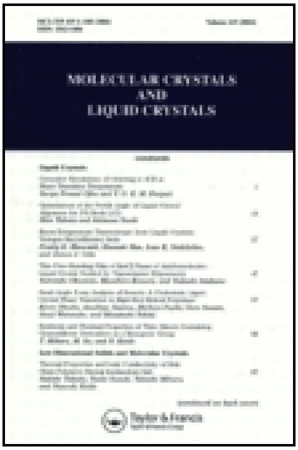

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# LIGAND-SENSITIZED AND UP-CONVERSION PHOTOLUMINESCENCE IN VACUUM-DEPOSITED THIN FILMS OF AN INFRARED ELECTROLUMINESCENT ORGANIC ERBIUM COMPLEX

Hiroyuki Suzuki [a] , Yoshiki Nishida [a] & Satoshi Hoshino [b]

[a] NTT Photonics Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan

[b] NTT Lifestyle and Environmental Technology Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan

Version of record first published: 15 Jul 2010

To cite this article: Hiroyuki Suzuki, Yoshiki Nishida & Satoshi Hoshino (2003): LIGAND-SENSITIZED AND UP-CONVERSION PHOTOLUMINESCENCE IN VACUUM-DEPOSITED THIN FILMS OF AN INFRARED ELECTROLUMINESCENT ORGANIC ERBIUM COMPLEX, Molecular Crystals and Liquid Crystals, 406:1, 27-37

To link to this article: http://dx.doi.org/10.1080/744818984

*Mol. Cryst. Liq. Cryst.*, Vol. 406, pp. 27/[221]–37/[231], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390263398

Taylor & Francis
Taylor & Francis Group

# LIGAND-SENSITIZED AND UP-CONVERSION PHOTOLUMINESCENCE IN VACUUM-DEPOSITED THIN FILMS OF AN INFRARED ELECTROLUMINESCENT ORGANIC ERBIUM COMPLEX

*Hiroyuki Suzuki and Yoshiki Nishida*
*NTT Photonics Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan*

*Satoshi Hoshino**
*NTT Lifestyle and Environmental Technology Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa, 243-0198, Japan*

*We observed ligand-sensitized and up-conversion photoluminescence (PL) in vacuum-deposited thin films of an infrared electroluminescent organic erbium complex, erbium (III) tris(8-hydroxyquinoline) (ErQ). The PL intensity at 1.55* μm *was increased by three orders of magnitude by changing the photo-excited species from* $Er^{3+}$ *to the organic ligand (Q). This strong enhancement was ascribable to ligand-sensitized PL based on the excited state energy transfer from Q to* $Er^{3+}$*. We simultaneously detected up-conversion PL from* $Er^{3+}$ *in the ultraviolet region. The up-conversion PL is emitted due to excited state absorption, which indicates that vacuum-deposited ErQ thin films are weak electron-phonon coupling systems.*

## 1. INTRODUCTION

The usefulness of organic emissive materials in the visible region has become established owing to the successful development of organic electroluminescence (EL) devices for display applications. In contrast, organic emissive materials and devices operating at wavelengths longer than 1 μm have not been important research targets due mainly to the difficulty involved in the development of organic infrared (IR) emissive materials and

---

*Corresponding author. E-mail: hiroyuki@aecl.ntt.co.jp

the lack of concrete application areas. Recent innovations in communication networks based on photonic technologies have stimulated research designed to extend the emission wavelength of organic materials to the IR region. This is because current photonic communication networks are constructed using silica optical fibers that have two main windows in their transmission loss spectra in the 1.3 and 1.5 µm wavelength regions.

A limited number of organic IR emissive materials have already been reported. They are divided into two types depending on whether or not they contain rare earth ions. The first type consists of organic materials containing no rare earth ions such as polymer nanocrystals [1] and an organic ionic dye [2,3]. Both exhibit EL peaking at around 1.2 µm. A wavelength of 1.2 µm can be used for high-speed local area networks (LANs) [4]. The other type of emissive material consists of organic complexes with trivalent rare earth ions such as $Er^{3+}$ [5–7], $Nd^{3+}$ [8,9] and $Pr^{3+}$ [10], and includes most of the organic IR emissive materials reported to date. The luminescence wavelengths emitted by these complexes are typical for the rare earth ions they contain, and so ascribable to their radiative 4f-4f transitions. Unlike the former materials in which the luminescence originates from allowed radiative transitions, the latter materials present us with the vital challenge of finding a way to improve the luminescence efficiency since the f-f transition is in principle a parity-forbidden process.

In this work, we examined the Photoluminescence (PL) characteristics of vacuum-deposited thin films of the most typical electroluminescent

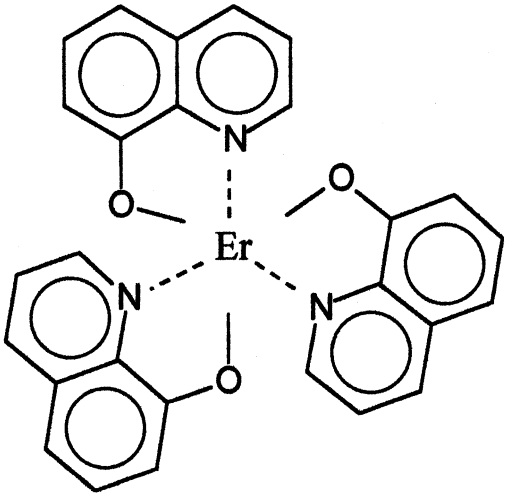

**FIGURE 1** Molecular structure of ErQ.

organic rare-earth complex in the 1.5 µm region, erbium (III) tris (8-hydroxyquinoline) (ErQ) (see Figure 1(a)) for the molecular structure) to determine both their advantages and limits as IR emissive materials, and provide a guideline for improving the luminescence efficiency. The PL properties of ErQ have not yet been examined in detail [5].

## 2. EXPERIMENTAL

We obtained ErQ by mixing erbium (III) chloride in aqueous solution with 8-hydroxyquinoline (8-Q) in methanol. ErQ thin films were vacuum-deposited on glass substrates with conventional apparatus. We measured the PL properties of ErQ thin films by using either an $Ar^+$ laser (six wavelengths: 457.9, 476.5, 488.0, 496.5, 501.7 and 514.5 nm) or a blue laser diode (wavelength: 405 nm) as an excitation source. We also examined the spectroscopic properties of 8-Q as an ErQ reference material. Since we were unable to prepare 8-Q thin films with the same apparatus due to its high vapor pressure, we measured its absorption and PL spectra in 1,2-dichloroethane and in powder samples, respectively. The PL spectra in the IR region were recorded with a 15-cm monochromator and an InGaAs charge-coupled-device (CCD), whereas those in the visible and ultraviolet regions were recorded with a different 15-cm monochromator and a Si CCD with enhanced UV sensitivity. We corrected the PL spectra for the spectral response of the detection system that we used unless otherwise noted. All the spectroscopic measurements were carried out at room temperature.

## 3. RESULTS

Figure 2(a) and (b), respectively, show the absorption spectra of a vacuum-deposited thin film of ErQ and of 8-Q in 1,2-dichloroethane. Weak absorption bands observed from an ErQ thin film in the 480–580 nm range are attributed to the 4f-4f transitions of $Er^{3+}$ [11]. A comparison of these two absorption spectra reveal that the strong absorption at around 380 nm originates from a transition of organic ligands (Q) with a red shift of about 0.70 eV caused by the charge transfer interaction between the central $Er^{3+}$and the attached Q. Dominant photoexcited species thus change from $Er^{3+}$ to Q in accordance with a shift in the excitation wavelength to the higher energy side, as indicated by the arrows in Figure 2(a). This means that photoexcitation at wavelengths shorter than about 450 nm leads to the considerably more efficient photogeneration of excited species since the $Er^{3+}$ absorptions are forbidden whereas that of Q is allowed.

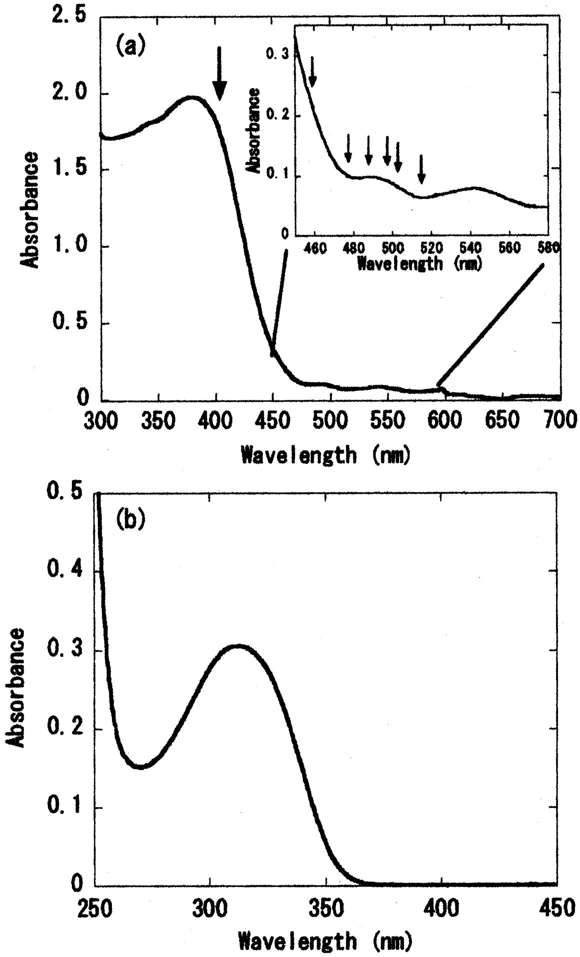

**FIGURE 2** Absorption spectrum of (a) a vacuum-deposited ErQ thin film and (b) 8-Q in 1,2-dichloroethane. The wavelengths used for the photoexcitation of the ErQ film are indicated by the arrows in (a).

Figure 3 shows the excitation wavelength dependence of the PL intensity of an ErQ thin film in the IR region (1.0–1.7 μm). As shown in the inset of Figure 3, the ErQ thin film exhibits two PL bands at 1.2 and 1.55 μm, which can be assigned to the $^4S_{3/2} \rightarrow {}^4I_{11/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of $Er^{3+}$, respectively [11]. The PL intensity at 1.55 μm, which is the most important emission for photonic communication applications, was enhanced by more than three orders of magnitude by shifting the excitation wavelength from 514.5 to 405 nm. The PL spectra of the ErQ

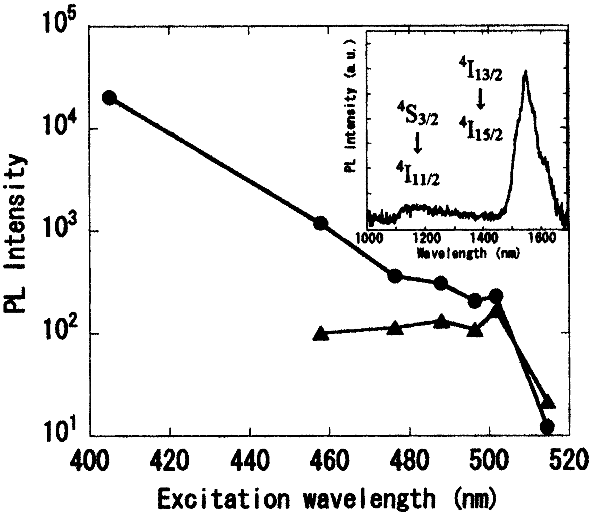

**FIGURE 3** The excitation wavelength dependence of the PL intensity in the 1.55 (circles) and 1.2 (triangles) μm bands. The inset shows the PL spectrum of a vacuum-deposited ErQ thin film in the IR region when it was excited at 457.9 nm.

thin film in the visible and near-IR regions are shown in Figures 4(a) and 5(a), respectively. Most of the PL bands detected in these two wavelength regions can be assigned to those originating from $Er^{3+}$ [11], as labeled in the two figures. The PL spectra from the visible to the IR regions indicate that a vacuum-deposited ErQ thin film is a weak electron-phonon coupling system since we detected a large number of PL bands ascribable to $Er^{3+}$. Unlike $Er^{3+}$ doped in inorganic systems [11–13], multiple phonon relaxation is not a dominant deactivation process for photoexcited states in this system. Figure 4(a) shows that there is an additional broad PL in the visible region. PL spectrum measurements of 8-Q powder samples revealed that this broad emission originates from the organic ligands of ErQ. Figures 4(b) and 5(b), respectively, show the excitation wavelength dependence of the PL intensity for various emission bands in the visible and near-IR regions. As shown in Figure 5(b), the PL intensity of the emission bands in the near-IR region changes in accordance with the absorption intensity of the ErQ thin film in the 514.5 to 476.5 nm wavelength region. The intensity of all the PL bands in the near-IR wavelength region increased when the ErQ film was excited at 457.9 nm. In contrast, although the PL intensity of the emission bands in the visible region also changes in accordance with the absorption intensity of the ErQ film for the 514.5 to 476.5 nm wavelength region, the PL intensity decreased

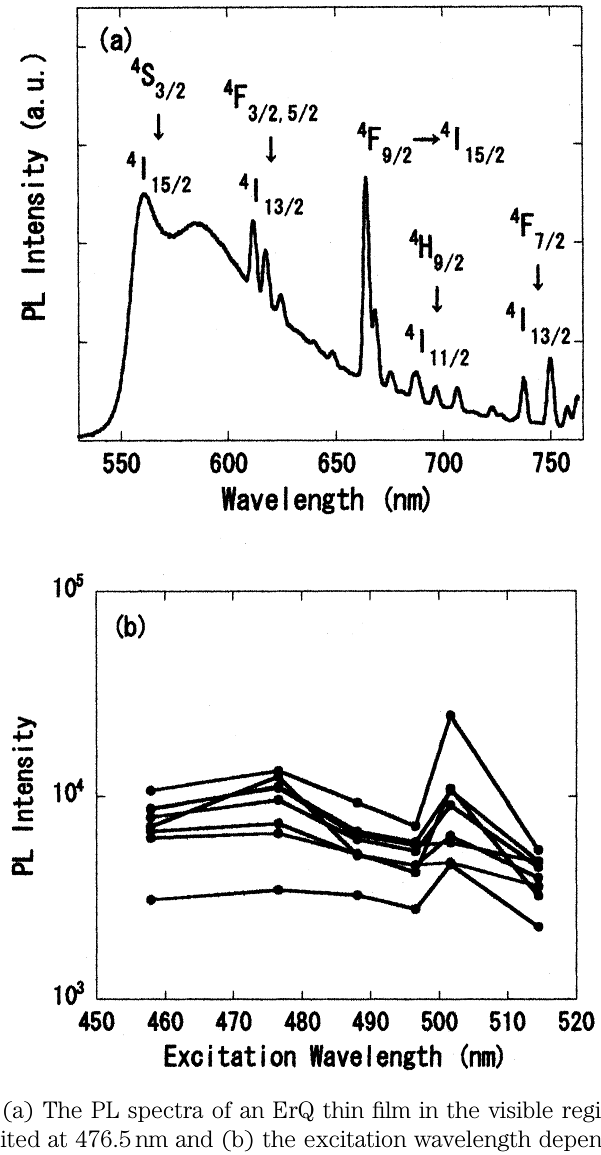

**FIGURE 4** (a) The PL spectra of an ErQ thin film in the visible region when the film was excited at 476.5 nm and (b) the excitation wavelength dependence of the PL intensity for emission bands located at shorter than 680 nm.

when the film was excited at 457.9 nm for emission bands located at shorter than 680 nm, as shown in Figure 4(b).

In addition to the PL bands described so far, we were able to observe up-conversion PL in the UV region, as shown in Figure 6. The up-conversion

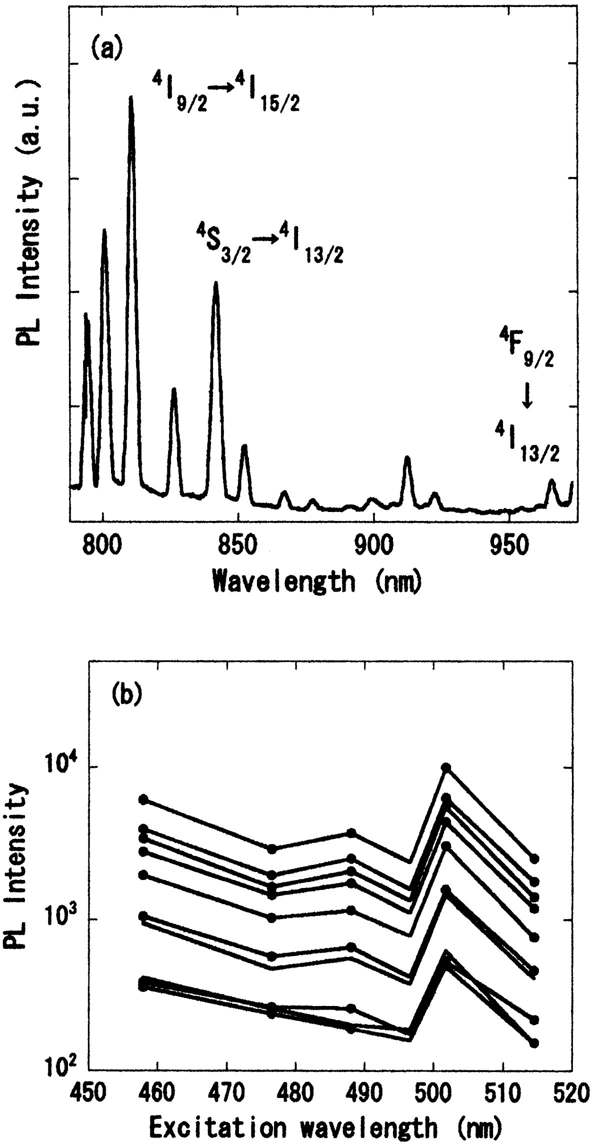

**FIGURE 5** (a) The PL spectra of an ErQ thin film in the near-infrared region when the film was excited at 488.0 nm and (b) the excitation wavelength dependence of the PL intensity for emission bands observed in the same wavelength region.

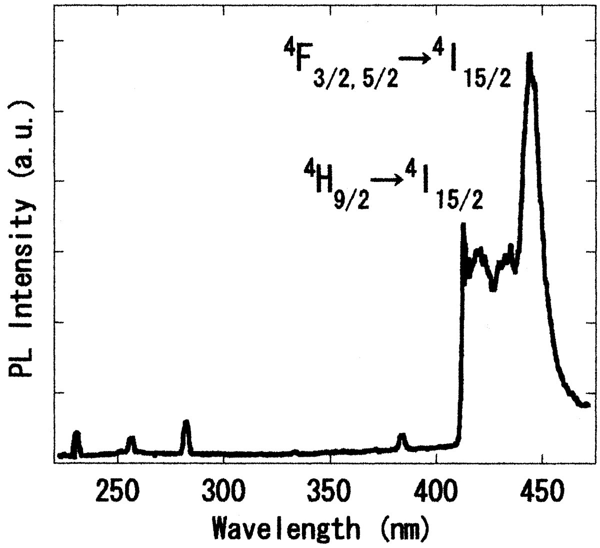

**FIGURE 6** Up-conversion PL spectrum in the UV region when the film was excited at 514.5 nm. This spectrum was uncorrected for the spectral response of the detection system used.

PL can be assigned to emissions originating from $Er^{3+}$, as labeled in the figure. The excitation wavelength dependence measurement reveals that the up-conversion PL intensity is at its largest with 514.5 nm excitation when an $Ar^+$ laser is used as the excitation source. We therefore conclude that the reduction in PL intensity at 1.55 μm (see Figure 3) is caused by the depopulation of the emitting $^4I_{13/2}$ state due to excited state absorption (ESA). The energy of the shortest wavelength up-conversion PL (about 5.3 eV) suggests that at least three-step absorption is occurring in the ErQ thin film during the photoexcitation.

## 4. DISCUSSION

Figure 7 is a schematic drawing of the PL process in ErQ thin films. This figure was drawn based both on the results obtained in this study and the established knowledge that the excited energy transfer from the first triplet excited states ($T_1$) of organic ligands to central rare earth ions is a dominant process in the excited state deactivation of organic rare earth complexes [14]. We roughly estimated the $T_1$ energy level of ErQ (about 2.0 eV) by using the first singlet excited state ($S_1$) energy of 8-Q (about 4.0 eV) and

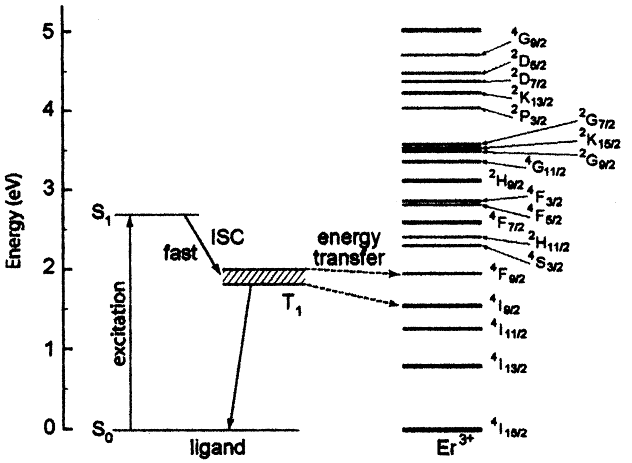

**FIGURE 7** A schematic drawing of the PL process in vacuum-deposited ErQ thin films. The $T_1$ state energy was depicted on the basis of the estimated values by the two methods.

ErQ (about 3.3 eV), and the $T_1$ energy of 8-Q (2.71 eV) [15]. Here, we assume that the energy difference between the $S_1$ and the $T_1$ states is the same for 8-Q and ErQ. Excited states of ErQ are generated efficiently by photoexcitation at 405 nm since, as described above, the absorption originates from an allowed transition of the organic ligands. Following the intersystem crossing (ISC) to the $T_1$ state, there is an energy transfer to the $^4F_{9/2}$ and/or $^4I_{9/2}$ levels of $Er^{3+}$. Since these two levels are located on the higher energy side of the $^4I_{13/2}$ state, a marked enhancement was observed in the PL at 1.55 μm. This ligand-sensitized PL is unique for organic rare earth complexes, and so provides an attractive way to increase the PL intensity originating from the parity-forbidden 4f-4f transition at 1.55 μm. It is interesting to synthesize organic $Er^{3+}$ complexes whose $T_1$ energy level is located between $^4I_{11/2}$ and $^4I_{13/2}$ with a view to achieving a PL efficiency enhancement at 1.55 μm. With these materials, it may be possible to realize the direct population of the $^4I_{13/2}$ level by excited state energy transfer from organic ligands. Another advantage of organic rare earth complexes is that their photoexcitation wavelength can be tuned for commercially available high-power laser diodes by changing the organic ligands.

As shown in Figures 4(b) and 5(b), the intensity of the PL bands in the visible and the near-IR regions exhibited different degrees of excitation wavelength dependence with excitation at 457.9 nm. It should be noted that the 457.9 nm light excites the organic ligands of ErQ, and thus the PL due to ligand-sensitization plays a dominant role. When we take account of the ligand-sensitized PL mechanism schematically depicted in Figure 7, the difference in the PL intensity for the excitation at 457.9 nm reflects the difference in the magnitude of the excited state population due to the excited state energy transfer from the organic ligands to $Er^{3+}$. Since the excited state energy transfer efficiency depends on the energy difference between the donor and acceptor states, the observed result reflects the $T_1$ energy of 8-Q, that is, it is located at an approximate energy of 1.8 eV (corresponding to 680 nm). This value agrees reasonably well with that obtained with the other method mentioned above (2.0 eV).

Another unique feature observed with ErQ thin films is up-conversion PL in the UV region caused by ESA. As inferred from the observation of many $Er^{3+}$PL bands, ESA is not a simple process and so a detailed understanding of the up-conversion PL process requires further study. However, we speculate that the first ESA occurs from the $^4I_{13/2}$ level since this ESA depopulates the $^4I_{13/2}$ level and results in the strong reduction observed in the PL intensity at 1.55 μm.

## 5. CONCLUSION

We have examined the PL characteristics of thin films of a typical infrared electroluminescent organic rare-earth complex, ErQ. Since ErQ thin film is a weak electron-phonon coupling system, it exhibits a large number of PL bands in the 0.5–1.7 μm range and efficient ESA, as confirmed by the observation of up-conversion PL in the ultraviolet region. We have shown that ligand-sensitized PL and ESA processes play essential roles in the PL process of ErQ thin films. The results obtained in this work will be beneficial for developing novel organic $Er^{3+}$ complexes with a higher emission efficiency at 1.55 μm.

## REFERENCES

[1] Tessler, N., Medvedev, V., Kazes, M., Kan, S., & Banin, U. (2002). Efficient near-infrared polymer nanocrystal light-emitting diodes. *Science*, *295*, 1506–1508.

[2] Casalboni, M., De Matteis, F., Prosposito, P., & Pizzoferrato, R. (1999). Optical investigation of infrared dyes in hybrid thin films. *Appl. Phys. Lett.*, *75*, 2172–2174.

[3] Suzuki, H. (2002). Infrared electroluminescence from an organic ionic dye containing no rare-earth ions. *Appl. Phys. Lett.*, *80*, 3256–3258.

[4] Koyama, F., Schlenker, D., Miyamoto, T., Chen, Z., Matsutani, A., Sakaguchi, T., & Iga, K. D. (2000). Data transmission over single-mode fiber by using 1.2-μm uncooled GaInAs-GaAs laser for Gb/s local area network. *12*, 125–127.

[5] Gillin, W. P. & Curry, R. J. (1999). Erbium (III) tris(8-hydroxyquinoline): A potential material for silicon compatible 1.5 μm emitters. *Appl. Phys. Lett.*, *74*, 798–799.

[6] Sun, R. G., Wang, Y. Z., Zheng, Q. B., Zhang, H. J., & Epstein, A. J. (2000). 1.54 μm infrared photoluminescence and electroluminescence from an erbium organic compound. *J. Appl. Phys.*, *87*, 7589–7591.

[7] Harrison, B. S., Foley, T. J., Bouguettaya, M., Boncella, J. M., Reynolds, J. R., Schanze, K. S., Shim, J., Holloway, P. H., Padmanaban, G., & Ramakrishnan. S. (2001). Near-infrared electroluminescence from conjugated polymer/lanthanide porphyrin blends. *Appl. Phys. Lett.*, *79*, 3770–3772.

[8] Kawamura, Y., Wada, Y., Hasegawa, Y., Iwamuro, M., Kitamura, T., & Yanagida, S. (1999). Observation of neodymium electroluminescence. *Appl. Phys. Lett.*, *74*, 3245–3247.

[9] Khreis, O. M., Curry, R. J., Somerton, M., & Gillin, W. P. (2000). Infrared organic light emitting diodes using neodymium tris-(8-hydroxyquinoline). *J. Appl. Phys.*, *88*, 777–780.

[10] Hong, Z., Liang, C., Li, R., Zang, F., Fan, D., Li, W., Hung, L. S., & Lee, S. T. (2001). Infrared and visible emission from organic electroluminescent devices based on praseodymium complex. *Appl. Phys. Lett.*, *79*, 1942–1944.

[11] Digonnet, M. J. F. ed. (1993). Rare earth doped fiber lasers and amplifiers. Marcel Dekker: New York.

[12] Polman, A. (1997). Erbium implanted thin film photonic materials. *J. Appl. Phys.*, *82*, 1–39.

[13] Zanatta, A. R. & Nunes, L. A. O. (1998). Green photoluminescence from Er-containing amorphous SiN thin films. *Appl. Phys. Lett.*, *72*, 3127–3129.

[14] Slooff, L. H., van Blaaderen, A., Polman, A., Hebbink, G. A., Klink, S. I., Van Veggel, F. C. J. M., Reinhoudt, D. N., & Hofstraat, J. W. (2002). Rare-earth doped polymers for planar optical amplifiers. *J. Appl. Phys.*, *91*, 3955–3980.

[15] Birks, J. B. (1970). Photophysics of Aromatic Molecules. Wiley-Interscience: London.