Luminescent Lanthanide Complexes: Visible Light Sensitised Red and Near-infrared Luminescence.
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Chapter 7

Interactions between push-pull chromophores and lanthanide β-diketonates

From the near-infrared luminescent complexes described in the previous three chapters we return to the visibly emitting europium(III) complexes, at least during the first part of this chapter. Accidentally a complex was discovered which produces photosensitised Eu$^{3+}$ luminescence upon excitation with visible light. This chapter starts out with a detailed study of this complex and similar ones. The concepts extracted from this study are then applied to near-infrared luminescent lanthanide complexes and to the design and synthesis of complexes more suited for practical application.

7.1 A surprising result

When colourless solutions of Michler’s ketone (4,4'-bis-(N,N-dimethylamino)-benzophenone, MK) and EuFOD (europium tris(6,6,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dione)) in benzene (both 1 mM) are mixed, a yellow colour develops instantaneously. Moreover, a red glow emerges from the solution under daylight illumination. The emission spectrum (Figure 7-2) demonstrates that this red glow is Eu$^{3+}$ luminescence: the sharp peaks are characteristic of lanthanide ion emission, Eu$^{3+}$ usually having its most intense emission around 615 nm. The corresponding excitation spectrum is in accordance with the observation that this luminescence can be excited by visible light. It extends well beyond 450 nm ($\lambda_{\text{max}}$ 414 nm). The quantum yield was found to be 0.17 in aerated solution and 0.20 after deoxygenation by four freeze-pump-thaw cycles (excitation at 420 nm, using quinine bisulfate in 1M H$_2$SO$_4$ as a reference$^2$).

These observations were made during experiments aimed at the observation of intermolecular energy transfer from organic sensitisers to lanthanide complexes and are quite surprising. The colour change indicates a ground-state interaction between the components. Moreover, the product of this interaction seems to defy the rule-of-thumb that only chromophores with their lowest singlet-singlet transitions in the UV can efficiently sensitise Eu$^{3+}$ luminescence.

* Especially in Eu$^{3+}$ β-diketonates, this so-called hypersensitive $^5D_1 \rightarrow ^7F_2$ transition is usually very intense.$^{[1]}$ See also Chapter 3.
Michler's ketone, Mk

EuFOD

**Figure 7-1.** Structural formulae of Michler's ketone and EuFOD.

It was hypothesised that Michler's ketone and EuFOD form a ground-state complex by interaction of the electron rich carbonyl group with the positively charged Eu$^{3+}$ ion. Such interactions are already well known from the use of lanthanide diketonates as NMR shift reagents,$^{[3, 4]}$ and in fact coordination of certain aliphatic substrates to EuFOD has been found to enhance its luminescence quantum yield.$^{[5]}$ Never before, however, has it been reported that complexation of chromophores to lanthanide β-diketonates yields efficiently luminescent Eu$^{3+}$ complexes that absorb visible light.

The new absorption band is probably due to a bathochromic shift of the first singlet-singlet transition of Michler’s ketone occurring upon complexation. This π-π* transition possesses charge-transfer character:$^{[6]}$ in the process of excitation, electron density is moved towards the carbonyl group and therefore it is quite likely that the transition energy is largely affected by the presence of a lanthanide ion. Since for a lanthanide complex to be luminescent, the triplet state of the antenna chromophore needs to lie at higher energies than the luminescent state of the ion, the singlet-triplet gap of the complexed MK must be small. It is known that free MK has such a small gap.$^{[7]}$

**Figure 7-2.** Corrected luminescence excitation ($\lambda_{\text{em}}=612$ nm) and emission ($\lambda_{\text{exc}}=450$ nm) spectra of a solution of 10$^{-5}$ M Michler's ketone and 10$^{-4}$ M EuFOD in benzene.
In the next sections we will confirm these hypotheses, and describe in more detail the structure and the photophysics of MK-EuFOD and related complexes.

7.2 Structure of the complex of MK and EuFOD

Upon closer inspection, the coordination of MK to lanthanide β-diketonates was found to occur only in non-coordinating solvents. Also, water molecules can compete with MK for free coordination sites on the lanthanide ion. Therefore, all reagents and solvents were dried before use. MK was purified according to a literature procedure.[8]

7.2.1 Spectrophotometric titration

The formation of a complex between MK and EuFOD in benzene can be monitored using UV-Vis absorption spectroscopy. Figure 7-3 shows a titration experiment, in which small amounts of a EuFOD stock solution are added to a solution of MK. It clearly shows 1:1 complex formation of MK with EuFOD. The absorption band of the complex resides at longer wavelengths, where MK and EuFOD themselves do not absorb. Analysis of the titration data (see Section 7.3.1) yields the formation constant for the MK-EuFOD complex in benzene, log $K = 4.85$. The extinction coefficient at 414 nm, the absorption maximum, was found to be $3.04 \times 10^4$ M$^{-1}$ cm$^{-1}$.

Figure 7-3. UV/Vis titration of a solution of Michler’s ketone in benzene with EuFOD. To 2.5 mL of a $10^{-5}$ M solution of MK in benzene, a EuFOD solution ($5 \times 10^{-4}$ M in benzene) is added in steps of 50 µL. The inset shows formation of the complex by means of its absorption at 414 nm as a function of the amount of EuFOD solution added. The solid line is the theoretical curve (Equation 7-2) for a 1:1 complex with log $K = 4.85$ and $\varepsilon_{\text{max}} = 3.04 \times 10^4$ M$^{-1}$ cm$^{-1}$. The dilution has been taken into account.
7.2.2 Other β-diketonates: change of ligands and of central ion

The effect of variation of the β-diketonate was explored. In benzene, the maximum of the absorption band varies from 398 nm for MK-Eu(dpm)$_3$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dionate) via 414 nm for MK-EuFOD to 430 nm for MK-Eu(hfa)$_3$ (hfa = 1,1,5,5,5-hexafluoro-2,4-pentanedionate). We tentatively attribute this to a variation of the electrostatic interaction between the MK chromophore and the lanthanide ion in the complexes, related to changes in chromophore-ion distances (see Chapter 7.2.3). Unlike MK-Eu(dpm)$_3$ and MK-EuFOD (both having 0.20 quantum yield in deoxygenated benzene at room temperature), the sensitised luminescence quantum yield of MK-Eu(hfa)$_3$ is very low ($6.2 \times 10^{-5}$ under the same conditions). This might be a result of too low a triplet energy of the antenna chromophore and we will discuss that later.

The same bathochromic shift of the MK absorption as induced by EuFOD is also observed with other lanthanides. Addition of either YbFOD, ErFOD, GdFOD or PrFOD to MK in benzene produces the same 414 nm absorption band in each case. This reflects the electrostatic nature of the interaction: all lanthanide ions carry a 3+ charge and the distance between the ion and the MK should be roughly equal in all complexes, since the structures of all the FOD chelates are expected to be practically the same. They will therefore have the same effect on the electronic energy levels of the chromophore. Obviously, the red glow is only observed with EuFOD.

Although the induced "optical shifts" are the same for different LnFODs, the shifts of the MK $^1$H nuclear magnetic resonances induced by these complexes are entirely different, which clearly shows that the effects have different origins (electrostatic vs. magnetic). For example, EuFOD causes a downfield shift whereas PrFOD shifts the resonances upfield. The protons closest to the carbonyl group are affected most, and the protons on the dimethylaminogroups are relatively unaffected. This supports our view that the MK interacts with the lanthanide diketonate through its carbonyl group.

7.2.3 Semi-empirical (SMLC/AM1) quantum chemical investigation

Results from molecular modeling also point in the direction of complex formation by means of the MK's carbonyl group. We implemented the SMLC (Sparkle Model for Lanthanide Complexes) modification$^{[9, 10]}$ to the AM1 method in the MOPAC 6.0 computer program which allows for the calculation of the structures of lanthanide complexes.

In SMLC/AM1 the lanthanide ion is represented by a trivalent positive point charge (a sparkle), ignoring the many electrons of the lanthanide ion which would seriously complicate quantum chemical calculations. This is justified since lanthanide complexes with organic ligands are based entirely on ionic interactions. The ligand is treated quantum chemically by the AM1 method. The SMLC parameters have been tuned to accurately reproduce the crystal structures of several β-diketonate complexes.$^{[9, 10]}

Figure 7-4 contains two structures found using the SMLC/AM1 model. Feasible structures of both EuFOD and MK-EuFOD are produced. In the latter structure, the distance between the MK carbonyl oxygen and the Eu$^{3+}$ ion, $r_{O-Eu}$, is 2.31 Å which is comparable
to the distance between the diketonate oxygens and the lanthanide, approximately 2.24 Å, and indicates binding interactions between MK and EuFOD.

Figure 7-4. Theoretical structures of anhydrous EuFOD (left) and MK-EuFOD (right) calculated using the SMLC/AM1 model. Hydrogen and fluorine atoms have been omitted for clarity.

The calculated heats of formation (Table 7-1) indicate that complexation of MK to EuFOD is energetically favoured over having the two components separated. Table 7-1 also shows that the complex with Eu(hfa)₃ is even more stable, which is reflected by a decrease of \( r_{O-Eu} \) to 2.17 Å.

We also optimised a structure in which the MK is pointing away from Eu(hfa)₃, denoted by Eu(hfa)₃-MK in Table 7-1. The small energy gain and the large distance from the nearest MK nitrogen to the lanthanide lead us to conclude that that is not the preferred way for MK to bind to the lanthanide \( \beta \)-diketonate.

Attempts to calculate electronic energy levels of the ligands - which is in principle possible using AM1 - failed due to convergence problems and probably require more advanced calculational strategies. SMLC/AM1, however, is currently the only model for lanthanide complexes that is able to reproduce non-ionic electrostatic interactions such as those in MK-EuFOD. The empirical molecular mechanics methods developed by van Veghel[11] and by Durand et al.[12] which are quite successful in predicting not only the structures but also the dynamics of ionic lanthanide complexes in solution, but - because of their non-quantum chemical nature - can not reproduce the charge distribution in the MK donor-\( \pi \)-acceptor system that leads to a binding interaction with lanthanide \( \beta \)-diketonates.
Table 7-1. Results from SMLC/AM1 calculations of MK, EuFOD, Eu(hfa)$_3$ and their complexes. The heats of complex formation ($\Delta H_{\text{complex}}^{\text{AM1}}$) were calculated by taking the difference between the heat of formation ($\Delta H_f^{\text{AM1}}$) of the complex and those of the individual components. For the complexes, the distance between the oxygen of MK and the Eu$^{3+}$ ion, $r_{\text{ion}}$, is given.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_f^{\text{AM1}}$ / kcal mol$^{-1}$</th>
<th>$\Delta H_{\text{complex}}^{\text{AM1}}$ / kcal mol$^{-1}$</th>
<th>$r_{\text{O-Eu}}$ / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>36.24574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EuFOD</td>
<td>-1286.59943</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MK-EuFOD</td>
<td>-1259.504</td>
<td>-9.15031</td>
<td>2.31</td>
</tr>
<tr>
<td>Eu(hfa)$_3$</td>
<td>-1123.99188</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MK-Eu(hfa)$_3$</td>
<td>-1103.92461</td>
<td>-16.17854</td>
<td>2.17</td>
</tr>
<tr>
<td>Eu(hfa)$_3$-MK</td>
<td>-1089.01785</td>
<td>-1.27174</td>
<td>8.38$^b$</td>
</tr>
</tbody>
</table>

a. Structure with the MK ‘pointing away’ from Eu(hfa)$_3$

b. distance between the lanthanide and the nearest MK nitrogen

7.3 Pathway to sensitised luminescence

The sensitisation pathway in luminescent lanthanide complexes generally consists of excitation of the antenna chromophore into its singlet state, subsequent intersystem crossing of the antenna to its triplet state and energy transfer from the antenna triplet to the lanthanide ion,$^{[13]}$ implying that the triplet energy must be sufficiently high. This is necessary even if the triplet state is not directly involved in the energy transfer (in the case of singlet energy transfer): a triplet state lower than the luminescent state of the lanthanide ion will quench it.$^{[14]}$ We will now discuss the energy levels of the coordinated MK antenna chromophore and the processes involved in producing sensitised luminescence.

7.3.1 The singlet state of the antenna

The energy of the antenna-centered singlet state initially populated by excitation can be estimated from the ground-state absorption spectrum of the complex. Figure 7-3 makes it evident that the absorption band corresponding to excitation of MK into its lowest singlet excited state shifts from $\lambda_{\text{max}}$ 348 nm to $\lambda_{\text{max}}$ 414 nm upon complexation. It would, however, be desirable to know the complete absorption spectrum of the complex. The problem is that the spectra in Figure 7-3 are always mixtures of MK, EuFOD and MK-EuFOD.

In Chapter 2, a method was laid out for decomposing sets of spectra (matrices) into the principal individual components, *Singular Value Decomposition* (SVD). Decomposition of a set of absorption spectra leads to vectors representing concentration information and vectors containing spectral data. These vectors are purely mathematical constructs, but can
be turned into physically meaningful curves by appropriate mathematical transformations, that make either the concentration or the spectral vectors fit to a physical model.

The SVD of the matrix built from the titration data of Figure 7-3 clearly indicates the presence of three distinct components (Figure 7-5): significant singular values are only found for these vectors. The concentration and spectral vectors have been plotted as a function of the amount of EuFOD added and the wavelength, respectively. The concentration-related vectors (top right in Figure 7-5) will be transformed into 'real' titration curves by taking suitable linear combinations. The coefficients for this target transformation are obtained using a Simplex method that minimises the difference between these linear combinations and the physical model describing the concentrations of the components as a function of the titration coordinate (see Section 2.7.2 in Chapter 2).

\[
A + B \rightleftharpoons AB
\] (7-1)

In this case, the physical model is a simple equilibrium:

The parameters that 'go into' this model are the equilibrium constant \( K \) and the added concentrations of component A (i.e. MK), \( c_A \), and of component B, \( c_B \). Using the Maple computer program (Waterloo Maple, Inc., Ontario, Canada) we find that the actual concentration of AB, \([AB]\) is given by

\[
[AB] = \frac{c_A c_B}{K + c_A + c_B}
\]
The actual concentrations of the other components are then easily found:

\[ [A] = c_A - [AB] \text{ and } [B] = c_B - [AB] \quad (7-3) \]

In our titrations both \( c_A \) and \( c_B \) are known, experimentally controlled parameters. Since there exists a range of wavelengths where only the complex absorbs and the absorbance is linearly related to \([AB]\), \( K \) is in this case easily obtained by fitting Equation 7-2 to the absorbance at 414 nm (Figure 7-3). Now that we have complete knowledge of the concentrations of all components, we can concentrate on finding the coefficients of the matrix that transforms the abstract concentration vectors.

The curves in the left part of Figure 7-6 are the concentration profiles that we obtain after transformation. The right part is the ‘side product’ of the transformation, the absorption spectra (as extinction coefficients vs. wavelength) of the individual components. Obviously, the spectra of MK and EuFOD can also be obtained directly, but now they are an indication of the validity of the data analysis method used. Moreover, we have now access to the pure absorption spectrum of MK-EuFOD. It is composed of the absorption spectrum of EuFOD, which is practically unchanged, and a shifted version of MK.

![Figure 7-6](image_url)

**Figure 7-6.** Concentration profiles (left) and absorption spectra (right) obtained by transforming the three principal components found in the SVD.

The absorption maxima of the three components and their assignments are collected in Table 7-2, both for benzene and methylcyclohexane solutions. In the latter solvent the shift of the absorption bands of MK upon complexation is of the same magnitude, but the free and the bound MK both have their absorption maxima at shorter wavelengths than when dissolved in benzene. The highly dipolar character of the excited state\[^{[6, 7]}\] of MK is likely to be the cause of this solvatochromism.
Table 7-2. Absorption maxima of MK, EuFOD, and MK-EuFOD in benzene and methylcyclohexane.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda) / nm, benzene</th>
<th></th>
<th>(\lambda) / nm, methylcyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK, (\pi-\pi^*)</td>
<td>346</td>
<td>EuFOD,</td>
<td>414</td>
</tr>
<tr>
<td>MK, (\pi-\pi^*)</td>
<td>312</td>
<td>MK-EuFOD</td>
<td>334</td>
</tr>
<tr>
<td>FOD, (\pi-\pi^*)</td>
<td>300</td>
<td>300</td>
<td>293</td>
</tr>
<tr>
<td>MK, (\pi-\pi^*)</td>
<td>240</td>
<td>254</td>
<td>254</td>
</tr>
</tbody>
</table>

From the absorption spectra and the emission spectra the energy of the lowest singlet excited state of the antenna chromophore in MK-EuFOD is estimated to be 22800 cm\(^{-1}\) (2.83 eV) in benzene and 23700 cm\(^{-1}\) (2.94 eV) in methylcyclohexane.

7.3.2 The triplet state of the antenna

The Gd\(^{3+}\) \(\beta\)-diketonates provide a way to study the triplet state energy of the coordinated MK. Having no electronic energy levels below 32000 cm\(^{-1}\) (310 nm), Gd\(^{3+}\) can not accept any energy from MK, but as mentioned in Section 7.2.2, it induces the same optical shift and eventually enhances singlet-triplet and triplet-singlet transitions in MK through its heavy atom effect. As a result in deoxygenated benzene, even at room-temperature, phosphorescence of MK-GdFOD is observed (excitation at 410 nm), as a broad band peaking at 540 nm (Figure 7-7).

![Figure 7-7](image)

Figure 7-7. Emission spectra of solutions of MK-GdFOD (left graph) and MK-Gd(hfa)\(_3\) (right graph) in benzene, excitation at 410 nm. Dotted lines: aerated solutions, solid lines: deoxygenated solutions.

From the emission spectrum of MK-GdFOD in methylcyclohexane glass at 77K (Figure 7-8), the triplet energy of the coordinated MK is estimated to be 19600 cm\(^{-1}\), which is indeed sufficient to efficiently populate the \(^5D_0\) luminescent state of Eu\(^{3+}\) (17500 cm\(^{-1}\)),
possibly via energy transfer to the $^5D_1$ state (19000 cm$^{-1}$) and subsequent relaxation to $^5D_0$ (see Section 7.3.3). The triplet energy of free MK is around 23000 cm$^{-1}$.[8]

![Figure 7-8. Low temperature emission spectra of MK-GdFOD (solid line) and MK-Gd(hfa)$_3$ (dotted line) (methylcyclohexane, 77K, excitation 420 nm).](image)

Figure 7-8 also contains the low-temperature emission spectrum of MK-Gd(hfa)$_3$ (methylcyclohexane, 77K). It reveals an antenna triplet energy of about 18800 cm$^{-1}$, which means that back energy transfer processes from Eu$^{3+}$ to the coordinated MK in MK-Eu(hfa)$_3$ might readily occur at room temperature. This explains why the quantum yield for sensitised Eu$^{3+}$ luminescence in this complex is so low (see Section 7.2.2).

The ligand centered triplet states of Gd(hfa)$_3$ and GdFOD (also those of the corresponding Eu$^{3+}$ diketonates) themselves were found to be 22400 and 22700 cm$^{-1}$, respectively, from the emission spectra ($\lambda_{\text{exc}} = 320$ nm) of methylcyclohexane solutions of these compounds at 77K. Because of their high energies, these states will not participate in the sensitisation process when the MK-Eu$^{3+}$ β-diketonates are excited in the MK centered long-wavelength absorption band.

### 7.3.3 Energy transfer

Upon laser excitation, MK-GdFOD displays intense excited state absorption bands in the microsecond time domain, which are the triplet-triplet absorptions of the coordinated MK antenna chromophore. Indeed, also these absorption bands are shifted to longer wavelengths compared to free MK (which has an excited state triplet-triplet absorption peaking around 500 nm[15]). We studied the transient absorptions (Figure 7-9) of three complexes using the tunable Coherent Infinity-XPO laser for excitation and a streak camera for analysis of the probe light (see Section 2.6.3, in Chapter 2). The complexes were dissolved in deoxygenated toluene. The streak images were subjected to SVD, and all showed only one principal component, from which the time-resolved and spectrally-resolved curves were constructed (Section 2.7, in Chapter 2).

The lowest triplet state of MK-GdFOD has a lifetime exceeding the time range of the experiment. Its lifetime is estimated to be 8 μs and can be regarded to be the triplet lifetime
in the presence of a lanthanide ion, but in the absence of energy transfer to that ion. The triplet state is quenched if energy accepting lanthanide ions are used. Thus, MK-EuFOD displays a very short-lived $T_{n} \rightarrow T_{1}$ absorption, which cannot be reliably measured in this microsecond time window. The triplet state of MK-YbFOD has a longer lifetime of 103 ns, which indicates a rather slow energy transfer process for this system. Yb$^{3+}$ has only one excited state at low energy (10200 cm$^{-1}$), and this may explain the slow rate of energy transfer.

In the nanosecond domain (Figure 7-10), the triplet-triplet absorption of MK-EuFOD becomes observable. Its kinetics simply follow the excitation pulse, which means that the triplet lifetime is shorter than 1 ns. The energy transfer from the antenna to the lanthanide ion in this complex is very fast, which is in line with the efficient photosensitisation that occurs. The spectra indicate (at least partial) involvement of the triplet state of the antenna. Singlet energy transfer still cannot compete with the extremely fast intersystem crossing in the bound Michler's ketone, which has a rate constant on the order of $10^{11}$ s$^{-1}$. Nevertheless, our results indicate that energy transfer from an organic donor to a lanthanide ion can reach rates significantly faster than $10^{9}$ s$^{-1}$.

### 7.3.4 The lanthanide luminescence step in MK-EuFOD

Rapid population of the excited states of Eu$^{3+}$ after excitation of MK-EuFOD at 440 nm is indeed observed in time-resolved luminescence spectroscopy. Two streak images (photon counting mode) of different time domains are shown in Figure 7-11. Paradoxically, the main emission band of the complex around 615 nm has a rise time of 1.2 µs. In the case of rapid energy transfer one would expect this rise time to be several orders of magnitude shorter. However, the main emissive state ($^{5}D_{0}$) is not directly populated from the antenna’s triplet state. The streak image shows narrow emission bands at shorter wavelengths which decay with that time constant of 1.2 µs. These stem from Eu$^{3+}$’s higher excited $^{5}D_{1}$ state, which is the lanthanide-centered state that is initially populated by energy transfer. We have not been able to see rising components in these emission bands, which is in line with the fast
antenna-to-ion energy transfer that is expected on basis of the observed short-lived triplet of MK-EuFOD.

A question that arises is what the emission spectrum of the higher excited \( ^5D_1 \) state of Eu\(^{3+} \) looks like. The streak image in the right half of Figure 7-12 contains this information. With the aid of the same principal component analysis method used in Section 7.3.1, we are able to separate the emission belonging to \( ^5D_1 \) from that from \( ^5D_0 \). In this case, only the part of the image after decay of the intense, short-lived ligand-centered emission was analysed, otherwise the information is completely dominated by this ‘spike’. The model used contains two components, one rising, one decaying exponentially, both with the same time constant. Figure 7-12 shows the reconstructed temporal and spectral curves belonging to the two emissive states. The energy difference between the \( ^5D_1 \rightarrow ^7F_j \) and the corresponding \( ^5D_0 \rightarrow ^7F_j \) bands is 1650 cm\(^{-1} \), indeed the gap between the \( ^5D_1 \) and \( ^5D_0 \) states.

Eu\(^{3+} \) ions are often used as luminescent probes to predict the spectroscopic properties of lanthanide-doped materials and in (bio)molecular structural studies. The relative inten-

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**Figure 7-10.** Time-resolved absorption spectroscopy for the same samples as in Figure 7-9, now in the nanosecond domain.

**Figure 7-11.** Fluorescence streak images of the emission of MK-EuFOD in toluene (\( \lambda_{\text{exc}} = 440 \text{ nm, approx. } 1.5 \text{ ns FWHM} \)). Left: millisecond domain, right: microsecond domain.
Figure 7-12. Left: Time-evolution of the population of the \( ^5\text{D}_0 \) (solid line) and the \( ^5\text{D}_1 \) (dotted line) states of Eu\( ^{3+} \) in MK-EuFOD. The lines are the model, the dots are the experimental profiles. The vertical line indicates the time after which the experimental data was analysed. Right: The emission spectra associated with the two states. The emission lines in the \( ^5\text{D}_1 \) spectrum have been assigned.

sities of the bands provide information about the direct chemical environment of the ion. Instead of the (usually) 3 or 4 emission bands in the Eu\( ^{3+} \) spectrum, twice as many information carrying bands become available by using time-resolved emission spectroscopy. In Chapter 3 we explained that all three Judd-Ofelt parameters can be estimated from the \( ^5\text{D}_0 \rightarrow \ ^7\text{F}_j \) emission spectrum alone. The additional spectral information can for example be used to make this determination more reliable.

The lifetimes of both excited Eu\( ^{3+} \) states are temperature-dependent (Figure 7-13), as is the quantum yield of sensitised luminescence. On basis of the \( ^5\text{D}_0 \) lifetime, the quantum yield of MK-EuFOD is expected to increase to 0.4 at 77 K. Such a temperature-dependence of the \( ^5\text{D}_0 \) emission has been observed for several Eu\( ^{3+} \) \( \beta \)-diketonates\(^{16-19}\) and is ascribed to (1) back energy transfer to the ligand and (2) activated deactivation through a nearby LMCT state. Temperature-dependence of the \( ^5\text{D}_1 \) lifetime has only been studied in glasses and crystals, where there are no ligand centered states that can quench this state, and less vibrational modes to mediate the relaxation to \( ^5\text{D}_0 \).

Finding a suitable photophysical model and a corresponding set of parameters to describe the curves in Figure 7-13 is a tricky business. A model is depicted in Figure 7-14a. Only the most likely processes have been indicated by arrows: the equilibrium between \( (\text{T}_1; \ ^7\text{F}) \) and \( (\text{S}_0; \ ^5\text{D}_0) \) has been omitted because of the relatively large gap between these states. We have included a low-lying ligand-to-metal charge transfer (LMCT) state. In

* When incorporating MK-EuFOD in a sucrose octaacetate (SOA) glass (m.p. 89 °C), the luminescence is absent when the glass is still hot, and appears as the SOA cools down to ambient temperature.
Eu$^{3+}$ β-diketonates (and several other types of Eu$^{3+}$ complexes) such states are known to provide an additional, non-radiative, deactivation path.

If we assume the equilibrium between ($T_1; 7F$) and ($S_0; 5D_1$) to be fast compared to the interconversion of ($S_0; 5D_1$) and ($S_0; 5D_0$), it may be possible to use the model in Figure 7-14b. Such a model was also used by Alpha et al.$^{[20]}$ to describe the temperature-dependent quantum yields and lifetimes of Eu$^{3+}$ cryptates. For such a kinetic scheme, an exact solution exists.$^{[21]}$

**Figure 7-13.** Temperature dependence of the excited state lifetimes of the $5D_1$ and $5D_0$ states in MK-EuFOD in toluene.

The values of $k_{fwd}$ and $k_0$ are taken from the $5D_1$ and $5D_0$ lifetimes at 77K, and are assumed to be temperature independent. This is only partially justified since multiphonon relaxation rates (i.e. rates of nonradiative relaxation mediated by matrix vibrations) are
PUSH-PULL CHROMOPHORES AS SENSITISERS

known to be slightly temperature-dependent in the temperature range of interest.\cite{22} The rate $k_{bk}$ must be related to $k_{fwd}$ by a Boltzmann-type formula:

$$k_{bk} = k_{fwd} \exp\left(\frac{-\Delta E_{01}}{kT}\right)$$

(7-4)

where $\Delta E_{01}$ should be the energy gap between the $^5D_1$ and $^5D_0$ states. The deactivation of the kinetically combined "antenna triplet + $^5D_1$" state, $k_1$, is modeled by an activated quenching process (which we believe to go through an LMCT state), described by maximal rate $k_Q$ and energy gap $\Delta E_Q$.

$$k_1 = k_Q \exp\left(\frac{-\Delta E_Q}{kT}\right)$$

(7-5)

The energy gaps, $\Delta E_{01}$ and $\Delta E_Q$, and $k_Q$ were adjusted by hand and several luminescence lifetime vs. temperature curves were calculated using the formulae in ref. \cite{20}. One of the better results is shown as solid lines in Figure 7-13. These curves are given by $k_{fwd} = 8.33 \times 10^5 \text{ s}^{-1}$, $k_0 = 2.20 \times 10^3 \text{ s}^{-1}$, $\Delta E_{01} = 1250 \text{ cm}^{-1}$, $\Delta E_Q = 1600 \text{ cm}^{-1}$ and $k_Q = 1.5 \times 10^{10} \text{ s}^{-1}$. The gap $\Delta E_{01}$ is too small compared to the 'real' spectroscopic gap between $^5D_1$ and $^5D_0$ (1650 cm$^{-1}$), which is probably a result of not including other (temperature-dependent) deactivation pathways. A more elaborate model is needed to accurately describe the temperature dependence of the decay times. Such a model would, however, require, more experimental data to get reliable fits. Moreover, extensive studies would be needed to remove all ambiguities in models and parameters.

### 7.4 Interlude

Michler’s ketone forms complexes with lanthanide β-diketonates by interaction of the electron rich carbonyl group with the positively charged lanthanide ion. This interaction causes the lowest singlet-singlet transition to shift to longer wavelengths. The crucial point is that the small energy gap between the singlet and triplet states of the MK chromophore is retained in the complex, which enables the visible light sensitisation of Eu$^{3+}$ in MK-EuFOD. In this complex, the energy transfer from the antenna to the ion occurs within a nanosecond and exclusively to the $^5D_1$ state. At room-temperature, back energy transfer and a low-lying LMCT state compete with sensitised luminescence.

The remaining part of this chapter will deal with two issues. Firstly, complexes with other push-pull chromophores will be investigated, not only in combination with Eu$^{3+}$ but also with the near-infrared luminescent lanthanide ions. Finally, we address the issue of
making complexes that are more stable in hydroxylic media while retaining the attractive properties of having visibly excited Eu$^{3+}$ luminescence.

### 7.5 Other push-pull chromophores

Formation of complexes between electron rich molecules (Lewis bases) and lanthanide β-diketonates is a general concept: the action of diketonates as NMR shift reagents is based on it. We therefore expected to find other chromophores to behave in a similar way as Michler’s ketone.

Several compounds were tested by adding solid LnFOD to solutions of these compounds and monitoring the resulting changes in their absorption spectra. Coumarins and some aromatic ketones such as acetonaphthone and 9-fluorenone did not display significant changes in their absorption spectra when LnFOD was present. In most cases, this is most likely to be a result of poor complex formation between the two components. It does not mean that there would be no spectral shift in the chromophore if a stable complex would be formed.

![Structures of push-pull chromophores exhibiting an optical shift](image)

**Figure 7-15.** Structures of push-pull chromophores exhibiting an optical shift when interacting with lanthanide β-diketonates.

We now focus our attention on compounds that do exhibit optical shifts under the action of LnFOD (Figure 7-15). All compounds were studied in dry toluene. Their absorption spectra before and after addition of LnFOD are drawn in Figure 7-16.

### 7.5.1 Bis(dimethylamino)xanthone (DMAX)

DMAX, which is structurally and photophysically similar to Michler’s ketone, was a kind gift of Prof. Dr W. Rettig (Technische Universität Berlin, Germany). Roughly speaking, the same optical shift in the ground-state absorption spectrum occurs upon addition of EuFOD, and excitation into this shifted absorption band gives rise to photosensitised Eu$^{3+}$ luminescence, just like with MK-EuFOD. In some details the absorption spectra of DMAX and its EuFOD adduct differ slightly from those of MK and MK-EuFOD, which is due to the bridging oxygen, which fixates the two (dimethylamino)phenyl moieties in DMAX, thereby changing its electronic structure.
Figure 7-16. Absorption spectra of solution of push-pull chromophores in toluene before (dotted line) and after (solid line) addition of LnFOD.

7.5.2 Benzanthrone (BA)

The official designation of BA is benz[de]anthracen-7-one. It is a triplet sensitiser (triplet energy 72 kcal/mol) and has been used to generate singlet oxygen. Several BA derivatives are commercial dyes such as 3-methoxybenzanthrone (C.I. Disperse Yellow 13). The basic photophysical characteristics of BA have been investigated by Bentley et al. 

The lowest singlet excited state of BA is of $\pi-\pi^*$ nature, in view of the high extinction coefficient and solvatochromism of the longest-wavelength absorption band. Indeed, this band is shifted further into the visible upon addition of LnFOD. The triplet level of BA is quite low compared to MK, and therefore no sensitised Eu$^{3+}$ is observed upon excitation of the the BA-EuFOD complex.

In contrast, energy transfer from BA to Yb$^{3+}$ in BA-YbFOD is fast. Preliminary time-resolved absorption measurements indicate that it occurs in the sub-nanosecond time range. Compared to the energy transfer in MK-YbFOD (Section 7.3.3) this is a more than 100-fold rate increase. In Chapters 4 and 5 we found that the distance between sensitiser and lanthanide ion is a crucial factor in the design of luminescent lanthanide complexes, especially in the case of Yb$^{3+}$. Here we see that if the energy gap between the sensitiser’s donating state and the lanthanide’s accepting level becomes too large, as is the case in MK-YbFOD, energy transfer slows down, even though donor and acceptor are in close contact.
7.5.3 Nile Red (NR)
Nile Red turns purple-blue when LnFOD is added to a solution of this highly fluorescent, polarity sensitive, hydrophobic dye. Moreover, some of its LnFOD adducts display photosensitised near-infrared luminescence. Since the photophysics of these complexes merit special attention, they will be discussed in a separate section below (Section 7.6).

7.5.4 Phenol Blue (PB)
The absorption band of PB is shifted towards the near-infrared* when it interacts with LnFOD, but no sensitised near-infrared luminescence was observed from any of the complexes. The reason for the absence of sensitised luminescence is not entirely clear. The excitation energy may already be rapidly dissipated within the PB itself by nonradiative processes. PB and all of its LnFOD adducts are conspicuously non-emissive, even at low temperatures. Another explanation may be a low lying antenna triplet state.

7.6 Nile Red based NIR luminescent complexes
Red light excitation of the blue coloured complex of Nile Red with either YbFOD or ErFOD leads to near-infrared luminescence from the respective lanthanide ion (Figure 7-17). The quantum yield of sensitised Er\textsuperscript{3+} luminescence is 40 times lower than that of NR-YbFOD. This reflects the lower intrinsic quantum yield of Er\textsuperscript{3+}, which has a slower radiative rate, but is at the same time more rapidly deactivated by non-radiative energy loss to matrix vibrations.

![Graph](image)

* Although the absorbance increases drastically going from PB to PB-LnFOD, the solution becomes less intensely coloured, because at the same time most of the absorption shifts to the far-red/near-infrared, where the human eye loses its sensitivity.
The case of Nile Red demonstrates once more that fluorescent dyes can be used as sensitizers for lanthanide ions. It is either through lanthanide-enhanced intersystem crossing and subsequent energy transfer from the dye’s triplet state or through direct singlet energy transfer that fluorescent dyes can populate the luminescent states of lanthanide ions. For the singlet pathway to sensitised lanthanide luminescence little direct experimental evidence is available in the literature. We discovered that in the case of NR-LnFOD there are clear indications for the occurrence of singlet energy transfer provided by NR antenna fluorescence. Although NR-GdFOD and e.g. NR-ErFOD have the same absorption spectra, their solutions have different colours, due to a much more intense fluorescence from the former.

7.6.1 Antenna fluorescence: evidence for singlet energy transfer

The fluorescence spectra in Figure 7-18 show that the fluorescence of NR in NR-GdFOD is shifted to longer wavelengths compared to the free dye (just like its absorption spectrum). The fluorescence is, however, only partially quenched, although among the lanthanides Gd$^{3+}$ is the most effective enhancer of intersystem crossing. Gd$^{3+}$ does not have any energy levels that are able to accept energy from the coordinated NR. In NR-YbFOD, where there exists a single lanthanide centered level, the antenna fluorescence is already quenched more. NR-ErFOD and NR-PrFOD possess many levels overlapping with the fluorescence of NR, and in these complexes there is hardly any antenna fluorescence.

Figure 7-18. Visible emission spectra of NR (dotted line) and NR-LnFOD (Ln = Gd, Yb, Er, Pr) in toluene ($\lambda_{exc} = 544$ nm in all cases). The intensities have been scaled to equal absorbances at the excitation wavelength.

In Section 4.3.2, we discussed the mechanisms by which lanthanide ions quench the fluorescence of chromophores: enhancement of intersystem crossing, singlet energy transfer and electron transfer quenching. The latter mechanism only occurs with Eu$^{3+}$ and Yb$^{3+}$, and only if the antenna has a sufficiently high singlet energy combined with a suitable oxidation potential. NR-GdFOD demonstrates that the lanthanide-enhanced intersystem
crossing alone cannot account for the fluorescence quenching in NR-YbFOD and NR-ErFOD. These considerations and the correlation between the number of potentially accepting states of the lanthanide ion and the fluorescence quantum yields lead us to conclude that Figure 7-18 contains clear-cut evidence for the occurrence of energy transfer from the antenna’s singlet state to the ion.

7.6.2 Further evidence for singlet energy transfer

Time-resolved absorption spectroscopy using the streak camera (sTA, Chapter 2) provides additional information about the antenna states involved in the sensitisation process on a nanosecond time scale, as we already saw in Section 7.3.3. The nanosecond sTA images of NR-GdFOD and of NR-YbFOD in deoxygenated toluene were analysed using singular value decomposition. For NR-GdFOD, two components were found, one of which is formed from the other with a time constant of 3.2 ns. We attribute these to the transient absorption spectra of the first excited singlet and triplet states of NR. The spectra associated to these species are shown in the left half of Figure 7-19. The absorption spectrum of the triplet state is markedly different from that of the singlet state.

The transient absorption image of NR-YbFOD in deoxygenated toluene only contains one component which more or less follows the excitation pulse (lifetime approximately 2 ns). The spectrum of this component matches that of the first singlet excited state of NR-GdFOD (Figure 7-19, right). This means that the triplet state in NR-YbFOD is not significantly populated, which supports our idea that in NR-YbFOD direct singlet energy transfer from NR to Yb\(^{3+}\) occurs. Conclusive evidence, however, can only be provided by experiments with better time-resolution, such as sub-picosecond transient absorption spectroscopy. The spectra in Figure 7-19 might serve as a road map for such investigations.

![Figure 7-19](image)

Figure 7-19. Transient absorption spectra (\(\lambda_{\text{exc}} = 590 \text{ nm}, 0.5 \text{ mJ/pulse}\)) of NR-GdFOD and NR-YbFOD in deoxygenated toluene extracted from the streak transient absorption(sTA) images using principal components analysis. Left: the spectra associated with the two principal components in the sTA image of NR-GdFOD. Right: The only principal component present in the sTA image of NR-YbFOD, together with the \(S_1\) absorption spectrum of NR-GdFOD.
7.7 Studies towards more stable complexes having push-pull chromophores as antennae

MK-EuFOD and related complexes have attractive photophysical properties, but they lack chemical stability: traces of water may already disrupt the complex. Moreover, these complexes are only soluble and stable in a limited number of solvents: alkanes, simple aromatics such as benzene, dichloromethane and the like. In the final part of this chapter we describe attempts to construct complexes that are more stable, even water-soluble, while retaining the important photophysical characteristics, such as visibly excited Eu$^{3+}$ luminescence.

Two approaches were used. One is to attach a push-pull chromophore to a ligand that binds lanthanide ions. The other is to modify Michler’s ketone to incorporate groups that provide binding sites. In both cases it is important that the chromophore is oriented such that the lanthanide ion is situated at its ‘pull’ side. This is necessary to make the shift of the absorption spectrum of the antenna go into the right direction. The two strategies are exemplified by the structures in Figure 7-20.

![DEAAP-crown and RJ2](image)

**Figure 7-20.** Structural formulae of two ligands synthesised to give Eu$^{3+}$ complexes that are more stable than MK-EuFOD, while still being excitable with visible light.

7.7.1 Syntheses

**DEAAP-Crown.** Although crown ethers are only moderately binding ligands for lanthanide ions, the crown ether was chosen because of its commercial availability and the relative ease with which the chromophore can be coupled to it, by having its bromide react with the nitrogen in the crown ether. In this way, the principle can be tested without getting involved in too much synthesis.

To a solution of 53 mg (0.2 mmol) 1-aza-18-crown-6 (Aldrich) and 29 mg K$_2$CO$_3$ (0.2 mmol) in 5 ml 1,4-dioxane was added 57 mg (0.2 mmol) α-bromo- p- (N, N-dimethyl-amino)-acetophenone (Lancaster) in 10 ml 1,4-dioxane. The mixture was stirred for 30 min at room temperature. Subsequently it was heated for three hours at 80 °C. The solvent was evaporated, and the residu was taken up in CHCl$_3$. This solution was filtered and evaporated.
\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.96 (2H, d), 6.64 (2H, d), 4.11 (2H, s, C(O)CH\(_2\)N), 3.6 (20H + 4H, m, crown + CH\(_3\)CH\(_2\)N), 2.99 (4H, t, NCH\(_2\)CH\(_2\)O), 1.20 (6H, t, CH\(_3\)CH\(_2\)N).

2,5-Bis[4-(dimethylamino)benzoyl]pyridine (RJ2). This ligand is synthesised by a Friedel-Crafts acylation. At 10 °C, 4.0 g (30 mmol) AlCl\(_3\) was suspended in 20 ml of dry diethyl ether. To this suspension was added a solution of 1.02 g (5 mmol) 2,6-pyridinedicarboxylic acid chloride in 20 ml ether. The mixture was stirred for 1 hour under a dry nitrogen atmosphere. During approximately 5 minutes, 3.14 ml (25 mmol) of N,N-dimethylylaniline was added dropwise while stirring at 10 °C. Then the mixture was refluxed for 3 h.

The mother liquor was poured into a mixture of 10 ml 45% NaOH and 15 ml water at 0 °C. The organic layer was separated and filtered. The water layer was extracted several times with ether. The organic phases were combined and evaporated. The crude product was recrystallised several times from ethanol, and obtained in low yield (<10%). The yield may drastically improve by optimising the work-up procedure, e.g. by using dichloromethane in the extraction.

\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\) (ppm) 3.0 (12H, s, CH\(_3\)), 6.75 (4H, AA', 3,5-phenyl), 8.1 (3H, m, 3,4,5-pyridyl), 8.35 (4H, BB', 2,6-phenyl).

### 7.7.2 Results

Dissolved in ethanol, both ligands display the bathochromic shift of their lowest singlet-singlet transition upon addition of EuCl\(_3\) to the solution. This means that the stability of the complexes is much higher than that of MK-EuFOD which dissociates in hydroxylic solvents. The quantum yield of sensitised Eu\(^{3+}\) luminescence is extremely low (<10\(^{-3}\)). The phosphorescence spectra of the Gd\(^{3+}\) complexes (methanol-ethanol 4:1 glass, 77 K) indicate triplet energies of 18800 and 17000 cm\(^{-1}\) for DEAAP-crown and RJ2 respectively, which are too low to efficiently sensitis\(e\) Eu\(^{3+}\). It is worth noting that upon cooling the solution of DEAAP-crown/Eu\(^{3+}\) to 77K, the Eu\(^{3+}\) luminescence becomes more intense, but directly after removing the sample from the coolant (liquid N\(_2\)) the luminescence disappears.

It seems that MK-EuFOD is quite a unique system, and that it will be difficult to synthesise Eu\(^{3+}\) complexes that are more stable, while retaining the interesting photophysical properties.

### 7.8 A water-borne latex carrying MK-EuFOD as a luminescent stain

Another way to bring a hydrophobic material in an aqueous environment is to encapsulate it in small polystyrene particles.\(^{[27]}\) The fluorescent latex spheres thus formed find applications in diagnostics and fluorescence microscopy. In fact, Eu\(^{3+}\) labelled latex spheres are offered by Molecular Probes, Inc., but require excitation wavelengths <380 nm. Here, we
describe the successful, albeit non-optimised, staining of small polystyrene particles with MK-EuFOD.

One ml of a concentrated solution (> 10\(^{-3}\) M) of MK-EuFOD in CH\(_2\)Cl\(_2\) was dispersed in 20 ml water. The dispersion was added dropwise to a thoroughly stirred suspension of 1.5 wt% polystyrene latex (kindly provided by Katrien Keune, University of Amsterdam, average particle size 150 nm). After one night of stirring, the organic solvent was stripped from the latex by vacuum evaporation. Big particles of polystyrene, formed due to the non-optimal staining conditions, were removed by centrifugation (6000 rpm, 1 day). For luminescence spectroscopy (Figure 7-22) the latex was diluted 100x with deionised water and filtered through 200 nm Whatman HPLC filters.

From this result, we conclude that it is indeed possible to encapsulate the MK-EuFOD complex in small polystyrene particles. The stained polystyrene particles show Eu\(^{3+}\) luminescence upon excitation with wavelengths exceeding 450 nm. The quantum yield is
expected to be as high as that of the complex in benzene, but this has to be confirmed either by direct measurement or by measurement of the luminescence lifetime. Moreover, the staining conditions need optimisation. Thus far, encapsulation of MK-EuFOD in polystyrene particles is the only successful strategy to make the system compatible with an aqueous environment.

7.9 Concluding remarks

Although discovered accidentally, the use of push-pull chromophores as photosensitisers for lanthanide luminescence is an intriguing and fruitful concept. Such chromophores traditionally have small singlet-triplet splittings: the overlap between the highest occupied and lowest unoccupied orbitals of these molecules is small leading to a small exchange energy. The smaller singlet-triplet splittings allow for the use of chromophores with absorption bands at longer wavelengths than non-push-pull systems. In the case of MK-EuFOD, photosensitised Eu$^{3+}$ luminescence is obtained upon excitation with unprecedented long wavelengths.

It is somewhat disturbing that any modification of the MK-EuFOD concept investigated thus far (exemplified by the ligands described in Chapter 7.7) leads to Eu$^{3+}$ complexes that are essentially non-luminescent. It appears that MK-EuFOD represents a unique optimum on the ‘quality surface’ of organoeuropium complexes.

The situation might be less critical with the near-infrared luminescent complexes, because of the lower energies of the luminescent states. The combination of Nile Red with near-infrared luminescent lanthanide β-diketonates shows that energy transfer from an organic chromophore to a lanthanide ion can be faster than $10^9$ s$^{-1}$, and potentially proceeds directly from the antenna’s singlet state.

References

PUSH-PULL CHROMOPHORES AS SENSITISERS 125


