

Bathochromicity of Michler's ketone upon coordination with lanthanide(III) β -diketonates enables efficient sensitisation of Eu^{3+} for luminescence under visible light excitation†

Martinus H. V. Werts, Marcel A. Duin, Johannes W. Hofstraat and Jan W. Verhoeven*

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, NL-1018 WS Amsterdam, The Netherlands. E-mail: jwv@org.chem.uva.nl

Received (in Exeter, UK) 15th March 1999, Accepted 23rd March 1999

The electronic absorption of Michler's ketone (MK) and related push-pull sensitizers undergoes a strong red shift upon coordination with lanthanide(III) β -diketonates, which enables unprecedentedly efficient sensitisation of Eu^{3+} luminescence for excitation at long wavelengths extending well into the visible region to above 450 nm.

The design of photoluminescent lanthanide complexes continues to be an active area of research,^{1,2} mainly because such complexes may be useful for application in fluorescent probes, and for the conversion and amplification of light. The long lifetimes of the excited states of the lanthanide ions are an advantage in these applications, and so is the spectral purity of their light emission. The ligands in luminescent lanthanide complexes contain, besides chelating groups, one or more sensitising chromophores ('antennae') which are needed to overcome the excitation bottleneck formed by the inherently small absorption cross sections of the lanthanide ions. The chromophores absorb the light and consecutively transfer the energy to the lanthanide ion.³ Bearing in mind possible applications, it would be most advantageous to have antenna chromophores that absorb significantly at wavelengths longer than 400 nm and then transfer the excitation energy efficiently and irreversibly to the ion. However, for luminescent Eu^{3+} and Tb^{3+} complexes, the excitation window appears to be limited to the near-UV due to the energetic constraints posed by the photophysics of sensitised lanthanide luminescence.⁴ Eu^{3+} complexes containing chromophores that absorb at wavelengths longer than 400 nm have been reported, but the overall luminescence quantum yields of these systems are generally low, because energy transfer is inefficient due to back energy transfer processes. For example, mixed complexes of certain β -diketonates and *o*-phenanthroline display absorption bands in the region 380–400 nm, but show luminescence quantum yields upon ligand excitation of 10^{-4} to 2×10^{-3} .⁵ Also in a series of Eu^{3+} Schiff base complexes studied recently,⁶ the quantum yield drops dramatically as the absorption maximum of the ligand approaches the visible region. In our ongoing search for improved antenna chromophores for lanthanide ions, experiments aimed at observing intermolecular energy transfer between organic chromophores and lanthanide chelates in organic solvents yielded surprising results.

When colourless solutions of Michler's ketone [4,4'-bis(*N,N*-dimethylamino)benzophenone] and $\text{Eu}(\text{fod})_3$ [europium tris(6,6,7,7,8,8,8-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 (Fig. 1) demonstrates that this red glow is europium(III) luminescence: the sharp peaks are characteristic of lanthanide ion emission, Eu^{3+} usually having its most intense emission around 615 nm.⁷ 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 (λ_{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 1 M H_2SO_4 as a reference⁸).

Michler's ketone and $\text{Eu}(\text{fod})_3$ apparently form a ground-state complex under the experimental conditions, most likely 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,^{9,10} and in fact coordination of certain aliphatic substrates to $\text{Eu}(\text{fod})_3$ have been found to enhance its luminescence quantum yield.¹¹ Never before, however, has it been reported that complexation of chromophores to lanthanide β -diketonates yields efficient 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: in the process of excitation, electron density is moved towards the carbonyl group making the transition solvatochromic.¹² Thus, it is quite likely that the transition energy is largely affected by the presence of the lanthanide ion.

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.¹³

The complex formation of MK with $\text{Eu}(\text{fod})_3$ in benzene can be monitored using UV-VIS absorption spectroscopy. The absorption band of the complex resides at longer wavelengths, where MK and $\text{Eu}(\text{fod})_3$ themselves do not absorb. Fig. 2 shows a titration experiment, in which small amounts of a $\text{Eu}(\text{fod})_3$ stock solution are added to a solution of MK. It clearly shows 1 : 1 complex formation of MK with $\text{Eu}(\text{fod})_3$. Analysis of the titration data yields the formation constant for the MK- $\text{Eu}(\text{fod})_3$ complex in benzene, $\log K = 4.85$. The extinction coefficient at 414 nm, the absorption maximum, was found to be $3.04 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

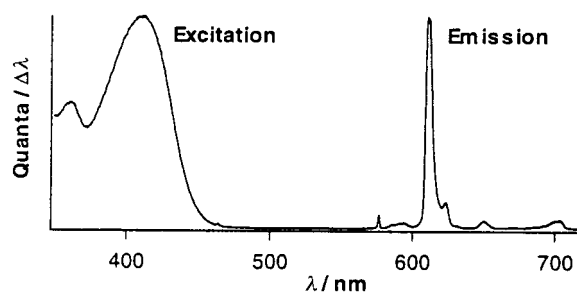


Fig. 1 Corrected luminescence excitation ($\lambda_{\text{em}} = 612 \text{ nm}$) and emission ($\lambda_{\text{exc}} = 450 \text{ nm}$) spectra of a solution of 10^{-5} M Michler's ketone and 10^{-4} M $\text{Eu}(\text{fod})_3$ in benzene.

† Supplementary data outlining the analysis methodology used and giving additional spectra are available from the RSC web site, see: <http://www.rsc.org/suppdata/cc/1999/799/>

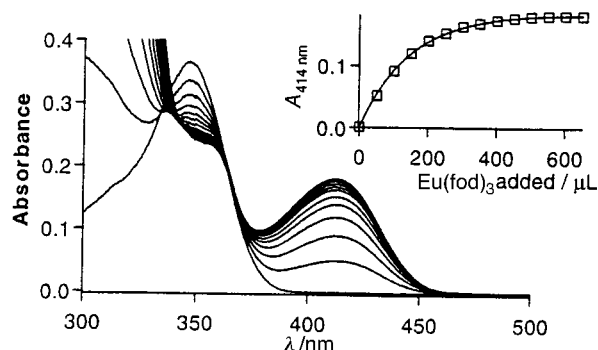


Fig. 2 UV-VIS titration of a solution of Michler's ketone in benzene with $\text{Eu}(\text{fod})_3$. To 2.5 ml of a 10^{-5}M solution of MK in benzene, a $\text{Eu}(\text{fod})_3$ solution ($5 \times 10^{-4}\text{M}$ in benzene) is added in steps of $50\ \mu\text{L}$. The inset shows formation of the complex by means of its absorption at 414nm as a function of the amount of $\text{Eu}(\text{fod})_3$ solution added. The solid line is the theoretical curve for a 1:1 complex with $\log K = 4.85$ and $\epsilon_{\text{max}} = 3.04 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$. The dilution has been taken into account.

The same bathochromic shift of the MK absorption as the one induced by $\text{Eu}(\text{fod})_3$ is also observed with other lanthanides. Addition of $\text{Yb}(\text{fod})_3$, $\text{Er}(\text{fod})_3$, $\text{Gd}(\text{fod})_3$ or $\text{Pr}(\text{fod})_3$ to MK in benzene produces in all cases the same 414nm absorption band. This reflects the electrostatic nature of the interaction: all lanthanide ions carry a 3+ charge and the distance between the ion and the MK is equal in all complexes. They will therefore have the same effect on the electronic energy levels of the chromophore. Obviously, the red glow is only observed with $\text{Eu}(\text{fod})_3$.

Although the induced 'optical shifts' are the same for different $\text{Ln}(\text{fod})_3$ species, the shifts of the MK ^1H nuclear magnetic resonances induced by these complexes are entirely different, which clearly shows that the effects have different origins (electrostatic vs. magnetic). For example, $\text{Eu}(\text{fod})_3$ causes a downfield shift whereas $\text{Pr}(\text{fod})_3$ shifts the resonances upfield. The protons closest to the carbonyl group are affected most, and the protons on the dimethylamino groups are relatively unaffected. This supports our view that the MK interacts with the lanthanide diketonate through its carbonyl group.

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,¹⁴ implying that the triplet energy must be sufficiently high. In view of the unprecedented observation of efficiently sensitised Eu^{3+} luminescence upon excitation with visible light the singlet-triplet gap of the coordinated MK must be exceptionally small compared to other organic chromophores used until now as sensitisers or (less likely) another mechanism such as the electron transfer mechanism proposed by Horrocks *et al.*¹⁵ must be involved.

The Gd^{3+} β -diketonates provide a way to study the triplet state energy of the coordinated MK. Having no electronic energy levels below $32000\ \text{cm}^{-1}$ (310nm), Gd^{3+} can not accept any energy from MK, but as mentioned above, it induces the same optical shift and eventually enhances singlet-triplet and triplet-singlet transitions in MK by its heavy atom effect. As a result in deoxygenated benzene, even at room temperature, phosphorescence of $\text{MK-Gd}(\text{fod})_3$ is observed (excitation at 410nm), as a broad band peaking at 540nm . From the emission spectrum of $\text{MK-Gd}(\text{fod})_3$ in methylcyclohexane glass at 77K , the triplet energy of the coordinated MK is estimated to be $19600\ \text{cm}^{-1}$, which is indeed sufficient to efficiently populate the $^5\text{D}_0$ luminescent state of Eu^{3+} ($17500\ \text{cm}^{-1}$), possibly via energy transfer to the $^5\text{D}_1$ state ($19000\ \text{cm}^{-1}$) and subsequent relaxation to $^5\text{D}_0$.¹⁶ The triplet energy of free MK is around $23000\ \text{cm}^{-1}$.¹³ These results clearly point to the occurrence of the 'usual' triplet pathway in the sensitisation of Eu^{3+} by MK without resort to more exotic mechanisms. The crucial point is that the very small singlet-triplet gap of MK is fully retained

upon coordination via its carbonyl oxygen to the lanthanide but that at the same time these energy levels are significantly lowered because the coordination stabilises the very polar excited states involved.

The effect of variation of β -diketonates was investigated as well. In benzene, the maximum of the absorption band varies from 398nm for $\text{MK-Eu}(\text{dpm})_3$ ($\text{dpm} = 2,2,6,6$ -tetramethylheptane-3,5-dionate) via 414nm for $\text{MK-Eu}(\text{fod})_3$ to 430nm for $\text{MK-Eu}(\text{hfa})_3$ ($\text{hfa} = 1,1,1,5,5,5$ -hexafluoropentane-2,4-dionate). We tentatively attribute this to a variation of the distance between the MK chromophore and the lanthanide ion in the complexes due to steric hindrance by the β -diketonate ligand. Unlike $\text{MK-Eu}(\text{dpm})_3$ and $\text{MK-Eu}(\text{fod})_3$ (both having 0.20 quantum yield in deoxygenated benzene), the sensitised luminescence quantum yield of $\text{MK-Eu}(\text{hfa})_3$ is very low (6.2×10^{-5} in deoxygenated benzene). This is probably a result of too low a triplet energy of the antenna chromophore. The phosphorescence spectrum of $\text{MK-Gd}(\text{hfa})_3$ (methylcyclohexane, 77K) reveals a triplet energy of about $18800\ \text{cm}^{-1}$, which means that back energy transfer processes from Eu^{3+} to the coordinated MK might readily occur at room temperature.

In conclusion, lanthanide β -diketonates have been found to form complexes with the carbonyl containing 'push-pull' chromophore Michler's ketone. This interaction brings about a bathochromic shift in the optical absorption spectrum of this chromophore. We note that this 'optical shift' effect is more general. In preliminary experiments, we also found bathochromic shifts in the dyes Nile Red and Phenol Blue induced by $\text{Ln}(\text{fod})_3$.¹⁷ A remarkable feature of the 'optically shifted', visible light absorbing MK chromophore is that it efficiently sensitises Eu^{3+} luminescence, which is an interesting property, e.g. for application as a luminescent label in time-resolved fluorescence microscopy, since visible light is less harmful to biological tissue than ultraviolet. A challenge in this respect is the development of more stable, water soluble complexes. This aspect and more details of the interesting photophysics of $\text{MK-Eu}(\text{fod})_3$ and related complexes are currently under investigation.

Notes and references

- 1 D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613.
- 2 M. Elbanowski and B. Makowska, *J. Photochem. Photobiol. A*, 1996, **99**, 85.
- 3 S. I. Weissman, *J. Chem. Phys.*, 1942, **10**, 214.
- 4 F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. Van der Tol and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 9408.
- 5 J.-C. G. Bunzli, E. Moret, V. Foiret, K. J. Schenk, W. Mingzhao and J. Linpei, *J. Alloys Compd.*, 1994, **207**, 107.
- 6 R. D. Archer, H. Chen and L. C. Thompson, *Inorg. Chem.*, 1998, **37**, 2089.
- 7 Especially in Eu^{3+} β -diketonates, this so-called hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is usually very intense. See e.g. L. R. Melby, N. J. Rose, E. Abramson and J. C. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117.
- 8 D. F. Eaton, *J. Photochem. Photobiol. B*, 1988, **2**, 523.
- 9 B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49.
- 10 A. F. Cockerill, G. L. O. Davies, R. C. Harden and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.
- 11 H. G. Brittain, *Inorg. Chem.*, 1980, **19**, 640.
- 12 E. J. J. Groenen and W. N. Koelman, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 58.
- 13 D. I. Schuster, M. D. Goldstein and P. Bane, *J. Am. Chem. Soc.*, 1977, **99**, 187.
- 14 G. A. Crosby, R. E. Whan and R. M. Alire, *J. Chem. Phys.*, 1961, **34**, 743.
- 15 W. D. Horrocks, Jr., J. P. Bolender, W. D. Smith and R. M. Supkowski, *J. Am. Chem. Soc.*, 1997, **119**, 5972.
- 16 Indeed, a weak $^5\text{D}_1 \rightarrow ^7\text{F}_0$ emission is observed at 530nm upon excitation of $\text{MK-Eu}(\text{fod})_3$ at 420nm .
- 17 A solution of Nile Red in benzene turns blue when solid $\text{Ln}(\text{fod})_3$ is added. Moreover, the complexed Nile Red efficiently sensitises the near-infrared luminescence of erbium(III) and ytterbium(III).