Luminescent Lanthanide Complexes: Visible Light Sensitised Red and Near-infrared Luminescence.
Werts, M.H.V.

Citation for published version (APA):
Chapter 1

The lanthanides, and their luminescent complexes

1.1 Introduction

Chemistry is about "taming the elements", understanding matter well enough to control its structure and its properties. This thesis is about designing, making and understanding luminescent materials. A broad range of naturally occurring and man-made materials that emit light is already known, from the stuff that makes fireflies glow to the semiconductors employed as lasing elements in compact disc players.

The kind of chemistry that we are going to work with is molecular chemistry, one of the most prolific enterprises in the science of chemistry. The notion that there exists such a thing as a molecule has proven to be quite fruitful. Our world partially consists of molecules and life depends on molecules. Chemists have been able to construct an inexhaustable variety of new molecules, sometimes inspired by nature, sometimes based on their own imagination. Thus, in this thesis, we are going to make luminescent molecules, or - put more precisely - molecules that combine with lanthanide ions to give luminescent lanthanide complexes in which lanthanides serve as the light emitting components.

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. The average Dutchman looks at lanthanide luminescence for at least 2 hours and 33 minutes a day. That is, if he only watches television. Computer screens too use lanthanide doped phosphors to convert cathode rays into visible information. The same type of materials is also found in fluorescent lighting.[1]

Lanthanide ions are also applied as the light generating and amplifying constituents in lasers (e.g. the neodymium(III):YAG laser) and optical amplifiers[2] (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 lanthanide-doped materials for these applications have thus far been inorganic glasses and crystals. Complexes of lanthanide ions with organic ligands hold the promise that for some applications they may provide alternatives. Scientists are working on

* luminescence: the emission of light by sources other than a hot, incandescent body. It is caused by the movement of electrons within a substance from more energetic states to less energetic states.
polymers doped with lanthanide complexes for optical amplification,[3-5] and the first prototypes of flat panel displays containing lanthanide complexes have seen the light.[6-8]

Currently, the most important use of luminescent lanthanide complexes is in medical diagnostics, where they are used to detect small amounts of biomolecules that can tell about the physical state of a patient. The well-known DELFIA (Dissociation Enhanced Lanthanide Fluorescence Immunoassay) detection scheme[9] of the Finnish company Wallac (now owned by PerkinElmer Lifesciences) is the basis of a large number of clinical tests, e.g. for testing newborn babies, in the diagnosis of many diseases and even to detect BSE (bovine spongiform encephalopathy, or mad cow disease).[10]

All these applications of lanthanide luminescence exist because of the initial scientific curiosity that led people to investigate the chemistry and physics of the lanthanide ions. On the other hand, the prospects of potential applications has stimulated further research which deepened the knowledge on lanthanide ions. In this Chapter, we will discuss several aspects of lanthanide ions and their (photo)luminescent complexes, beginning with a short historiography and ending with an overview of luminescent lanthanide complexes.

Table 1-1. Lanthanum and the lanthanides: electronic configuration, ionic radius, and some electrochemical[11] properties of their tervalent ions.

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Symbol</th>
<th>M$^{3+}$</th>
<th>M$^{3+}$ radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>Lanthanum</td>
<td>La</td>
<td>[Xe]</td>
<td>1.061</td>
</tr>
<tr>
<td>58</td>
<td>Cerium</td>
<td>Ce</td>
<td>[Xe]4f$^1$</td>
<td>1.034</td>
</tr>
<tr>
<td>59</td>
<td>Praseodymium</td>
<td>Pr</td>
<td>[Xe]4f$^2$</td>
<td>1.013</td>
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<tr>
<td>60</td>
<td>Neodymium</td>
<td>Nd</td>
<td>[Xe]4f$^3$</td>
<td>0.995</td>
</tr>
<tr>
<td>61</td>
<td>Promethium</td>
<td>Pm</td>
<td>[Xe]4f$^4$</td>
<td>0.979</td>
</tr>
<tr>
<td>62</td>
<td>Samarium</td>
<td>Sm</td>
<td>[Xe]4f$^5$</td>
<td>0.964</td>
</tr>
<tr>
<td>63</td>
<td>Europium</td>
<td>Eu</td>
<td>[Xe]4f$^6$</td>
<td>0.950</td>
</tr>
<tr>
<td>64</td>
<td>Gadolinium</td>
<td>Gd</td>
<td>[Xe]4f$^7$</td>
<td>0.938</td>
</tr>
<tr>
<td>65</td>
<td>Terbium</td>
<td>Tb</td>
<td>[Xe]4f$^8$</td>
<td>0.923</td>
</tr>
<tr>
<td>66</td>
<td>Dysprosium</td>
<td>Dy</td>
<td>[Xe]4f$^9$</td>
<td>0.908</td>
</tr>
<tr>
<td>67</td>
<td>Holmium</td>
<td>Ho</td>
<td>[Xe]4f$^{10}$</td>
<td>0.899</td>
</tr>
<tr>
<td>68</td>
<td>Erbium</td>
<td>Er</td>
<td>[Xe]4f$^{11}$</td>
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<tr>
<td>69</td>
<td>Thulium</td>
<td>Tm</td>
<td>[Xe]4f$^{12}$</td>
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<tr>
<td>70</td>
<td>Ytterbium</td>
<td>Yb</td>
<td>[Xe]4f$^{13}$</td>
<td>0.858</td>
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<tr>
<td>71</td>
<td>Lutetium</td>
<td>Lu</td>
<td>[Xe]4f$^{14}$</td>
<td>0.848</td>
</tr>
</tbody>
</table>

$E_{\text{red}} = -0.35$ V vs NHE

$E_{\text{red}} = -1.05$ V vs NHE
1.2 History

1.2.1 Discovery and purification 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 fractional crystallisations: C. James once performed 15000 recrystallisations to obtain ‘pure’ Tm(BrO$_3$)$_3$.

These difficulties are a result of the lanthanides 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.

Until World War II, the only 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$_4$. Among the lanthanide ions, Eu$^{3+}$ is by far most easily reduced. McCoy generously provided other scientists with samples of Eu$^{3+}$. In fact, the first studies on Eu$^{3+}$ complexes in solution (Section 1.2.2) were made possible by these gifts.

The Manhattan project during World War II yielded the first large-scale separation methods for lanthanide ions. The ion-exchange chromatographic methods 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.

Rare earth ions are more common than the name implies: La, Ce and Nd are more abundant on earth than Pb, and over 100 minerals containing them have been described. However, only a few of these minerals contain lanthanides in sufficient amount to warrant commercial extraction. Among the major sources are bastnasite, monazite, and xenotime. However, Eu is present only at about 0.1% or less in these ores and is present in about 1 ppm in the earth’s crust. Pm, which is radioactive, does not occur in nature, and was first made by man in 1945.
1.2.2 A brief history of the photophysical studies on lanthanide ions

The unusually sharp absorption lines of rare earth compounds were first observed by Becquerel\textsuperscript{[13]} in 1906 when he measured the spectrum of the mineral xenotime ($\text{YPO}_4$ containing traces of Er, Ce and Th). Low temperature studies carried out in Kamerlingh Onnes’ laboratories\textsuperscript{[14]} showed that the lines could be as narrow as those of the absorption lines of free atoms or molecules. The crystal absorption lines were also shown to exhibit a considerable Zeeman splitting in an applied magnetic field. However the origin of the spectra remained a mystery.

Around 1930, Bethe,\textsuperscript{[15]} Kramers\textsuperscript{[16]} and Becquerel\textsuperscript{[17]} 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 remains 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 puzzle\textsuperscript{[18]} and showed using a very simple and highly 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\textsuperscript{11} 5d\textsuperscript{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. Freed \textit{et al.}\textsuperscript{[19]} found that the relative intensities of the absorption lines of $\text{Eu}^{3+}$ were different in different solvents, and Weissman\textsuperscript{[20]} discovered that complexes of $\text{Eu}^{3+}$ with certain ultraviolet absorbing ligands were highly luminescent when excited with ultraviolet light. Since $\text{Eu}^{3+}$ itself has only a few, very weak absorption bands, solutions of this ion are not very brightly photoluminescent. Obviously, certain organic ligands can serve to photosensitise the luminescence of lanthanide ions. It was also found\textsuperscript{[21]} 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 two decades after the war. 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\textsuperscript{6} energy levels of all trivalent lanthanides in the IR, visible and UV spectral region was given by Dieke in the 1960s.\textsuperscript{[22]} Because of the small influence of the host lattice on the levels the diagram is applicable to trivalent lanthanides in any compound. Figure 1-1 contains an adapted version of the original diagrams by Dieke and Carnall \textit{et al.}\textsuperscript{[23]}
Figure 1-1. Term scheme indicating the electronic energy levels of several lanthanide ions. The commonly observed luminescent state has been marked with a filled circle. The next lower-lying state (the ‘highest non-luminescent state’) is indicated by an open circle.
The calculation of the intensities of the induced electric dipole transitions between energy levels of the lanthanide ions became possible through the theoretical work of Judd\cite{24} and Ofelt\cite{25} published in 1962. 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. Application to ions in complexes with organic ligands is much rarer.

Also at the beginning of the 1960s (twenty years after the first report\cite{20}), systematic studies of luminescent lanthanide complexes and their photophysics appeared.\cite{26-32} 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. 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.\cite{33-35}

### 1.3 Photophysics of lanthanide ions

#### 1.3.1 Electronic 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. 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. Put simply, depending on their number, there are many ways to distribute the electrons over the 7 4f-orbitals, but some distributions are energetically more favourable. The interactions that split up the levels belonging to the [Xe] 4f$^n$ 5d$^0$ configuration are clarified in Figure 1-2, where we have taken the Eu$^{3+}$ ion as an example.

Of the interactions, the Coulombic, representing the electron-electron repulsions within the 4f orbitals, is the largest and yields terms with a separation in the order of $10^4$ cm$^{-1}$. These terms are in turn split into several J-levels by spin-orbit coupling, which is relatively large ($10^3$ cm$^{-1}$) because of the heavy lanthanide nucleus. 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. In this work, we will largely ignore this fine structure, although it may be used to gather information about the symmetry of the coordination environment.\cite{36}
1.3.2 Radiative transitions

In the free ion, only magnetic dipole (MD) transitions are allowed. These are selected by the $\Delta J = 0, \pm 1$ (but $J = 0 \leftrightarrow J = 0$ is forbidden) rule. Their intensity is easily calculated\(^{37}\) 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\(^{3+}\). In a coordinating environment, electric dipole (ED) transitions are induced as the ligand field mixes odd-parity configurations slightly into the [Xe] 4f\(^7\) 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 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\(^{3+}\).

Both MD and induced ED transitions of lanthanide ions are weak compared to the ‘fully allowed’\(^{38}\) 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 M\(^{-1}\) cm\(^{-1}\) with bandwidths of less than 0.2 nm. This makes the long-lived photoluminescence of lanthanide ions difficult to excite.
1.3.3 Nonradiative relaxation of excited lanthanide ions

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 place. Under favourable conditions, emission from ‘higher’ excited states is indeed observed, and that process is the basis of upconversion,\(^{[39,40]}\) 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,\(^{[41,42]}\) in which a highly excited ion emits sequentially two photons.

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.\(^{[43]}\) 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 between the vibronic wavefunctions. A semi-quantitative treatment was given by Haas and Stein.\(^{[44]}\)

As a result of vibration-mediated nonradiative decay, luminescence of a given lanthanide ion occurs mainly from one state (indicated by the filled circles in Figure 1-1), which is the state that has a large gap with the next-lower 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, the emission of lanthanide ions stem (almost) exclusively from one level, and therefore the number of emission lines is limited (Table 1-2).

One should, however, not expect the nonradiative decay rate to depend only on the energy gap and the number of ‘fitting’ matrix vibrations. Multiphonon relaxation still involves electronic transitions in the ion without a change in parity. Weber\(^{[43]}\) pointed out that also for this process selection rules apply, although these only affect a few transitions, such as \(5\text{D}_1 \leftrightarrow 5\text{D}_0\) in Eu\(^{3+}\) (and Tb\(^{3+}\)). Indeed, even in organic media, weak luminescence from the ‘higher excited’ \(5\text{D}_1\) state is observed (see e.g. Chapter 7).

1.4 Luminescent lanthanide complexes

1.4.1 Introduction

We mentioned in Section 1.2.2 that the first report of a brightly photoluminescent lanthanide complex dates back to 1942.\(^{[20]}\) That work can be considered the starting point for the research and development of luminescent lanthanide complexes. It took, however, about twenty years before photochemists developed a serious interest in these materials. Again
Table 1-2. The typical emission bands of the lanthanide ions Eu\(^{3+}\), Tb\(^{3+}\), Nd\(^{3+}\), Er\(^{3+}\), and Yb\(^{3+}\) in solution.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Transition</th>
<th>Emission</th>
<th>Ion</th>
<th>Transition</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(^{3+})</td>
<td>(5^D_0 \rightarrow 7^F_0)</td>
<td>580 nm</td>
<td>Nd(^{3+})</td>
<td>(4^F_{3/2} \rightarrow 4^F_{9/2})</td>
<td>880 nm</td>
</tr>
<tr>
<td></td>
<td>(7^F_1)</td>
<td>590 nm</td>
<td></td>
<td>(4^F_{11/2})</td>
<td>1060 nm</td>
</tr>
<tr>
<td></td>
<td>(7^F_2)</td>
<td>613 nm</td>
<td></td>
<td>(4^F_{13/2})</td>
<td>1330 nm</td>
</tr>
<tr>
<td></td>
<td>(7^F_3)</td>
<td>650 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(7^F_4)</td>
<td>690 nm</td>
<td>Er(^{3+})</td>
<td>(4^I_{13/2} \rightarrow 4^I_{15/2})</td>
<td>1550 nm</td>
</tr>
<tr>
<td></td>
<td>(7^F_5)</td>
<td>710 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb(^{3+})</td>
<td>(5^D_4 \rightarrow 7^F_6)</td>
<td>490 nm</td>
<td>Yb(^{3+})</td>
<td>(2^F_{5/2} \rightarrow 2^F_{7/2})</td>
<td>980 nm</td>
</tr>
<tr>
<td></td>
<td>(7^F_5)</td>
<td>545 nm</td>
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<td>(7^F_2)</td>
<td>650 nm</td>
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</table>

twenty years later, at the beginning of the 1980s, the field received a new impulse when it became clear that lanthanide complexes could find wide-spread use in medical diagnostics.\(^9\) In the second half of that decade, lanthanide ions also started to receive the attention of the growing group of supramolecular chemists.

Luminescent lanthanide complexes consist of a lanthanide ion encapsulated in a ligand. Generally speaking, the ligand can be tailored to contain built-in functionalities that give the overall complex desired properties. Parameters such as solubility (e.g. compatibility with polymers or aqueous solutions), electrochemical activity, binding affinity for other molecular building blocks, responsivity to external stimuli (such as the presence of certain ions\(^{45, 46}\) etc.) are all influenced by the overall structure of the ligand.

![energy transfer](image)

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**Figure 1-3.** General architecture of luminescent lanthanide complexes
In most cases (Figure 1-3) - and very much so in the present work - the ligand contains a light-absorbing group in the form of an organic chromophore. Such a group is generally referred to as the antenna chromophore, in analogy to the light harvesting centra in photosynthetic reaction centra. The photonic energy absorbed by this antenna can be transferred to the encapsulated lanthanide ion, thus circumventing the photoexcitation bottleneck posed by the small absorption cross-sections of the lanthanide ions. This concept of photosensitisation of lanthanide luminescence will be detailed in Section 1.4.3.

An important function of the ligand in all luminescent lanthanide complexes is to be a tight container for the ion and to protect the lanthanide ion from being quenched by high-energy vibrations, especially if the complex is to be used in aqueous solution, since O-H is a well-known quencher for lanthanide ions. More on the radiative and nonradiative processes occurring in excited lanthanide ions in luminescent complexes in Section 1.4.5. First, we will give a small overview of the coordination chemistry of lanthanide ions.

### 1.4.2 Coordination chemistry of lanthanide ions

All of the trivalent lanthanide ions (Ln\(^{3+}\)) share a number of common coordination properties. Their coordination chemistry exhibits some variability across the lanthanide series, but this variability is much less pronounced than is found among transition-metal ions. The Ln\(^{3+}\) ions may be classified as "hard" acids. Therefore, it is expected (and observed) that among the donor atoms most commonly used the binding preference is O > N > S. Furthermore, it is generally agreed that Ln\(^{3+}\)-ligand coordination occurs predominantly via ionic bonding interactions, leading to a strong preference for negatively charged donor groups that are also "hard" bases, and neutral donors that possess large ground-state dipole moments such as amide carbonyl oxygens. Water molecules and hydroxide ions are particularly strong ligands for Ln\(^{3+}\), so that in aqueous solution only ligands containing donor groups having negatively charged oxygens (such as carboxylate, sulfonate, phosphonate, phosphinate) can bind strongly. In aqueous solution, donor groups containing neutral oxygen of nitrogen atoms generally bind only when present in multidentate ligands that contain at least one or two other donor groups having negatively charged oxygen.

The predominantly ionic character of Ln\(^{3+}\)-ligand interactions and the relatively low charge-to-ionic radius ratios of the Ln\(^{3+}\) ions account for several additional aspects of lanthanide coordination chemistry. First, there is little or no directionality in the Ln\(^{3+}\)-ligand interactions so that primary coordination numbers and complex geometries are determined almost entirely by ligand characteristics (conformational properties and the number, sizes and charged nature of donor groups). The only lanthanide property of importance in this regard is the ionic radius. Lanthanide complexes exhibit coordination numbers ranging from six to twelve, with eight and nine being the most common.

### 1.4.3 Photosensitisation of lanthanide luminescence

The trick that is usually applied to efficiently photoexcite lanthanide ions in spite of their extremely weak absorption lines, is to have an organic antenna chromophore absorb the
light and transfer this energy to the lanthanide ion. One might expect that electronic energy transfer to lanthanide ions is not so readily achieved as energy transfer to organic chromophores whose electronic transitions are fully allowed. Nevertheless a plethora of organic chromophores have been found to sensitise the photoluminescence of lanthanide ions. The first compounds found to be suitable sensitisers are β-diketones (such as 1) and simple aromatics (dipicolinic acid, 3, and salicylic acid, 4). All of these compounds form complexes with lanthanide ions ensuring that the distance between the sensitiser and the ion is small. Only in that case efficient sensitisation can take place.

The highly distance-dependent energy transfer is likely to take place via an electron exchange (Dexter-type) mechanism. A dipole-dipole (Förster type) mechanism would require that at least the electronic transition of the energy acceptor (i.e. the ion) is allowed. Results from studies on energy transfer from triplet excited acetonaphthone and acetylfluorene to lanthanide ions indeed support an exchange mechanism. Other studies on polycyclic aromatic hydrocarbons corroborate this. A comparison of the complexes in Chapters 4 and 5 will underline the extreme distance dependence of the (Dexter-type) intracomplex energy transfer, which is presumably operational in luminescent lanthanide complexes.

However, it is not only the distance that is a crucial factor in determining the rate and eventually the efficiency of energy transfer. An expression for the rate of exchange (Dexter) energy transfer is given by Equation 1-1.

\[
k_{ET}(\text{exchange}) \propto \frac{h}{2\pi} J^2 \exp\left(-\frac{2R_{DA}}{L}\right)
\]

where \(J\) is a spectral overlap integral, and \(R_{DA}\) is the donor-acceptor separation. \(P\) is related to specific orbital interactions and \(L\) determines the length scale of the exchange interaction. Both \(P\) and \(L\) are not easily related to experimentally accessible parameters. For \(L\) sometimes the sum of the van der Waals radii of donor and acceptor are taken.
Thus, apart from being critically dependent on energy donor-acceptor distance, also the 'spectral overlap', \( J \), of the emission of the donating state and the absorption of the ion is important for the rate of energy transfer. In the case of Dexter type transfer this spectral overlap integral represents merely a matching of the energy levels involved. It is therefore independent of the oscillator strengths of the transitions in the donor and the acceptor. For its evaluation, the emission spectrum of the donor and the absorption spectrum of the acceptor are normalised so that both their areas are unity.

Recently, Malta et al. have embarked upon a detailed theoretical analysis of the energy transfer rates in sensitiser-containing lanthanide complexes.\(^{[52-54]}\) They obtained expressions for the energy transfer probabilities based on Coulombic and exchange mechanisms. As one could expect, these expression are quite similar to the well-known Förster and Dexter formulations. The main difference is that they contain some lanthanide-specific terms. These terms have thus far not been connected to experimentally accessible quantities and some of them will probably never be. As a result, quantitative agreement between theory and experiment is difficult to achieve. Nevertheless the expressions give rise to some important selection rules, and none of them rule out the antenna singlet state for achieving energy transfer.

Although the theoretical treatment of energy transfer from an organic 'antenna' to a lanthanide ion does not rule out the possibility of energy transfer from the singlet state of the antenna, experimental investigations\(^{[26-28, 55]}\) have indicated that in general the triplet state of the antenna is involved in photosensitisation. Although Kleinerman\(^{[56]}\) pointed out that these studies still do not rigorously exclude the singlet state as a potential energy donor, singlet energy transfer is not observed in lanthanide complexes because it is usually too slow to compete with other processes like antenna fluorescence and especially intersystem crossing.\(^{[57, 58]}\)

The mechanism of photosensitisation in lanthanide complexes that is currently generally accepted is illustrated in Figure 1-4. Excitation of the antenna into its (allowed) singlet-singlet transition is followed by intersystem crossing (ISC) after which the antenna is in its triplet state. ISC competes with other processes that occur from the antenna's singlet state, in particular fluorescence. From the triplet excited antenna, the energy migrates to the lanthanide ion. Also this process competes with other ways that deactivate the antenna triplet state, such as quenching by molecular (triplet ground state) oxygen. Oxygen sensitive sensitised lanthanide luminescence is a clear sign that energy transfer from the antenna to the ion is rather slow.

According to the scheme in Figure 1-4, the quantum yield of the lanthanide luminescence that is excited via the antenna chromophore, \( \Phi_{\text{tot}} \), is the product of the yields of the individual three steps: intersystem crossing (\( \Phi_{\text{ISC}} \)), energy transfer (\( \Phi_{\text{ET}} \)) and lanthanide luminescence (\( \Phi_{\text{Ln}} \)). The factors determining \( \Phi_{\text{Ln}} \) will be described in Section 1.4.5.

\[
\Phi_{\text{tot}} = \Phi_{\text{ISC}} \Phi_{\text{ET}} \Phi_{\text{Ln}}
\]  
(1-2)
Generally accepted view of the energy conversion process in luminescent lanthanide complexes.

Figure 1-4 contains another implication. Irrespective of the actual antenna states involved in the sensitisation process, the triplet state of the antenna needs to be sufficiently higher in energy than the luminescent state of the lanthanide ion. Energy transfer from a lanthanide ion back to the triplet state of the antenna might be relatively slow, but can nevertheless effectively compete with the slow radiative rate of excited lanthanide ions. Such back energy transfer is irreversible if the triplet state is lower, but if the triplet is situated only slightly higher that the luminescent state of the ion, back energy transfer can still occur as a thermally activated process.\(^{[32, 57]}\)

The fact that the lowest (triplet) excited state of the antenna chromophore should have a sufficiently high energy puts a constraint on the chromophores that can actually be applied as photosensitisers for a certain lanthanide ion. Both intersystem crossing and energy transfer are ‘downhill’ processes. The vast majority of luminescent lanthanide complexes that have been studied today are based on \(\text{Eu}^{3+}\) and \(\text{Tb}^{3+}\) which luminesce in the visible and on basis of the above considerations it can be estimated\(^{[59]}\) that the long-wavelength edge of the excitation window for these complexes is in the ultraviolet. This is less desirable in view of applications of such complexes as luminescent labels, since the use of UV excitation causes extensive scattering and excitation of background fluorescence from biological material, requires quartz optics, and is harmful to vital biomatter.

If one would use lanthanide ions with luminescent states that are less energetic than those of \(\text{Eu}^{3+}\) and \(\text{Tb}^{3+}\), it would become possible to use antenna chromophores absorbing at longer wavelengths. The prospect of using visible light to excite the long-lived, narrow band emission of lanthanide ions is one of the incentives to carry out the work presented in Chapters 4, 5, 6, and 7 of this thesis.

1.4.4 The influence of the lanthanide ion on the antenna chromophore

Apart from the influence that the antenna chromophore has on the lanthanide ion, namely that it photosensitises its luminescence, there are also effects that the ion has on the
chromophore. Within the paradigm of Figure 1-4, these effects (which have received relatively little attention in the literature) have three sources: (1) the triple positive charge of the ion, (2) its heavy nucleus and, particularly in the case of Eu$^{3+}$ and Yb$^{3+}$, (3) its electrochemical activity.

The charge of the ion and the related electric field usually leads to (often relatively small) changes in the absorption spectrum and the locations of the electronic energy levels of the antenna chromophore. This electrostatic perturbation is likely to be highly distance and orientation dependent, and big changes in the absorption spectrum of an antenna chromophore may be indicative of a close contact between ion and sensitiser, which is beneficial for energy transfer. Extreme cases of changes in the absorption spectra of antenna chromophores that are a result of the presence of a lanthanide ion can be found in Chapter 7.

The most noticeable effect on the photophysics of organic chromophores that both the heavy nucleus and the electrochemical activity of lanthanide ions may have is quenching of the chromophores’ fluorescence. In the first case, the heavy, paramagnetic nucleus enhances intersystem crossing$^{[21, 60-62]}$ leading to formation of more triplet excited antennae at the expense of antenna fluorescence. This is favourable for the sensitisation process: the lanthanide ion helps the chromophore to behave like a good sensitisier.

In complexes with lanthanide ions having low reduction potentials, Eu$^{3+}$ and Yb$^{3+}$, the antenna fluorescence may also be quenched by a electron transfer fueled by the energy contained in the excited singlet of the antenna.$^{[63]}$ In the case of Eu$^{3+}$ this gives rise to a ligand-to-metal charge transfer (LMCT) state, (antenna$^{+}$; Eu$^{2+}$), that decays nonradiatively, thus leading to a dramatic reduction of the overall sensitised luminescence quantum yield. The occurrence of LMCT has been identified as the most prominent cause of the failure of various chromophores to sensitisie Eu$^{3+}$ luminescence.$^{[64-66]}$

Charge recombination from the LMCT state of Yb$^{3+}$, (antenna$^{+}$; Yb$^{2+}$), may leave the Yb$^{3+}$ in an excited state. Horrocks et al.$^{[67]}$ were the first to point out this possibility, which is unique to Yb$^{3+}$ complexes. It constitutes a sensitisation mechanism which is quite different from the excitation-intersystem crossing-energy transfer scheme (Section 1.4.3), but this does not mean that photosensitised Yb$^{3+}$ is exclusively generated by this ‘internal redox’ mechanism, as Horrocks et al. suggest. In Chapters 4 and 7, it will be shown that in most cases the ‘conventional’ (triplet) mechanism is operational.

1.4.5 Luminescence; nonradiative deactivation of lanthanide ions

The overall quantum yield $\Phi_{\text{tot}}$ of a luminescent lanthanide complex (Equation 1-2) is partially determined by the quantum yield of the lanthanide luminescence step, $\Phi_{\text{Ln}}$. Nonradiative relaxation of the excited state of lanthanide ions is a generally occurring process, as we already pointed out in Section 1.3.3, and therefore $\Phi_{\text{Ln}}$ is always less than 1. Especially matrices containing high-energy vibrations such as organic ligands and aqueous solutions are very effective in mediating this type of relaxation. If $k_{r}$ is the sum of the rate of the radiative processes occurring from the luminescent state of the lanthanide ion and
\(k_{\text{nr}}\) the sum of the nonradiative processes, the quantum yield of lanthanide luminescence is given by

\[
\Phi_{\text{Ln}} = \frac{k_r}{k_r + k_{\text{nr}}} \tag{1-3}
\]

The radiative rate is related to the probabilities of the luminescent transitions and depends on the lanthanide ion and the coordinating environment (see also Section 1.3.2). It is usually in the order of 1000 s\(^{-1}\), but its precise value in luminescent lanthanide complexes has never been studied systematically, not even for Eu\(^{3+}\) and Tb\(^{3+}\) complexes. We will discuss this problem further in Chapter 3.

The radiationless transitions from the luminescent states of lanthanide ions \((k_{\text{nr}})\) and complexes in solution have received much more attention.\(^{[44, 68-74]}\) Particularly, complexes of Eu\(^{3+}\) and Tb\(^{3+}\) have been studied in great detail. For these two ions, especially the O-H oscillator is an effective luminescence quencher. For a lanthanide complex to be successfully luminescent in aqueous solution, it needs a ligand that shields the ion from quenching water molecules.

Exchanging O-H for O-D (e.g. by dissolving the lanthanide salt or complex in D\(_2\)O instead of H\(_2\)O) usually leads to a dramatic increase in observed lifetime and quantum yield of lanthanide luminescence. O-D is a lower energy vibration, and a less efficient quencher, since more vibrational quanta are needed to bridge the gap between the luminescent state of the lanthanide ion and the next lower one (Section 1.3.3). Selective deuteration of the surrounding matrix provides a way to study the contributions of different vibrations to \(k_{\text{nr}}\).

Recently, the non-radiative deactivation of excited lanthanide ions in complexes with organic ligands was studied systematically by Beeby \textit{et al.}\(^{[74]}\) Their paper contains a good overview of the work that has been done on elucidating the role of different vibrational oscillators in quenching the luminescence of lanthanide ions. Moreover, they provide additional data, and give estimates of the contributions that various types of vibrations make to \(k_{\text{nr}}\) (Table 1-3).

Water molecules that are directly bound to the lanthanide ion are the most efficient quenchers. Therefore it is of the utmost importance in the design of luminescent complexes for application in aqueous solution that water molecules be excluded from the first coordination sphere of the ion. Apart from the water molecules bound directly to the ion, the role of closely diffusing O-H oscillators should also not be underestimated: they limit e.g. the luminescence lifetime of Yb\(^{3+}\) complexes in aqueous solution to 5 \(\mu\)s.

It should be noted that there may be contributions to \(k_{\text{nr}}\) other than energy transfer to vibrations in the coordination environment of the ion. States that lie only slightly higher than the luminescent state can, with the aid of thermal activation, provide an alternative deactivation path and contribute to \(k_{\text{nr}}\). Especially LMCT states in Eu\(^{3+}\) complexes
Table 1-3. Contributions (s\(^{-1}\)) of various commonly encountered ligand and solvent vibrations to the rate of nonradiative deactivation (\(k_{nr}\)) of the luminescent states of Tb\(^{3+}\), Eu\(^{3+}\) and Yb\(^{3+}\) as reported by Beeby et al.\(^{74}\)

<table>
<thead>
<tr>
<th></th>
<th>Tb(^{3+})</th>
<th>Eu(^{3+})</th>
<th>Yb(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>bound H(_2)O (per molecule)</td>
<td>2.0 x 10(^2)</td>
<td>8.3 x 10(^2)</td>
<td>1.0 x 10(^6)</td>
</tr>
<tr>
<td>closely diffusing H(_2)O (total)</td>
<td>60</td>
<td>2.5 x 10(^2)</td>
<td>2.0 x 10(^5)</td>
</tr>
<tr>
<td>C-H (per oscillator(^a))</td>
<td>0</td>
<td>25</td>
<td>1 x 10(^4)</td>
</tr>
<tr>
<td>amine N-H (per oscillator(^b))</td>
<td>90</td>
<td>1.2 x 10(^3)</td>
<td>1 x 10(^4)</td>
</tr>
<tr>
<td>amide N-H (per oscillator)</td>
<td>0</td>
<td>75</td>
<td>1 x 10(^4)</td>
</tr>
</tbody>
</table>

\(^a\) different for different types of C-H, values given are typical values
\(^b\) from small data set

(Section 1.4.4) are notorious. This too should be taken into account when designing luminescent lanthanide complexes.

1.4.6 Examples

In this section, some examples of luminescent lanthanide complexes will be discussed. We do not intend to give a comprehensive overview. Numerous review papers exist,\(^{54, 57, 66, 75-79}\) and the reader is referred to those papers for such an overview. Here we will limit ourselves to some special cases. Since this thesis will describe work on near-infrared luminescent complexes, we will pay special attention to other work on near-infrared luminescent complexes.

Derivatives of the first two examples (5 and 6) are actually used as labels in homogeneous immunoassays,\(^{80, 81}\) in which they serve as luminescence energy donors that transfer their energy to fluorescent acceptors on a microsecond time scale. A signal is generated only when donor and acceptor are close together, \textit{i.e.} attached (via antibodies) to the same analyte.

Complex 5\(^{82, 83}\) is the result of many years of optimising the ligand structure,\(^{84}\) and has excellent photophysical properties (Table 1-4) such as appreciable extinction coefficients at relatively long wavelengths combined with a high quantum yield for a lanthanide complex in aqueous solution. In the Eu\(^{3+}\) complex, the energy transfer from antenna to ion is expected to be optimal.

The photophysical properties of 6\(^{85}\) are less favourable: its absorption maximum lies at a short wavelength (300 nm) and its overall luminescence quantum yield is much lower than that of 5 because of incomplete energy transfer and thermally accessible LMCT states. On the other hand, 6 has an elegant architecture in which the ion is completely surrounded by sensitisers, and which leads to kinetically and thermodynamically stable complexes.

A more straightforward approach to luminescent Eu\(^{3+}\) and Tb\(^{3+}\) complexes is to take a ligand that is known to tightly bind lanthanides (such as EDTA or DTPA) and to attach to it a UV absorbing chromophore. Ligand 7, which has in fact salicylic acid (4) built in as a
sensitiser, combines with Tb$^{3+}$ to give highly luminescent complexes.$^{[86, 87]}$ Its Eu$^{3+}$ complexes are less successful, probably due to deactivation of the antenna by means of an LMCT process. Selvin and co-workers used carbostyryl 124 as antenna chromophore to obtain ligand 8,$^{[88-90]}$ the lanthanide complexes of which they applied in luminescence resonance energy transfer experiments to measure distances in biomolecular studies.$^{[91]}$ Later,$^{[62]}$ the effectiveness of carbostyryl as a sensitiser was questioned.

The group of Parker$^{[76, 92]}$ has developed quite some expertise in synthesising cyclen (= 1,4,7,10-tetraazacyclododecane) derivatives such as 9$^{[93, 94]}$ and 10$^{[62]}$ and employing those as ligands in luminescent lanthanide complexes. Lanthanide complexes of derivatives of 9 (e.g. with R = CH$_2$Ph) are extremely stable, and in those complexes the ion is almost completely shielded from the solvent. As a result, the Tb$^{3+}$ complex achieves an impressive overall quantum yield of 0.44. The Eu$^{3+}$ complex does not luminesce that well, but that is probably a result of the phenyl group not being a suitable sensitiser for this ion. Also the Tb$^{3+}$ complex would benefit from a ‘better’ sensitiser than the phenyl group, especially one that absorbs at longer wavelengths.

Ligands 11$^{[45]}$ and 12$^{[95]}$ are both sensitiser containing ligands whose binding arms consist of chiral side groups. As a result, the lanthanide luminescence is partially circularly polarised$^{[96, 97]}$ with the polarisation depending on the configuration of the chiral groups.
The phenanthridine group in 11 sensitises both Eu$^{3+}$ and Tb$^{3+}$ luminescence, and protonation shifts its absorption band from 350 to 385 nm, making these complexes luminescent pH sensors. Moreover, the sensitisation efficiency in these complexes is oxygen concentration dependent (because of slow energy transfer). Thus, at the same time they are oxygen sensors.

The palladium porphyrin in 12 sensitises the near-infrared Yb$^{3+}$ and Nd$^{3+}$ luminescence, and also in complexes of 12 with these ions the sensitised luminescence is quenched by oxygen. However, when the porphyrin interacts with (or: intercalates into) DNA the quenching effect of oxygen is reduced, leading to an overall enhancement of NIR luminescence. Another example of porphyrin sensitised near-infrared lanthanide luminescence was used by Gaiduk et al.$^{[98]}$

Certain calixarenes have also been found to bind lanthanide ions. The tetraamide 13 was the first calixarene reported to give luminescent lanthanide complexes.$^{[99]}$ In this structure, the lanthanide ion is most probably situated in the 'lower rim' between the ether and the amide oxygens. Calixarene 14$^{[59]}$ contains triphenylene as a sensitising chromophore, which improves the photoluminescence characteristics, but also makes them oxygen sensitive. It appears that just attaching a triplet sensitisier to a ligand binding moiety without minimising the distance between sensitisier and ion usually leads to intracomplex energy transfer rates that are too slow to make the sensitised luminescence oxygen independent.

Very recently, also near-infrared luminescent lanthanide-calixarene complexes have been reported. Fluorescein, which we demonstrated to be a sensitisier for the near-infrared
Luminescence of Yb$^{3+}$, Nd$^{3+}$ and Er$^{3+}$ (see Chapters 4 and 5), was subsequently incorporated by Oude Wolbers et al. into a calixarene ligand similar to 14.$^{[100]}$

Another type of 'supramolecular' hosts for lanthanide ions are the m-terphenyls, such as 15.$^{[101, 102]}$ Their lanthanide complexes are well soluble in organic solvents and polymers, which makes them interesting for polymer fiber optics and lanthanide-doped organic LEDs. In the case of 15, the triphenylene was found to give energy transfer to both the visibly emitting Eu$^{3+}$ and Tb$^{3+}$ ions, and to the near-infrared Nd$^{3+}$, Yb$^{3+}$ and Er$^{3+}$.

Like in the lanthanide complexes of the triphenylene-modified calixarene 14, energy transfer does not occur completely. It was found$^{[101]}$ that the lanthanide complexes 15 probably exist in two conformers, one in which sensitisation occurs and one in which it does not. In the case of azatriphenylene-derivatives 16-18,$^{[103, 104]}$ the ion is closer to the chromophore. Indeed, the sensitisation is fast and oxygen-independent. In dry acetonitril, 16 forms brightly luminescent complexes with Eu$^{3+}$ and Tb$^{3+}$ ions, achieving quantum yields as high as 0.67.$^{[103]}$

Ligands 17 and 18 form luminescent Eu$^{3+}$ and Tb$^{3+}$ complexes in aqueous solution. In spite of the shielding polyaminopolycarboxylic acid moiety and the excellent sensitisation,
complexes with 18 do not have extremely high quantum yields (about 5%). This is most probably due to incomplete protection of the ions from quenching solvent molecules. This protection appears to be much better in complexes with ligands 19 and 20. However, these have less attractive light absorbing characteristics.

Table 1-4 summarises the main photophysical properties of some of the Eu$^{3+}$ and Tb$^{3+}$ complexes that we mentioned in this chapter. It gives an idea which excitation wavelengths and extinction coefficients to expect when working with visibly luminescent lanthanide complexes in (aqueous) solution.

Data on near-infrared luminescent complexes is far more scarce. Table 1-5 contains representative data from recent work on these complexes, which all appeared during the period that the work on this thesis was carried out.
### Table 1-4. Photophysical properties of some of the luminescent lanthanide complexes described in this chapter. The values between parentheses are for deoxygenated solutions.

<table>
<thead>
<tr>
<th>solvent</th>
<th>antenna absorption</th>
<th>Eu(^{3+}) complex</th>
<th>Tb(^{3+}) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\text{max}} / \text{nm})</td>
<td>(\varepsilon_{\text{max}} / \text{M}^{-1}\text{cm}^{-1})</td>
<td>(\Phi_{\text{tot}})</td>
</tr>
<tr>
<td>5</td>
<td>H(_2)O</td>
<td>335</td>
<td>14000</td>
</tr>
<tr>
<td>6</td>
<td>H(_2)O</td>
<td>303</td>
<td>28000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H(_2)O</td>
<td>342</td>
<td>10500</td>
</tr>
<tr>
<td>9</td>
<td>H(_2)O</td>
<td>250</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>10</td>
<td>H(_2)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>H(_2)O</td>
<td>346</td>
<td>0.004</td>
</tr>
<tr>
<td>13</td>
<td>H(_2)O</td>
<td>280</td>
<td>30000</td>
</tr>
<tr>
<td>15</td>
<td>MeOH</td>
<td>340</td>
<td>300</td>
</tr>
<tr>
<td>16</td>
<td>MeCN</td>
<td>347</td>
<td>6440</td>
</tr>
<tr>
<td>17</td>
<td>H(_2)O</td>
<td>352</td>
<td>10100</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>352</td>
<td>25500</td>
</tr>
<tr>
<td>19</td>
<td>H(_2)O</td>
<td>336</td>
<td>10000</td>
</tr>
<tr>
<td>20</td>
<td>H(_2)O</td>
<td>295</td>
<td>0.2</td>
</tr>
</tbody>
</table>

### Table 1-5. Near-infrared luminescent lanthanide complexes described in this chapter. Note that the luminescence lifetimes are now in microseconds.

<table>
<thead>
<tr>
<th>ligand</th>
<th>ion</th>
<th>solvent</th>
<th>antenna absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Yb(^{3+})</td>
<td>H(_2)O</td>
<td>(250)</td>
</tr>
<tr>
<td>15</td>
<td>Yb(^{3+})</td>
<td>DMSO</td>
<td>(340)</td>
</tr>
<tr>
<td></td>
<td>Nd(^{3+})</td>
<td></td>
<td>(300)</td>
</tr>
<tr>
<td></td>
<td>Er(^{3+})</td>
<td></td>
<td>(580)</td>
</tr>
<tr>
<td>21</td>
<td>Nd(^{3+})</td>
<td>acetone</td>
<td>(~10)</td>
</tr>
</tbody>
</table>

Tb complex is oxygen sensitive

R = CH\(_2\)Ph

phenanthridine deprotonated

direct excitation of the ion
As we will see in this thesis, the luminescence quantum yields of near-infrared luminescent lanthanide complexes are generally low. In this respect, complex $21^{[106]}$ is interesting, since it attains a quantum yield of 3%, which is a world record for Nd$^{3+}$ in organic media. This relatively high quantum yield is achieved by excluding high-energy vibrations from the first coordination sphere of the ion, and keeping quenching solvent molecules far away from the ion.

1.5 Scope of this thesis

The core of this work (Chapters 4, 5, and 6) concerns the photosensitisation of near-infrared luminescent lanthanide complexes. One part addresses questions of fundamental nature, such as “what processes occur between the absorption of light by the antenna chromophore and the emission of lanthanide luminescence?”, “how fast are they?” and “what influences these processes?”. The other part consists of trying to use near-infrared luminescent complexes as labels for biomolecules. The combination of visible light excitation with long-lived near-infrared emission that these complexes offer might be advantageous for such an application.

More or less accidentally we discovered that Michler’s ketone combines with EuFOD to give a luminescent Eu$^{3+}$ complex that can be excited at unprecedented long wavelengths, with blue light. This discovery afforded interesting leads for further research, which is described in Chapter 7. The problem of predicting the radiative rates of excited lanthanide ions is addressed in Chapter 3. Contributions were also made to the refinement of the spectroscopic and mathematical tools that are used to investigate the molecular photophysics (Chapter 2) of luminescent lanthanide complexes.
It is the white powder that is obtained after smashing a fluorescent lamp (Caution: this should be done in the hood, and only after warning the other people working in the lab that there may be a little implosion).

References


