

## Novel lanthanide complexes for visible and IR emission

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### Abstract

In this work we report the synthesis and photophysical properties of a novel ligand and its lanthanide complexes based on macrocycle 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid bearing 8-hydroxyquinoline as antenna. Visible and IR sensitized emission is obtained because of the efficient energy transfer from the antenna to the emitting ion. The interaction between ions and antenna is accounted for by suitable quantum chemical calculations. The good stability of the complexes and their solubility in organic solvents make them good candidates for the fabrication of plastic waveguides and optical amplifiers.

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### 1. Introduction

Organic semiconductors are innovative materials for a new generation of low-cost, technologically advanced devices, which encompasses light emitting diodes, thin film transistors, photodetectors and solar cells. Their use in optical telecommunications is also quite attracting, but efficient IR emission from organic semiconductors is not easy to obtain. The use of organolanthanides has been attracting increasing interest since devices based on erbium for 1.5  $\mu\text{m}$  emission, neodymium for 0.9, 1.0 and 1.3  $\mu\text{m}$  emission and ytterbium for 0.98  $\mu\text{m}$  emission have been demonstrated [1,2]. Significant technological improvements can be expected by using these materials since their solubility in common organic solvents allows their incorporation in polymeric matrices in concentration ( $10^{21}$  ions/cm<sup>3</sup>) higher than that in glass or semiconductor hosts ( $10^{19}$  ions/cm<sup>3</sup>). This in principle allows the fabrication of plastic optical amplifiers of a few centimetres in length for low-cost optical links.

Moreover, as the excited state levels of the emitting ion are populated by an intramolecular energy transfer from the optically excited ligand [3], which acts as an efficient light-harvesting antenna, both direct (in the infrared) and indirect (in the ligand absorption band in the near UV–vis) pumping is possible. The use of organic ligands can then overcome the low absorption coefficient of the lanthanides, thus reducing the pumping threshold. As both the absorption of the organic ligand and the emission of the lanthanide ion can be tuned, a variety of materials exhibiting a wide range of optical properties can be envisaged and has indeed been prepared, thus providing access to all the three IR transparency spectral windows of interest for telecommunications.

In order to manipulate optical signals, several components with different functions, like splitters, switches and (de-) multiplexers are integrated on small substrates. Plastic optical fibers have clear technical advantages over glass fibres such as flexibility and a large core diameter, which enables efficient connection for a local area network. Low loss (100 db/km) optical fibers, which can be used between 500 and 1300 nm, have been successfully prepared [4,5]. The bases of these integrated devices are planar optical waveguides that consist of

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a high refractive index material embedded in materials with a lower refractive index. Light is guided through the high refractive index material (the core) as a result of the total internal reflection at the interface. In many cases, the integrated optic devices are based on organic polymeric materials deposited on proper substrates (silicon wafers; silica) by spin coating from solution and patterns can be created with standard lithographic techniques.

Furthermore, high refractive index contrast can be achieved with different polymers thus producing a strong confinement of the light in the core of the guide and relatively strong bends are possible without too large losses. Each manipulation of the signal may result in intensity losses and the on-chip integration of optical amplifiers with other components is therefore desired. The most important optical amplifier for long distances is  $\text{Er}^{3+}$ -doped fibre amplifier and also other lanthanide ions such as  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  are used.

In integrated optics it would be convenient to incorporate the lanthanide ions in the device. The inorganic lanthanide salts cannot be dispersed into an organic matrix. A way to do so is to solubilize or disperse the lanthanide ion in organic polymers by exploiting the good solubility of lanthanide chelates in common organic solvents. Moreover, ligands with suitable electrical transport properties offer the opportunity for excitation of the lanthanide ions via electroluminescence, thus allowing the possibility of electrical pumping.

In this paper, novel lanthanide complexes possessing high stability constant ( $10^{20}$ ) combined with good thermal and chemical behaviour are reported. They exhibit an efficient energy transfer from the light-harvesting antenna to the emitting ion both in the IR and visible spectral region. Their photophysical properties are accounted for by suitable quantum chemical calculations.

## 2. Experimental results and discussion

Among the large number of ligands already used, those based on the macrocycle 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) bearing a phenanthroline moiety [6] have attracted our attention. This ligand has an interesting characteristic: the macrocycle saturates seven of nine coordination sites of rare earths thus increasing the stability of the complex. By using the same structural motif, namely to saturate the coordination sphere of the ion with a macrocycle bearing a light-harvesting antenna, a novel ligand bearing 8-hydroxyquinoline as antenna has been synthesized. Details of the synthesis will be published elsewhere [7].  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$  complexes have been prepared by mixing the ligand and the lanthanide salt in water solution, keeping the pH around 7. The complexes are soluble in common polar organic solvents, including water. Fig. 1 shows a sketch of the molecular structure of the ligand and of its complexes.

Figs. 2 and 3 show the absorption and emission spectrum of the complexes with  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$ , respectively. Both the absorption spectra show a broad absorption at 360 nm and

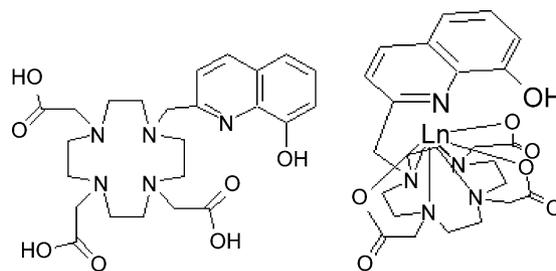


Fig. 1. Molecular structure of the ligand (left) and of its lanthanide complexes (right).

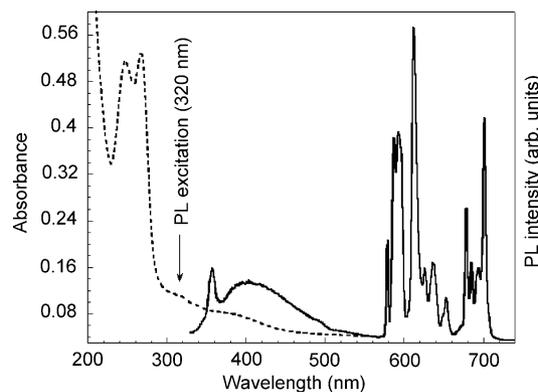


Fig. 2. Absorption (dotted line) and emission (full line) spectra of the  $\text{Eu}^{3+}$  complex. The sharp peak superimposed to the ligand emission is the Raman scattering from water solvent.

sharper bands below 300 nm which arise from the electronic transitions of the ligand. At this concentration ( $10^{-5}$  M) ion absorption is not detected. Emission spectra, which have been obtained by exciting at 320 nm for the Eu complex and 360 nm for the Er complex, contain both the typical sharp emission peaks of the lanthanides in the red and in the IR and the broad and structureless emission from the lowest singlet state of the ligand at 400 nm. The presence of this latter emission is indicative of an incomplete energy transfer to the excited levels of the ion. Energy transfer from the light-harvesting antenna to the emitting ion can take place through two different mechanisms.

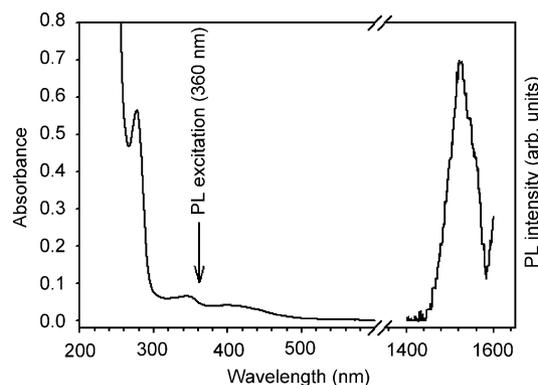


Fig. 3. Absorption (left) and emission (right) spectra of the  $\text{Er}^{3+}$  complex.

1. Short range exchange Dexter transfer in the region of the spatial overlap between the wavefunction of the  $\pi$  electrons of the antenna and the f electrons of the ion.

In this case the transfer probability  $W_{\text{ex}}$  by exchange interaction can be written as [8]:

$$W_{\text{ex}} = \frac{1}{\tau} \exp \left[ \frac{2R_0}{L} \left( 1 - \frac{R}{R_0} \right) \right] \quad (1)$$

with

$$\frac{\exp(2R_0/L)}{\tau} = \frac{2\pi}{\hbar} K^2 \int f_{\text{D}}(E) f_{\text{A}}(E) dE \quad (2)$$

where  $\tau$  is the life time of the excited state of the ligand in absence of the transition metal,  $L$  the Bohr radius,  $R$  the distance between the ligand and the transition metal ion and  $K$  a constant with the dimension of an energy.  $f_{\text{D}}(E)$  and  $f_{\text{A}}(E)$  are the normalized donor (D) emission and acceptor (A) absorption, respectively.

Eq. (1) shows that a high transfer rate is obtained when donor and acceptor are in close contact each other in order to allow an exchange interaction. This latter condition is fulfilled in the case of intramolecular energy transfer as in the present metallorganic complexes, in which the D–A distances are in the range of few Å. This is usually the main energy transfer mechanism between triplet states because the efficiency of this process is independent from the oscillator strength of the involved electronic transitions.

2. Long range dipole–dipole coupling (Förster), which involves transfer from dipole-allowed excited singlet states. In this case the transfer rate is given by [9]:

$$W_{\text{DA}} = \frac{1}{\tau_{\text{D}}} \left( \frac{R_0}{R} \right)^6 \quad (3)$$

with

$$R_0^6 = \frac{9\chi^2 \ln 10 c^4 \Phi_0}{128\pi^5 n^4 N} \int_0^\infty f_{\text{D}}(\nu) \varepsilon_{\text{A}}(\nu) \frac{d\nu}{\nu^4} \quad (4)$$

where  $R_0$  is the Förster radius defined in terms of the usual parameters, namely  $\chi$  the orientational factor,  $N$  the number of molecules,  $\Phi_0$  the luminescence quantum yield of the antenna,  $n$  the refractive index,  $f_{\text{D}}$  the (normalized) emission spectrum of the antenna and  $\varepsilon_{\text{A}}$  the extinction coefficient of the transition metal ion.

In the complex we are investigating, both these mechanisms account for the observed energy transfer to the transition metal ion which can take place from the lowest singlet excited state  $S_1$  and the lowest triplet excited state  $T_1$  of the antenna, provided that there is a good spectral overlap between the lowest excited states  $S_1$  and  $T_1$  of the donor, on which the excitation is funnelled after thermalization, and some excited levels of the emitting ion. In the present case, the lowest excited state of the 8-hydroxyquinoline are located at 2.2 eV for the  $T_1$  state and at 3.35 eV for the  $S_1$  state [10] so that a good spectral overlap is found with the  $^5D_0$

and  $^4F_{9/2}$  for the exchange transfer to the  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$ , respectively, and with the  $^5D_4$ ,  $^5G_6$  and  $^2H_{9/2}$  for dipole transfer to  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$ , respectively [11]. It is noticeably that the infrared photoluminescence quantum efficiency of the  $\text{Er}^{3+}$  complex is comparable with that of the  $\text{ErQ}_3$  [Er(III) tris(8-hydroxyquinoline)], that is actually the benchmark for this kind of complexes.

### 3. Quantum chemical calculations

In order to achieve information on the interaction between the lanthanide ion and the antenna, we have performed a quantum chemical investigation on the somewhat smaller  $\text{ErQ}_3$  complex. This choice has been dictated by the fact that in this complex the ligand and the antenna coincide thus reducing the computational load. Moreover, this is the most studied  $\text{Er}^{3+}$  complex emitting in the IR region and consequently a large amount of experimental data are available.

The geometry optimization of the complex was performed at semiempirical level using the PM3 Hamiltonian. This choice allows to reduce the computational time of the calculation but, on the other hand, raises the problem of the lanthanide ion descriptions. Possible approaches are:

- (i) replacing the ion with a point charge [12];
- (ii) introducing in the chosen semiempirical model a “ghost” atom with a suitable parameterizations for reproduce, for example, the geometry of the real system [13].

Both the methodologies were used in literature and the latter is known as Sparkle Model [13] for the calculation of Lanthanide Complexes (SMLC).

In this work we have used an intermediate approach which consists in replacing the lanthanide atom with another one parameterized in the actual semiempirical model. This choice has the following advantages:

- (i) it is superior to the point charge approximation in that the core interactions between the coordinating atom and its first neighbours are explicitly taken into account;
- (ii) it is not required the parameterization intrinsic to the SMLC method.

The main hypothesis of this approach is that, in the framework of a semiempirical approximation (where the f electron are not taken explicitly into account), the geometry of the complex was mainly affected by the coulomb interactions (related to the charge–ion radius ratio) of the ligands with the coordinating atom.

Relaxations of the first, showing that in this case a single antenna molecule comes into close contact with the coordinating ion and undergoes [14] substantial deformation (Fig. 4 and Table 1).

On the basis of the above geometry we are presently performing [14] CIS ZINDO calculations [15] in order to obtain

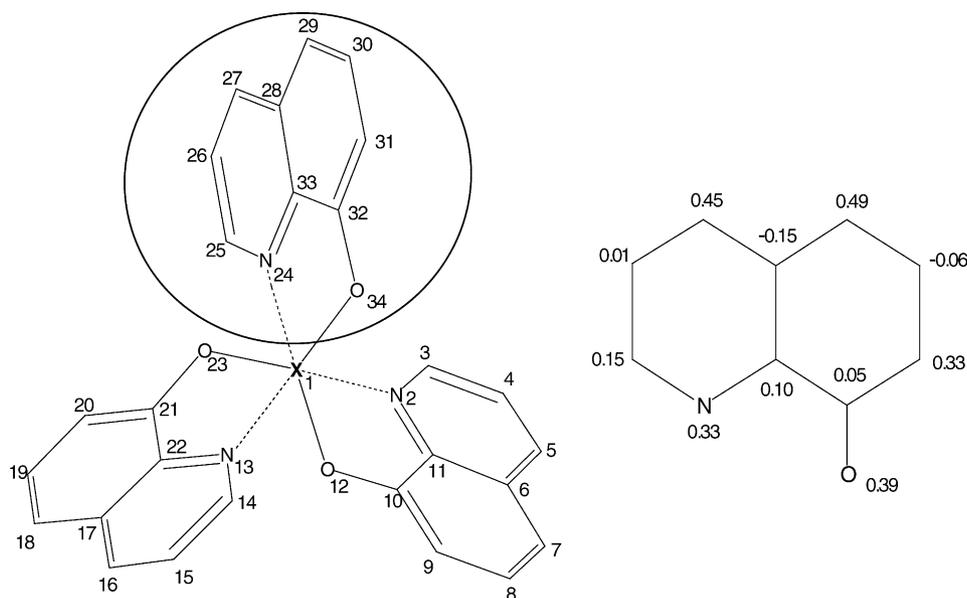


Fig. 4. Schematic structure of the first optimised triplet state, the ligand circled carrying the triplet exciton. On the right the atomic spin distribution is reported.

Table 1  
Bond lengths in the first triplet state (all distances are in nm)

X1–N2	0.2443	X1–N13	0.2384	X1–N24	0.1929
X1–O12	0.1787	X1–O23	0.1802	X1–O34	0.1887
N2–C3	0.1341	N13–C14	0.1340	N24–C25	0.1412
C3–C4	0.1416	C14–C15	0.1416	C25–C26	0.1370
C4–C5	0.1376	C15–C16	0.1375	C26–C27	0.1416
C5–C6	0.1422	C16–C17	0.1423	C27–C28	0.1407
C6–C7	0.1410	C17–C18	0.1410	C28–C29	0.1416
C7–C8	0.1386	C18–C19	0.1385	C29–C30	0.1412
C8–C9	0.1396	C19–C20	0.1394	C30–C31	0.1373
C9–C10	0.1412	C20–C21	0.1412	C31–C32	0.1465
C10–C11	0.1436	C21–C22	0.1440	C32–C33	0.1440
C10–O12	0.1310	C21–O23	0.1312	C32–O34	0.1269
C6–C11	0.1426	C17–C22	0.1428	C28–C33	0.1429
N2–C11	0.1383	N13–C22	0.1386	N24–C33	0.1384

excited state energies to provide a theoretical estimate of the spectral overlap between the antenna and the coordinated ion and therefore of the transfer rate.

#### 4. Conclusions

We have synthesized and optically characterized a new ligand and its lanthanide complexes. These complexes show a remarkable chemical stability thanks to the presence of DO3A macrocycle, while keeping an efficient light-harvesting antenna, like the 8-hydroxyquinoline. Both  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$  complexes exhibit good transfer from the optically excited antenna to the emitting ions. In particular the emission intensity of the  $\text{Er}^{3+}$  chelate is comparable with that of  $\text{ErQ}_3$  which is, up to now, one of the best IR lanthanide complex emitters. The structure of the complex is currently under investigation to determine whether the antenna is directly coordinated to the ion or is attached only to the macrocycle.

In the latter case, the only mechanism responsible for the sensitization of the ion emission would be the long range dipole–dipole interaction involving the first excited singlet state, while in the first case both singlet and triplet states are involved. Theoretical calculations on the relaxation upon photoexcitation show that the quinolinic unit, if coordinated by the ion, comes into close contact with the metal center. This relaxation could enhance the energy transfer rate through the triplet state thus providing indication on the type of ion–antenna interaction.

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