© 2000 The Chemical Society of Japan

Photosensitized Luminescence of Neodymium(III) Coordinated with 8-Quinolinolates in DMSO-d_6

Mitsunori Iwamuro, Tomoko Adachi, Yuji Wada, Takayuki Kitamura, Nobuaki Nakashima,[†] and Shozo Yanagida*

Material and Life Science, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871

†Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-0022

(Received January 26, 2000)

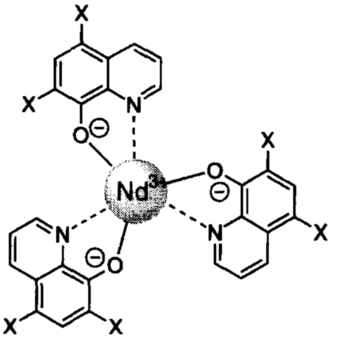
Some quinolinol derivatives possessing suitable triplet state energy were examined to sensitize the luminescence of neodymium ion (Nd(III)) as coordinating ligands. Photosensitized luminescence in the near-infrared region of four neodymium(III) complexes: tris(8-quinolinolato)neodymium(III) ([Nd(q)$_3$]), tris(5,7-dichloro-8-quinolinolato)-neodymium(III) ([Nd(Clq)$_3$]), tris(5,7-dibromo-8-quinolinolato)neodymium(III) ([Nd(Brq)$_3$]) and tris(5,7-diiodo-8-quinolinolato)neodymium(III) ([Nd(Iq)$_3$]), were observed by selective excitation of the ligand moieties in DMSO-d_6. Highly efficient intramolecular energy transfer from the excited ligand moieties to the central Nd(III) ion was successfully achieved by using the halogenated ligands.

Nd(III)-containing systems have been regarded as the most popular infrared luminescent materials, especially in inorganic media. On the other hand, we have attempted to develop Nd(III) complexes in organic media, which are potential materials for use in organic laser systems,[1] organic electroluminescence devices[2] or biological applications.[3] Effective luminescence of Nd(III) was successfully observed in organic media when the nonradiative transition via vibrational excitation of surrounding organic molecules was suppressed by using low vibrational ligands and deuterated solvent.[4] In addition, introduction of low vibrational bulky ligands suppresses the cross relaxation[5] that happens during excitation migration of excited Nd(III) complexes in the system.[1,6—8]

On the other hands, the absorption of Nd(III) is very weak because the electronic transition in the *f*-orbital is forbidden by the selection rule. Such an intrinsic low absorption coefficient of Nd(III) ($\varepsilon < 50\ \mathrm{M^{-1}\,cm^{-1}}$, $1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$) is also responsible for the difficulty in observing intense luminescence. Photosensitization via intramolecular energy transfer from the excited organic ligands to the central Nd(III) should increase the population of the excited state of Nd(III), giving the enhanced luminescence of the metal ion. When the ligand moieties of the complex as chromophore are selectively excited to the singlet excited state, the intersystem crossing to the triplet state of the chromophore leads to sensitization via intramolecular energy transfer from the triplet state to the excited levels of Nd(III). Very recently, the photosensitized luminescence of Nd(III) using fluorescein, eosin, *m*-terphenyl derivatives, and azatriphenylene as sensitizing chromophores was observed in liquid systems such as D_2O, methanol-d_4, acetonitrile, and dimethylsulfoxide-d_6 (DMSO-d_6).[9—12] The energy accepting levels ($^2G_{7/2}+^4G_{5/2}$) of Nd(III) are positioned at around 585 nm (17100 cm^{-1}). We recently designed some low vibrational bulky fluorinated β-diketones as sensitizing ligands and clarified that the photosensitized luminescence efficiency of Nd(III) increased with increase of overlapping of the phosphorescence of the β-diketonates with the absorption band of the *f*–*f* transitions ($^4I_{9/2}$ (ground state) $\rightarrow$ $^2G_{7/2}+^4G_{5/2}$) of Nd(III).[13] In this system, however, the intramolecular energy transfer efficiency (Φ_{tot}) was still low (< 35%), because the triplet state of the β-diketonato ligands did not have suitable energy to undergo efficient energy transfer to Nd(III), and so a large part of the excited triplet energy was lost by radiation as phosphorescence. We recently found that tris(8-quinolinolato)-neodymium(III) complex and halogen-containing complexes showed enhanced photosensitized luminescence in DMSO-d_6 solutions.[14] In the present paper, the photosensitized luminescence properties of these Nd(III) complexes are examined in detail and the efficiency of the intramolecular energy transfer is discussed because such complexes possess an appropriate triplet state energy around 17100 cm^{-1} (λ = 585 nm) in their lanthanide complexes.[15,16]

Experimental

Materials. The formulas and abbreviations for the four Nd(III) complexes discussed in the present study are shown in Fig. 1. Neodymium(III) nitrate hexahydrate (99.5%) and gadolinium(III) nitrate hexahydrate (99.5%) were purchased from Wako Pure Chemical Industries Ltd. Deuterated dimethylsulfoxide (DMSO-d_6, 99.9%) was obtained from Aldrich Chemical Co. Inc. All other chemicals were reagent grade and were used as received. All of the Nd(III) and Gd(III) complexes were synthesized by reactions of the corresponding ligands with neodymium or gadolinium nitrate hexahydrate in the presence of a small amount of aqueous ammonia in a water solution (pH = 7) at room temperature. The chemical



X	
H	$Nd(q)_3$
Cl	$Nd(Clq)_3$
Br	$Nd(Brq)_3$
I	$Nd(Iq)_3$

Fig. 1. Chemical structures of Nd(III) complexes.

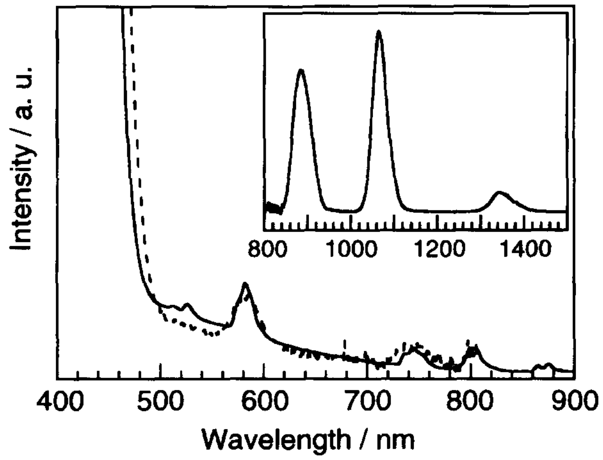


Fig. 2. Absorption (broken line) and excitation spectrum (solid line, λ_{em} = 1070 nm) of $[Nd(q)_3]$ in DMSO-d_6 (5 mM). The figure in the insert is the luminescence spectrum excited at λ = 425 nm.

components of all of the complexes were identified by FT-IR and elemental analyses.[17] DMSO-d_6 used as a solvent for optical measurements was degassed and dried by continuous stirring for 24 h in vacuo using calcium hydride. Further purification of the solvents was carried out by performing bulb-to-bulb distillation in vacuo two times.

Sample Preparation and Optical Measurements. The sample preparation for the optical measurements was carried out by the method reported previously as follows:[18] Well-dried Nd(III) complexes (5 μmol) were dissolved in 1 ml of purified anhydrous DMSO-d_6 in a quartz cell under vacuum (0.1 Pa). The concentration of the solutions was 5 mM. The optical path length of the cell for all the measurements was 10 mm.

UV-vis absorption spectra were recorded on a Hitachi Model U-3300 spectrophotometer in the 400—900 nm spectral range. Fluorescence and phosphorescence spectra in the 400—800 nm spectral range were recorded on a Hitachi Model F-4500 fluorescence spectrophotometer in EPA rigid glass solvent (ether : isopentane : ethanol = 5 : 5 : 2 volume) at liquid nitrogen temperature (77 K). Absorption band intensities of the *f–f* transitions were determined by integration of the areas of the bands and are presented as oscillator strength values P calculated according to the previously reported method.[19] Judd–Ofelt parameters Ω_t (t = 2, 4, and 6) were calculated using the six integrated absorption band intensities at λ = 500—900 nm on the spectra as we reported previously.[18]

Luminescence spectra in the near infrared region (800—1500 nm) at room temperature were obtained using a 500 W Xe lamp (JASCO, LH-X500) as a light source, a monochromator (JASCO, PS-H150) and a liquid nitrogen-cooled Ge detector. The luminescence lifetime of all samples was determined using a Q-switched Nd : YAG laser (Spectra-Physics, Quanta-Ray, DCR-2, 20 Hz, 20 mJ/pulse, fwhm = 7 ns, λ = 1064 nm), and a Si photodiode (Hamamatsu Photonics, S 3759 5H, time response $\leq$1 ns). A nanosecond pulse for sample excitation (λ = 532 nm, power = 1 mJ, diameter = 5 mm) was obtained by second harmonic generation using a KDP crystal. Luminescence from the samples was filtered by low-cut optical filters (Hoya, R66 and R68) that were placed in front of the detector. The response of the photodiode was monitored by a digital oscilloscope (Tectronix, TDS380P, 400 MHz) that was synchronized to single pulse excitation. The Quantum yield of the Nd(III) complexes was determined by ligand excitation and direct excitation of Nd(III) by the same procedure using an integral sphere (diameter 9 cm) as described in the previous study.[20]

Results and Discussion

Absorption Properties. The absorption spectrum of $[Nd(q)_3]$ in DMSO-d_6 is shown in Fig. 2. The large broad band edge observed below 500 nm was ascribed to the π–π* transition of quinolinolato ligand moiety. Five weak absorption bands were observed at λ = 500—520, 550—640, 730—770, 780—830, and 860—880 nm. These absorption bands are attributed to the Nd(III) *f–f* transitions of $^4I_{9/2}$ (ground state) $\rightarrow {}^4G_{7/2} + {}^2G_{9/2}$, $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^4S_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2} + {}^2H_{9/2}$, and $^4I_{9/2} \rightarrow {}^4F_{3/2}$, respectively. The transition probability of these transitions gave the information about the symmetrical structure in the solution. In particular, the $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ transitions are known as the hypersensitive transition of neodymium, which is peculiarly sensitive to changes in the coordination structure around the ion and of which the oscillator strength (P) is enhanced as the symmetry of the ligand field is reduced.[21,22] As seen in Table 1, three halogen-containing Nd(III) complexes: $[Nd(Clq)_3]$, $[Nd(Brq)_3]$, and $[Nd(Iq)_3]$, were found to have larger P values than $[Nd(q)_3]$. The symmetrical difference between $[Nd(q)_3]$ and the halogenated derivatives is due to their coordination number in DMSO-d_6 solution. The $[Nd(q)_3]$ and the halogen-containing complexes in solid state have one and two coordination water molecules, respectively, as confirmed by elemental analyses. In the DMSO-d_6 solution, the coordinating water molecules are exchangeable for the corresponding number of DMSO-d_6 molecules because the donor number of water (18.0) is smaller than that of DMSO (29.8).[7] So the $[Nd(q)_3]$ and the halogen-containing complexes are situated in

Table 1. Oscillator Strength of Absorption Bands and Judd–Ofelt Parameter of the Nd(III) Complexes

Complex	Oscillator strength $P \times 10^6$	Judd–Ofelt parameter / 10^{-20} cm^2 Ω_2	Ω_4	Ω_6
$[Nd(q)_3]$	48.7	21.81	6.28	12.17
$[Nd(Clq)_3]$	53.7	23.69	7.26	12.89
$[Nd(Brq)_3]$	53.0	24.71	6.37	12.31
$[Nd(Iq)_3]$	57.7	26.26	7.19	14.17

an asymmetric environment of the seven and eight (square antiprism)[23] coordinated structures, respectively, leading to lack of a center of symmetry in the coordination sphere. The increased transition probabilities of the halogen-containing complexes was considered due to their having a more reduced symmetric ligand field than $[Nd(q)_3]$ does. This fact was confirmed by Judd–Ofelt analysis. Changes in the Ω_t (t = 2, 4, and 6) parameters obtained in the analysis arise from the influence of the ligand field and chemical bonding properties around the Nd(III) center. The Ω_2 is particularly sensitive to changes in the ligand field of the complex, and a more asymmetric ligand field results in a greater increase in Ω_2. The Ω_2 value obtained from the halogen-containing complexes were larger than $[Nd(q)_3]$ (Table 1). These results suggest that one or two DMSO-d_6 molecules should coordinate to Nd(III) in all of the complexes.

The excitation spectrum obtained by monitoring the luminescence of $[Nd(q)_3]$ at λ = 1070 nm is also shown in the same spectral region as the absorption. Since the shape of the excitation spectrum is similar to that of the absorption spectrum, the efficient intramolecular energy transfer occurs from the excited quinolinolato moieties to the central Nd(III).

Near-Infrared Luminescence Properties. A photosensitized luminescence spectrum of $[Nd(q)_3]$ in DMSO-d_6 is shown in the insert of Fig. 2. The luminescence in the near-infrared region given by the excitation of the quinolinolato ligand moieties (λ_{EX} = 425 nm) consists of the three bands at λ = 884, 1065, and 1341 nm, which are attributed to the Nd(III) *f*–*f* transitions of $^4F_{3/2}$ (emitting level) $\rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively. The intensity of the luminescence at λ = 1070 nm was 42 times higher than that obtained by the direct excitation of Nd(III) at λ_{EX} = 585 nm. The halogen-containing Nd(III) complexes also showed the similar luminescence spectra to those of $[Nd(q)_3]$. However, all of the halogen-containing complexes showed a quantum efficiency of the photosensitized luminescence (Φ_{tot}) which was more than twice the value for $[Nd(q)_3]$. This result should be due to decreasing of high-vibrational C–H bonds which deactivate the excited $^4F_{3/2}$ state by their own vibrational excitation. In fact, the luminescence lifetime and the luminescence quantum efficiency (Φ_{Nd}) at direct excitation of central Nd(III) of the halogen-containing complexes gave larger values than those of $[Nd(q)_3]$ (Table 2).

Triplet State Energy. According to Crosby's study on the photosensitized luminescence of lanthanide(III) complexes, the energy transfer from the excited ligands to lanthanide ions takes place through their lowest triplet states.[15] This mechanism has been investigated by Bhaumic[24] and several other researchers.[25] The gadolinium (III) (Gd) complexes are selected for the determination of the triplet state energy of ligand moieties.[15,26] Figure 3 shows the energy diagrams of the 8-quinolinolato ligand, Nd(III) and Gd(III). The emitting level ($^6P_{7/2}$) energy of Gd(III) is much higher than the singlet state energy of the quinolinolato derivatives. Therefore the ligands can not sensitize Gd(III). The shortest phosphorescence band in the low-temperature phosphorescence spectrum was taken as the 0–0 transition of the triplet levels. As shown in Fig. 4 (solid line), the low temperature spectrum of $[Gd(q)_3]$ mainly consists of two luminescence bands, which are assigned to fluorescence (emission from the excited singlet state) at λ_{Flu} = 490 nm and phosphorescence (emission from the excited triplet state) at λ_{Phos} = 582 nm. All spectral data are listed in Table 3. The triplet energy of each quinolinolato derivative was found to be around 17100 cm^{-1}; thus, all of the complexes had suitable triplet state energy which agreed well with the energy accepting levels ($^4G_{5/2}$ and $^2G_{7/2}$) of Nd(III). In the present Nd(III) complexes, only fluorescence was observed in the low-temperature spectrum (Fig. 4, dotted line), indicating that the triplet energy should be quenched by Nd(III).

Overlap Integral. Since the intramolecular energy transfer from the triplet state of the organic ligand as a donor (D*) to the excited levels of the lanthanide ion as an ac-

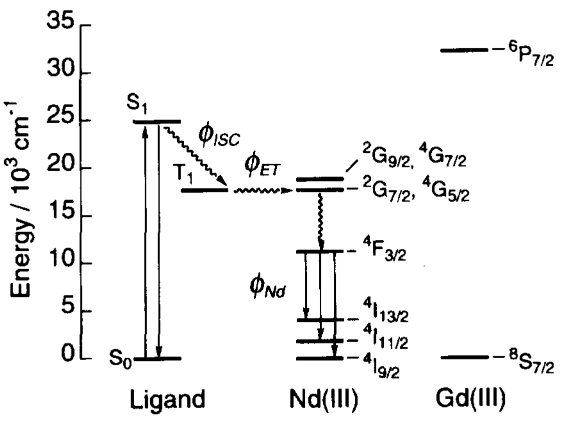


Fig. 3. Schematic energy structure and intramolecular energy transfer mechanism for the Nd(III) complexes.

Table 2. Luminescence Properties of the Nd(III) Complexes

Complex	λ_{Ex}/nm[a)]	λ_{Lum}/nm[a)]	Lifetime/μs[c)]	Efficiency/% Φ_{tot}[a)]	Efficiency/% Φ_{Nd}[b)]
$[Nd(q)_3]$	425	884, 1065, 1341	2	0.4	1.6
$[Nd(Clq)_3]$	448	892, 1072, 1355	3	1.0	3.7
$[Nd(Brq)_3]$	447	884, 1068, 1349	3	1.0	3.9
$[Nd(Iq)_3]$	447	886, 1070, 1348	3	0.9	4.4

a) Excitation of ligand moieties at λ = 425—448 nm. b) Excitation of Nd(III) at λ = 585 nm.
c) Excitation of Nd(III) at λ = 532 nm.

Table 3. Fluorescence and Phosphorescence Data of the Gd(III) and Nd(III) Complexes

Complex	λ_{Flu}/nm	λ_{Phos}/nm (energy/cm^{-1})	Complex	λ_{Flu}/nm	Overlap integral $J\times10^3$
[Gd(q)$_3$]	490	582 (17200)	[Nd(q)$_3$]	485	10.8
[Gd(Clq)$_3$]	486	601 (16600)	[Nd(Clq)$_3$]	479	8.0
[Gd(Brq)$_3$]	491	601 (16600)	[Nd(Brq)$_3$]	498	9.4
[Gd(Iq)$_3$]	489	605 (16500)	[Nd(Iq)$_3$]	499	7.2

All spectra were measured by the ligand excitation at λ = 425—448 nm in EPA at 77 K.

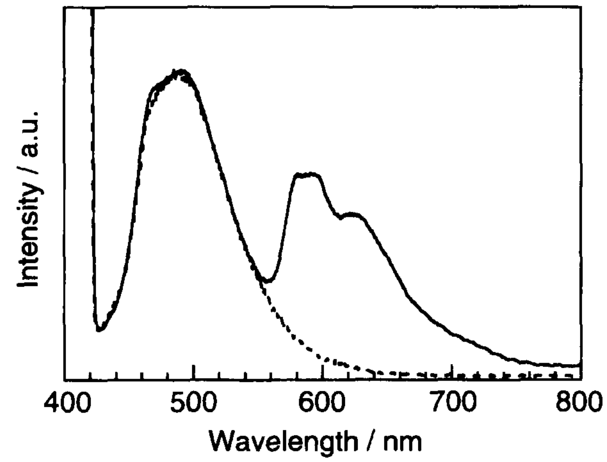


Fig. 4. Emission spectra in visible region of [Gd(q)$_3$] (solid line) and [Nd(q)$_3$] (dotted line) in EPA rigid glass solvent at low temperature (77 K). Both spectra were normalized at λ = 490 nm.

ceptor (A*) is of a spin-forbidden type, the energy is transferred by the resonant exchange interaction. According to the Dexter exchange-interaction theory,[27] the transition probability ($P(\mathrm{D}^* \rightarrow \mathrm{A}^*)$) for the energy transfer is proportional to the overlap integral of the spectra, J.

$$P(\mathrm{D}^* \rightarrow \mathrm{A}^*) = kz^2J, \quad (1)$$

$$J = \int f_{\mathrm{D}}(\lambda)\varepsilon_{\mathrm{A}}(\lambda)\mathrm{d}\lambda, \quad (2)$$

$$\int f_{\mathrm{D}}(\lambda)\mathrm{d}\lambda = \int \varepsilon_{\mathrm{A}}(\lambda)\mathrm{d}\lambda = 1, \quad (3)$$

where, kz^2 is a constant that is dependent on the mutual distance between the central ion and its coordinated atom. The overlap integral (J) is defined by Eq. 2, in which f_{D} is the phosphorescence spectrum of the ligand moiety, ε_{A} is the molar absorption coefficient of the lanthanide ion and λ is the wavelength. Therefore, in the present study, the integral $\int f_{\mathrm{D}}(\lambda)\varepsilon_{\mathrm{A}}(\lambda)\mathrm{d}\lambda$ represents the overlap between the experimental phosphorescence spectrum of the ligand moieties as an energy donor $f_{\mathrm{D}}(\lambda)$ and the experimental absorption spectrum of the central Nd(III) as an energy acceptor $\varepsilon_{\mathrm{A}}(\lambda)$ over the same spectral region. Thus, the functions $\int f_{\mathrm{D}}(\lambda)\mathrm{d}\lambda$ and $\int \varepsilon_{\mathrm{A}}(\lambda)\mathrm{d}\lambda$ are normalized as shown in Eq. 3. All normalized phosphorescence spectra used in the calculation of J were obtained from the differential spectra between Gd(III) complexes and Nd(III) complexes. The resulting J values are listed in Table 3. According to the results in the study of tris[bis(pentafluorobenzoyl)methanato]neodymium(III) with the overlap integral 1.5×10^{-3}, compared to the energy transfer efficiency of 34.7%. All of the complexes have very large J values which are sufficient to allow almost 100% intramolecular energy transfer.

Conclusion

Effectively photosensitized luminescence of Nd(III) in the near-infrared region was successfully observed in DMSO-d_6 solutions using tris(8-quinolinolato)neodymium(III) and three halogen-containing complexes. Their excited triplet energy determined from the corresponding Gd(III) complexes agree well with the energy accepting levels, $^4\mathrm{G}_{5/2}$ and $^2\mathrm{G}_{7/2}$, of Nd(III); the overlap integral between the phosphorescence spectrum of the ligand moieties and the absorption spectrum of Nd(III) gave very large value. The phosphorescence energy in all Nd(III) complexes was quenched completely by the energy transfer to Nd(III), and the highly efficient energy transfer was successfully achieved, giving remarkable photosensitized luminescence of Nd(III) in fluid organic solutions

The authors are grateful to Dr. T. Yatsuhashi, Department of Chemistry, Faculty of Science, Osaka City University, for the measurement of the luminescence lifetimes. We would also like to thank Daikin Chemical Co., Ltd. for the generous gift of fluorinated compounds. This study was supported in part by a Grant-in-Aid for Scientific Research (A) No. 06403023 from the Ministry of Education, Science, Sports and Culture, and by a Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists (to M. Iwamuro).

References

1 A. Heller, *J. Am. Chem. Soc.*, **89**, 167 (1967).

2 Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, and S. Yanagida, *Appl. Phys. Lett.*, **74**, 3245 (1999).

3 E. Soini and I. Hemmilä, *Clin. Chem.* (*N. Y.*), **25**, 353 (1979); E. G. Dickson, A. Pollak, and E. Diamandis, *Pharm. Ther.*, **66**, 207 (1995); H. Mikola, H. Takalo, and I. Hemmilä, *Bioconjugate Chem.*, **6**, 235 (1995).

4 A. Heller, *J. Am. Chem. Soc.*, **88**, 2058 (1966); G. Stein and E. Wurzberg, *J. Chem. Phys.*, **62**, 208 (1975).

5 J. A. Caird, A. J. Ramponi, and P. R. Staver, *J. Opt. Soc. Am. B*, **8**, 1391 (1991).

6 A. Beeby and S. Faulkner, *Chem. Phys. Lett.*, **266**, 116 (1997).

7 Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J.-H.

Kim, N. Nakashima, and T. Yamanaka, *Chem. Phys. Lett.*, **248**, 8 (1996); Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, and S. Yanagida, *J. Phys. Chem.*, **100**, 10201 (1996).

8 Y. Hasegawa, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, and S. Yanagida, *Chem. Phys. Lett.*, **260**, 173 (1996).

9 M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, and J. W. Verhoeven, *Chem. Phys. Lett.*, **276**, 196 (1997).

10 M. P. Oude Wolbers, F. C. J. M. Van Veggel, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 2275.

11 F. J. Steemers, W. Verboom, J. W. Hofstraat, F. A. J. Geurts, and D. N. Reinhoudt, *Tetrahedron Lett.*, **39**, 7583 (1998).

12 S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. Van Veggel, D. N. Reinhoudt, L. H. Slooff, A. Polman, and J. W. Hofstraat, *J. Appl. Phys.*, **86**, 1181 (1999).

13 M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, T. Kitamura, N. Nakashima, T. Yamanaka, and S. Yanagida, *Chem. Lett.*, **1997**, 1067; M. Iwamuro, Y. Wada, Y. Kitamura, N. Nakashima, and S. Yanagida, *Phys. Chem. Chem. Phys.*, in press.

14 M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura, and S. Yanagida, *Chem. Lett.*, **1999**, 539.

15 G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, **34**, 743 (1961).

16 W. P. Gillin and R. J. Curry, *Appl. Phys. Lett.*, **74**, 798 (1999).

17 Selected analytical data. Tris(8-quinolinolato)neodymium(III): IR (KBr) 3300—3500 (br., O–H), 1383 (C=N), and 1105 cm^{-1} (C–O). Anal. Found: C, 54.60; H, 3.30; N, 7.05%. Calcd for $C_{27}H_{18}N_3O_3Nd\cdot H_2O$ (as a monohydrate): C, 54.53; H, 3.39; N, 7.07%. Tris(5,7-dichloro-8-quinolinolato)neodymium(III): IR (KBr) 3300—3500 (br., O–H), 1375 (C=N), 1108 (C–O), and 958, 883 cm^{-1} (C–Cl). Anal. Found: C, 37.84; H, 1.87; N, 4.77%. Calcd for $C_{27}H_{12}N_3O_3Cl_6Nd\cdot 2H_2O$ (as a dihydrate): C, 39.58; H, 1.97; N, 5.13%. Tris(5,7-dibromo-8-quinolinolato)neodymium(III): IR (KBr) 3300—3500 (br., O–H), 1370 (C=N), 1105 (C–O), and 937, 859 cm^{-1} (C–Br). Anal. Found: C, 29.14; H, 1.41; N, 3.63%. Calcd for $C_{27}H_{12}N_3O_3Br_6Nd\cdot 2H_2O$ (as a dihydrate): C, 29.86; H, 1.48; N, 3.87%. Tris(5,7-diiodo-8-quinolinolato)neodymium(III): IR (KBr) 3300—3500 (br., O–H), 1368 (C=N), 1104 (C–O), and 921, 843 cm^{-1} (C–I). Anal. Found: C, 23.69; H, 1.19; N, 3.12%. Calcd for $C_{27}H_{12}N_3O_3I_6Nd\cdot 2H_2O$: C, 23.70; H, 1.18; N, 3.07%.

18 M. Iwamuro, Y. Hasegawa, Y. Wada, K. Murakoshi, N. Nakashima, T. Yamanaka, and S. Yanagida, *J. Lumin.*, **79**, 29 (1998).

19 W. T. Carnall, P. R. Fields, and B. G. Wybourne, *J. Chem. Phys.*, **42**, 3797 (1965).

20 K. L. Eckerle, W. H. Venable, Jr., and V. R. Weidner, *Appl. Opt.*, **15**, 703 (1976).

21 B. R. Judd, *Phys. Rev.*, **127**, 750 (1962).

22 G. S. Ofelt, *J. Chem. Phys.*, **37**, 511 (1962).

23 I. B. Liss and W. G. Bos, *J. Inorg. Nucl. Chem.*, **39**, 443 (1977); M. F. Richardson, W. F. Wagner, and D. E. Sands, *Inorg. Chem.*, **7**, 2495 (1968); M. Sayeed and N. Ahmad, *J. Inorg. Nucl. Chem.*, **43**, 3197 (1981); S. T. Frey, M. L. Gong, and W. De W. Horrocks, Jr., *Inorg. Chem.*, **33**, 3229 (1994); R. C. Holz and L. C. Thompson, *Inorg. Chem.*, **32**, 5251 (1993).

24 M. L. Bhaumic and M. A. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965).

25 F. Halverson, J. S. Brinen, and J. R. Leto, *J. Chem. Phys.*, **40**, 2790 (1964); M. Tanaka, G. Yamaguchi, J. Shiokawa, and C. Yamanaka, *Bull. Chem. Soc. Jpn.*, **43**, 549 (1970); W. M. Watson, R. P. Zerger, J. T. Yardley, and G. D. Stucky, *Inorg. Chem.*, **14**, 2675 (1975); J.-A. Yu, R. B. Lessard, L. E. Bowman, and D. G. Nocera, *Chem. Phys. Lett.*, **187**, 263 (1991); P. K. Sharma, A. R. Van Doorn, and A. G. J. Staring, *J. Lumin.*, **62**, 219 (1994); M. Latva, H. Takalo, K. Simberg, and J. Kankare, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 995; L. Ying, A. Yu, X. Zhao, Q. Li, D. Zhou, C. Huang, S. Umetani, and M. Matasai, *J. Phys. Chem.*, **100**, 18387 (1996); F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. Van der Tol, and J. W. Verhoeven, *J. Am. Chem. Soc.*, **117**, 9408 (1995); F. J. Steemers, H. G. Meuris, W. Verboom, D. N. Reinhoudt, E. B. Van der Tol, and J. W. Verhoeven, *J. Org. Chem.*, **62**, 4229 (1997); B. Yan, H.-J. Zhang, and J.-Z. Ni, *Chin. J. Chem.*, **15**, 243 (1997); E. B. Van der Tol, H. J. Ramesdonk, J. W. Verhoeven, F. J. Steemers, E. G. Kerver, W. Verboom, and D. N. Reinhoudt, *Chem. Eur. J.*, **4**, 2315 (1998).

26 M. L. Bhaumic and M. A. El-Sayed, *J. Phys. Chem.*, **69**, 275 (1965); S. Sato and M. Wada, *Bull. Chem. Soc. Jpn.*, **43**, 1955 (1970); B. Yan, H.-J. Zhang, S.-B. Wang, and J.-Z. Ni, *J. Chin. Chem. Soc.*, **44**, 567 (1997).

27 D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).