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Making sense of lanthanide luminescence

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ABSTRACT

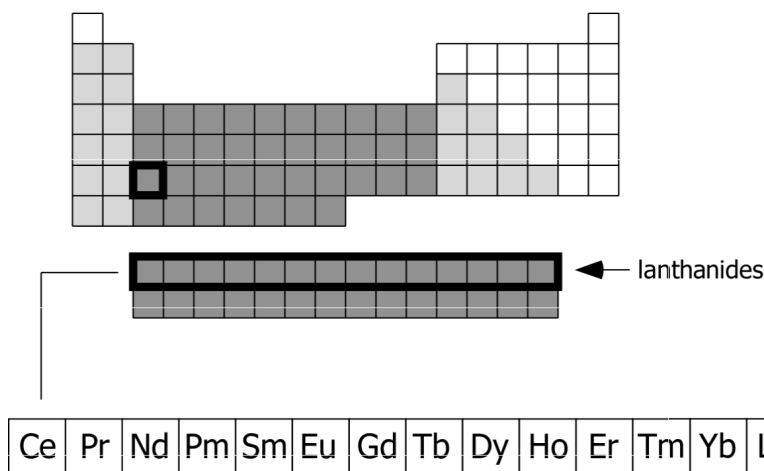
The luminescence of trivalent lanthanide ions has found applications in lighting, lasers, optical telecommunications, medical diagnostics, and various other fields. This introductory review presents the basics of organic and inorganic luminescent materials containing lanthanide ions, their applications, and some recent developments. After a brief history of the discovery, purification and early spectroscopic studies of the lanthanides, the radiative and nonradiative transitions of the 4f electrons in lanthanide ions are discussed. Lanthanide-doped phosphors, glasses and crystals as well as luminescent lanthanide complexes with organic ligands receive attention with respect to their preparation and their applications. Finally, two recent developments in the field of luminescent materials are addressed: near-infrared luminescent lanthanide complexes and lanthanide-doped nanoparticles.

Keywords: *lanthanide, luminescence, nanoparticles, photonics*

1. Introduction

Photonics, broadly defined as the science and technology for understanding, controlling and exploiting the interaction of light and matter, furnishes enabling technologies for telecommunications, solar energy, lighting, displays, biotechnology, medical

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cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium

Fig. 1. The place of the lanthanides in the Periodic Table. Lanthanum (La) is sometimes also counted under the lanthanides.

diagnostics, bio-imaging *etc.* Lanthanide ions hold a special place in photonics because of their unique photophysical properties, especially with respect to the generation and amplification of light. The luminescence of trivalent lanthanide ions (Ln^{3+}) has been and is being studied in several scientific domains, ranging from laser physics to molecular biology. Many reviews have appeared,^{1–14} mostly focussing on specific aspects. For more profound introductions of the use of lanthanide luminescence in a certain field the reader is warmly advised to delve into those papers and books. This review aims to introduce the basics of lanthanide luminescence, to show the connections between research in different domains and to indicate some (but inevitably not all) modern developments concerning lanthanide luminescence. This review will deal only with the luminescence of the trivalent lanthanide ions, the most prevalent form in which the lanthanides exist in nature. Figure 1 indicates how to find the lanthanides in the Periodic Table: they are in the “footnote”.

Lanthanide luminescence spectra are characterized by sharp peaks, whose spectral positions are independent of the embedding matrix, but whose intensities and fine structure may vary (Figure 2).

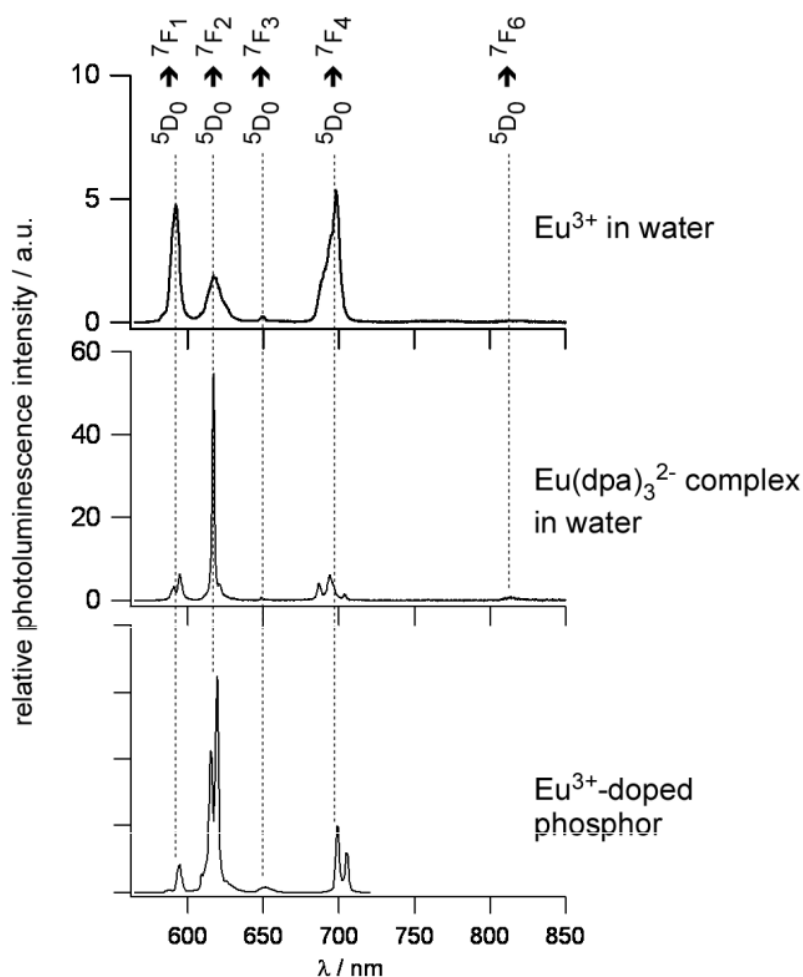


Fig. 2. Emission spectra of the Eu^{3+} ion in different environments. The radiative transitions take place from the $^5\text{D}_0$ level. The fine structure observed on some transitions (in particular on $^5\text{D}_0 \rightarrow ^7\text{F}_4$) is due to the crystal field splitting. The spectra of Eu^{3+} and $\text{Eu}(\text{dpa})_3^{2-}$ in water were taken from ref. 15. “dpa” stands for 2,6-dipicolinate. The spectral data for the phosphor (of composition $\text{Y}_{0.845}\text{Al}_{0.07}\text{La}_{0.06}\text{Eu}_{0.025}\text{VO}_4$) was taken from ref. 16.

If one succeeds in introducing lanthanide ions into a particular material, be it a crystal, a glass, a liquid, a molecular material such as a polymer, this material will become luminescent. A lot of work on luminescent materials based on lanthanide ions is about finding ways to introduce these ions into a material while keeping the ions brightly luminescent and the material intact.

Although lanthanides are often referred to as rare earth elements, they are not scarce.* In our technology-filled lives they are ubiquitous, especially where the emission of light is involved. Conventional televisions and computer screens use lanthanide doped phosphors to convert cathode rays into visible information. Flat panel displays often rely on lanthanide luminescence as well. The same type of materials is also found in fluorescent lighting.⁴ It is the white powder that is obtained when breaking a fluorescent lamp.

Lanthanide ions are also applied as the light generating and amplifying constituents in lasers (*e.g.* in the Nd^{3+} :YAG laser) and optical amplifiers¹⁷ (EDFA's: erbium(III) doped fiber amplifiers). Over the past few years, the latter have become a key component in optical telecommunications, where light instead of electricity carries information. The materials for these applications have thus far been inorganic glasses and crystals doped with lanthanide ions. Lanthanide-doped luminescent materials are a fine example of how applications arise from "fundamental" research and how these applications in turn stimulate basic research.

Lanthanide ions can form soluble complexes with organic ligands and such complexes hold the promise that for some photonic applications they may provide low-cost alternatives to inorganic materials. Lanthanide complexes may be incorporated in easily processible polymers. Work is being done on polymers doped with lanthanide complexes for optical amplification,^{13,18} and the first prototypes of flat panel displays containing lanthanide complexes have seen the light.^{6,19} Lanthanide complexes are under consideration as the active elements for OLEDs (Organic Light Emitting Diodes), together with various organic molecules and metal-organic complexes.

Currently, the most important commercialised use of luminescent lanthanide complexes is in medical diagnostics, where they are used to detect small amounts of biomolecules that can tell about the physiological state of a patient. DELFIA (Dissociation Enhanced Lanthanide Fluorescence Immunoassay) is a well-known medical diagnostic detection scheme¹ that forms the basis of a large number of clinical tests, *e.g.* for testing newborn babies

* Lanthanum, cerium and neodymium are more abundant on earth than lead, and over 100 minerals containing them have been described. The major sources for commercial extraction are bastnasite, monazite, and xenotime. Europium is present only at about 0.1% or less in these ores and is present in about 1 ppm in the earth's crust. Promethium, which is radioactive, does not occur in nature, and was first made by man in 1945.

(for cystic fibrosis, hypothyroidism and congenital adrenal hyperplasia), in the diagnosis of many diseases and even to detect BSE (bovine spongiform encephalopathy, or mad cow disease).²⁰ All these diagnostic tests rely on molecular biological methods based on biomolecular recognition processes such as antibody-antigen interactions that translate the concentration of a biomarker (biomolecular species related to the pathology to be diagnosed) into a concentration of lanthanide ions. In DELFIA, the luminescence of the lanthanide ion is detected after adding reagents that optimise (or reveal) the lanthanide luminescence. The intensity of the luminescence will be related to the concentration of biomarker initially present in the sample. The advantage of using lanthanide complexes for detection is that they offer a very high detection sensitivity, with very low background signals, without the need for radioactive labels that have been used previously. An alternative lanthanide-based biomolecular detection scheme is homogeneous time-resolved fluorescence (HTRF).⁵⁵

2. A brief history

Discovery and isolation of the lanthanides

In 1752, the Swedish mineralogist Cronstedt (who was also the first to describe zeolites) discovered a new heavy mineral in a mine near Ryddarhyttan in his home country. At the time, it was thought to be a calcium-iron silicate and the then unknown rare earths were mistaken for calcium. Gadolin (Finland), in 1794, isolated an oxide from a heavy black mineral at Ytterby (also in Sweden) and named the oxide 'ytterbia'. Half a century later, in 1842, Mosander further separated 'ytterbia' by oxalate and hydroxide precipitation. He named the three fractions 'yttria', 'erbia' and 'terbia'. These 'earths' turned out to be complicated mixtures as well. The isolation of lanthanum, the lanthanides, yttrium, and scandium was not completed until 1908–1909 owing to the difficulties in separating them by repetitive fractional crystallisations. Charles James, an early expert in the isolation of kilogram quantities of pure lanthanide salts, once performed many thousands of recrystallisations to obtain 'pure' $\text{Tm}(\text{BrO}_3)_3$.

The difficulties in separating the individual lanthanides are a result of them having very similar chemical properties. Their dominant valence state is plus three, and they show only small differences in complex formation and solubility. These small differences are due to their decrease in size with increasing atomic number (the 'lanthanide contraction'). It was only

through the aid of (X-ray) spectroscopy that in 1913 it was conclusively shown that there exist only 14 elements between La and Hf. At the end of the 1910s, Bohr interpreted this as gradual filling of the 4f shell, an extension of the 4th quantum group from 18 to 32 electrons.

Before the Second World War, a major advance in separating lanthanide ions was made by McCoy, who purified considerable quantities of Eu by reducing Eu^{3+} to Eu^{2+} with Zn amalgam followed by precipitation as EuSO_4 .²¹ Among the lanthanide ions, Eu^{3+} is by far most easily reduced (to Eu^{2+} , which then can precipitate with sulfate ions). McCoy provided other scientists with samples of Eu^{3+} . In fact, the first spectroscopic studies on Eu^{3+} complexes in solution (see below) were made possible by these gifts. The Manhattan project during the Second World War yielded the first large-scale separation methods for lanthanide ions. The ion-exchange chromatographic methods developed there are based on the (small) difference in the stability of chelates (at the time citrate complexes). Together with the liquid-liquid extraction methods developed in the early 1950s these methods are still used in the commercial production of lanthanides.

Early studies on the photophysics of lanthanide ions and their coordination complexes

The unusually sharp absorption lines of rare earth compounds, already known from early spectroscopic observations by Bunsen on “didymium sulfate” crystals in 1866, were studied in detail by J. Becquerel²² in 1906 when he measured the spectrum of the mineral xenotime (YPO_4 containing traces of Er, Ce and Th). The crystal absorption lines were shown to exhibit a considerable Zeeman splitting in an applied magnetic field. However the origin of the spectra remained a mystery. Around 1930, Bethe,²³ and Kramers and Becquerel suggested that the lines may be due to electronic transitions within the 4f configuration, which from now on we will refer to as f–f transitions. The electrons in the 4f shell are shielded from the surroundings by the filled 5s and 5p shells, and therefore do not play a role in the chemical bonding between the lanthanide ion and the containing matrix (ligands). As a consequence the influence of the matrix on the optical transitions within the 4f shell is small, resulting in sharp-line spectra resembling those of the free ions, whether in crystals or in solution.

If these transitions are indeed intraconfigurational, the question remained as to how these transitions acquire their strength:

formally they are forbidden by the Laporte (or parity) selection rule. In 1937, van Vleck addressed this puzzle²⁴ and showed using a simple and instructive model of f–f transitions that they become partially allowed as electronic dipole transitions by admixture of configurations of opposite parity, such as the $4f^{n-1} 5d^1$ configuration. Some f–f transitions are allowed as magnetic dipole transitions, and both schemes yield oscillator strengths of the same order of magnitude.

The 1930s and early 1940s also witnessed the first spectroscopic studies of lanthanide ions in solution, in particular using the purified Eu^{3+} samples provided by McCoy. Freed *et al.*²⁵ found that the relative intensities of the absorption lines of Eu^{3+} were different in different solvents, and Weissman²⁶ discovered that complexes of Eu^{3+} with certain ultraviolet absorbing ligands were highly luminescent when excited with ultraviolet light. Since Eu^{3+} itself has only a few, very weak absorption bands, solutions of this ion alone are not very brightly photoluminescent. Thus, Weissman had discovered that certain organic ligands can photosensitise the luminescence of lanthanide ions: “. . .the excitation may be accomplished, under suitable conditions, through light absorption by other constituents of the rare earth compound with subsequent transfer of energy to the rare earth ion.”. It was also found²⁷ that lanthanide ions quench the fluorescence of organic ligands.

At that time, the optical spectra of lanthanide ions and the underlying electronic energy level structure were only qualitatively understood. The formidable task of finding, calculating and assigning the energy levels was carried out by many research groups in the 1940–1950s. Advances in theoretical methods, particularly by Racah in the 1940s, enabled quantitative fits of the energy level positions throughout the lanthanide series to be performed. The first overview of the $4f^n$ energy levels of all trivalent lanthanides in the IR, visible and UV spectral region was given by G. H. Dieke in the 1960s. Because of the almost negligible influence of the host lattice on the levels the diagram is applicable to trivalent lanthanides in any compound. Energy level diagrams for the lanthanide ions can be found in various references.^{28,29}

The calculation of the intensities of the induced electric dipole transitions between energy levels of the lanthanide ions became possible through the theoretical works of Judd and Ofelt published independently in 1962.¹⁰ Nowadays, the Judd-Ofelt theory is often used to describe and predict the electronic spectra of lanthanide ions present in glasses and crystals, in particular to predict the

luminescent properties on basis of the absorption spectra.³ Application to ions in complexes with organic ligands is much rarer.¹⁵

Also at the beginning of the 1960s (twenty years after the first report of the luminescence of lanthanide complexes in solution),²⁶ more systematic studies of luminescent lanthanide complexes and their photophysics appeared.^{30–35} These studies were mainly concerned with the β -diketonate complexes of Eu^{3+} and Tb^{3+} , and revealed many of the photophysical concepts still used today in the development of luminescent lanthanide complexes. One of the reasons for this sudden interest in luminescent lanthanide complexes was that they were shown to be suitable compounds for ‘organic’ lasers and optical amplifiers.^{36–38}

3. Radiative and non-radiative transitions in trivalent lanthanide ions

All luminescence is the result of the competition of radiative and non-radiative pathways in the relaxation of an electronically excited species. Lanthanide luminescence forms no exception. The multitude of electronic energy levels due to the f electrons allows for a rich cascade of radiative and non-radiative relaxation processes in excited lanthanide ions. Understanding lanthanide luminescence therefore requires knowledge of the electronic energy levels related to the 4f orbitals and the radiative and non-radiative decay channels.

Electronic structure and energy levels

Going from La^{3+} to Lu^{3+} , the 4f orbitals are filled with electrons. These electrons have little interaction with the chemical environment of the ion, as the 4f orbitals are shielded from it by the electrons in the 5s and 5p shells, which are lower in energy, but spatially located outside the 4f orbitals. This explains the similarity in chemical properties of all lanthanide ions, which for example leads to the difficulties in separation. The electronic transitions that are responsible for the line-like absorption and luminescence spectra are transitions within the $5s^2 5p^6 4f^n$ configuration, and are therefore only marginally affected by the matrix.

The occurrence of different energy levels belonging to the same configuration is a result of several interactions within the ion. Depending on the number of electrons, there are many different ways to distribute the electrons over the seven 4f-orbitals, but some

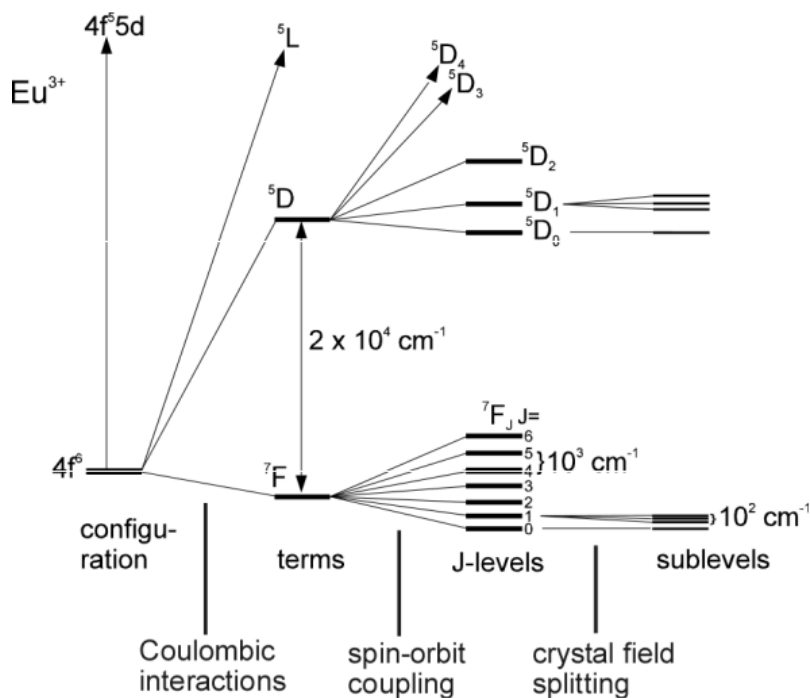


Fig. 3. The interactions leading to the different electronic energy levels for the $[Xe] 4f^6 5d^0$ configuration of Eu^{3+} (six electrons in the $4f$ orbitals).

distributions of electrons are energetically more favourable than others. The interactions that split up the levels belonging to the $[Xe] 4f^n 5d^0$ configurations are clarified in Figure 3, where the Eu^{3+} ion has been taken as an example.

The Coulombic interaction, which represents the electron-electron repulsions within the $4f$ orbitals, is the largest among the $4f$ electronic interactions and yields terms with a separation in the order of 10^4 cm^{-1} . Each of these terms is split into several J-levels by spin-orbit coupling, which is relatively large (10^3 cm^{-1}) in lanthanide ions because of their heavy nuclei. We have now arrived at the *free ion levels* that are described by the term symbols $(2S+1)L_J$. $2S+1$ represents the total spin multiplicity, L the total orbital angular momentum and J the total angular momentum of the f electrons.

When present in a coordinating environment, such as a crystal or an organic ligand, the individual J-levels are split up further by the electric field of the matrix, which is usually referred to as the crystal field. These splittings are usually small (10^2 cm^{-1}) and, depending on the spectral resolution of the spectrometer, appear as fine

structure on the individual bands. Often this fine structure is ignored, although it may be used to gather information about the symmetry of the coordination environment.³⁹

Radiative transitions

In the hypothetical free lanthanide ion, only magnetic dipole (MD) transitions are allowed. These are selected by the $\Delta J = 0, \pm 1$ (but $J = 0 \rightarrow J = 0$ is forbidden) rule. Their probability is relatively easily calculated⁴⁰ and practically independent of the surrounding matrix. One example of a purely MD transition is the ${}^5D_0 \rightarrow {}^7F_1$ emission line of Eu^{3+} (see Figure 2). In a coordinating environment, electric dipole (ED) transitions are induced as the ligand field mixes odd-parity configurations slightly into the $[\text{Xe}] 4f^n 5d^0$ configuration. Most of the absorption and emission lines are such induced ED transitions. Some transitions acquire strength both by MD and ED schemes: the emission spectrum of Tb^{3+} is dominated by mixed ED/MD transitions.

Since ED transitions in lanthanide ions are induced by the ligand field their strengths (or: probabilities) are quite sensitive to it. Strongly asymmetric or strongly interacting ligand fields lead to relatively intense ED transitions. The intensities of some ED transitions are extremely sensitive to coordinating environment, which means that they can be either completely absent or very intense, depending on the ligand field. An example of such a *hypersensitive transition* is the ${}^5D_0 \rightarrow {}^7F_2$ emission line of Eu^{3+} (Figure 2).

Both MD and induced ED transitions of lanthanide ions are weak compared to the ‘fully allowed’ transitions found in organic chromophores. In the case of luminescence, this gives rise to radiative lifetimes in the order of milliseconds, depending on the lanthanide ion and its matrix, which is 6 orders of magnitude as long as the radiative lifetimes of organic fluorophores. On the other hand, also the absorption bands are weak, typically resulting in extinction coefficients in the order of $1 \text{ M}^{-1} \text{ cm}^{-1}$ with bandwidths of less than 0.2 nm. This makes the long-lived photoluminescence of lanthanide ions difficult to excite. Later on we will see that ways exist to circumvent this excitation bottleneck.

Figure 4 schematises the types of electronic transitions in lanthanide ions, both of radiative and non-radiative nature. If highly excited lanthanide ions could only decay radiatively, their emission spectra would become extremely rich in lines, since in principle radiative transitions between any two states can take

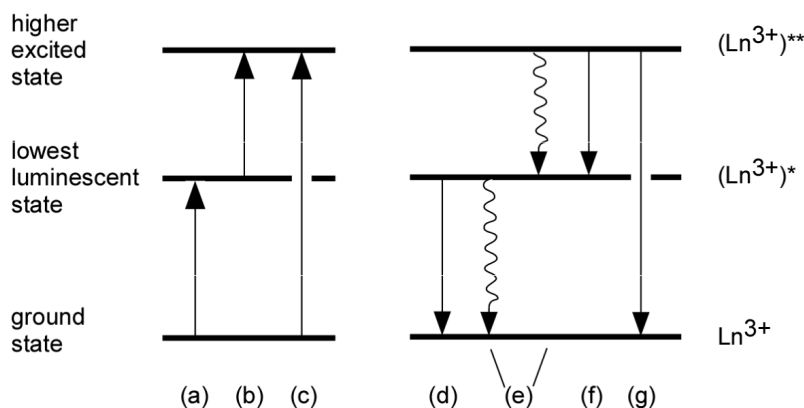


Fig. 4. Electronic transitions in lanthanide ions: (a) absorption/excitation, (b) excited state absorption, (c) direct excitation into a higher excited state, (d) "conventional" emission from the lowest luminescent state, (e) non-radiative relaxation, (f) radiative transition between excited states, (g) emission from a higher excited state.

place. Under favourable conditions, emission from 'higher' excited states is indeed observed, and such processes are the basis of *upconversion* (UC),⁹ in which an already excited ion is excited into a higher lying luminescent state, converting two low-energy photons into one high-energy photon, and *quantum cutting* (QC),⁴¹ in which a highly excited ion emits sequentially two photons. Both UC and QC have important technological implications. UC can convert a flux of near-infrared light into visible light, whereas QC offers the prospect of highly energy-efficient conversion of ultra-violet light into visible light.

Nonradiative relaxation of excited lanthanide ions

The excited states of lanthanide ions, however, do not decay solely by radiative processes. In glasses and crystals, the electronic excitation energy can be dissipated by vibrations of the surrounding matrix, a process known as *multiphonon relaxation*.⁴² A similar process occurs also in complexes with organic ligands, and is even of bigger importance in such systems, since in organic media suitable high-energy vibrations are more common.

The efficacy of matrix vibration mediated nonradiative relaxation is inversely proportional to the number of vibrational quanta that are needed to bridge the gap between a given energy level and the next-lower one. This energy gap law is a result of the overlap

Table 1 Commonly observed emission bands of the lanthanide ions Eu^{3+} , Tb^{3+} , Nd^{3+} , Er^{3+} , and Yb^{3+} in solution. See Figure 5 for examples of the corresponding emission spectra

Ion	Transition	$\lambda_{\text{emission}}$	Ion	Transition	$\lambda_{\text{emission}}$	
Eu^{3+}	${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$	580 nm	Nd^{3+}	${}^4\text{F}_{3/2} \rightarrow {}^4\text{F}_{9/2}$	880 nm	
	$\rightarrow {}^7\text{F}_1$	590 nm		$\rightarrow {}^4\text{F}_{11/2}$	1060 nm	
	$\rightarrow {}^7\text{F}_2$	613 nm		$\rightarrow {}^4\text{F}_{13/2}$	1330 nm	
	$\rightarrow {}^7\text{F}_3$	650 nm	Er^{3+}	${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$	1550 nm	
	$\rightarrow {}^7\text{F}_4$	690 nm		Yb^{3+}	${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$	980 nm
	$\rightarrow {}^7\text{F}_5$	710 nm				
Tb^{3+}	${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$	490 nm				
	$\rightarrow {}^7\text{F}_5$	545 nm				
	$\rightarrow {}^7\text{F}_4$	590 nm				
	$\rightarrow {}^7\text{F}_3$	620 nm				
	$\rightarrow {}^7\text{F}_2$	650 nm				

between the vibronic wavefunctions. A semi-quantitative treatment was given by Haas and Stein.⁴³ The nonradiative decay rate does not depend exclusively on the energy gap and the number of matrix vibrations that fit this gap. Multiphonon relaxation still involves electronic transitions in the ion without a change in parity. Weber⁴² has pointed out that also for this process selection rules apply, although these only affect a few transitions, such as ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ in Eu^{3+} (and Tb^{3+}). Indeed, even in organic media, weak luminescence from the ‘higher excited’ ${}^5\text{D}_1$ state can be observed.

As a result of vibration (or phonon)-mediated nonradiative decay, luminescence of a given lanthanide ion occurs mainly from one state, which is the state that has a large gap with the next lower lying level. More highly excited states are quickly deactivated to this state, since the higher states form a ‘ladder’ consisting of relatively small gaps that efficiently undergo multiphonon relaxation. Especially in organic media and in aqueous solution, where matrix vibrations of high energy are ubiquitous,^{46,47} the emission of lanthanide ions stems (almost) exclusively from one level, and therefore the number of emission lines is limited. Table 1 contains a small overview of the commonly observed emission lines of certain lanthanide ions in solution and in organic and biological media, and Figure 5 shows examples of observed spectra.

4. Lanthanide-doped luminescent materials

The practical application of lanthanide luminescence requires the ions to be incorporated into a matrix that is robust and compatible

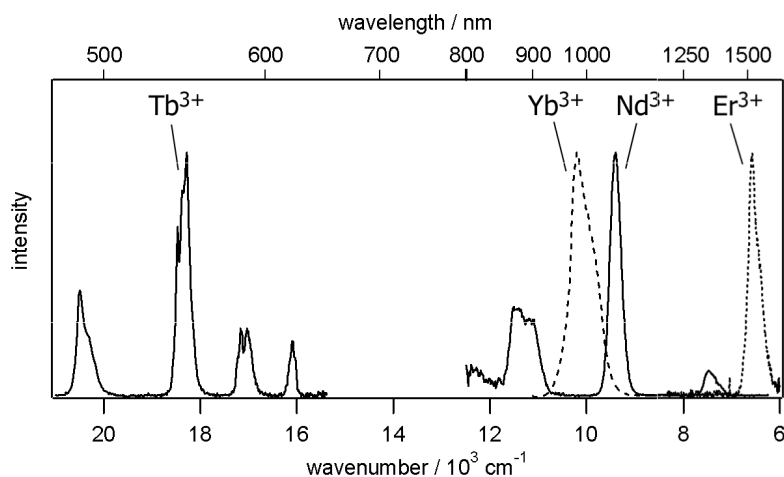


Fig. 5. Emission spectra of complexes of different lanthanide ions in solution (buffered H_2O or D_2O , pH 8.3). The complexes are actually sensitiser-modified Ln(DTPA) complexes,^{44,45} that will be discussed later in the text.

with respect to the intended application. The luminescent powders called *phosphors*[†] used to convert the UV radiation generated by the mercury or xenon plasma inside fluorescent lighting need to deliver a homogeneous and stable light output even after prolonged exposure to this highly energetic radiation. Similarly, phosphors for cathodoluminescence, found in cathode ray tubes, need to resist the continuous electron bombardment. When making use of lanthanide luminescence for the detection of biological molecules, the luminescent material needs to be compatible with biological and aqueous environments and the individual light emitters should be small enough not to interfere with any of the biochemical processes in the sample under study. What follows here is an overview of the most common types of lanthanide based materials and their fabrication.

Phosphors

Phosphors are luminescent inorganic materials with preferably a homogeneous grain size which is usually on the order of several micrometers. The grains can be smaller, in which case they may be

[†] Confusingly, elemental phosphorous is not a phosphor. The glow of (white) phosphorous, initially mistaken to be “cold” light, is actually the slow burning of phosphorous in air.

called *nanophosphors*. Phosphors are luminescent because of the presence of small amounts of *activators*. The stable luminescence of trivalent lanthanide ions make them attractive activators. In fluorescent lighting, phosphors convert ultraviolet radiation generated by a mercury or Xe plasma into visible light. In cathode ray tubes, phosphors emit light upon electron bombardment. Phosphors for these applications have already largely been optimised. A recent review can be found in ref. 4.

Historically, the fluorescence and the phosphorescence of certain inorganic materials has been known since antiquity. The first synthetic phosphor, known as “Bolognian Phosphorous”, was prepared and reported by Vincenzo Casciarolo in Bologna in 1603. At the start of the 20th century, scintillation screens based on ZnS:Ag phosphors (zinc sulfide doped with silver ions) developed by Geiger were instrumental in the discovery of the atomic nucleus by Rutherford and co-workers. The first patent application for the use of phosphors in fluorescent lighting was filed by Germer, Meyer and Spanner in 1926. General Electric commercialised the first fluorescent lamp in 1938. Before, all electric lighting had been produced by incandescence (which produces more heat than light) or by gas discharges (which often partially generates ultraviolet radiation reducing lighting efficiency, or uses rare gases).

Phosphors are synthesised by various methods: homogeneous precipitation, solvothermal methods, and more recently combustion synthesis. In homogenous precipitation, small crystalline grains are produced by slowly introducing a precipitating agent (such as oxalic acid) into a solution of inorganic ions. After precipitation the phosphors are “annealed” by calcination at high temperatures ($>1000^{\circ}\text{C}$, often in air) which removes all organic material and water. In solvothermal synthesis the phosphor grains grow in a solution (either aqueous or organic) of the precursor materials at elevated pressure and high temperatures. Pressure and temperature are two parameters than can be carefully controlled to obtain the desired size of particles. Combustion synthesis⁴⁸ is a recently discovered method for synthesising phosphors, in which the energy needed for melting and mixing the starting materials is generated by the exothermic reaction of the starting materials themselves. The starting materials are often oxygen rich metal nitrates and organic fuels such as carbohydrazide. The compounds are mixed in solution which is then heated in an oven at moderate temperatures (400°C). The solvent evaporates and at the exothermic reaction starts resulting in a spectacular, self-sustaining fire of which the temperature can rise up to 1400°C . Finally the

luminescent phosphor is recovered as the “ashes” of the combustion process.

Doped crystals and glasses

For lasers and optical amplifiers, limpid materials are needed that have transparency in the spectral region where light generation and amplification takes place. Both glasses⁵ and crystals⁷ can meet these requirements. Artificial crystals of high purity are grown by well-established techniques, notably the Czochralski method, in which a crystal is very slowly drawn from a melt. In luminescent crystals, the “activating” lanthanide ions replace a small fraction of the ions of the host crystals. The most widely known lanthanide-doped crystal is without a doubt $\text{Nd}^{3+}:\text{YAG}$ which is crystalline $\text{Y}_3\text{Al}_2(\text{AlO}_4)_3$ in which a certain fraction of the Y^{3+} ions has been replaced by Nd^{3+} . Doping levels can be high ($> 10\%$) but too high concentrations of active lanthanide ions can lead to decreased photonic performance due to interactions between neighbouring ions.

Glasses are usually fabricated by intimately mixing the precursor materials, melting them at high temperatures, cooling the melt to vitrify the material, followed by an annealing step before cutting and polishing. The precursor materials may include gases, in which case the other materials are molten in an atmosphere of the gases needed (*e.g.* HF can be the source of fluoride in the synthesis of fluoride glasses).⁵ Glasses can be either doped with lanthanide ions, or lanthanide ions can be integral part of the glass forming composition. Fibers can be drawn from glass, and Er^{3+} -doped glass fibers are important elements in optical telecommunications as they can be used to amplify optical signals.¹⁷ The inhomogeneity in surroundings of the ions embedded in glasses is reflected by a broadening of all transitions which is advantageous for optical amplification purposes as the useful photonic bandwidth is increased with respect to crystalline materials.

Luminescent lanthanide complexes

Complexes of lanthanide ions with organic ligands are a class of luminescent materials that are different from the inorganic materials discussed above. However, their luminescence, in particular their emission spectra, bear close resemblance to those of lanthanide-doped phosphors, crystals and glasses. Table 2 compiles a few of the differences between the classes.

Table 2 Comparison of lanthanide-doped inorganic materials and luminescent lanthanide complexes

Doped inorganics	Lanthanide complexes
Usually large objects (> 100 nm)	Molecular objects, compatible with polymers and biological environments
Physicochemical properties tuned by surface modification	Physicochemical behaviour can be tuned at the atomic level through molecular chemistry
Facile generation of NIR luminescence, upconversion (UC) and quantum cutting (QC)	Nonradiative deactivation impedes UC and QC, and makes NIR luminescence weak
Traditionally used for lighting, CRT displays and optical telecoms technologies	Used in medical diagnostic tests, bioimaging, and for luminescent doping of polymers
Functionalised nanophosphors now being studied for compatibility with living biosystems and for doping of polymers	Lanthanide complexes now serious candidates for application in flat panel displays (OLED technology) and future lighting

Particular attention is drawn to the importance of non-radiative deactivation in luminescent lanthanide complexes. These processes are also present in inorganics (electron-phonon relaxation), but the ubiquity of molecular high-energy vibrations in organic ligands and solvents makes that non-radiative relaxation of excited lanthanide ions is much more efficient in these materials. Especially the O–H vibrations of water are good quenchers of lanthanide luminescence. Many of the efforts in the development of luminescent lanthanide complexes are aimed at protecting the ion from these quenchers, and thus enable luminescence in aqueous and biological media. For the visibly luminescent Eu^{3+} and Tb^{3+} complexes, effective protecting ligands have been developed,^{2,11,12,14} but – as we will see below – real challenges remain in preventing the non-radiative deactivation in complexes of near-infrared luminescent ions that are intrinsically more sensitive to quenching by molecular vibrations.

The production of luminescent lanthanide complexes consists mainly of the chemical synthesis of the ligand. Usually the lanthanide ion is introduced only after the ligand has been built up in full. The complex formation takes place readily in solution (if the ligand is any good!) although certain cage-like systems may need some activation energy to push the ion into place. The

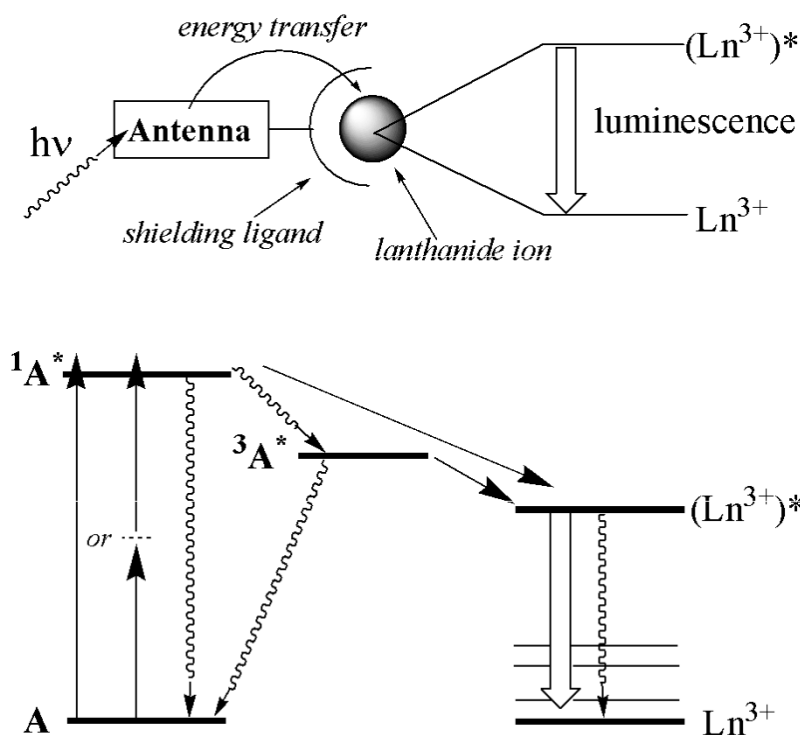


Fig. 6. Architecture and energy diagram of luminescent lanthanide complexes ('A' stands for the antenna chromophore, Ln^{3+} for the lanthanide ion).

synthesis of the ligand can be addressed with the complete arsenal of organic chemical reactions, which explains the enormous variety of lanthanide complexes that have been synthesised over the years.

The general molecular architecture of lanthanide complexes for photonic applications is sketched in Figure 6. One part of the ligand is designed to strongly bind and shield the lanthanide. Ln^{3+} ions have high coordination numbers (8, 9) and occupying as many as possible will contribute to the success of the ligand in protecting the ion against quenching. In this part mostly coordinating groups such as carboxylic acids, amides, pyridines *etc.* are found.

The ligand incorporates an organic chromophore to enhance the effective absorption cross section: the chromophore absorbs the light and transfers the energy to the lanthanide ion. In analogy to the light harvesting molecules found in natural photosynthetic systems, these sensitising chromophores are sometimes referred to as *antenna chromophores*. These antennae are often indispensable as Ln^{3+} light absorption bands are narrow ($\Delta\lambda < 1 \text{ nm}$) and weak

($\varepsilon < 1 \text{ M}^{-1} \text{ cm}^{-1}$, or $\sigma < 4 \times 10^{-21} \text{ cm}^2$, where ε stands for the extinction coefficient and σ for the absorption cross section). Organic dyes exhibit absorption cross sections 10^4 to 10^5 times as high, and over a much broader spectral range. The figure-of-merit of luminescent tracers and molecular probes for bioimaging and detection is the *brightness*, the product $\varepsilon\Phi$ of the extinction coefficient (ε) and the luminescence quantum efficiency (Φ). Intensely absorbing sensitising chromophores are therefore needed to raise the overall brightness by raising the extinction coefficient.

Although many different types of light absorbing molecules may act as antennae for exciting lanthanide ions, both the internal photonic energetics of the complex and application-related considerations impose certain constraints on the sensitiser. As can be gathered from Figure 6 the energies of the excited states of the sensitiser need to be sufficient to transfer energy to the luminescent state of the lanthanide ion.[‡] In the case of Eu^{3+} and Tb^{3+} complexes this limits the choice of sensitisers to those absorbing in the UV or in the blue⁵¹ part of the spectrum at best. For applications longer excitation wavelengths are preferred: highly energetic UV radiation can induce more damage especially in organic and biological systems. Recently developed near-infrared luminescent lanthanide complexes can use visible light (*vide infra*) but with the drawback – at present – of low luminescence quantum yields.

The efficiency of energy transfer from the antenna to the ion is highly distance dependent. For optimal photosensitisation the chromophore is preferably directly bound to the ion, as is the case in one of the first effective sensitisers of lanthanide luminescence, 2,6-dipicolinic acid.[§] Experimental demonstrations of the necessity of close proximity of ion and sensitiser can be found for example found for triphenylene, which is much more effective as a

[‡] The exact mechanism of the energy transfer is still under debate. Organic chromophores have both singlet and triplet excited states and one of the questions is to what extent the triplet state plays a rôle as an intermediate state in the organic-to-lanthanide energy transfer. Experimental evidence suggests that direct energy transfer from the excited singlet state to the lanthanide ion may take place, but that the triplet state is partially or even completely responsible for the photosensitisation, depending on the precise architecture of the complex and the photophysical properties of the sensitiser.^{31,49,50}

[§] This molecule is also abundantly present in bacterial spores, and sensitised lanthanide luminescence can be used to detect small quantities of this compound.⁵²

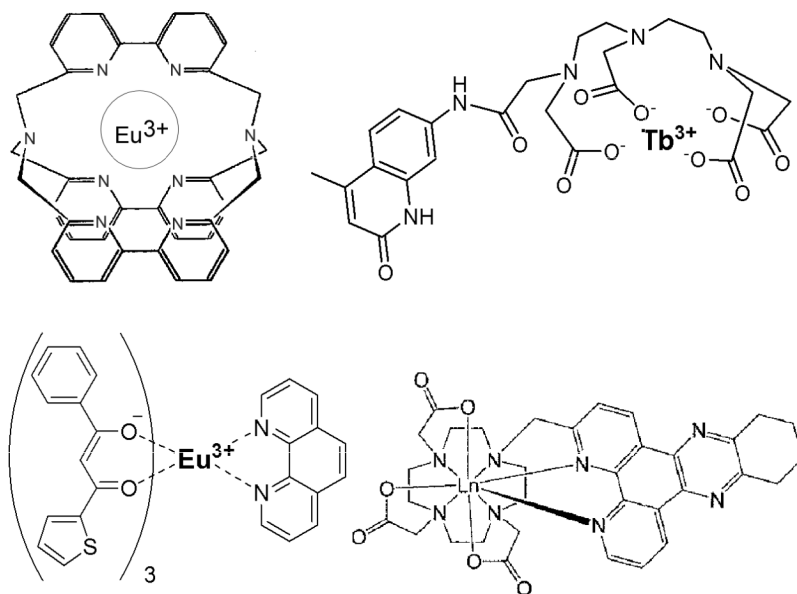


Fig. 7. Examples of visibly luminescent lanthanide complexes for near-UV excitation. Clockwise starting from top left: a Eu^{3+} cryptate, cs124-DTPA-Tb, a β -diketonate complex and an azatriphenylene-functionalized DOTA complex.

sensitiser when directly bound to the lanthanide ion in the form of its aza-derivative⁵³ than when appended as a light absorbing unit to a calixarene ionophore.⁵⁴

Some examples of visibly luminescent complexes are compiled in Figure 7. The elegant cage of the Eu^{3+} cryptate shows how a bipyridine unit can be at once a binding, protecting and photosensitising ligand. This cryptate forms the basis of various biophotonic detection schemes where biological binding events are signalled by a resonance energy transfer from the luminescent state of the cryptate to a red-absorbing energy acceptor, usually allophycocyanin.⁵⁵ Another donor used in this type of resonance energy transfer⁵⁶ (often referred to as fluorescence resonance energy transfer, FRET) is cs124-DTPA-Tb of which the synthesis is based on the idea to have a light absorber with an amino group react with one of the carboxylic acid residues of the well-known DTPA^{**} ligand.⁵⁷

^{**} diethylenetriaminepentaacetic acid. The (non-luminescent) Gd^{3+} complex of DTPA is frequently used as a contrast agent in magnetic resonance imaging under the trade name Magnevist.

The β -diketonate complex is an example of a Eu^{3+} complex that is soluble in organic solvents and can be incorporated in polymers. Materials of this type are used for anti-counterfeiting inks found in passports and certain Euro bank notes. The phenyl-thenoyl substituted β -diketone ligands are the sensitizers, whereas the *o*-phenanthroline serves to improve the protection of the ion against the binding of quenching O–H groups. The Tb^{3+} complex of the functionalised cyclic DOTA ligand has recently been successfully used in fluorescence microscopy on living cells.⁵⁸ The antenna chromophore is the potent azatriphenylene sensitizer initially developed by Verhoeven *et al.*⁵³

Since lanthanide complexes can be designed to be sensitive to pH, temperature, oxygen or other analyte concentrations^{14,59} they may become useful probes for live cell imaging. Multiphoton microscopy is a rapidly emerging technique for such imaging. Studies of lanthanide complexes under such multiphoton excitation are rare,^{60–63} and further work is necessary to identify complexes that have a suitable response towards multiphoton excitation under biological conditions. We note that multiphoton excited luminescence, which involves the *simultaneous* absorption of several photons, is different from the upconversion luminescence described for lanthanide-doped phosphors, which is based on the *sequential* absorption of photons.

5. Near-infrared lanthanide luminescence in aqueous, organic and biological media

Most of the work on luminescent lanthanide complexes and the luminescence of lanthanide ions in organic, aqueous and liquid environments has been concerned with the visibly luminescent Eu^{3+} and Tb^{3+} ions. Two other visibly luminescent ions, Dy^{3+} and Sm^{3+} (*cf.* Figure 1) have also received much attention, albeit to a lesser extent which is likely related to their inferior luminescence quantum yields in these media as a result of their more efficient nonradiative relaxation mediated by smaller gaps between the lowest luminescent state and the lower lying energy levels. Gd^{3+} is known to possess very high luminescence quantum yields in solution but it emits far into the UV (310 nm), which makes it less interesting for applications, either in biological detection or elsewhere.

The luminescence of the other lanthanide ions in organic and aqueous media has long been considered to be too weak to merit vivid scientific interest, but recently this situation has changed.

Complexes of some of these lanthanides have been known for quite some time to exhibit near-infrared luminescence. In 1958 Crosby and Kasha³⁰ described for instance the photosensitised emission of Yb^{3+} chelates, whereas solutions of neodymium(III) complexes were studied for laser action in the 1960s.³⁸ Until the early 1990s there have been some reports of Yb^{3+} -porphyrin complexes^{64,65} and the ability of coloured metal indicators to act as photosensitisers for Nd^{3+} and Yb^{3+} .^{66,67}

Systematic studies of near-infrared luminescence in organic and aqueous media began in the middle of the 1990s with reports on Nd(III) ,^{45,68,69} Yb(III) ^{45,70} and Er(III) ^{45,71}. For erbium(III), of importance for optical telecommunications, these were the first reports of its luminescence in an organic environment opening possibilities for the development of Er^{3+} doped polymers. It was demonstrated that dyes such as fluorescein and eosin could be incorporated as successful antenna chromophores for Nd^{3+} , Yb^{3+} and Er^{3+} into the ligand architecture.⁴⁵ Other types of antenna chromophores were identified such as organometallic complexes.⁷² The efficiency of the sensitisation processes depends critically on the distance between the ion and the sensitiser: the antenna chromophore needs to be in close contact with the lanthanide to ensure efficient transfer, as was demonstrated for the fluorescein-type of antenna chromophore. The intensity of the ligand fluorescence and the sensitivity of the sensitised lanthanide luminescence towards the presence of oxygen in solution are effective indicators for the efficiency of the sensitisation process. When in close contact with the energy-accepting lanthanide ion (Nd^{3+} , Er^{3+} or Yb^{3+}), the fluorescence of the fluorescein chromophore is completely quenched, and no sensitivity towards the presence of oxygen is found, indicating optimal sensitisation.⁷³ Complexes in which the chromophore is situated at approximately 0.5 nm of the ion still display relatively intense ligand-centered fluorescence and sensitivity to dissolved oxygen.⁴⁵

The nonradiative decay channels in Yb^{3+} -based complexes in solution have been characterized quantitatively,⁴⁷ showing that not only directly bound water molecules quench its luminescence, but that quenching is also caused by closely diffusing water molecules. This is important information for the development of Yb^{3+} complexes for application in biological systems where water is omnipresent as it stresses the need of encapsulating the luminescent ion in a large protecting ligand. The reduction in nonradiative deactivation of the luminescent state of near-infrared lanthanide ions is crucial for their application, be it as lumino-

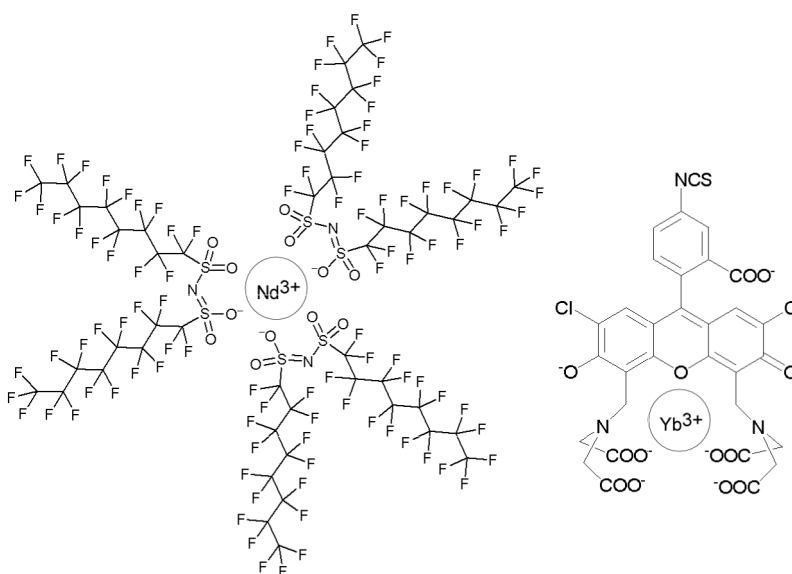


Fig. 8. Examples of near-infrared luminescent lanthanide complexes. Left: Nd^{3+} complexes with reduced non-radiative deactivation due to replacement of C–H by C–F oscillators. Right: $\text{Yb}(\text{FxCITC})$, a near-infrared luminescent label for the labeling of biological molecules.

phores or as elements for light amplification. Molecular vibrations in the ligand that encapsulates the ion, in particular C–H, N–H and O–H, are very capable quenchers of NIR lanthanide luminescence. An illustrative example of efforts to reduce this problem is the complex developed by Hasegawa *et al.*⁷⁴ where all of the C–H oscillators have been replaced by the lower-energy C–F group (Figure 8, left). The experimentally determined luminescence quantum yield of this complex reaches a record value of 3%, which is obviously low compared to lanthanide ions in glasses and crystals or organic dyes in solution whose quantum yields can often exceed 50%. A recent, supplementary strategy for maintaining near-infrared luminescence, is the encapsulation of the ions in aromatic shells which rigorously prevents quenching solvent molecules from approaching the lanthanide ion.⁷⁵

A sub-optimal photoluminescence quantum yield is not necessarily a major problem. Other factors come into play when developing applications. In medical diagnostic and imaging applications the luminescence signal generated is proportional to the product of the extinction coefficient of the complex and the quantum yield, the brightness $\epsilon\Phi$, which means that also the

extinction coefficient is an important factor. Additional factors come into play as well: the optical transparency of the embedding matrix, which is much better in the near-infrared for biological material. Especially Yb^{3+} should be a good ion for luminescent complexes in biological applications, as it has all of its emission concentrated in one narrow spectral band around 980 nm, where an average biological medium is at its most transparent. Use of an Yb^{3+} complex, $\text{Yb}(\text{FxITC})$ (Figure 8), in a fluoroimmunoassay has been demonstrated.⁷⁶

Another important parameter is the photostability of the lumiphores, as this determines the total number of photons that will be emitted by the complex before it is destroyed by a photoinduced process. Data on the photostability of lanthanide complexes is very scarce. The photostability of lanthanide complexes is expected to be superior to that of organic fluorophores, since the excitation energy only remains on the organic ligand a very short time before it is transferred to the lanthanide ion which usually does not undergo any photochemical transformations.

Concerning the luminescence of the remaining lanthanide ions, the ions Pr^{3+} , Tm^{3+} and Ho^{3+} display even weaker luminescence in solution than Yb^{3+} , Nd^{3+} and Er^{3+} , and the luminescence of their complexes has only recently been measured.^{77,78}

6. Lanthanide doped nanoparticles

It has been mentioned before that inorganic hosts such as glasses and crystals have less effective non-radiative deactivation channels for excited lanthanide ions than do molecular hosts. Near-infrared luminescence, emission from higher excited states and luminescence upconversion are therefore more readily observed for lanthanides in such inorganic hosts. For biological detection and for the doping of lanthanide ions into polymeric hosts it is interesting to have objects with the luminescent properties of inorganic phosphors but with sizes comparable to molecules (only several nanometers) and with similar solubility and physicochemical behaviour. Such Ln^{3+} doped “nanophosphors” are currently under active development, especially using “wet chemical” synthetic methods which are often relatively low cost and easily scaled up. We will focus here on particles that are dispersable (soluble) in organic and aqueous solvents since those are most interesting for application in either bioimaging or as photonically active elements in polymer based waveguides.

In a pioneering work in this field,⁷⁹ the micrometer-sized grains of an industrial europium(III)-doped phosphor powder were ground into smaller phosphor particles. These smaller particles were coated with negatively charged polyelectrolytes and subsequently with proteins (such as avidin) to render them biocompatible. Imaging was achieved using pulsed excitation and delayed detection in a conventional fluorescence microscope which suppresses the autofluorescence of the biological sample making use of the fact that the decay times of biofluorescence (on the order of nanoseconds) are orders of magnitude shorter than the decay of lanthanide luminescence (approx. 1 millisecond). Specifically designed upconverting phosphors of composition $Y_2O_3:S:(Yb,Er)$ have been used for upconversion luminescence detection in nucleic acid microarrays.⁸⁰ Very sensitive detection of the upconverted green luminescence can be achieved under 980 nm NIR excitation. The particles used are on the order of several hundreds nanometers in size, which can still be considered very large compared to molecular dimensions.

Smaller particles have been investigated recently: Ln^{3+} -doped $LaPO_4$ ⁸¹ and LaF_3 ⁸² nanoparticles with sizes in the 5–15 nm range. Indeed, near-infrared luminescence from the Nd^{3+} and Er^{3+} -doped particles appear to suffer less non-radiative deactivation than in complexes with organic ligands, although near the surface of the particles efficient quenching still occurs. In 12 nm sized $NaYF_4:(Yb,Er)$ and $NaYF_4:(Yb,Tm)$ particles upconversion luminescence is observed under NIR excitation.⁸³

This type of doped inorganic nanoparticles lack the excellent light absorption properties of organic chromophores, necessitating the weak direct excitation of lanthanide ions, although Ce^{3+} has been used to enhance the ultraviolet absorption of Tb^{3+} particles.⁸¹ A different strategy to obtain Ln^{3+} -doped nanoparticles with efficient light absorption is the incorporation of lanthanide ions into semiconductor nanoparticles, which has been achieved recently.⁸⁴ The overall photoluminescence quantum yield of these doped quantum dots was found to be very low ($<10^{-3}$) but ample room exists for the improvement of these materials through advances in the control of size-distribution and the introduction of protecting capping layers. Further functionalisation of the nanoparticle surface is necessary to make them biocompatible.^{85,86} Especially in the controlled surface modification of inorganic nanoparticles by organic molecules much work remains to be done to improve colloidal stability and biological compatibility.

7. Conclusions and outlook

This introductory review to lanthanide luminescence has necessarily not treated all of the aspects of the science and technology of lanthanide luminescence. One intriguing application of the photophysical intricacies of lanthanide-contained materials that we have not mentioned is the use of ytterbium doped materials for optical refrigeration.⁸⁷ This process is based on a material whose highly efficient fluorescence emission at room temperature is of slightly higher average energy than the light absorbed, which means that the material slowly loses energy while photoluminescing. The thermal populations of closely lying crystal-field levels of Yb^{3+} in ground and excited states and the transition probabilities between these states lie at the basis of this paradox. The use of lanthanide photophysics for optical refrigeration is yet another demonstration of the richness of effects that can be observed with the large number of different energy levels inherent to the 4f electrons of lanthanide ions. It may very well be that fundamental studies on the photonics of materials containing one, two or more different types of interacting lanthanide ions will lead to the observation of new effects. Many of these findings may at first seem only of fundamental scientific interest, and many will remain within the academic realm, but some may lead to yet unforeseen applications, which are likely to lie in the field of lighting and optical information transport and processing.

As we have seen, each type of host for lanthanide ions has its strengths and weaknesses for the construction of luminescent materials. Organic ligands generally induce efficient non-radiative deactivation of lanthanide ions, in particular for highly excited states, but offer tunability of their physicochemical and biological behaviour through molecular chemistry. Inorganic hosts give rise to richer lanthanide photophysics through reduced non-radiative deactivation channels, but are not as easily processed as organic materials and are often bio-incompatible. As we have seen in this review, the traditional weaknesses of the different types of hosts are currently being addressed: surface-modified nanoparticles may eventually be used in organic and biological media for polymer optical amplifiers or biological imaging, and luminescent lanthanide complexes may generate light in electroluminescent devices, or work efficiently as near-infrared emitters.

The work on lanthanide luminescence is a wonderful demonstration that scientific research is really a continuum of “fundamental” and “applied” research. Interdisciplinarity, potential medical nano-

biotechnological applications, it is all there in lanthanide luminescence. Looking into the future is difficult, and we will not draw up a “to do” list for further developments of lanthanide luminescence and its applications. The concerted research efforts of scientists from different horizons will determine how bright the future will be for luminescent lanthanide ions.

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