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Structure and Emission Properties of Er_3Q_9 (Q = 8-Quinolinolate)

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We report the first combined optical and structural investigation of the water free Er-quinolinolate complex, an organo-lanthanide system of interest for 1.5-μm telecom applications. Structural data demonstrate that the complex has a trinuclear structure (Er_3Q_9) which provides the Er metals with an octa-coordination by the organic ligand and prevents solvent and water molecules from entering the lanthanide coordination sphere. The results of the structural analysis allow us to infer that the strong Er luminescence quenching exhibited by the Er_3Q_9 complex is due uniquely to resonant energy transfer to the aromatic C–H vibrations of the ligand, providing the correct tools to design more efficient emitters.

Er-doped silica fibers are currently at the heart of the optical amplification technology used in the long-haul communication systems operating in the 1.5-μm spectral window. A drawback of this technology stems from the weak optical transitions of Er ions and their very low solubility in all inorganic matrices, resulting in long and expensive amplifiers. In the past decade, organo-Er complexes have been extensively investigated as a promising alternative. The attractiveness of these materials arises from their high solubility in plastic waveguides, the high absorption cross-sections in the visible, and the potential for electrical pumping. Such complexes could enable the realization of a new generation of low-cost optical amplifiers in the centimeter-length scale, featuring superior optical and mechanical figures of merit,[1] and are suitable for the fabrication of photonic integrated circuits.[1]

The erbium(III) organic complex ErQ_3, where Q is the anion of 8-hydroxyquinoline,[2] can be considered as a prototype organo-lanthanide system for 1.5-μm telecom applications and has gathered much attention especially after the demonstration of the first electrically excited organo-lanthanide IR emitter.[3] In order to enhance the emission efficiency of ErQ_3[3] (and similar complexes with 5,7-halogen substituted Q[4]), researchers have studied its properties in different solvents to evidence possible environmental effects. The interpretation of experimental results has so far relied on the common assumption of an Er mononuclear structure[5] with octahedral coordination geometry.[3,4] It is generally assumed that, in this unsaturated structure, the Er coordination sphere is easily fulfilled by water molecules, which are supposed to be the most important IR quenchers especially when present in the first coordination sphere. In this report, we show the first combined structural and optical investigation of the Er(III) complex of 8-hydroxyquinoline ligand prepared as described in footnote 6. To the best of our

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(1) (a) Kuriki, K.; Koike, Y.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2347–2356. (b) 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. *J. Appl. Phys.* **2002**, *91*, 3955–3979.

(2) The corresponding AlQ_3 complex, used as an electron-transport emitting layer, represents a milestone in the development of organic light-emitting diodes, since this compound provides an excellent combination of stability and efficiency. Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161–174.

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(5) X-ray data obtained on low-crystallinity ErQ_3 are reported in the following: Magennis, S. W.; Ferguson, A. J.; Bryden, T.; Jones, T. S.; Beeby, A.; Samuel, I. D. W. *Synth. Met.* **2003**, *138*, 463–469.

(6) The synthesis follows: a few drops of NH_3 28% were added to a mixture of HQ (0.157 g, 1.08 mmol) in H_2O (100 mL) under mixing. After 30 min, a water solution of $Er(NO_3)_3{\cdot}5H_2O$ (0.160 g, 0.361 mmol) was added to the above mixture, which is allowed to react for 2 days. A yellow precipitate is formed, collected by filtration, washed with water, NaOH 0.1 M, and water, and dried in the oven. Analytical results agree with the $ErQ_3{\cdot}H_2O$ formulation. This solid was dissolved in hot CH_3CN, the solvent was rotary evaporated to incipient precipitation, and yellow crystals of $Er_3Q_9{\cdot}CH_3CN$ were obtained (yield 46%). IR spectra of the products before and after crystallization are superimposable, except for the peaks due to water.

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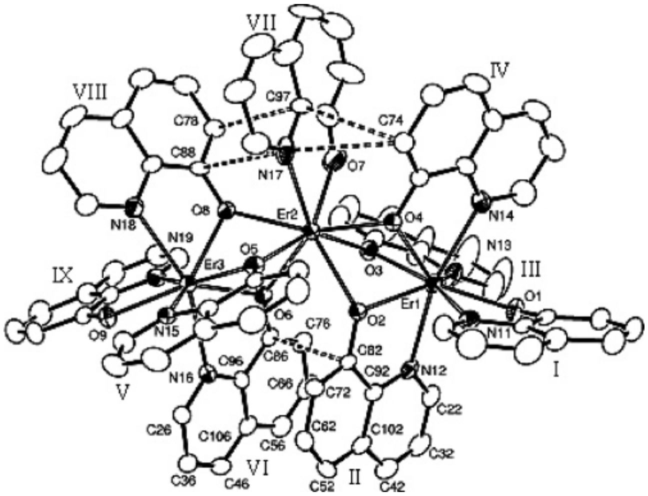

Figure 1. Perspective view of Er_3Q_9. Dashed bonds represent π interactions. Thermal ellipsoids are drawn at the 25% probability level.

knowledge, this is the first X-ray structure of lanthanide (Er, Nd, Gd) quinolinolate (and similar 5,7-halogen ligands) complexes, despite the several reports on their optical properties.[1,3−5,7] The X-ray data analysis of the obtained Er-quinolinolate crystals[8] shows that the trinuclear complex Er_3Q_9 depicted in Figure 1 is formed. Each metal presents a distorted antiprismatic geometry with the two outer metals bound by four nitrogen and four oxygen atoms whereas the inner erbium is coordinated by a nitrogen and seven oxygen atoms [bond length ranges: $Er-O_{bridge} = 2.306(4)-2.480(3)$ Å, $Er-O = 2.243(5)-2.276(3)$ Å, $Er-N = 2.456(5)-2.533(7)$ Å]. The molecule is bent [Er(1)−Er(2)−Er(3) angle = 133.48(1)°], and in the inner pocket the II and VI quinolinolate anions are π stacked [II−IV dihedral angle = 2.0(1)°]. The minimum distance is exhibited by the C(82) and C(86) atoms (3.201(3) Å). On the opposite side of the molecule, the VII quinolinolate is also interacting with the IV and VIII quinolinolate anions [minimum distances: N(17)−C(74) = 3.155(8) Å and N(17)−C(88) = 3.067(7) Å], but the quinolinolate molecules are skewed with respect to each other with the dihedral angles between the planes of 34.7(1)° (IV−VII) and 30.2(1)° (VII−VIII).

The ESI-mass spectrum[9] (Figure 2) shows that the trinuclear structure is preserved in solution, and this result is in agreement with UV−vis−NIR spectroscopic results which show that DMSO (dimethyl sulfoxide) solution and solid sample spectra (diffuse reflectance = DR) exhibit similar features.

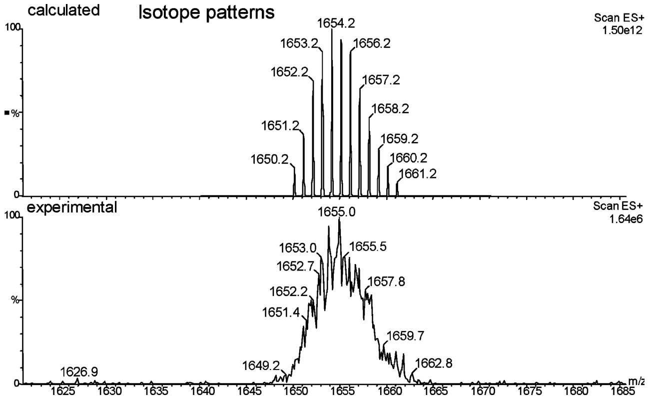

Figure 2. Expanded region of the ES(+) mass spectrum of Er_3Q_9 in CH_3CN/MeOH, 3/1; m/z $[Er_3Q_8]^+$= 1654.98.

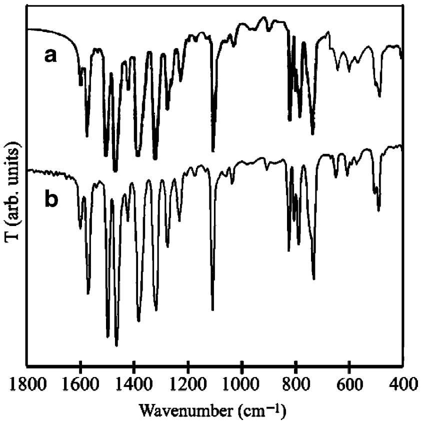

Figure 3. Infrared spectra [cm^{-1}, KBr pellets] of ErQ_3 (a, taken from ref 10) and of Er_3Q_9 (b, this work). Transmittance is in arbitrary units.

We point out that the infrared spectrum of Er_3Q_9 matches the literature spectrum assigned to ErQ_3,[10] as shown in Figure 3. This suggests that the common assumption of an ErQ_3 mononuclear structure[5] with octahedral coordination geometry based on analytical and IR spectral characterization needs revision. To date, the formation of polynuclear complexes with increased lanthanide coordination numbers through bridging of quinolinolate ligands had never been taken into consideration either for erbium or similar lanthanide complexes (neodimium[7] and gadolinium[4]), although the synthesis of other polynuclear organo-lanthanide complexes is not uncommon.[11]

The Er emission spectrum and decay dynamics are investigated in Er_3Q_9 crystals by spectrally resolved and time-resolved optical spectroscopy. Figure 4 displays continuous-wave (CW) DR and photoluminescence (PL) spectra taken on Er_3Q_9 crystals.[12]

Optical absorption and emission from the Er(III) ions are shown to occur near 1.52 μm, corresponding to the $^4I_{15/2} \leftrightarrow$

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(7) Khreis, O. M.; Curry, R. J.; Somerton, M.; Gillin, W. P. *J. Appl. Phys.* **2000**, *88*, 777−780.

(8) Data collection was performed on a Bruker AXS Smart 1000 area detector diffractometer (Mo Kα; $\lambda = 0.71073$ Å). Structure solution was by direct methods and refined on F^2. Crystal data follow: formula $C_{83}H_{57}Er_3N_{10}O_9$, crystal size $0.15 \times 0.10 \times 0.10$ mm³, triclinic $P\bar{1}$, $a = 12.352(1)$ Å, $b = 16.775(1)$ Å, $c = 18.199(1)$ Å, $\alpha = 83.488(1)°$, $\beta = 79.302(1)°$, $\gamma = 83.831(1)°$, $V = 3667.0(4)$ Å³, $Z = 2$, $F(000) = 1802$, μ(Mo Kα) = 3.468 mm⁻¹. Least-squares refinement based on 8675 reflections with $I > 2\sigma(I)$ gave final $R = 0.0390$ and $R_w = 0.0487$. Acetonitrile solvent molecules were severely disordered and were treated using the SQUEEZE PLATON program.

(9) Mass spectra were obtained with a Micromass ZMD spectrometer; experimental details and the full spectrum are reported as Supporting Information.

(10) Aly, H. F.; Abdel Kerim, F. M.; Kandil, A. T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4340−4344.

(11) Hyeon, J.-Y.; Edelmann, F. T. *Coord. Chem. Rev.* **2003**, *247*, 21−78.

(12) CW PL was excited using a UV single line (near 350 nm) of an Ar-ion laser. A pump fluence of ~1 W/cm² was used at normal incidence. Measurements were made at room temperature in inert (He) atmosphere. The PL signal was dispersed in a single spectrometer (with an 8-nm band-pass), detected by an amplified InGaAs detector, and analyzed using a lock-in amplifier. CW DR spectra were taken on Er_3Q_9 crystals dispersed in KBr, using a Cary 5 spectrophotometer equipped with a diffuse reflectance accessory

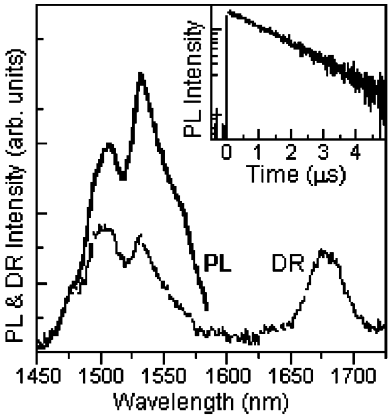

Figure 4. Main panel: CW photoluminescence (thick solid line labeled as PL) and diffuse reflectance (thin solid line labeled as DR) spectra of crystalline powder of Er_3Q_9. Inset: Er(III) PL time decay curve.

$^4I_{13/2}$ transition manifolds. The spectra show evidence of Stark splitting of the level manifolds[13] induced by the local electric field acting on the metal ions. The two inequivalent coordination configurations within the Er_3Q_9 complex also contribute to the (inhomogeneous) broadening of the Stark-split lines.

The DR and PL spectra are very similar in shape, with small variation in relative intensity between the Stark lines: the stronger PL band at 1530 nm is rationalized in terms of spectral diffusion of the metal-ion electronic excitations toward low-energy states. The peak observed in DR near 1680 nm is attributed to absorption by the first overtone of the stretching mode of the aromatic C−H groups of the quinolinolate molecules ($\nu = 3047\ \text{cm}^{-1}$), whereas no absorbance by O−H vibrations is detected. Thus, the combined structural and spectroscopic results allow us to ascribe the Er luminescence quenching in the Er_3Q_9 complex uniquely to the aromatic C−H vibrations of the ligand. The Er emission dynamics following ultrafast photoexcitation of the quinolinolate ligands is shown in the inset of Figure 4.[14] The emission build-up occurs in the time scale of a few nanoseconds. Although there are two unequivalent coordination sites in the trinuclear complex, nearly single-component decay is observed within the available dynamic range. Er intrinsic deactivation toward the aromatic C−H groups occurs with a time constant of 2.2 μs, at least 3 orders of magnitude faster than the radiative lifetime of this emission, in agreement with previous reports.[1] Measurements made in nondeuterated DMSO degassed solutions of Er_3Q_9 (1.0×10^{-3} M) show very similar results with nearly the same PL lifetime. The experimental decay time is consistent with the transfer time (2 μs) from the Er ions to the aromatic C−H groups of the ligand calculated in the framework of the Förster's resonance energy transfer theory[15] applied to the trinuclear molecular structure shown in Figure 1. The nearly single-exponential behavior can be explained considering that Er−Er energy migration within an Er_3Q_9 molecule occurs in the 10-ns time scale according to Förster's theory, much faster than the Er nonradiative decay time; as a result, Er excitations are effectively delocalized over the three metal ions and experience only a coordination configuration average.

In conclusion, we studied for the first time the structural and emission properties of the Er_3Q_9 trinuclear complex, in which the Er metals are fully coordinated by the quinolinolate (Q) ligand molecules. Resonant activation of aromatic C−H vibrations of the ligand by the Er electronic excitations is inferred to be the only cause of IR luminescence quenching near 1.5 μm and to yield the Er PL lifetime of 2.2 μs, which is in agreement with both other groups' experimental results and our model calculations based on Förster's resonance energy transfer theory. These findings allow us to draw the general conclusion that the aromatic C−H groups sitting in the Er inner coordination sphere represent an ultimate, though very severe, limit to the IR emission yield of organo-Er complexes, where O−H and other vibration modes do not come into play. Moreover, our results provide a sound framework for the design of new complexes with enhanced emission efficiency. For this purpose, several candidates[1,16] under investigation appear to be promising.

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Supporting Information Available: X-ray data for $Er_3Q_9{\cdot}CH_3CN$ as CIF file (CCDC-246193), structural and characterization details, and ESI-mass data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Polman, A. *J. Appl. Phys.* **1997**, *82*, 1−39.

(14) Transient PL measurements were carried out using 150-fs-long pulses at 380 nm (obtained by frequency doubling the output pulses of a Ti:sapphire-based amplified laser system operating at the repetition frequency of 1 kHz) as the excitation source. The samples were excited at normal incidence with a fluence of ≈10 mJ/cm², at room temperature. The laser and visible frequencies were cut using color-glass filters, and the optical signal in the 1.5-μm region was detected using an amplified InGaAs photodiode with a response time of less than 2 ns, and averaged using a digitizing scope.

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