Novel Erbium(III)-Encapsulated Complexes Based on π-Extended Anthracene Ligands Bearing G3-Aryl-Ether Dendron: Synthesis and Photophysical Studies

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Abstract: A series of inert and photo-stable Er(III)-encapsulated complexes based on π-extended dendritic anthracene ligands bearing G3-aryl-ether dendron ([G3-AnX]-CO_2H), which retain different π-bridging systems, such as single (X= S), double (X= D) and triple (X= T) bonds was designed and synthesized to establish the structure-property relationship. The near infrared emission intensities of Er(III)-encapsulated complexes were enhanced dramatically by increasing the π-conjugated extension of anthracene ligands. The time-resolved luminescence spectra show monoexponential decays with a lifetime of 2.0~2.4 ms for Er^{3+} ions in thin films, and calculated intrinsic quantum yields of Er^{3+} ions are in the range of 0.025~0.03%. As a result, all Er(III)-encapsulated dendrimer complexes exhibit the near IR emission with the following order: Er^{3+}-[G3-AnD]$_3$(terpy) > Er^{3+}-[G3-AnS]$_3$(terpy) $\approx$ Er^{3+}-[G3-AnT]$_3$(terpy), because Er^{3+}-[G3-AnD]$_3$(terpy) has a higher relatively spectral overlap J value and energy transfer efficiency. In addition, the lack of detectable phosphorescence and no significant spectral dependence of the π-extended anthracene moieties on the solvent polarity support energy transfer from their singlet state to the central Er^{3+} ion taking place in Er^{3+}-[G3-AnX]$_3$(terpy).

Keywords: Er(III)-encapsulated complexes, π-extended anthracene ligand, near-IR emission, energy transfer efficiency.

Introduction

Recently, luminescent lanthanide (Ln) complexes have attracted much attention because of their academic interests and potential candidates in a wide variety of photonic applications such as planar waveguide amplifiers, plastic lasers, light-emitting diodes, and luminescent probes.[1-5] The absorption and emission cross section of Ln^{3+} ion is intrinsically small in absorption and photoluminescence (PL) due to the fact that the $4f^n$-$4f^n$ electronic transitions are forbidden, whereas the luminescent lifetime is relatively long. To overcome these shortcomings, recently, organic ligands are being used to excite Ln^{3+} ions via an energy transfer from the luminescent ligand to the Ln^{3+} ion. In most cases,[2-16] Ln^{3+} ions are usually coordinated to the organic luminescent ligands, acting as sensitizers, which efficiently absorb and transfer the energy of light to excite Ln^{3+} ions via energy transfer process.[6,7] This sensitization process is much more effective than the direct excitation of Ln^{3+} ions, since the

absorption coefficients of organic chromophores are many orders of magnitude larger than the intrinsically low molar absorption coefficients of Ln^{3+} ions. Moreover, very recently, several research groups have focused on developing the efficient artificial light-harvesting Ln(III) complexes, in which the use of dendrimers for light harvesting systems has been widely demonstrated.[8-16]

The encapsulation of Ln^{3+} ion into a luminescent dendrimer can lead to a system capable of shielding central Ln^{3+} ion from nonradiative environment and efficiently transferring excited energy from the peripheral chromophores to the focal point of the dendrimer.

For example, Fréchet *et al.* reported the site isolation and antenna effects on luminescent properties of spherical Ln(III)-cored dendrimer complexes based on Eu^{3+},Tb^{3+} and Er^{3+} ions.[8,11,16] To achieve the site isolation of Ln^{3+} ions, Ln^{3+} ions were surrounded by the dendritic shell of the aryl-ether typed dendrons. However, among them, the chemical structure of Er(III)-cored dendrimer complexes was not characterized clearly, and Er(III)-cored dendrimer complexes did not exhibit near infrared (NIR) emission.[8] Although the

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aryl-ether typed dendron was widely used as light-harvesting antenna, its spectral overlap integral (J) between the emission band of peripheral antenna and the absorption band of Ln^{3+} ion and quantum yield were not satisfactorily large to obtain the effective energy transfer. Thus, the aryl-ether typed dendron provides the site isolation of Ln^{3+} ions.[8,11]

To enhance the NIR emission intensity and maintain the effective energy transfer process, therefore, our research efforts have been focused on developing a series of Ln(III)-encapsulated complexes with artificial light-harvesting systems using dendritic luminescent ligands based on metallo-porphyrins[17] and anthracene units.[18] These Er(III)-cored dendrimer systems consist of Ln(III)-cored supramolecular complexes and light-harvesting dendritic photon antenna, in which a proper cascade-typed energy gradient is maintained within the light-harvesting dendrons through luminescent ligand to Er^{3+} ion. Surprisingly, we found that the site-isolation effect was dominant over the light-harvesting effect in the series of Ln(III)-cored dendrimer complexes, due to low quantum yield of aryl-ether dendron ($\Phi_f = 0.02$). In other words, well-known aryl-ether dendrons are not effective to sensitize Ln^{3+} luminescence, but are able to shield Ln^{3+} ion. Much stronger emission intensity of Er^{3+}-[G3-AnS]$_3$(terpy) in thin film was obtained 3.8×10^3 times or 1.82×10^4 times by indirect excitation of the dendritic ligand ($\lambda_{ex} = 290$ nm or 395 nm), respectively, than by the direct excitation of Er^{3+} ion ($\lambda_{ex} = 488$ nm ($^4F_{7/2}$) or 523 nm ($^2H_{11/2}$)). It supports that an efficient energy transfer from dendritic anthracene ligand to Er^{3+} ion takes place. As a result, this sensitization process is much more effective than the direct excitation of Er^{3+} ions.

In this paper, we report the synthesis and characterization of a series of the inert and photo-stable Ln(III)-encapsulated complexes based on different π-bridging centered anthracene ligands bearing G3-aryl-ether dendron systematically and precisely. Also, here, we include their photophysical results to be discussed in relation to the structure-property relationship among the present luminescent lanthanide complexes.

Experimental

Material Synthesis. Palladium(II) acetate (Pd(OAc)$_2$), tri-o-tolylphosphine (TOP), triphenylphosphine (PPh$_3$), triethylamine, 2-methyl-3-butyn-2-ol, 4-iodobenzoic acid, and dichloro(triphenylphosphine)palladium(II) were obtained from Aldrich Chemical Co. and used without further purification. The third generation aryl-ether dendron ([G3]-Br) was synthesized according to the procedure described in the literature[19] and the detailed synthetic procedure of [G3-An]-Br has been described elsewhere.[18] The starting materials, 4-vinylbenzoic acid methyl ester (1) were prepared by literature method,[20] and the general synthetic strategy for π-

extended dendritic anthracene ligands is Heck reaction[21] and Sonogashira cross-coupling protocol.[22] The vinyl-bridged anthracene derivative ([G3-AnD]-CO$_2$H) was synthesized by the well-known Heck reaction of 4-vinylbenzoic acid methyl ester with [G3-An]-Br and then hydrolyzed. The acetyl-bridged anthracene derivative [G3-AnT]-CO$_2$H was prepared by Sonogashira cross-coupling of 2-methyl-3-butyn-2-ol with [G3-An]-Br. The protecting group was removed with NaOH/toluene, and the resulting alkyne ([G3-AnT]-H) was coupled with 4-iodobenzoic acid to give [G3-AnT]-CO$_2$H as a yellow powder. A series of novel Ln(III)-cored complexes having G3-aryl ether dendron was synthesized through the ligand-exchange reaction using ErCl$_3$ developed in our laboratory.[23-25]

Synthesis of [G3-AnS]-CO$_2$H and Ln^{3+}-[G3-AnS]$_3$(terpy). The detailed synthetic procedures of [G3-AnS]-CO$_2$H and Ln^{3+}-[G3-AnS]$_3$(terpy) were described elsewhere.[18]

Synthesis of [G3-AnD]-CO$_2$Me. [G3-An]-Br (3.50 g, 1.82 mmol) was dissolved in 20 mL of dry DMF at 50 °C under a nitrogen atmosphere. Palladium (II) acetate ((CH$_3$CO$_2$)$_2$Pd; 27 mg, 0.13 mmol) and tri(o-tolyl)phosphine (TOP: 170 mg, 0.55 mmol) were added, dissolved and stirred for 1 h. To the resulting solution, 4-vinylbenzoic acid methyl ester (0.29 g, 1.82 mmol) and tributylamine (5.2 mL) were added and heated overnight at 100 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo. The crude mixture was purified by column chromatography (3.1 g, 85%). ν_{max}(KBr pellet)/cm^{-1} 3030, 2870, 1719, 1596, 1450, 1292, 1156, 1053, 832, and 737; δ_H (300 MHz, CDCl$_3$, Me$_4$Si) 8.36 (d, 2H), 8.08 (d, 2H), 7.80-7.65 (m, 4H), 7.40-7.26 (m, 46H), 7.18 (d, 2H), 7.05-7.01 (m, 2H), 6.79 (d, 2H), 6.69-6.66 (m, 12H), 6.62 (t, 1H), 6.54 (m, 6H), 5.12 (s, 2H), 5.01 (d, 20H), 4.95 (s, 8H), 3.98 (s, 3H).

Synthesis of [G3-AnD]-CO$_2$H. KOH (0.5 g, 9.17 mmol) was added to a solution of [G3-AnD]-CO$_2$Me (2.3 g, 1.15 mmol) in 20 mL of ethanol/THF (7:3 v/v). The reaction mixture was stirred for 12 h at reflux temperature. The reaction mixture was evaporated to dryness to vacuo. The residual was dissolved with water and then acidified with HCl. This solid was washed sequentially with water and hexane, giving a yellowish solid (1.98 g, 87%). ν_{max}(KBr pellet)/cm^{-1} 3029, 2867, 1687, 1595, 1449, 1293, 1153, 1049, 831, and 735; δ_H (300 MHz, CDCl$_3$, Me$_4$Si) 8.37 (d, 2H), 8.22 (d, 2H), 7.79-7.70 (m, 4H), 7.40-7.26 (m, 46H), 7.18 (d, 2H), 7.05-6.99 (m, 2H), 6.78 (d, 2H), 6.69-6.66 (m, 12H), 6.61 (t, 1H), 6.55 (m, 6H), 5.11 (s, 2H), 4.99 (d, 20H), 4.96 (s, 8H); MALDI-TOF-MS: m/z calcd for C$_{134}$H$_{110}$O$_{17}$ 1990.7743, found (M+2H)$^+$ 1992.5470.

Synthesis of [G3-AnT]-OH. The mixture of [G3-An]-Br (2.95 g, 1.53 mmol), CuI (30 mg, 0.15 mmol), PPh$_3$ (40 mg, 0.15 mmol), 2-methyl-3-butyn-2-ol (0.3 mL, 3.07 mmol) and PdCl$_2$(PPh$_3$)$_2$ (12 mg, 0.015 mmol) in 15 mL of NEt$_3$ under nitrogen was refluxed for 24 h. The solvent was evaporated

in vacuo. The crude mixture was purified by column chromatography (2.6 g, 88%). δ_H (300 MHz, CDCl$_3$, Me$_4$Si) 8.58 (d, 2H), 7.71 (d, 2H), 7.58 (m, 2H), 7.41-7.25 (m, 44H), 7.16 (d, 2H), 6.76 (d, 2H), 6.69-6.66 (m, 12H), 6.60 (t, 1H), 6.55 (m, 6H), 5.08 (s, 2H), 4.98 (s, 20H), 4.94 (s, 8H), 2.26 (bs, 1H), 1.85 (s, 6H).

Synthesis of [G3-AnT]-H. NaOH (0.27 g, 6.74 mmol) was added to a solution of [G3-AnT]-OH (2.6 g, 1.35 mmol) in 20 mL of toluene. The solution mixture was heated to 80 °C for 12 h. The solvent was evaporated *in vacuo*. The crude mixture was purified by column chromatography (2.2 g, 87%). v_{max}(KBr pellet)/cm^{-1} 3278 (-C≡CH), 3030, 2968, 1595, 1450, 1295, 1155, 1051, 831, and 736; δ_H (300 MHz, CDCl$_3$, Me$_4$Si) 8.74 (d, 2H), 7.79 (d, 2H), 7.63 (m, 2H), 7.44-7.32 (m, 44H), 7.23 (d, 2H), 6.83 (d, 2H), 6.78-6.72 (m, 12H), 6.65 (t, 1H), 6.62 (m, 6H), 5.14 (s, 2H), 5.06 (s, 20H), 5.02 (s, 8H), 4.08 (s, 1H).

Synthesis of [G3-AnT]-CO$_2$H. The mixture of [G3-AnT]-H (2.20 g, 1.180 mmol), CuI (0.02 g, 0.12 mmol), PdCl$_2$ (PPh$_3$)$_2$ (0.01 g, 0.12 mmol), PPh$_3$ (0.03 g, 0.12 mmol), and 4-iodobenzoic acid (0.38 g, 1.53 mmol) in 50 mL NEt$_3$/toluene was refluxed for 12 h. After cooling to room temperature, the crude mixture was filtered and purified by column chromatography (1.6 g, 68%). v_{max}(KBr pellet)/cm^{-1} 3030, 2986, 2192 (C≡C), 1687, 1596, 1450, 1293, 1154, 1050, 831, and 734; δ_H (300 MHz, CDCl$_3$, Me$_4$Si) 8.71 (d, 2H), 8.22 (d, 2H), 7.88 (d, 2H), 7.75 (d, 2H), 7.62 (m, 2H), 7.41-7.25 (m, 44H), 7.17 (d, 2H), 6.77 (d, 2H), 6.69-6.66 (m, 12H), 6.61 (t, 1H), 6.55 (m, 6H), 5.10 (s, 2H), 4.99 (s, 20H), 4.95 (s, 8H); MALDI-TOF-MS: m/z calcd for C$_{134}$H$_{108}$O$_{17}$ 1988.7587, found (M+H)$^+$ 1989.8315.

Synthesis of Ln^{3+}-[G3-AnX]$_3$(terpy) (X=D and T): General Procedure. A mixture of [G3-AnX]-CO$_2$H (3.0 equiv.) and KH (3.3 equiv.) was stirred in freshly distilled THF at room temperature for overnight until there was no more H$_2$ gas to generate. After the completion of salts, the methanol solution of anhydrous ErCl$_3$ (1.0 equiv.) and 2,2':6',2"-terpyridine (1.1 equiv.) was added to the reaction solution, and then stirred for 2 days. The resulting solution was filtered and the solvents were removed. The resultant solid was washed sequentially with methanol, hexane, and diethyl ether, yielding a yellowish solid. The complexes all gave similar IR spectra.

Er^{3+}-[G3-AnD]$_3$(terpy): 98%. v_{max}(KBr pellet)/cm^{-1} 1595, 1510, 1449, 1294, 1155, 1051, 832, and 736; Anal. Calcd for C$_{417}$H$_{338}$N$_3$O$_{51}$Er: C, 78.57; H, 5.34; N, 0.66; Er, 2.62, found: C, 79.29; H, 5.82; N, 0.69; Er, 2.55.

Er^{3+}-[G3-AnT]$_3$(terpy): 86%. v_{max}(KBr pellet)/cm^{-1} 2196, 1598, 1516, 1452, 1296, 1154, 1050, 832, and 738; Anal. Calcd for C$_{417}$H$_{332}$N$_3$O$_{51}$Er: C, 78.65; H, 5.25; N, 0.66; Er, 2.63, found: C, 77.95; H, 5.74; N, 0.58; Er, 2.71.

General Measurements. ^{1}H NMR spectra were recorded with the use of Varian Oxford 300 MHz spectrometers; chemical shifts were reported in ppm units with tetramethyl-

ylsilane as an internal standard. Infrared spectra were measured on KBr pellets using a Perkin-Elmer Spectrometer. The mass spectra were taken by a JEOL JMS-AX505WA mass spectrometer. MALDI-TOF mass spectrometry was performed on a Voyager-DETM STR Biospectrometry. The elemental analyses were carried by means of EA1110 (CE Instrument). Steady-state absorption spectra were recorded by a Shimadzu UV-2401PC spectrophotometer and photo-luminescence spectra were measured by steady-state fluor-imeter (Edinburgh FS920) with 450W Xe-lamp. The excitation light from 300 mm focal length monochromator was focused on the sample. The fluorescence from the sample was collected and refocused to the emission monochromator with 300 mm focal length. Visible emission spectra were taken with a PMT system (Hamamatsu R955) and NIR emission spectra were taken with the liquid nitrogen cooled by Ge-detector (Edinburgh EI-L). All spectra were taken at the room temperature. The quantum yields (ϕ_f) of ligand and complexes were determined using standard reference (9,10-diphenylanthracene in cyclohexane, ϕ_f=0.95).[26] The micro-second time-resolved emission measurements were carried out by using a Nd:YAG laser. The third harmonic generation (355 nm, 5 ns pulse width at 10 Hz repetition rate) of Nd:YAG laser (EXSPLA NT342) system was used to excite the ligand moiety. The emission spectrum was analyzed with a monochromator (Acton spectrapro 2300i) and detected with a photomultiplier followed by a boxcar averager (Stanford Research System) or a digital oscilloscope (Agilent infiniium 54832B DSO).

Results and Discussion

Chemical Structures and Synthesis of a Series of the Er(III) Encapsulated Complexes Based on π-Conjugated Anthracene Ligands Bearing G3-Aryl-Ether Dendron.

We have synthesized the inert and photo-stable Er(III)-encapsulated complexes based on π-extended dendritic anthracene (An) ligands, by introducing vinyl and ethynyl linkage into 9,10-diphenylanthracene (DPA) unit, in order to establish the structure-property relationship as well as
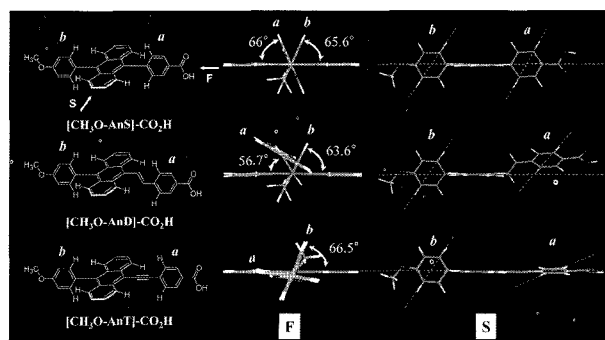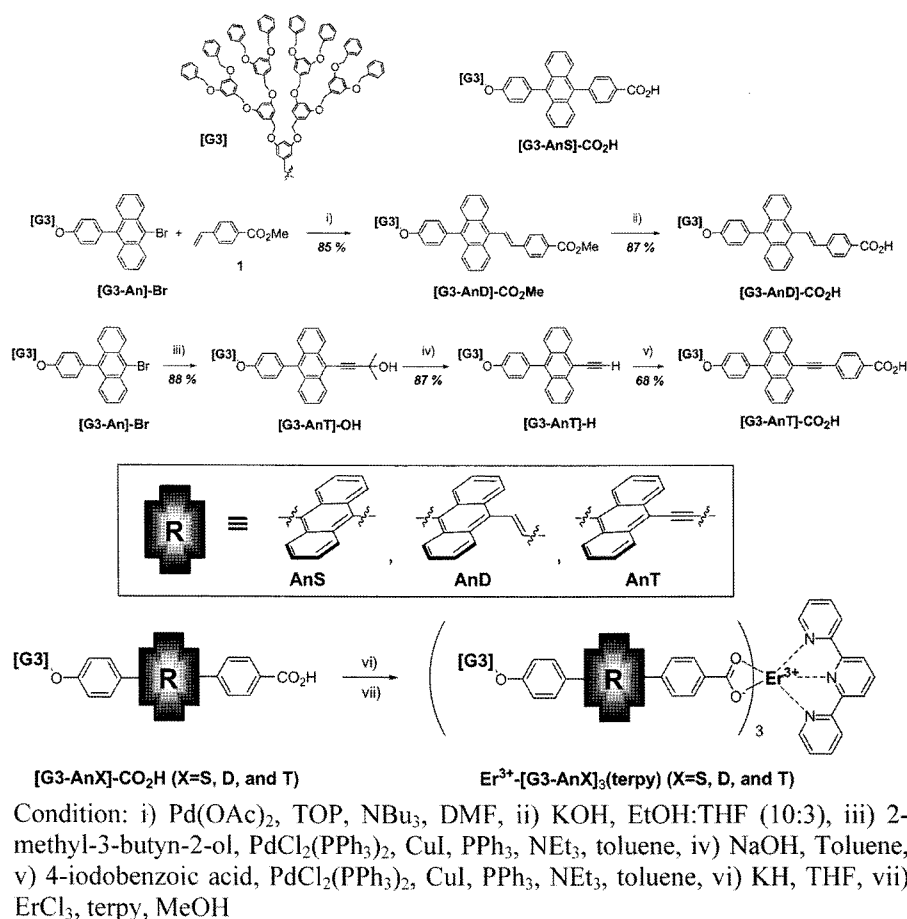

Scheme I. Snapshot of anthracene ligands ([CH$_3$O-AnX]-CO$_2$H, X=S, D, and T), derived from a semi-empirical method (AM1).

move the longer wavelength of the pumping laser for effectively exciting Er(III) complexes. To enhance the sensitization process in Er(III) complexes, we chose π-extended anthracene ligands bearing G3-aryl-ether dendron as well as having different π-bridging systems, such as single (S), double (D) and triple bonds (T), because the quantum yield (ϕ_f) of π-extended anthracene ligands bearing G3-aryl-ether dendron is close to unity in the solution and in the crystalline state.[27] Fluorescence quantum yields of most organic chromophores are only observed in a dilute solution because of the concentration quenching.

In the case of π-extended anthracene ligands, the dihedral angle between π-extended phenyl group and anthracene unit is estimated to be 63.6~66.5°, using a semi-empirical method (AM1), due to a great steric hindrance between π-extended phenyl group and anthracene unit (see Scheme I). It causes no effect of concentration on the quantum yield of its derivatives. Also, the π-extended anthracene ligand bearing G3-aryl-ether dendron is one of the most promising candidates for antenna chromophores to efficiently absorb and transfer the energy of light to excite Er^{3+} ions via energy transfer process. Very recently, we demonstrated that a series of the stable and inert Ln(III)-encapsulated complexes based on

dendritic anthracene ligand (Ln^{3+}-[Gn-AnS]$_3$(terpy)) exhibits strong NIR emission bands via highly efficient energy transfer from the excited states of the peripheral antenna to Ln^{3+} ions (Er^{3+}, Nd^{3+}, and Yb^{3+} ions).[18] Their photophysical studies indicate that the energy transfer (ET) efficiency between the anthracene ligand in the dendritic anthracene ligands and Ln^{3+} ion was evaluated to be in the range of 90 to 97%.

In our previous reports, additionally, some of the key parameters,[18] governing the enhancement of the NIR emission in Ln(III) complexes, are the type of luminescent lanthanide complexes such as a directly chelated complex or an indirectly chelated complex as well as the coordination number of Ln^{3+} ions with the complexed ligands: (1) The directly luminescent Ln(III)-chelated complexes have much higher PL efficiency than the indirectly luminescent Ln(III)-chelated complexes, due to much higher intersystem crossing (ISC) efficiency in the direct chelated complex.[23a] Our directly chelated complexes possess a luminescent group directly coordinated to Ln^{3+} ions. But, the indirectly chelated complex has the luminescent group indirectly coordinated to Ln^{3+} ions. As a result, the indirectly chelated complex does not have an external heavy atom effect which is induced by the heavy and paramagnetic Ln^{3+} ion. (2) Highly

Condition: i) Pd(OAc)$_2$, TOP, NBu$_3$, DMF, ii) KOH, EtOH:THF (10:3), iii) 2-methyl-3-butyn-2-ol, PdCl$_2$(PPh$_3$)$_2$, CuI, PPh$_3$, NEt$_3$, toluene, iv) NaOH, Toluene, v) 4-iodobenzoic acid, PdCl$_2$(PPh$_3$)$_2$, CuI, PPh$_3$, NEt$_3$, toluene, vi) KH, THF, vii) ErCl$_3$, terpy, MeOH

Scheme II. Chemical structures of aryl-ether dendrons and synthesis of Ln(III)-encapsulated complexes.
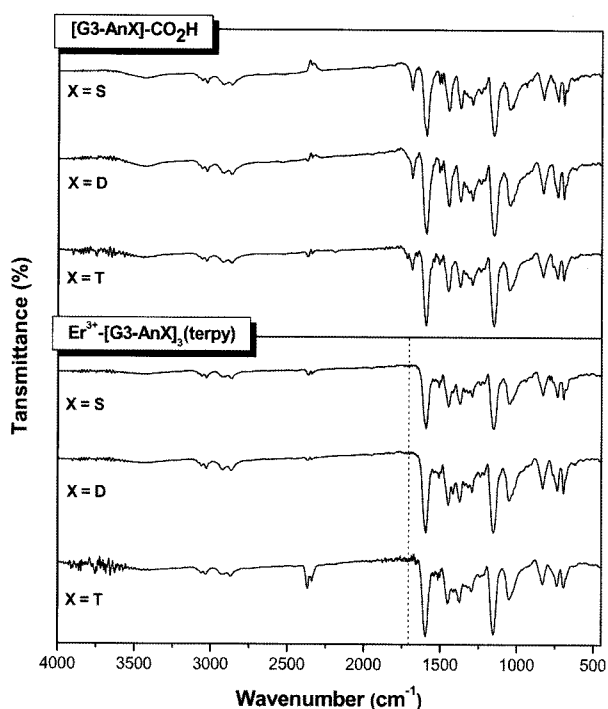
Figure 1. FTIR spectra of a series of [G3-AnX]-CO₂H and Er³⁺-[G3-AnX]₃(terpy) (X=S, D and T).

coordinated Ln(III)-cored complexes (at least 8 to 9 coordination number) have much higher PL efficiency than unsaturated 6-coordinated complex.[24a] Therefore, 2,2′:6′,2″-terpyridine (terpy) unit used in this paper may be expected to effectively block luminescent deactivating molecules, leading to the formation of 9-coordinated, direct Ln(III)-chelated complexes. The chemical structures of the π-extended anthracene ligands bearing G3-aryl-ether dendron and their stable, inert and direct Er(III)-encapsulated complexes are shown in Scheme II.

The third generation aryl-ether dendron-functionalized π-extended anthracene ligands ([G3-AnX]-CO₂H; X=S, D, and T) were synthesized. Treatment [G3-An]-Br with 2-methyl-3-butyn-2-ol by Sonogashira cross-coupling and deprotection of the dimethylhydroxy group in [G3-AnT]-OH with NaOH afforded [G3-AnT]-H. The resulting terminal alkyne ([G3-AnT]-H) was cross-coupled with 4-iodobenzoic acid to give [G3-AnT]-CO₂H. The chemical structures of all dendritic ligands were identified by FTIR, ¹H NMR, MALDI-TOP mass, elemental analysis, absorption and emission spectroscopies. In particular, the observed δ values for methyl protons in [G3-AnT]-OH and for terminal alkyne proton (-C≡CH) in [G3-AnT]-H are 1.85 and 4.08 ppm, respectively. Moreover, in FTIR spectrum, a vibrational band at 3278 cm⁻¹, corresponding to the -C≡C-H stretch vibration of the terminal alkyne, was clearly visible, together with a band at 1595 cm⁻¹ which may be attributed to the aromatic C=C stretch vibration. After coupling of the terminal alkyne

with 4-iodobenzoic acid, yielding the [G3-AnT]-CO₂H, the terminal alkyne proton was clearly disappeared in ¹H NMR and the -C≡C- and C=O stretch vibrations for the corresponding ethynyl-bridged anthracene derivative ([G3-AnT]-CO₂H) were observed at 2192 and 1685 cm⁻¹, respectively. In FTIR spectra, as shown in Figure 1, the carboxylic acid of all dendritic ligands ([G3-AnX]-CO₂H) exhibits around 1690 cm⁻¹. In comparison with these ligands, all FTIR spectra for Er(III)-cored dendrimer complexes are very similar to exhibit two characteristic bands of asymmetric (~1600 cm⁻¹) and symmetric (~1400 cm⁻¹) stretching vibration modes of the carboxylate group. It indicates that the carboxylic acid group was converted into carboxylate anion as a result of the formation of the stable Er(III)-cored complexes.[25]

Absorption and Luminescence Properties of π-Conjugated Anthracene Ligands Bearing G3-Aryl-Ether Dendron and Their Er(III)-Encapsulated Complexes.

In a previous article, we reported that a series of inert and photostable encapsulated lanthanide(III) complexes of Er³⁺-[Gn-AnS]₃(terpy) based on dendritic anthracene ligands has shown for the first time to exhibit strong near-IR emission bands via efficient energy transfer from the excited states of the peripheral antenna to the Ln³⁺ ions (Er³⁺, Yb³⁺, and Nd³⁺).[18] It was found that the near-IR emission intensities of Ln³⁺ ions in the encapsulated Ln³⁺ dendrimer complexes were dramatically enhanced on increasing the generation number (*n*) of dendrons, owing to site-isolation and light-harvesting effects. Also, all Ln(III)-cored dendrimer complexes bearing G3-aryl-ether dendron have an excellent thermal- and photo-stability and a good solubility. Thus, it led to an easy thin film preparation by spin-coating the corresponding solution. Our main research efforts have been focused on developing luminescent lanthanide complexes with highly efficient lanthanide emission for the use in a wide variety of real applications, such as planar waveguide amplifiers and light-
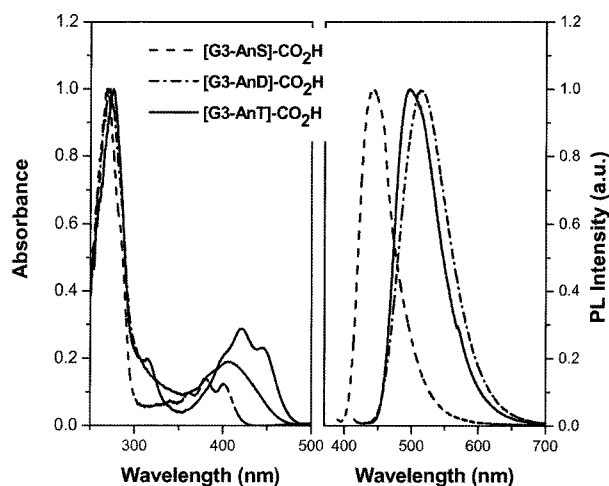

Figure 2. Normalized UV-vis absorption and emission spectra of π-extended anthracene ligands in thin film.

emitting diodes, etc.[1] It is necessary to study their photophysical behaviors in thin films. These Ln(III)-cored dendritic anthracene complexes have the similar absorption and emission features to those of the corresponding thin films. Here, we mostly discussed their photophysical properties in thin films.

UV-vis absorption and PL spectra of π-extended anthracene ligand bearing G3-aryl-ether dendron ([G3-AnX]-CO_2H, X=S, D, and T) in thin film are shown in Figure 2. The absorbance of the aryl-ether typed dendrons in dendritic π-extended anthracene ligands appeared at 285 nm and the anthracene units absorbed at the wavelength range of 350 to 480 nm simultaneously. The introduction of the aryl-ether dendron into π-extended anthracene ligands does not also influence the restriction rotation barrier between adjacent π-extended phenyl ring and anthracene ring hydrogens (see Scheme I). This restricted rotation barrier leads to the fact that π-extended anthracene ligands with the aryl-ether dendron have well-resolved structures, similar to that of 9,10-DPA derivative.[27] Also, similar UV-vis absorption behavior of π-extended anthracene ligand ([G3-AnX]-CO_2H, X=S, D, and T) was observed in THF solutions. One could note the expected shift in the absorption maxima to longer wavelengths on going from alkane π-bridging centered anthracene ligand ([G3-AnS]-CO_2H) through alkyne π-bridging centered anthracene ligand ([G3-AnT]-CO_2H) to alkene π-bridging centered anthracene ligand ([G3-AnD]-CO_2H), due to increase in π-conjugation length. Surprisingly, in contrast to the recent report in which the absorption maxima of alkyne π-bridged chromophores are blue-shifted relative to their alkene counterparts in donor-π-acceptor molecules,[27] alkyne π-bridging centered anthracene ligand is more red-shifted than two others, since alkyne π-bridging centered anthracene ligand has more effective π-conjugation than two others, as illustrated in Scheme I.

The fluorescence of the G3-aryl-ether dendron, appeared at the maximum wavelength of 345 nm, was totally quenched when they were excited at 285 nm of the dendron absorption band, but the significant decrease in the fluorescence of aryl-ether dendron is accompanied by a strong increase in the fluorescence intensity of the π-extended anthracene moiety. These results show that a highly efficient energy transfer from the aryl-ether dendron to the π-extended anthracene moiety takes place. Instead of the excitation wavelength of 285 nm, at which the aryl-ether dendrons mainly absorbed, in addition, in order to evaluate the relative fluorescent quantum efficiencies of π-extended anthracene unit in dendritic anthracene ligands, we selected another excitation wavelength of the maximum absorption wavelength for each π-extended anthracene ligand because each π-extended anthracene ligand can be excited at its maximum absorption wavelength. Upon the excitation of [G3-AnX]-CO_2H at its maximum absorption wavelength, the fluorescence quantum efficiency of dendritic anthracene ligands in THF was
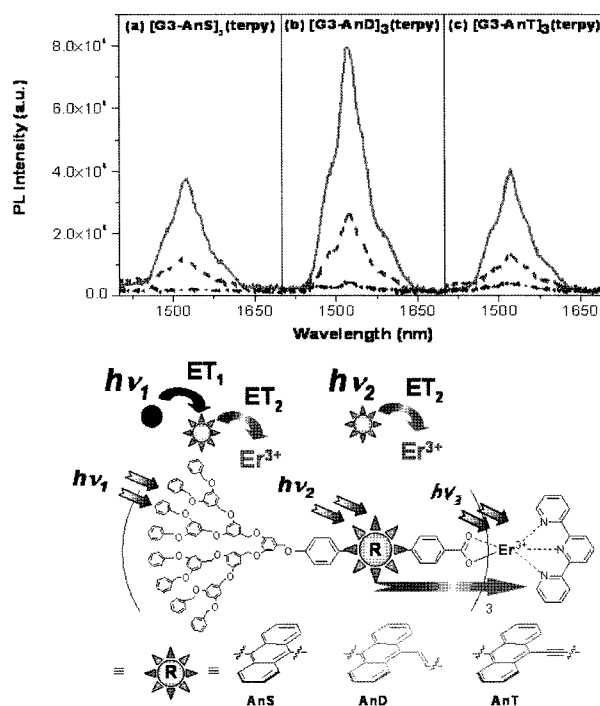
Figure 3. Near IR emission spectra of Er^{3+}-[G3-AnX]$_3$(terpy) in thin film as a function of excitation wavelength (hv_1 (solid, red,), $\lambda_{ex}=A_{max}$; hv_2 (dash, blue), $\lambda_{ex}=290$ nm; hv_3 (dash dot, black), $\lambda_{ex}=$ 488 nm).

determined by comparison with 9,10-diphenylanthracene as a standard,[26] as summarized in Table I.

The fluorescence quantum yield (ϕ_{rel}) of the anthracene moiety in [G3-AnS]-CO_2H in thin film state as free ligand is set to unity. In contrast to the fluorescence quantum yield (ϕ_{rel}) of the anthracene moieties in solution, in thin film state, [G3-AnD]-CO_2H has higher fluorescence quantum yield than [G3-AnS]-CO_2H or [G3-AnT]-CO_2H by 1.44 or 1.55 times, respectively. A series of the Er(III)-cored dendrimer complexes, Er^{3+}-[G3-AnX]$_3$(terpy), has a similar UV-vis absorption phenomena to a series of the corresponding [G3-AnX]-CO_2H ligands in thin film. All Er(III)-cored dendrimer complexes showed strong NIR emission bands at 1,530 nm, originated from $4f$-$4f$ electronic transition of the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) of the partially filled $4f$ shell. As shown in Figure 3, much stronger emission intensities of Er^{3+}-[G3-AnX]$_3$(terpy) in thin film were obtained by indirect excitation of the dendritic ligand ($\lambda_{ex}=290$ nm or $\lambda_{ex}=A_{max}$), respectively, than by the direct excitation of Er^{3+} ion ($\lambda_{ex}=488$ nm ($^4F_{7/2}$)). It supports that an efficient energy transfer from dendritic anthracene ligand to Er^{3+} ion takes place, associated with the site-isolation and light-harvesting effects.

Previously, in order to distinguish the site-isolation effect from the light-harvesting effect, we compared the NIR intensity of Er^{3+} ion, upon excitation of anthracene unit at 395

nm or 357 nm with that of Er^{3+} ion, upon excitation of aryl-ether dendron unit at 290 nm in Er(III) complexes. As a result, the NIR intensity of Er^{3+} ion, upon excitation of anthracene unit at 395 nm, was stronger than that upon excitation of aryl-ether dendron unit at 290 nm by 4.8 times. It clearly indicates that the aryl-ether dendrons are not effective to sensitize Er^{3+} luminescence through anthracene units, but are able to shield Er^{3+} ion, so-called, the site-isolation effect. This effect should be dominant over the light-harvesting effect in the series of Er^{3+}-[Gn-AnS]$_3$(terpy).[18] It is considered to be due to the intrinsically low quantum yield of aryl-ether dendron (ϕ_f = 0.02) for exciting anthracene units. In other words, aryl-ether typed dendrons in dendritic ligands could not effectively sensitize the Er^{3+} luminescence through anthracene units, but, they render the efficient site-isolation effect enough to prevent intermolecular interaction between Er^{3+} ions, which limits NIR intensity.[1,8]

Fluorescence Quenching and Relative Quantum Yields of Er(III)-Encapsulated Dendrimer Complexes. The fluorescence of the π-extended anthracene moiety ([G3-AnX]-CO_2H ligands), upon the photoexcitation at the maximum absorption wavelength for each π-extended anthracene ligand in thin film, which is mainly absorbed by the π-extended anthracene units, is thoroughly studied in the present Er(III) complexes. We chose the photoexcitation wavelength of the maximum absorption wavelength for each π-extended anthracene ligand, because Er^{3+} ions do not have any significant absorbance at 390 nm and thus the direct excitation of Er^{3+} ions should be negligible. The relative fluorescence intensities of the π-extended moiety in Er(III) complexes are shown in Figure 3, where the fluorescence intensity of the π-extended anthracene moiety in [G3-AnS]-CO_2H and the fluorescence quantum yield (ϕ_{rel}) of the anthracene moiety in [G3-AnS]-CO_2H as free ligand is set to unity. The fluorescence intensity of the π-extended anthracene moiety was dramatically quenched in the Er(III) complexes, due to the efficient energy transfer from the anthracene ligand to Er^{3+} ion. As a result, the significant decrease of the fluorescence intensity for the π-extended anthracene moiety in Er(III) complexes is accompanied by a strong increase in the NIR
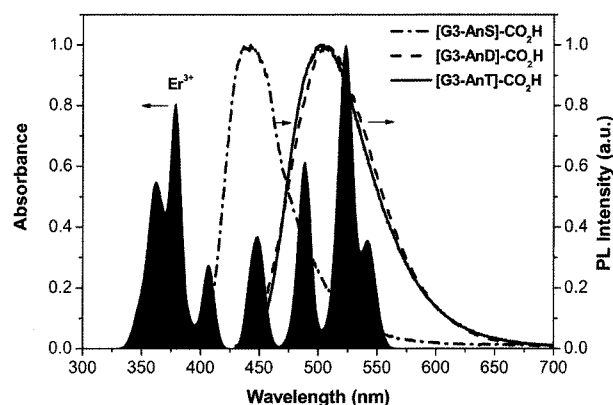
**Figure 4.** UV-vis absorption of $ErCl_3$ in water and PL spectra of π-extended anthracene units in thin films.

emission of the Er^{3+} ions. With these results, the relative fluorescence quantum yields of the π-extended anthracene moiety in Er(III) complexes were determined and summarized in Table I. As quantitatively compared the emission intensity in the visible region of the π-extended anthracene moiety in [G3-AnS]-CO_2H (ϕ_{rel} =1), the relative fluorescence quantum yield for the π-extended anthracene moiety in Er(III) complexes is determined to be 0.03 for Er^{3+}-[G3-AnS]$_3$(terpy), 0.03 for Er^{3+}-[G3-AnD]$_3$(terpy), and 0.05 for Er^{3+}-[G3-AnT]$_3$(terpy), respectively. These results imply that the energy transfer process between dendritic π-extended anthracene ligand and Er^{3+} ion takes place efficiently, since the spectral overlap integral between the emission band of anthracene derivative and the absorption bands of Er^{3+} ion is sufficiently large (see Figure 4). Based on the fluorescence quenching amount of the ligand in Ln(III) complexes, the energy transfer (ET) efficiency between the anthracene ligand in the dendritic anthracene ligands and Ln^{3+} ion was evaluated to be in the range of 95% to 98%.

In addition, our photophysical studies indicate that no detectable phosphorescence and no significant spectral dependence of the π-extended anthracene moieties on the solvent polarity (see Figure 5) support the energy transfer

Table I. Photophysical Results of Dendritic Anthracene Ligands and Their Er(III) Complexes

Samples	ϕ^a	$\phi_{rel}{}^b$	Rel. Spectral Overlap (J)	Rel. Area of Er Emission	τ_{obs} (μs)^c	ϕ_{Ln}(%)^d
[G3-AnS]-CO_2H	0.80	1	1	-	-
[G3-AnD]-CO_2H	0.21	1.44	1.55		
[G3-AnT]-CO_2H	0.60	0.93	1.56		
Er^{3+}-[G3-AnS]$_3$(terpy)	0.39	0.03 (97%)		1	2.0	0.025
Er^{3+}-[G3-AnD]$_3$(terpy)	0.11	0.03 (98%)		1.92	2.4	0.030
Er^{3+}-[G3-AnT]$_3$(terpy)	0.34	0.05 (95%)		0.87	2.1	0.026

^{a}Quantum yield in THF solution. ^{b}Relative quantum yield of anthracene unit ($\lambda_{ex} = A_{max}$) in thin film (Decreased ratio of fluorescence intensity is given in parentheses). ^{c}The detection wavelength was 1,530 nm (λ_{ex} = 355 nm, thin film). ^{d}Calculated from $\phi_{Ln} = \tau_{obs}/\tau_R$, where τ_R is radiative lifetime of Ln (8 ms for Er^{3+}).
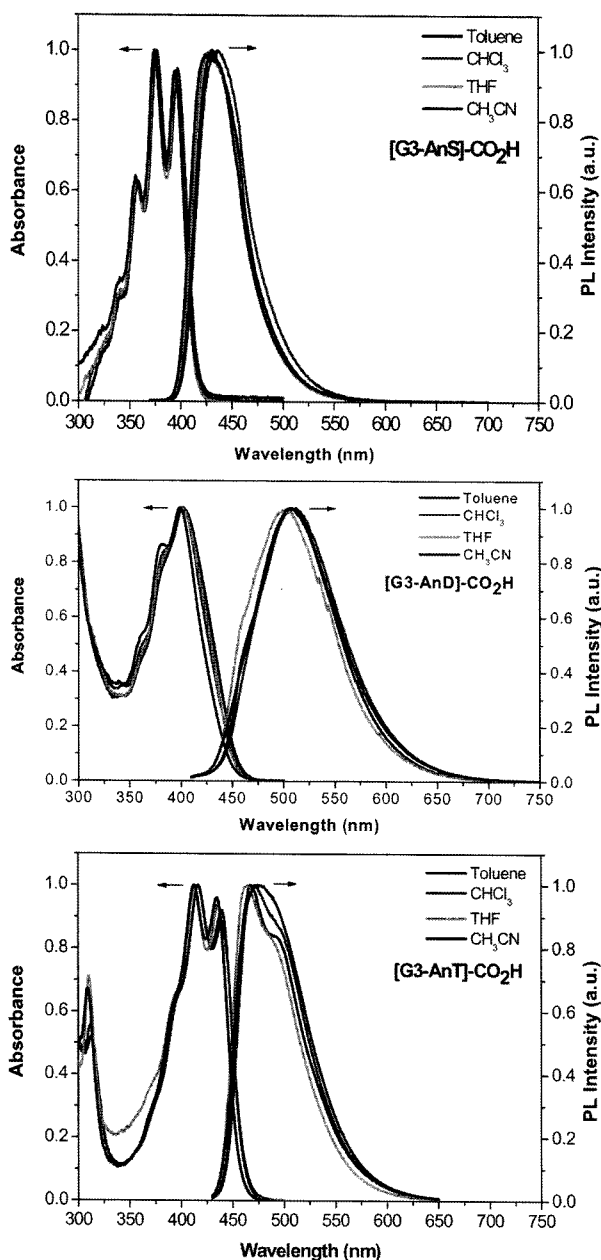
Figure 5. Effect of solvent polarity on absorption and emission spectra of [G3-AnX]-CO₂H (X=S, D, and T).

from their singlet state to central Er^{3+} ion taking place in than Er^{3+}-[G3-AnX]₃(terpy).[18,28,29] The latter result allows us to exclude the possibility of the energy transfer process via a charge transfer complex.[29] As a result, the fluorescence quenching of the ligand in Er(III) complexes could imply that excited singlet energy might be transferred to Er^{3+} ion. Upon the photoexcitation wavelength of the maximum absorption wavelength for each π-extended anthracene ligand, all Er(III)-cored dendrimer complexes showed strong NIR emission bands at 1,530 nm, originated from 4f-4f electronic transition of the first excited state ($^{4}I_{13/2}$) to the ground

state ($^{4}I_{15/2}$) of the partially filled 4f shell. Among them, much stronger emission intensity of Er^{3+}-[G3-AnD]₃(terpy) in thin film was obtained 1.92 times or 2.21 times than Er^{3+}-[G3-AnS]₃(terpy) or Er^{3+}-[G3-AnT]₃(terpy), respectively (see Table I).

With our results, it can be concluded that some of the key parameters, governing the enhancement of the NIR emission in luminescent Ln(III) complexes, are the higher relative spectral overlap J value (see Figure 4) and the higher relative energy transfer efficiency of the luminescent ligands, because all Er(III)-cored dendrimer complexes based on π-conjugated anthracene ligands bearing G3-aryl-ether dendron, which retain different π-conjugated systems, such as single, double and triple bonds, have a similarly chemical structure, due to a higher rotation barrier caused by a great steric hindrance between π-extended phenyl group and anthracene unit. Very recently, similar result was reported by our group.[30]

Radiative Lifetime and Quantum Yield of Lanthanide (III) Ions. The time-resolved luminescence spectra in the NIR region show monoexponential decays with a luminescence lifetime of 2.0 μs for Er^{3+} ion in Er^{3+}-[G3-AnS]₃(terpy) thin film, 2.4 μs for Er^{3+} ion in Er^{3+}-[G3-AnD]₃(terpy) thin film, and 2.1 μs for Er^{3+} ion in Er^{3+}-[G3-AnT]₃(terpy) thin film. The PL quantum yields (($\phi_{Ln} = \tau_{obs}/\tau_R$) were calculated from the observed lifetimes ($\tau_{obs} = (k_r + k_{nr})^{-1}$) and the radiative lifetimes ($\tau_R = k_r^{-1}$) of the Ln^{3+} ions. The radiative lifetimes were taken from the literature,[31] with typical lifetimes of 8 ms for Er^{3+} ion. The radiative lifetime is a very important parameter in the photophysical properties of NIR emission because the overall rate of non-radiative deactivation, determined by both τ_{obs} and τ_R and non-radiative process (k_{nr}), influences the observed luminescence lifetime. Calculated intrinsic quantum yields of NIR Ln^{3+} ion emission were not much different to be 2.5×10^{-2} % for Er^{3+} ion in Er^{3+}-[G3-AnS]₃(terpy) thin film, 3.0×10^{-2} % for Er^{3+} ion in Er^{3+}-[G3-AnD]₃(terpy) thin film, and 2.6×10^{-2} % for Er^{3+} ion in Er^{3+}-[G3-AnT]₃(terpy) thin film. However, by comparison of their relative area of Er^{3+} emission, among them, Er^{3+}-[G3-AnD]₃(terpy) in thin film exhibits much stronger emission intensity by 1.92 times or 2.21 times than Er^{3+}-[G3-AnS]₃(terpy) or Er^{3+}-[G3-AnT]₃(terpy), respectively. Surprisingly, after 5 ns and 10 Hz pulse laser with the power of 13 mJ per pulse irradiated to Er^{3+}-[G3-AnS]₃(terpy) for 2 h, its PL intensity remains constant. It indicates the excellent photo-stability of the present Ln(III)-cored dendrimer complexes. Also, they are thermally stable up to 250 °C. They have a good solubility in common organic solvent and it allows them to make thin films directly by spin-coating their solutions. In addition, Er^{3+}-[G3-AnX]₃(terpy) has a very broad NIR emission band with the full-width-at-half-maximum (FWHM) of 70-77 nm, which is very important for the real wavelength division multiplexing (WDM) applications.[3,32]

Conclusions

It is the first demonstration that a series of the inert and photo-stable lanthanide(III)-encapsulated complexes based on π-extended anthracene ligands bearing G3-aryl-ether dendron exhibits strong near IR emission bands via efficient energy transfer from the excited states of the π-conjugated anthracene ligands to Er^{3+} ions. A significant decrease in the fluorescence of anthracene ligand is accompanied by a strong increase in the near IR emission of the Er^{3+} ions. The near IR emission intensities of Er^{3+} ions in the Ln(III)-encapsulated dendrimer complexes were dramatically enhanced with increasing the π-conjugated extension of anthracene ligands, due to the effective energy transfer efficiency between the excited state of the π-conjugated anthracene ligand and Er^{3+} ion. Their photophysical studies indicate that the energy transfer efficiency between the anthracene ligand in the dendritic anthracene ligands and Ln^{3+} ion was evaluated to be in the range of 95 to 98%. The time-resolved luminescence spectra show monoexponential decays with a lifetime of 2.0 ~2.4 μs for Er^{3+} ions in thin films and calculated intrinsic quantum yields of Er^{3+} ions are in the range of 0.025~0.03%. As a result, all Er(III)-encapsulated dendrimer complexes exhibit the near IR emission with the following order: Er^{3+}-[G3-AnD]₃(terpy) > Er^{3+}-[G3-AnS]₃(terpy) ≈ Er^{3+}-[G3-AnT]₃ (terpy), where Er^{3+}-[G3-AnD]₃(terpy) has relatively the higher spectral overlap *J* value and energy transfer efficiency. Also, their photophysical studies support the energy transfer from their singlet state to central Er^{3+} ion taking place in Er^{3+}-[G3-AnX]₃(terpy). All Er(III)-cored dendrimer complexes have an excellent thermal- and photo-stability and a good solubility as well as a very broad near IR emission band.

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