

Enhanced Luminescence of an Erbium (III) Ion-Association Ternary Complex with a Near-Infrared Dye

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A near-infrared (NIR) luminescent erbium (III) ternary complex has been prepared with an ion-associating sensitizer of IR5, a NIR dye whose large absorption cross section covers the visible spectrum around 488 nm and especially the NIR spectrum around 980 nm. In this paper NIR photoluminescence from the complex in bulky powder is obtained. The 1.54 μm emission of erbium ion upon 980 nm laser diode (LD) excitation is remarkably enhanced, as a result of effective indirect excitation of erbium ion via IR5 (harvesting most excitation light). The luminescence mechanisms upon indirect excitation are simply described. It is suggested that the investigated complex is potentially an active substance for the fabrication of planar optical amplifiers operating at 1.5 μm , which in particular can be conveniently based on cheap pumping sources such as 980 nm LDs and are compatible with the current optical communication network.

1. Introduction

Erbium (III) ion used as an active element in planar optical amplifiers operating at 1.5 μm has attracted considerable attention.^{1,2} Unfortunately, it has an intrinsically small molar absorption coefficient in the UV–vis–near-infrared (NIR) spectrum due to its forbidden characteristic of intra-4f transitions, which is unfavorable for pumping efficiency. However, the molar absorption coefficient of some organic chromophore is 3–5 orders of magnitude larger than that of erbium ion. Generally, one solution to enhance luminescence of erbium (III) ions is to indirectly excite erbium ions through their luminescent excited states that are populated via an energy transfer process from the triple states of organic chromophores to them. And this energy transfer process can be realized either through direct coordination of a sensitizer molecule multidentate with a number of donor atoms or through coordination of a simple ligand covalently attached with a sensitizer molecule. Recently, near-infrared emission originating from sensitizer-functionalized ligand-based lanthanide (Er^{3+} , Nd^{3+} , and Yb^{3+}) complexes has been reported.^{2–6} Nevertheless, the sensitizers are limited to visible fluorescent dyes, which brings about several drawbacks for the near-infrared emission of erbium ions such as the following: (a) Mismatch between the triplet state of the organic sensitizer which is generally above 13 500 cm^{-1} and the luminescent level $^4\text{I}_{13/2}$ of Er^{3+} ion which is relatively low at about 6500 cm^{-1} . The large energy gap may result in a low energy transfer quantum yield and consequently low overall luminescent quantum yield. (b) Limitation of the excitation light wavelength to the UV–vis spectrum. This disadvantage makes it incompatible with as-available optical telecommunication applications based on silica fibers, in which typically a semiconductor laser diode presenting 980 nm light is popular as one of the pumping sources owing to its relatively low cost.¹

Considering that the erbium organic complexes are promoted to fabricate erbium-doped polymers^{2,7} or sol–gel-derived hybrid organic–inorganic materials⁸ for planar optical amplifiers, it is necessary to design an erbium complex with intense absorption in the NIR spectrum so as to especially employ the semiconductor laser diodes as pump sources with high efficiency.

Hence, we propose a commercially available NIR dye (IR5, i.e., Q-switch 5) as a sensitizer for near-infrared emission of Er^{3+} ions. The reasons are that its molar absorption coefficient for the band at 980 nm, which just belongs to the vibronic sideband of the principle absorption band at 1090 nm, is large enough^{9,10} and its first triplet state T_1 is low enough, about 7500 cm^{-1} according to our preliminary study. An alternative strategy in the design of an erbium complex with IR5 is to synthesize a ligand that comprises an erbium-coordinating moiety and the sensitizer IR5, namely an IR5-functionalized ligand. However, this strategy is difficult to carry out since it involves complicated organic synthesis procedures. As we know, lanthanide ternary complexes formed by ion-association of an anion binary complex with a basic dye cation such as rhodamine dye are employed in spectrofluorometric analysis.¹¹ This leads to the possibility of obtaining a similar lanthanide ternary complex with IR5 dye since IR5 dye is also classified as a basic dye with a large cation segment. On the basis of all the above concepts, an erbium ion-association ternary complex with IR5 dye moiety (IR5 tetrakis(hexafluoroacetylacetonato) erbium(III) ($\text{Er}(\text{HFA})_4\text{IR5}$)) (see Figure 1) has been designed for potential optical applications. In the complex, the IR5 functional segment bound through Coulombic interaction is close enough to the erbium ion, which may give rise to efficient energy transfer from IR5 segment to erbium ion. In this paper, we prepared the complex and investigated its near-infrared luminescence properties.

2. Experimental Section

The precursor ternary complex tetrakis(hexafluoroacetylacetonato) erbium(III) ($\text{Er}(\text{HFA})_4\text{K}$) (see Figure 1) was syn-

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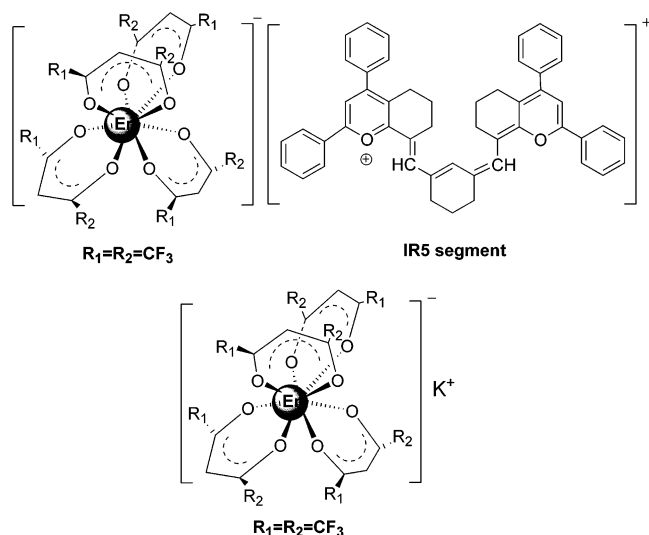


Figure 1. Chemical structures of the ion-association ternary complex $\text{Er}(\text{HFA})_4\text{IR5}$ (top) and the precursor complex $\text{Er}(\text{HFA})_4\text{K}$ (bottom).

thesized using the procedure of Melby et al. with a slight modification.¹² The complex had first been characterized by FT-IR (Nicolet Avatar360 FT-IR) and elemental analysis (CE Instruments Eager 200). Then the complex $\text{Er}(\text{HFA})_4\text{IR5}$ was prepared by mixing 1 equiv of IR5 dye salt with 1 equiv of $\text{Er}(\text{HFA})_4\text{K}$ in chloroform solution (added with a small amount of dimethylformamide) where the ion exchange reaction occurred as $\text{Er}(\text{HFA})_4\text{K} + \text{IR5 dye salt} \rightarrow \text{Er}(\text{HFA})_4\text{IR5} + \text{KClO}_4$; subsequently the mixture was kept for 24 h, and finally the precipitated potassium perchlorate and the solvent were removed. The recrystallized complex was dried in vacuo, and its identification was confirmed by FT-IR, elemental analysis, and UV-vis spectroscopy. FT-IR (KBr pellet, cm^{-1}): $[\text{Er}(\text{HFA})_4\text{K}]$ 1680(s), 1449(m), 1208(s), 1150(s), 851(m), 725(s), 663(w), 451(w); $[\text{IR5 dye salt for comparison}]$ 3056(w), 2932(w), 2862(w), 1491(w), 1425(m), 1267(s), 1121(s), 1090(s), 828(m), 766(m), 701(s), 623(m); $[\text{Er}(\text{HFA})_4\text{IR5}]$ 3058(w), 2931(m), 2861(w), 1684(s), 1494(m), 1447(m), 1419(m), 1274(w), 1205(s), 1136(s), 840(w), 801(w), 762(s), 723(m), 701(s), 668(w), 617(w), 455(w). Anal. Calcd. for $\text{Er}(\text{HFA})_4\text{K}$: C, 23.2; H, 0.4; Er, 16.2. Found: C, 22.6; H, 0.5; Er, 16.0. Anal. Calcd. for $\text{Er}(\text{HFA})_4\text{IR5}$: C, 50.3; H, 2.8; Er, 10.0. Found: C, 51.4; H, 3.2; Er, 9.7. UV-vis (nm) for $\text{Er}(\text{HFA})_4\text{IR5}$: 500, 616, 691(sh), 883(sh), 966, 1015(sh), 1091.

Measurements of absorption spectra were performed on a double-beam Perkin-Elmer Lambda spectrometer with a spectral resolution of 1 nm. Visible fluorescence spectra were recorded on a Hitachi Model F-4500 fluorescence spectrophotometer. The NIR photoluminescence spectra were determined at room temperature using a spectrometer equipped with a monochromatic (Spex 1269, SPEX Industries Inc., USA) and a liquid nitrogen cooled Ge detector (EO-817L, Yellow River Systems Inc., USA). The integral time was aptly selected according to the photoluminescence intensity, and the spectral resolution was 2 nm for all photoluminescence measurements. The phosphorescence measurement was performed at 77K with liquid nitrogen cooling.

3. Results and Discussion

3.1. Absorption, Fluorescence, and Phosphorescence Spectra. Absorption spectra of 1×10^{-2} mol/L $\text{Er}(\text{HFA})_4\text{K}$ and 2×10^{-5} mol/L $\text{Er}(\text{HFA})_4\text{IR5}$ in chloroform solution are shown

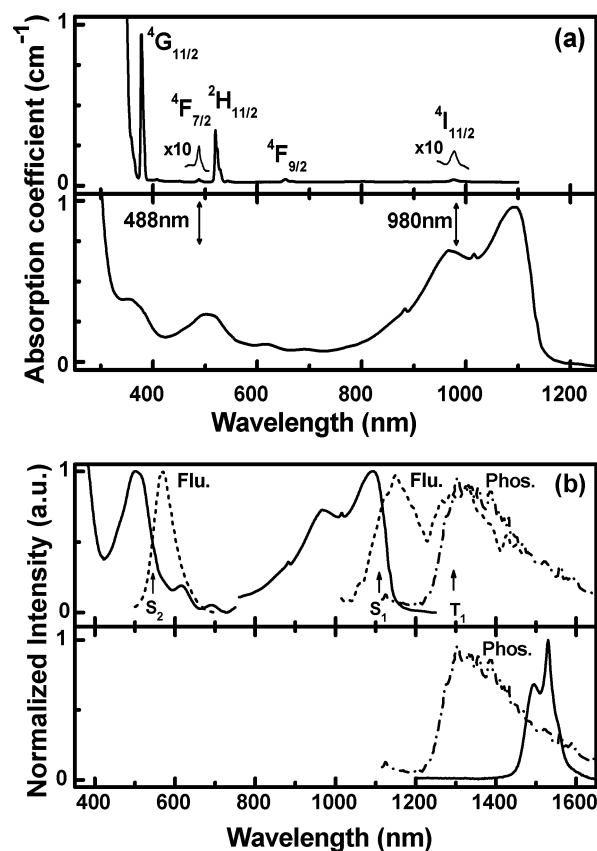


Figure 2. (a) Absorption spectra of $\text{Er}(\text{HFA})_4\text{K}$ dissolved in chloroform (1×10^{-2} mol/L, top) and $\text{Er}(\text{HFA})_4\text{IR5}$ in chloroform (2×10^{-5} mol/L, bottom). The absorption bands of $\text{Er}(\text{HFA})_4\text{K}$ are specified to the transitions from ground level $^4\text{I}_{15/2}$ to $(^2s+1)\Gamma_j$. Two 10-fold enlarged absorption bands at around 488 nm and 980 nm are also shown as a guide for the eye. (b) Normalized absorption spectrum of IR5 dye salt in chloroform solution (solid line), fluorescence spectrum in the visible region and NIR fluorescence spectrum of IR5 dye salt in chloroform solution excited at 500 and 980 nm (short-dash line), respectively, and phosphorescence spectrum of bulky IR5 dye salt excited at 488 nm at 77 K (dash-dot-dash line) (top); normalized phosphorescence spectrum of IR5 dye salt and absorption spectrum of Er^{3+} ion around 1500 nm (solid line) (bottom).¹⁴

in Figure 2a. The absorption spectrum of $\text{Er}(\text{HFA})_4\text{K}$ exhibits the intrinsic absorption bands of the erbium ion. But in the absorption spectrum of $\text{Er}(\text{HFA})_4\text{IR5}$ the absorption bands attributed to the IR5 segment are so intense and wide as to cover up all those of the erbium ion, which confirms the existence of the IR5 segment in the complex. In particular, upon comparison of the two absorption bands at around 488 nm and 980 nm between $\text{Er}(\text{HFA})_4\text{IR5}$ and $\text{Er}(\text{HFA})_4\text{K}$, we can find that the molar absorption coefficients in both bands for the former are over 3 orders of magnitude larger than those for the latter due to the presence of the IR5 segment. The normalized fluorescence spectra in the visible and near-infrared region for the IR5 dye salt are also obtained to determine the singlet state levels of the IR5 segment. From the crossing of the normalized absorption and fluorescence spectra¹³ for the IR5 dye salt as indicated in Figure 2b, the energy levels of the first singlet state S_1 and the second singlet state S_2 are estimated to be 9000 cm^{-1} and $18\,400 \text{ cm}^{-1}$, respectively. Also in Figure 2b the phosphorescence spectrum of the IR5 dye salt in bulky powder is shown, from the crossing of which and fluorescence spectrum the energy level of the first triplet state T_1 is analogously evaluated as being about 7700 cm^{-1} (but that of the second triplet state T_2 cannot be directly evaluated from this).

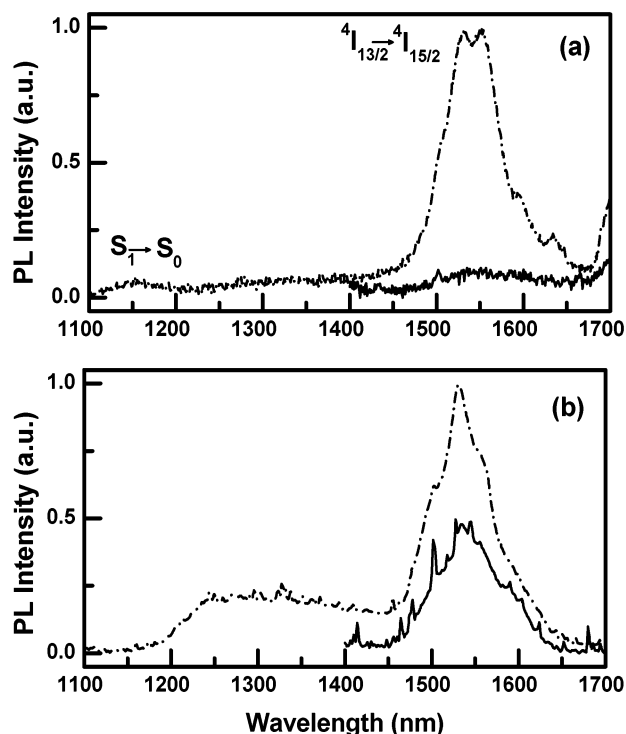


Figure 3. NIR photoluminescence spectra of the complexes $\text{Er}(\text{HFA})_4\text{IR5}$ (dash-dot-dash line) and $\text{Er}(\text{HFA})_4\text{K}$ (solid line) in bulky powder excited by the 980 nm LD laser line with output power about 100 mW (integral time 0.1 s) (a) and the 488 nm line from an Ar^+ laser with nearly equal output power (integral time 0.8 s) (b) at room temperature. The marked transitions $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ and $\text{S}_1 \rightarrow \text{S}_0$ refer to erbium ion and the IR5 segment, respectively.

3.2. Photoluminescence. NIR photoluminescence spectra of the two complexes $\text{Er}(\text{HFA})_4\text{IR5}$ and $\text{Er}(\text{HFA})_4\text{K}$ have been obtained at room temperature using two kinds of excitation sources, a 980 nm semiconductor laser diode and an Ar^+ laser with a 488 nm line, as shown in Figure 3. The investigated samples are measured in bulky powder in order to avoid partial dissociation and additional coordination for the complexes, which probably take place in solution. In addition, the excitation light was not intensively focused on the samples since the samples may be decomposed upon large excitation density. The intensities of the broad emission bands with a full width at half-maximum (fwhm) value up to 80 nm, corresponding to the transition $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ of erbium ion, for the complex $\text{Er}(\text{HFA})_4\text{IR5}$ upon excitation at both wavelengths exhibit 10-fold and 2-fold greater intensity than those of the complex $\text{Er}(\text{HFA})_4\text{K}$, respectively. The obvious spectral noise for $\text{Er}(\text{HFA})_4\text{K}$ is due to its weak luminescence signal. It should be noted that a difference between the profiles upon different excitation wavelengths can be seen for $\text{Er}(\text{HFA})_4\text{IR5}$, two comparable peaks at 1530 nm and 1555 nm from 980 nm excitation but one peak at 1530 nm with a 1557 nm shoulder from 488 nm excitation. The change in the relative peak intensities is a manifestation of a change in the relative transition probabilities between the seven Stark levels of $^4\text{I}_{13/2}$ and eight levels of $^4\text{I}_{15/2}$,¹⁵ but the actual cause and significance remain unknown here. A suspected cause for decreasing the relative strength at short wavelength is tentatively deemed to result from the reabsorption process of Er^{3+} ions. The reabsorption process (at ca. 1530 nm) can distort the emission spectrum, particularly for the solid samples used in the photoluminescence measurements and the large photoluminescence intensity in the case of 980 nm excitation. It is obvious that the luminescent yield of

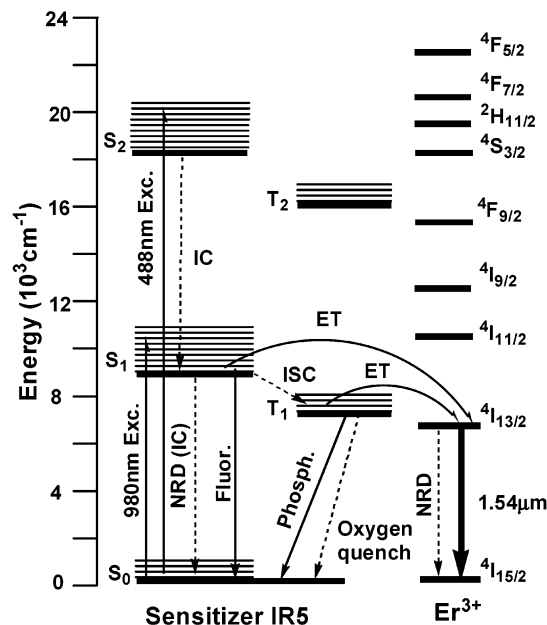


Figure 4. Schematic energy diagram describing the sensitization mechanism of NIR photoluminescence from the bulky $\text{Er}(\text{HFA})_4\text{IR5}$ complex via the IR5 segment. Here the abbreviations IC, NRD, ISC, and ET are the terms internal conversion, nonradiation deactivation, intersystem crossing, and energy transfer, respectively.

$\text{Er}(\text{HFA})_4\text{IR5}$ upon exciting at 980 nm is higher than that upon exciting at 488 nm since the background noise for the latter appears a little distinct, probably owing to different photoluminescence mechanisms which correlate with excitation sources (vide infra). In Figure 3b the unexpected broad band around 1300 nm for $\text{Er}(\text{HFA})_4\text{IR5}$, which becomes obvious since the emission of Er^{3+} at 1500 nm is depressed, is considered to be the emission from singlet oxygen $^1\text{O}_2$ (ca. 1275 nm). In Figure 3 there is very weak or absent IR5-related fluorescence ($\text{S}_1 \rightarrow \text{S}_0$) that is present in the fluorescence spectra of the IR5 dye salt.

For the complex $\text{Er}(\text{HFA})_4\text{K}$, the absorption bands around 980 nm and 488 nm are not assigned to electronic transitions of the ligand HFA but to the intrinsic absorption transitions $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ of Er^{3+} (see Figure 2a). Only a direct excitation process for the luminescence of Er^{3+} ions may occur when this bulky complex is excited at 980 nm and 488 nm, precluding the indirect excitation process via ligands. In the case of the complex $\text{Er}(\text{HFA})_4\text{IR5}$, according to the absorption coefficients above-mentioned at the two absorption bands around 488 nm and 980 nm, it is reasonable to deduce that the excitation light is mainly absorbed by the IR5 segment, which implies that the indirect excitation process via IR5 is expected to be dominant for enhanced $\text{Er}(\text{HFA})_4\text{IR5}$ luminescence, and the direct excitation process is negligible.

3.3. Indirect Excitation Mechanism. Furthermore, we present a simplified model to explain the mechanism of NIR photoluminescence from $\text{Er}(\text{HFA})_4\text{IR5}$ upon indirect excitation via the IR5 segment, as depicted in Figure 4. The data for the energy levels for Er^{3+} are adopted from ref 16. The energy levels of the singlet states and the first triplet state of the IR5 segment are estimated as above. And the energy levels of the second triplet state T_2 is calculated according to the assumption that the lowest singlet–triplet split for the NIR dye monomer is small, about 1000–3000 cm^{-1} , since the actual value cannot be identified by the same method as T_1 .^{17,18} Thus the energy level of the second triplet state T_2 is about 17 000 cm^{-1} .

3.3.1. On Excitation at 980 nm. According to Malta et al.,¹⁹ the selection rules for energy transfer from the excited singlet or triplet state of the sensitizer to the $(^{2s+1})T_J$ levels of lanthanide ions are as follows: $|\Delta J| = 0, 1$ ($J = J' = 0$ forbidden) for the electron exchange energy transfer mechanism (Dexter mechanism) and $|\Delta J| = 2, 4, 6$ for the dipolar or multipolar energy transfer mechanism (Förster mechanism). Upon exciting the bulky $\text{Er}(\text{HFA})_4\text{IR5}$ at 980 nm, the IR5 segment as an “antenna” exhausts most of the excitation photons due to its large absorption cross section, which then raises the electrons of IR5 from the ground-state S_0 to the excited-state S_1 . Pathways to deactivate S_1 are described as follows: (a) First undergo intersystem crossing (ISC) passing through the lowest triplet state T_1 ($S_1 \rightarrow T_1$) at an enhanced rate due to the external heavy atom effect of paramagnetic erbium ion (in the case of this work, weak IR5-related fluorescence in the presence of Er^{3+} may be the proof for this, see Figure 3a),²⁰ then intramolecular transfer energy (ET) to the radiative excited level $^4I_{13/2}$ of the erbium ion chiefly via the Dexter mechanism ($|\Delta J| = 1$),³ since the IR5 segment is considered to adjoin closely to the outer coordination sphere of the erbium ion through the Coulombic effect as suggested in Figure 1 and the close energy correspondence for T_1 (ca. 7700 cm^{-1}) and $^4I_{13/2}$ (6500 cm^{-1}) is evident. The actual distance between Er^{3+} and the IR5 segment cannot be determined directly. Nevertheless, on the basis of the space-filling model of $\text{Er}(\text{HFA})_4\text{IR5}$ where all atoms are represented by their van der Waals radius,^{2,6} the rough distance (from the central Er^{3+} ion of dodecahedra $[\text{Er}(\text{HFA})_4]^-$ perpendicular to the conjugated plane of the IR5 segment) can be presumed estimated to be less than 7 Å. This agrees with the small distance (<10 Å) needed for efficient energy transfer by the Dexter mechanism. Furthermore, in Figure 2b the normalized phosphorescence spectrum of the IR5 dye salt and the $I_{15/2} \rightarrow ^4I_{13/2}$ transition absorption spectrum of Er^{3+} in the range of 1200–1650 nm exhibit spectral overlap between them. As expected, the manifold level $^4I_{13/2}$ is the only acceptor level of Er^{3+} , with the T_1 of the IR5 segment the donor level. According to Dexter,²¹ the spectral overlap integral (J) of the phosphorescence spectrum of the IR5 dye salt and the absorption spectrum of Er^{3+} can be given by $J = \int f_D(\lambda) \epsilon_A(\lambda) d\lambda$ with the phosphorescence of the donor and appropriate transition absorption of the acceptor normalized ($\int f_D(\lambda) d\lambda = 1$ and $\int \epsilon_A(\lambda) d\lambda = 1$, respectively). The calculated J value in this case is 2.41×10^{-3} , which is a moderate value to ensure the energy transfer process. Finally, this pathway is abbreviated as $S_1 \rightarrow T_1 \rightarrow \text{Er}^{3+}(^4I_{13/2})$. (b) S_1 directly transfers energy to the $^4I_{13/2}$ level of the Er^{3+} ion via the Dexter mechanism ($|\Delta J| = 1$) possibly due to a lower energy gap with the corresponding level ($^4I_{13/2}$ is the only excited state of Er^{3+} below S_1).²² Nevertheless, it is commonly considered to be inefficient because energy transfer via the singlet state is not fast enough to compete with the fluorescence or the intersystem crossing. This pathway is abbreviated as $S_1 \rightarrow \text{Er}^{3+}(^4I_{13/2})$. (c) Internal conversion (IC) to S_0 by nonradiative decay while deactivating S_1 to the vibrational mode of the surrounding moieties such as CH or even to $^1\text{O}_2$. (d) Fluorescence ($S_1 \rightarrow S_0$). Both pathways a and b lead to NIR emission of Er^{3+} ions, with the IR5 segment acting as the sensitizer. Moreover, when pathways a and b are compared, pathway a in which energy flows from triplet state to Er^{3+} ion through the Dexter mechanism should be the most dominant pathway for NIR emission.¹⁹ In Figure 3a, the rather weak fluorescent intensity arose from the IR5 segment in comparison to that due to Er^{3+} ions and the enhancement in erbium ion

emission can be attributed to efficient energy transfer from the IR5 segment to the Er^{3+} ion.

3.3.2. On Excitation at 488 nm. When $\text{Er}(\text{HFA})_4\text{IR5}$ is excited at 488 nm, the second singlet state S_2 of the IR5 segment is primarily populated through the transition $S_0 \rightarrow S_2$, because of the above-mentioned reasons. Since the internal conversion between S_2 and S_1 is considered to take place extremely fast in less than 10^{-11} s with respect to the intersystem crossing from S_2 to T_2 (generally in 10^{-7} s), S_2 deactivates to S_1 rather than to T_2 .¹⁷ After that, a process similar to that for the 980 nm excitation will happen. Surely, the external heavy atom effect of Er^{3+} may promote the intersystem crossing $S_2 \rightarrow T_2$. Given that, T_2 should transfer energy via the Dexter mechanism only to the $^4I_{13/2}$ level of Er^{3+} ($\Delta J = 1$) or via the Förster mechanism only to the $^4I_{11/2}$ level of Er^{3+} ($\Delta J = 2$) according to the selection rules. However, the energy gap between T_2 and $^4I_{13/2}$ or between T_2 and $^4I_{11/2}$ is so large as to be over 10 000 cm^{-1} or 6000 cm^{-1} , which will result in a very small energy transfer rate from T_2 to $^4I_{13/2}$ or from T_2 to $^4I_{11/2}$. Hence, we exclude the $S_2 \rightarrow T_2 \rightarrow \text{Er}^{3+}$ pathway from contributing to energy transfer from the IR5 segment to Er^{3+} . Conclusively, combined with the as-discussed main energy transfer process on 980 nm excitation, the main energy transfer process leading to the NIR luminescence of Er^{3+} on 488 nm excitation is denoted as $S_2 \rightarrow S_1 \rightarrow T_1 \rightarrow \text{Er}^{3+}(^4I_{13/2})$. It is noted that the molar absorption coefficient of IR5 at 488 nm is less than half of that at 980 nm, which results in relatively low luminescence intensity when excited at 488 nm.

4. Conclusions

In summary, the enhanced NIR photoluminescence of erbium ion has been achieved from the erbium ion-association ternary complex sensitized by the near-infrared dye IR5 upon 488 nm excitation and upon 980 nm excitation. The results suggest that the complex has promising applications in erbium-doped optical materials. Indirect excitation mechanisms for the investigated complex are deduced mainly to be $S_1 \rightarrow T_1 \rightarrow \text{Er}^{3+}(^4I_{13/2})$ for 980 nm excitation and $S_2 \rightarrow S_1 \rightarrow T_1 \rightarrow \text{Er}^{3+}(^4I_{13/2})$ for 488 nm excitation. Further work is in progress concerning more evidence for the two mechanisms. Also, the intensified NIR luminescence of this complex pumped at 980 nm provides the possibility to incorporate the complex into polymers or hybrid organic–inorganic matrixes to fabricate planar amplifiers compatible with the existing optical communication network.

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References and Notes

- (1) Polman, A. *J. Appl. Phys.* **1997**, *82*, 1.
- (2) Slooff, L. H.; Van Blaaderen, A.; Polman, A.; Hebbink, G. A.; Klink, S. I.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Hofstra, J. W. *J. Appl. Phys.* **2002**, *91*, 3955.
- (3) Slooff, L. H.; Polman, A.; Cacialli, F.; Friend, R. H.; Hebbink, G. A.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Appl. Phys. Lett.* **2001**, *78*, 2122.
- (4) Werts, M. H. V.; Verboeven, J. W.; Hofstra, J. W. *J. Chem. Soc., Perkin Trans. 2* **2000**, 433.
- (5) Korovin, Y.; Rusakova, N. *J. Fluoresc.* **2002**, *12*, 159.
- (6) Slooff, L. H.; Polman, A.; Klink, S. I.; Hebbink, G. A.; Grave, L.; van Veggel, F. C. J. M.; Reinhoudt, D. N.; Hofstra, J. W. *Opt. Mater.* **2000**, *14*, 101.

- (7) Lin, S.; Feuerstein, R. J.; Mickelson, R. *J. Appl. Phys.* **1996**, *79*, 2868.
- (8) (a) Li, C. Y.; Ingenhoff, J.; Najafi, S. I.; Chisham, J.; MacLachan, M.; Andrews, M.; Kao, Y.; Mackenzie, J. D.; Ohtsuki, T.; Peyghambarian, N. *Proc. SPIE* **1995**, 2397, 430. (b) Etienne, P.; Coudry, P.; Porque, J.; Moreau, Y. *Opt. Commun.* **2000**, *174*, 413.
- (9) Reynolds, G. A.; Drexhage, K. H. *J. Org. Chem.* **1977**, *42*, 885.
- (10) Kopainsky, B.; Qiu, P.; Kaiser, W.; Sens, B.; Drexhage, K. H. *Appl. Phys. B* **1982**, *29*, 15.
- (11) Haddad, P. R. *Talanta* **1977**, *24*, 1 and references therein.
- (12) Mebly, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.
- (13) Additionally, in Figure 2b NIR profiles of absorption and fluorescence spectra for the IR5 dye salt appear an obvious deviation from mirror symmetry. This can be explained as that emission at about 1275 nm from singlet oxygen $^1\text{O}_2$ comprises the NIR fluorescence spectrum, as a consequence of oxygen quenching the excited states of the IR5 dye. Oxygen quenching should be noticed due to the lower energy of the excited states especially for IR5 dye, which may depress the luminescence yield.
- (14) Due to weak phosphorescence intensity and the influence of $^1\text{O}_2$, the phosphorescence spectrum seems a little anamorphic. The overlapping between the phosphorescence and fluorescence spectra of IR5 dye is ascribed to overlapping of its singlet split and triplet split states. The absorption spectrum of Er^{3+} ion around 1500 nm is measured on a melt-derived $50\text{SiO}_2\text{50PbF}_2\text{3ErF}_3$ glass by our group, since the undistorted spectrum around 1500 nm of Er^{3+} ion in solution is difficult to obtain due to the vibration absorption of OH and CH.
- (15) Miniscalco, W. J. *J. Lightwave Technol.* **1991**, *9*, 234.
- (16) Carnall, W. T.; Fields, P. R.; Rajnak, K. *J. Chem. Phys.* **1968**, *49*, 4424.
- (17) Schäfer, F. P. *Dye Laser*; Springer-Verlag: Berlin, Heidelberg, New York, 1973.
- (18) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721.
- (19) (a) Malta, O. L. *J. Lumin.* **1997**, *71*, 229. (b) Gonçálves e Silva, F. R.; Malta, O. L. *J. Alloys Compd.* **1997**, *250*, 427. (c) Malta, O. L.; Gonçálves e Silva, F. R. *Spectrochim. Acta, Part A* **1998**, *54*, 1593. (d) de Sá, G. F.; Malta, O. L.; de Mello Donegá, C.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; da Silva, E. F. *Coord. Chem. Rev.* **2000**, *196*, 165. (e) Gonçálves e Silva, F. R.; Malta, O. L.; Reinhard, C.; Güdel, H.-U.; Piguet, C.; Moser, J. E.; Bünzli, J.-C. G. *J. Phys. Chem. A* **2002**, *106*, 1670.
- (20) (a) Klink, S. I.; Grave, L.; Reinhoudt, D. N.; van Veggel, F. C. J. M.; Werts, M. H. V.; Geurts, F. A. J.; Hofstra, J. W. *J. Phys. Chem. A* **2000**, *104*, 5457. (b) Klink, S. I.; Oude Alink, P.; Grave, L.; Peters, F. G. A.; Hofstra, J. W.; Geurts, F. A. J.; van Veggel, F. C. J. M. *J. Chem. Soc., Perkin Trans. 2* **2001**, 363. (c) Hebbink, G. A.; Grave, L.; Woldering, L. A.; Reinhoudt, D. N.; van Veggel, F. C. J. M. *J. Phys. Chem. A* **2003**, *107*, 2483. (d) Tobita, S.; Arakawa, M.; Tanaka, I. *J. Phys. Chem.* **1984**, *88*, 2697. (e) Tobita, S.; Arakawa, M.; Tanaka, I. *J. Phys. Chem.* **1985**, *89*, 5649.
- (21) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
- (22) (a) Hebbink, G. A.; Klink, S. I.; Grave, L.; Oude Alink, P. G. B.; van Veggel, F. C. J. M. *ChemPhysChem* **2002**, *3*, 1014. (b) Vögtle, F.; Gorka, M.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *ChemPhysChem* **2001**, *2*, 769.