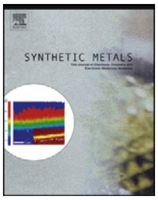
Synthetic Metals 161 (2012) 2693–2699

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Predictive modeling of the vibrational quenching in emitting lanthanides complexes

Angelo Monguzzi[a,*], Alberto Milani[b], Agniezka Mech[a], Luigi Brambilla[b], Riccardo Tubino[a], Carlo Castellano[c], Francesco Demartin[c], Francesco Meinardi[a], Chiara Castiglioni[b]

[a] Dipartimento di Scienza dei Materiali, Università Milano Bicocca, via. R. Cozzi 53, 20125 Milano, Italy
[b] Dipartimento di Chimica, Materiali, Ing. Chimica "G. Natta", Politecnico di Milano, P.zza L. Da Vinci 32, 20133 Milano, Italy
[c] Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, Via G. Venezian 21, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 29 June 2011
Received in revised form 2 September 2011
Accepted 1 October 2011
Available online 22 October 2011

Keywords:
Near infrared emitters
Lanthanides complexes
Emission quenching
Vibrational intensities

ABSTRACT

Organic complexes of lanthanides trivalent ions such as Nd^{3+} and Er^{3+} are receiving increasing attention in view of their use as dopants in polymeric telecommunication devices. Their employment is however currently limited by their small emission quantum yield (QY) due to non-radiative deactivation of near infrared (NIR) transitions through electronic-vibrational energy transfer (ET). A complete modeling of this quenching effect is presented here and successfully tested on a purpose-made Er^{3+} complex. This method provides "a priori" information/predictions regarding the emission properties of new complexes thus establishing useful guidelines for the design and synthesis of new molecules and for the engineering of materials suitable in technological applications.

1. Introduction

Lanthanide complexes exhibit narrow emission bands originating from forbidden 4*f* intrashell transitions of metal ions responsible for their luminescent properties. In organic fluorescent compounds, the energy of the triplet state is usually degraded through thermal deactivation processes without photon emission. Thus, the internal quantum efficiency for devices operating with organic fluorescent compounds is limited to 25%. In contrast, for lanthanide complexes with π-conjugated ligands, lanthanide ions are excited via intramolecular ET from singlet and triplet excited states of the ligands. Thus, there is no limitation, up to 100%, of the internal quantum efficiencies for devices using lanthanide ion chelates as emitters [1,2].

Neodymium (Nd^{3+}) and erbium (Er^{3+}) trivalent ions are currently used as near infrared emitting active elements in devices due to their transitions at 1340 nm (Nd^{3+}, $^4I_{13/2} \rightarrow {}^4F_{3/2}$) and 1530 nm ($Er^{3+}$, $^4I_{13/2} \rightarrow {}^4I_{15/2}$). In the last years, many studies have been focused on finding novel and cheap gain materials in the 1.53 μm window for integrated optoelectronic devices based on Er^{3+} ions emission to be used in telecom applications [3]. To this end, polymeric matrices have been considered because they possess several advantages (in respect of their silica counterparts) like low-cost, flexibility, high packaging density and simple processing steps. They can be doped by Er^{3+} complexes, which provide the desired emission wavelength and possess the solubility necessary to avoid quenching effects even at high concentrations. Moreover, thanks to their large absorption cross section, organic ligands work as light harvester for the lanthanide ion, indirectly excited by energy transfer (ET), thus circumventing the problems related to the weak and narrow (forbidden) transitions typical of lanthanides ions and therefore the need to use high power pump lasers for Er^{3+} direct optical excitation at 980 and 1480 nm. At these excitation wavelengths, excited-state absorption is a factor strongly limiting the optical gain, apart from the fact that such pump lasers constitute a significant fraction of the cost of a NIR optical amplifier.

The principal limiting factor in NIR emitting Er^{3+} complexes is the very low photoluminescence (PL) quantum yield (QY); the conclusions of several studies on rare-earth ions luminescence quenching in organic solutions and inorganic glasses have established that culprit for this low efficiency is the presence of nearby high-energy vibrational centers, in particular O–H and C–H bonds [4–14]. These bonds play a major role in the quenching process, since their first overtones are resonant with the erbium emission transition. Vibrational modes such as the oxygen/lanthanide bond are ineffective, in spite of their proximity to the Er atom, because of their low (less than 500 cm^{-1}) and weak stretching fundamental frequency. For these bonds, more than ten vibrational quanta are necessary to match the ion transition energy, thus making the transfer ineffective. Also other higher energy vibrational modes

---

[*] Corresponding author.
E-mail address: angelo.monguzzi@mater.unimib.it (A. Monguzzi).

0379-6779/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2011.10.002

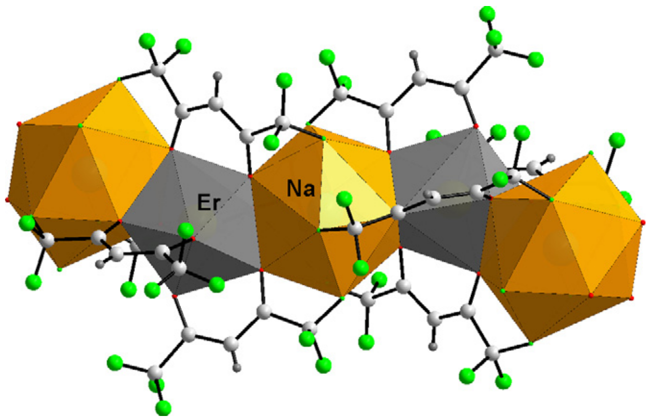


Fig. 1. A portion of the polymeric structure of the $Er(C_5HO_2F_6)_4Na$ complex.

usually present in organic molecular structures, such as C=O and C=C stretching, require more than two vibrational quanta to meet the resonance conditions necessary to conserve energy in the transfer process (see Fig. 1 in Ref. [21]).

The physical mechanism responsible for this quenching is generally identified with a dipole–dipole energy transfer from the electronically excited ion towards the high energy states (overtones) of the vibrational center. High frequency vibrations such as O–H and C–H bonds most liable for this effect are generally present as functional groups of the organic ligand and/or as residual water (or solvent) molecules from the chemical synthesis of the complexes. The effectiveness of this adverse non-radiative deactivation is clearly indicated by the NIR photoluminescence lifetime of the Er^{3+} ion, which from the value of $\sim 10^{-3}$ s typical in inorganic solids, drops to $\sim 10^{-6}$ s or less in most organic complexes. Understandably, much recent experimental efforts in this field have been devoted to the synthesis of O–H and C–H free complexes by halogenation and by avoiding contaminations by water during the synthesis. By using this strategy, very recently it has been possible to achieve lifetimes of up of $\sim 3 \times 10^{-4}$ s and QY of about 2% for Er ions [15–18].

It should be stressed that (i) the synthesis of fully-fluorinated complexes is chemically cumbersome and (ii) even if such compounds can be obtained they are more sensitive and unstable compared to their un-halogenated counterparts because of the electron-withdrawing properties of halogenated groups. Guidelines for the chemical design of new highly efficient emitters can be in principle obtained by a proper modeling of the non radiative quenching processes exerted onto the ion by the ligand. In this paper we will present a theoretical model for the quenching based on “a priori” calculations which will be tested on a purpose-made Er^{3+} complex, and it will be shown how starting from the molecular structure of the selected compound its luminescence QY can be predicted with good accuracy.

2. Model and discussion

The mechanism of non-radiative quenching in lanthanide ions implies electromagnetic coupling between the downward electronic transition of the lanthanide ion and the oscillator of the vibrational transitions of groups surrounding the ion with energy matching the electronic transition [19–25]. This coupling can be described within the framework of the dipole–dipole Förster energy transfer (ET), with the difference that in this case the energy acceptor is a vibrational oscillator. By considering the number g_i of energy acceptors A_i in close proximity to the emitting ion, their relative distance (R_{A_iD}) and the radiative lifetime τ_{rad} of the ion transition, the transfer rate k_{ET} can be written as

$$k_{ET} = \sum_i \frac{g_i}{\tau_{rad}} \left(\frac{R_0}{R_{A_iD}} \right)^6 . \qquad (1)$$

R_0 is the Förster radius, a characteristic parameter of each donor–acceptor system which depends on the transition dipoles and on the spectral overlap between donor emission and acceptor absorption by $R_0 = 0.21\,[\theta^2 n^{-4} Q_D J(\upsilon)]^{1/6}$, where n is the refraction index of the material, θ is the factor which considers the reciprocal spatial orientation of the dipole moments involved in the transfer and Q_D is the donor emission QY. The overlap integral $J(\upsilon) = \int F_D(\upsilon)\varepsilon_A(\upsilon)(c/n\upsilon)^4 d\upsilon$, where $F_D(\upsilon)$ is the normalized erbium emission spectrum and $\varepsilon_A(\upsilon)$ is the vibrational absorption coefficient of the quencher, is the index of the effective resonance between the transitions involved (c is the speed of light). By assuming that the quencher absorption spectrum can be approximated by a lorentzian shape, $J(\upsilon)$ can be expressed as a function of the vibrational transition moments $\mathbf{M}_{0n}$ by

$$J(\upsilon) = \int \left(\frac{c}{n\upsilon_{PL}} \right)^4 F(\upsilon)\Gamma(\upsilon) d\upsilon \left(\frac{4\pi^3 \upsilon_{0n}}{3\hbar\varepsilon_0 c^2} \right) \left| M_{0n} \right|^2 \qquad (2)$$

where $\Gamma(\upsilon) = (\Delta\upsilon/2\pi)[(\upsilon - \upsilon_{0n})^2 + (0.5\Delta\upsilon)^2]^{-1}$ is the normalized Lorentz function, υ_{PL} is the frequency of the ion emission peak, υ_{0n} is the frequency of the resonant vibrational absorption and $\Delta\upsilon$ is the full width at half maximum (FWHM) of the peak. Therefore, in order to make a quantitative prediction of the extent of the non-radiative decay originating from ET, the transition moments $\mathbf{M}_{0n}$ of the vibrational overtones in resonance with the electronic transition of the ion considered must be evaluated. An analytical model has been developed to calculate the intensities of the overtone bands based on the knowledge of the intensities of the associated fundamental transitions, thus obtaining the following recurrent relationship [20,21].

$$\frac{\left| \mathbf{M}_{0n} \right|^2}{\left| \mathbf{M}_{01} \right|^2} \approx \frac{n!}{n^2} x_e^{n-1} . \qquad (3)$$

This model introduces the effect of mechanical anharmonicity x_e in the local mode approximation, while neglecting electrical anharmonicity. Based on Eq. (3) and by considering an anharmonic constant of 0.0190 for the C–H bond, one finds the following relationship involving the square of the transition dipole $\mathbf{M}_{01}$ which rules the intensity of the fundamental and that of the first overtone $\mathbf{M}_{02}$,

$$\left| \mathbf{M}_{02} \right|^2 \approx 0.5 x_e \left| \mathbf{M}_{01} \right|^2 \approx 0.0095 \left| \mathbf{M}_{01} \right|^2 \qquad (4)$$

The transition dipole of the fundamental vibration can be estimated from the associated IR intensity $A = (1/Cd)\int \ln(I_0/I) d\upsilon$ as [26,27]:

$$A = \frac{1}{cd} \int \ln\left(\frac{I_0}{I} \right) d\nu = \xi \left| \mathbf{M}_{01} \right|^2 \left(\frac{2\omega}{\hbar} \right) = \xi \left| \frac{\partial \mathbf{M}}{\partial \mathbf{Q}} \right|^2 \qquad (5)$$

The quantity A can be computed with good accuracy by Density Functional Theory calculations (DFT), thus providing a tool for a screening (solely based on theoretical predictions) among many different organic ligand on the basis of their quenching efficiency. To demonstrate the predictive capability of the model proposed in the following section we will estimate the PL yield of a purpose-made Er^{3+} complex and compare the results of the calculation with experimental data.