyclic derivatives of azacryptands, macrobicyclic N,N -dioxides, macrobicyclic polypyridines, carcerands, bispherands, or cavitacryptands. The supramolecular ligands have been designed and synthesized in order to provide enough coordination sites for the formation of stable $\text{Er}(\text{III})$ -chelated complexes. For getting a higher optical amplification gain, also, the energy levels of the supramolecular ligands were adjusted to maintain the effective energy transfer process from supramolecular ligands to $\text{Er}(\text{III})$ ions. Furthermore, to maximize the light-harvesting effect, new aryl ether-typed dendrons as photon antennas have been incorporated into lanthanide-cored supramolecular systems.

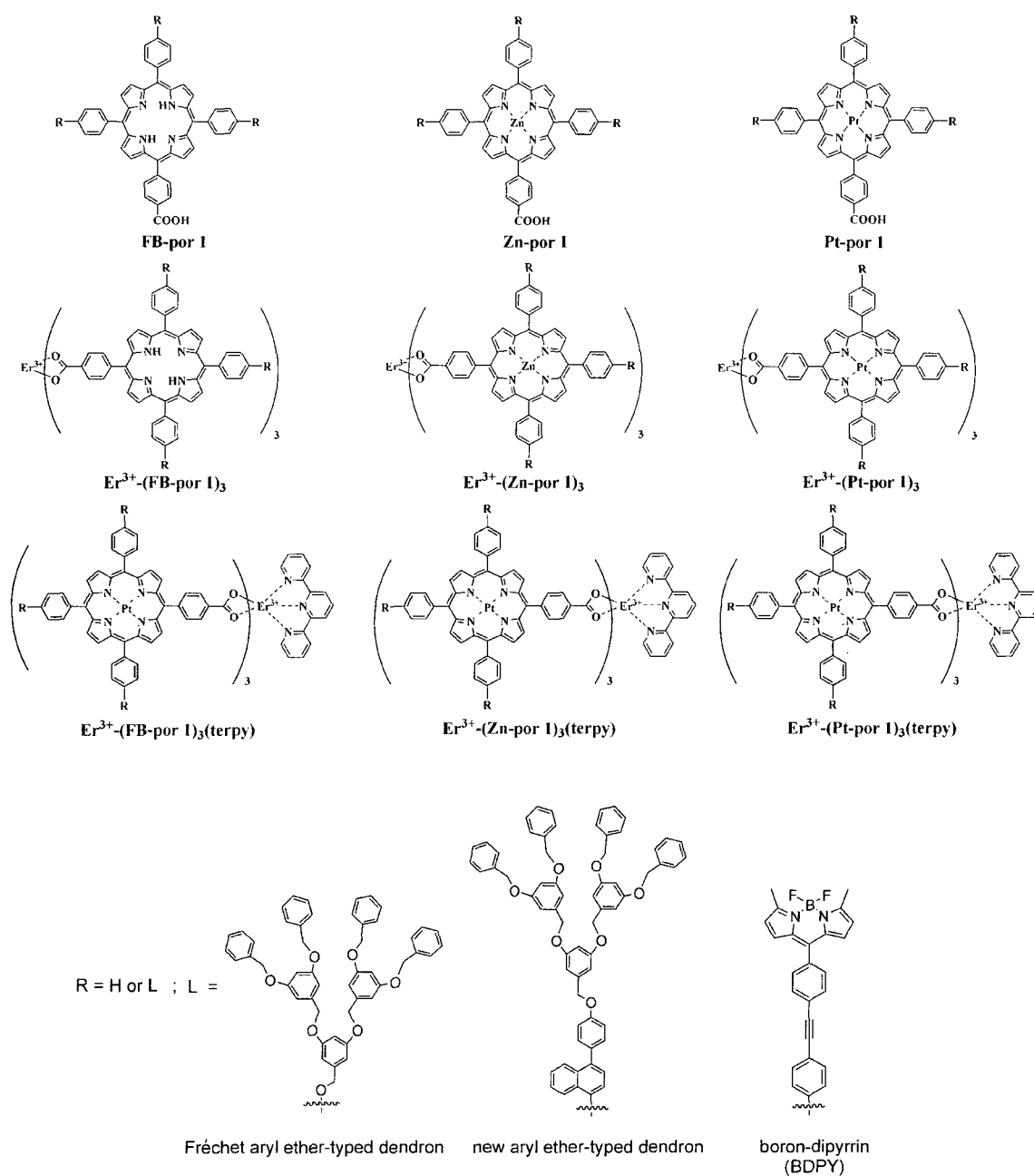
The basic concept of novel lanthanide-cored supramolecular systems with highly efficient light-harvesting dendritic arrays is described in Scheme I. Our supramolecular systems have both lanthanide-cored supramolecular complexes and light-



Scheme II. Synthetic routes to porphyrin derivatives.

harvesting dendritic photon antenna with such proper energy gradient. In our supramolecular systems, many exterior chromophores efficiently absorb and transfer the light through the interior chromophores to the supramolecular ligands via energy transfer process, so-called the light-harvesting effect, leading to the formation of the singlet state of the supramolecular ligands. And then, the singlet state of the supramolecular ligands is converted into their triplet state by ISC process. The triplet state of the supramolecular ligands must be tailored to maintain the upper energy level than the lower excited energy level ($\text{Er}^{3+}, {}^4\text{I}_{13/2}$) of the lanthanide ions, and

then transitioned to the lower excited energy level ($\text{Er}^{3+}, {}^4\text{I}_{15/2}$) of the lanthanide ions through the lattice relaxation process (or the vibrational relaxation process). Finally, it loses the photon energy in a radiative decay to fall back to the ground state ($\text{Er}^{3+}, {}^4\text{I}_{15/2}$) of the lanthanide ions, emitting the stimulated light at $1.54 \mu\text{m}$. It is very important to note that the accumulating photon energy from the triplet state of the supramolecular ligands can excite the lanthanide ions as much as possible, thus maximizing the optical amplification gain. Also, the optophysical properties of the lanthanide-encapsulated supramolecular systems are optimized and maximized



Scheme III. Lanthanide(III)-cored supramolecules based on porphyrin derivatives with highly efficient light-harvesting dendritic arrays.

during artificially light gathering and transferring by way of using principles of naturally existing photo-synthetic antenna.⁴⁶

Lanthanide(III)-Cored Supramolecules based on Porphyrin Derivatives. To maximize the optical amplification efficiency, we have designed and synthesized lanthanide(III)-cored supramolecules based on porphyrin derivatives with light-harvesting dendritic arrays for optical amplification using the metal-ligand exchange reaction, as shown in Schemes II and III. Porphyrin derivatives were chosen for supramolecular ligands, since they are well-known as photon antenna for natural photosynthetic system.⁴⁶ Also, supramolecular ligands should have the following properties: First, they have enough donor atoms (8-12) such as oxygen and nitrogen, and specific isolation space for guest metal ions. It is possible to obtain the encapsulation of lanthanide ions and the isolation from light quenchable solvents such as water. Second, they have specific functional groups, in which they will be used to couple with antenna systems or light-harvesting systems. Third, the energy level of the triplet state of metalloporphyrins has the spectral overlap well with the $^4F_{9/2}$ sublevel of Er(III) ions to maintain the effective energy transfer process from metalloporphyrin ligands to Er(III) ions.

The porphyrin derivatives were synthesized according to a procedure described by Lindsey *et al.* (see Scheme II).⁴⁷ Their chemical structures were identified by FT-IR, $^1\text{H-NMR}$, UV-vis absorption and emission spectroscopies. A $^1\text{H-NMR}$ spectrum of free base porphyrin (FB-Por 1) showed two characteristic peaks at 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. 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. Also, Zn-Por 1 and 2 showed a very intense band at 420 nm for B-band, whereas the weak bands at 547 and 585 nm were assigned to the Q bands. Generally, metalloporphyrins were more symmetrical macrocycles than free base 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 2 and FB-Por 1 showed a moderate band at 596 nm and a strong band at 646 nm (see Figure 7). Initially, we synthesized Er-cored supramolecular complexes using the starting material of Er(III) acetate, according to the previous Fréchet's method.^{10,48} But, the reaction did not take place because of the chemical stability of Er(III) acetate.⁴⁹ So, we achieved successfully the synthesis of Er-cored supramolecular complexes based on porphyrins using ErCl_3 in a novel synthetic method, yielding the 6- and 9-coordinated complexes to form a more stable complex and to shield the erbium (III)-chelated complexes more efficiently (see Scheme III).⁵⁰

The successful synthesis of Er-chelated model complexes was proved by FT-IR, absorption and emission spectroscopies.⁴⁹ But, the paramagnetic properties of Er complexes could not permit NMR characterization of the corresponding complex. FT-IR spectra of carboxylate groups in Er complexes showed two characteristic peaks in the region of 1600 and 1400 cm^{-1} . Their emission spectra, obtained from the different excitation wavelengths corresponding to the absorption maximum positions of porphyrins, showed an intra 4f shell from its first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) taking place at 1.54 μm (see Figure 8). These results indicate that the saturated 9-coordinated complex has the higher PL efficiency than the unsaturated 6-coordinated complex. In the latter complex, three H_2O molecules should be at least coordinated in the unsaturated 6-coordinated complex. It was confirmed with the determination of the releasing water amount from thermal gravimetric analysis (TGA). In these

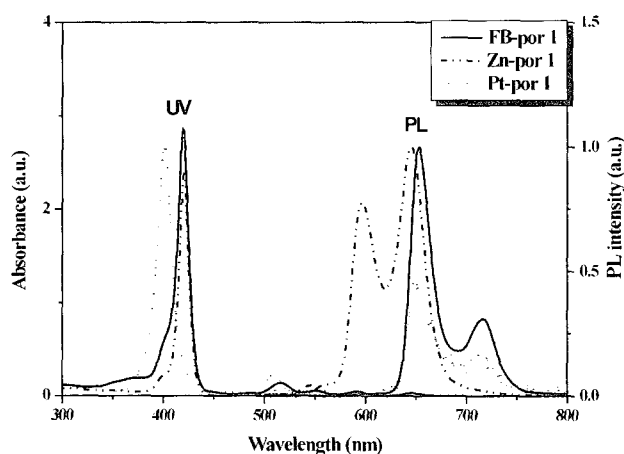


Figure 7. The UV-vis absorbance and emission spectra of FB-por 1, Zn-por 1, and Pt-por 1.

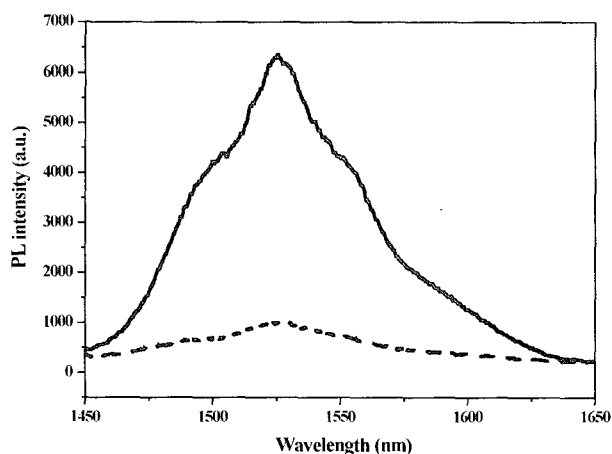
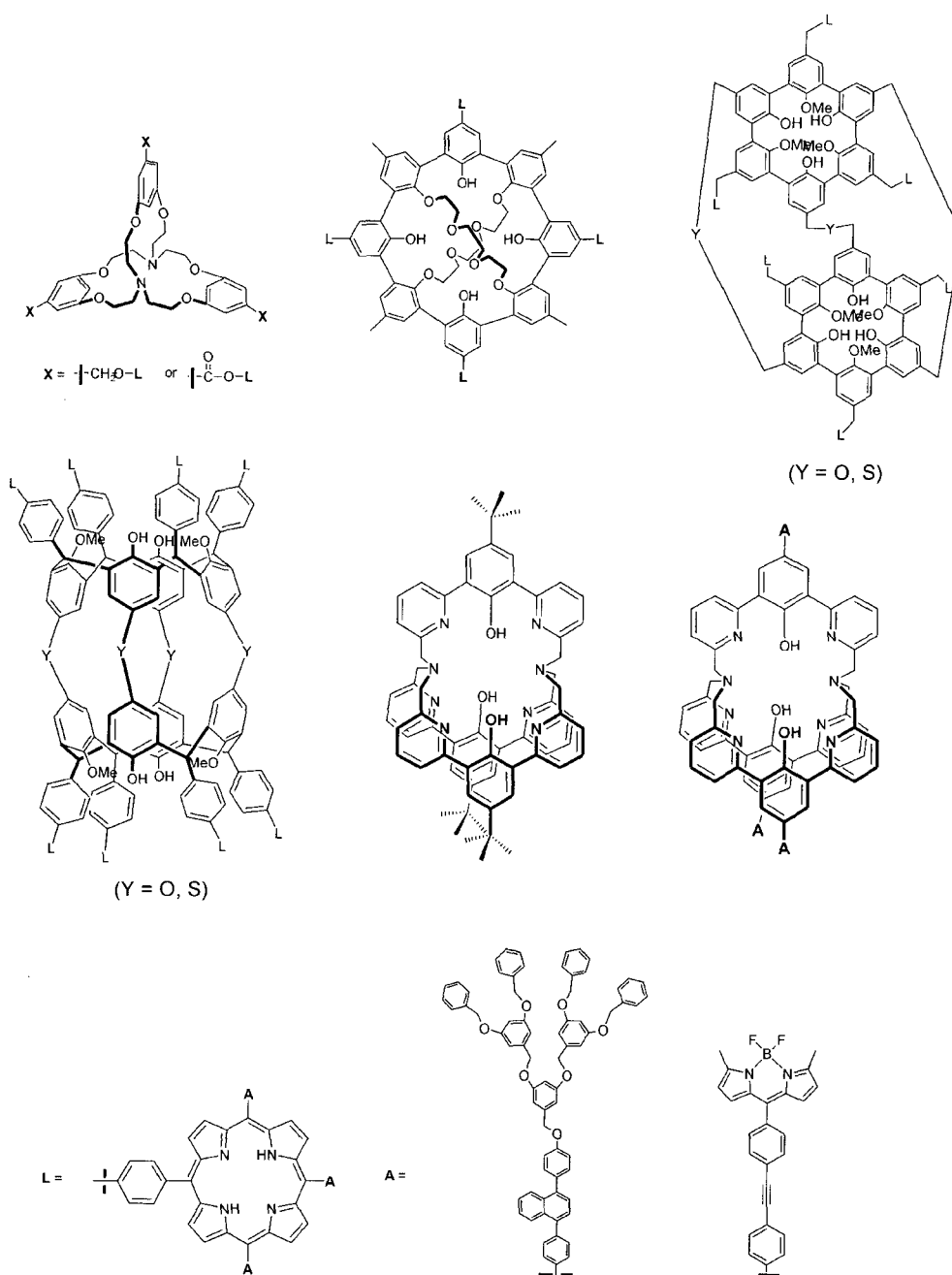


Figure 8. Near IR emission spectra of Er^{3+} -(Pt-por 1)₃ (dash) and Er^{3+} -(Pt-por 1)₃-(terpyridine) (bold) (Powder, $\lambda_{\text{ex}} = 488 \text{ nm}$ from Ar^+ laser).

H₂O molecules, the lattice vibration relaxation of O-H bonds effectively quenches the near IR emission corresponding to the characteristic $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of trivalent erbium ions, reducing the intensity of the near IR emission. Also, the instability of the unsaturated 6-coordinated complex has the more chance of nonradiative relaxation decay than the saturated 9-coordinated complex. It induces the lower intensity of the near IR emission.

Lanthanide(III)-Cored Supramolecules based on Macrobicyclics Derivatives. The excited state of the lanthanide

ions is effectively quenched by interactions with high energy vibrations like O-H and N-H groups. Also, the poor solubility of lanthanide ion (Ln³⁺) in inorganic media leads to clustered Ln³⁺ species, limiting the amplification achievable. To remove two problematic issues and achieve high amplification gain through the site isolation and the light-harvesting effect, we have also designed and synthesized lanthanide(III)-cored supramolecules with highly efficient light-harvesting dendritic arrays. Here, the supramolecular ligands based on macrobicyclics derivatives, such as azacryptand, macrobicyclic *N,N*-



Scheme IV. Lanthanide(III)-cored supramolecules based on macrobicyclics with highly efficient light-harvesting dendritic arrays.

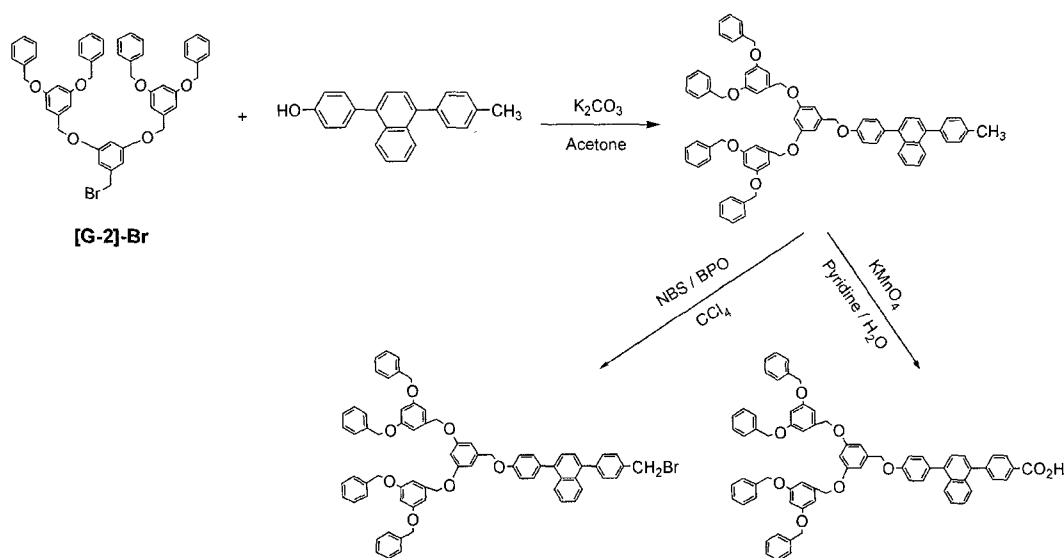
dioxide, macrobicyclic polypyridine, carcerand, bispherand, and cavitacryptand, which are very tightly bound in the lanthanide ions and form overall neutral complexes with lanthanide ions, have been designed to isolate the lanthanide ion from the quenching molecules (solvents and H₂O) and to offer at least 8-9 hard donor atoms (O and N atoms) towards lanthanide ions for the encapsulation of lanthanide ions with supramolecular ligands (see Scheme IV). Also, the light-harvesting dendritic arrays may be expected to block the faces of the macrobicyclic structures towards luminescent deactivating molecules.

Highly Efficient Light-Harvesting Dendritic Arrays as Photonic Antennas. Recently, dendrimer-typed light-harvesting materials have been extensively studied.^{10,48,51-53} As presented in Scheme IV, in dendrimer-typed light-harvesting materials, many exterior chromophores, as photon antennas, efficiently absorb and transfer lights to the central laser dyes through the energy transfer. The central laser dyes gather lights from the surface antennas. This is so-called the light-harvesting effect. With this light-harvesting effect, the central laser dyes can be efficiently excited and then deactivated in a radiative decay, making the ultra-highly efficient radiations possible. The light-harvesting efficiency in the dendrimer is influenced by the generation number of dendrimer and energy gradients. Even with the small amount of low photon energy irradiating at the dendrimers, the central dye molecules would accumulate the low energy through the multi-phonon process as well as the energy transfer process, to cause the higher photon energy.⁵¹ Therefore, the opto-physical properties of lanthanide(III)-cored supramolecular systems can be optimized and maximized during artificial light gathering and transferring by way of using principles of naturally existing photo-synthetic antenna, in which the light is absorbed and transferred to the core of the integrated systems to

cause light-harvesting effect.

Several dendrimers involving a porphyrin or metalloporphyrin core and absorbing chromophore groups at the outside have been investigated. Fréchet and coworkers have reported aryl-ether type dendrimers with zinc porphyrin and tetraphenylporphyrin cores.⁵² And, they have investigated the effects of generation number, solvent on the photophysical property and morphology of dendrimers. In an attempt to mimic natural photosynthetic antenna complexes for the light harvesting effect, boron-dipyrrin (BPDY) pigments have been appended to a free base or metalloporphyrin core.⁵³ In this case, the energy transfer process occurred with efficiency more than 85%. Artificial photosynthetic antennas, such as aryl-ether type and boron-dipyrrin dye, absorb UV and green light and transfer the absorbed light to the dendrimer's core. This photosynthetic antenna system represents an analogy to the photosynthetic system of nature. Kawa and Fréchet have also reported the site isolation and antenna effects on luminescent properties of spherical Eu(III)-cored dendrimer.^{10,48} The poor solubility of Ln cations in inorganic media leads to clustered Ln³⁺ species, limiting the amplification achievable. To achieve the site isolation of Ln³⁺ cations, lanthanide ions were surrounded by the dendritic shell such as aryl-ether type dendron. The enhanced luminescent intensities depend significantly on the morphology of the dendrimer and efficient energy transfer from the photonic antennas to rare earth ion at the focal point. Although the aryl ether type dendron was widely used to photonic antennas, its spectral overlap between the photonic antennas and the metal-coordinated ligand was not satisfied, limiting the enhanced luminescent intensity. So, it indicates the importance of an energy gradient for the efficient transfer of the excitation energy.

Very recently, we have designed and synthesized several new aryl ether-typed dendric light-harvesting arrays to opti-



Scheme V. A synthetic example of new aryl ether-functionalized dendrons based on naphthalene derivatives as photonic antennas.

mize and maximize the energy transfer efficiency.⁵⁴ For an example, the naphthalene moiety was synthesized by the well-known Suzuki cross coupling with moderate yield. It was incorporated into the second generation of the Fréchet aryl ether-typed dendron, yielding new aryl ether-typed dendron based on naphthalene (see Scheme V). In our preliminary study, new naphthalene-based dendron is a good candidate for artificial photonic antenna to our lanthanide-cored supramolecular systems with Er(III) and Eu(III) ions.⁵⁵

Summary

Polymeric materials with ultrahigh amplification gain for planar waveguide optical amplifiers are not yet investigated both in Korea and elsewhere around the globe. For such materials, very recently, exploratory host-guest systems have been actively studied by doping lanthanide-chelated complex into inorganic/polymer matrices for the purpose of increasing the solubility of lanthanide ion, which could be considered as one effective way of doping lanthanide ions into polymer matrix. However, in the host-guest system, the limited concentration of lanthanide metals due to their low solubility and the phase separation between the lanthanide ion and silica, all of which lead to the low amplification gain, should be addressed as the main problematic issues.

Such efforts are just in the early stage and not only the basic concept not established, but also the structure-property relationship is not yet clearly understood. Therefore, the dependences of lanthanide ion and ligand structure on amplification principles (such as the optical amplification lifetime, excited state dynamics, etc) need to be systematically established. Based on the relationship established, the design and synthesis of ultrahighly efficient lanthanide ion-chelated complexes using molecular engineering approach need to be investigated. In addition, the development of "smart materials" with higher doping concentration of lanthanide ion complexes, in which the nonradiative process is totally eliminated even at high doping concentration of lanthanide ion complexes, must be thoroughly studied. In this paper, the highly efficient light-harvesting integrated supramolecular systems based on lanthanide-cored dendritic or supramolecular complexes were systematically designed and synthesized to optimize optophysical properties during artificially light gathering and transferring by way of using principles of naturally existing photo-synthetic antenna, in which the light is absorbed and transferred to the core of the integrated systems to cause light-harvesting effect. Also, the lanthanide-cored dendritic or supramolecular complexes synthesized are to provide excellent solubility to the polymeric matrix as well as to alleviate the ion-ion interaction by way of eliminating the coagulation between lanthanide complexes. In addition, the establishment of basic principles of amplification, including the dependence of lanthanide ion complexes and ligand structure on excited state dynamics and lifetimes, elucidation

of basic energy transformation and transfer mechanisms, will be investigated with regard to understand the structure-property relationships.

Based on the structure-property relationships determined, ultrahighly efficient light-harvesting supramolecular structures were optimized and their application as the future optical amplification devices will be examined. In addition, the forementioned supramolecular structure was modified through molecular engineering and utilized for investigating new functional supramolecules, which will be designed and synthesized for the application to plastic laser technology. Its attempt is the first of its kind throughout the world.

Utilizing our developed materials, we will have the leverage to lead the world in tomorrow's communication technology and the technological impact will be similar to the integrated circuit development in semiconductor industries. This will not only be considered to be the material revolution in the heart of exploratory materials in optical information and communication, but also will open up many new areas of applications of polymeric materials for use in ultrahigh speed communication and information systems for the future generation. We can have applications to use in planar waveguide-typed integrated optical amplifiers, plastic lasers, and green/red as well as NIR light-emitting diodes.

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