

VISIBLE AND NEAR-INFRARED EMITTING LANTHANIDE COMPLEXES FOR LUMINESCENT SOLAR CONCENTRATORS

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ABSTRACT: Lanthanide (Ln) complexes consisting of rare earth ions such as Europium (Eu^{3+}) or Ytterbium (Yb^{3+}) with highly absorbing organic ligands attached, offer advantages over the fluorescent dyes and quantum dots that are more often considered for use in luminescent solar concentrators (LSCs). The large Stokes shift of such complexes (>200 nm) eliminates the re-absorption losses presented by other fluorophores, caused by the overlap of their absorption and emission spectra. This paper investigates the potential improvement in fluorescent quantum yield (FQY) that can be achieved through deuteration and fluorination of the secondary co-ordinating sphere – the solvent environment. This involves replacing hydrogen (H) atoms with deuterium (D) or fluorine (F). Due to their higher atomic weights, the bonds they form with carbon vibrate at lower energies thereby shifting the vibrational modes to longer wavelengths. This reduces quenching of the excited state of the Ln ions and results in improved FQY.

KEYWORDS: Concentrators, Photoluminescence, Reabsorption, Lanthanide complexes

1 INTRODUCTION

Luminescent Solar Concentrators (LSCs) are planar, non-imaging optical devices used to concentrate sunlight onto small areas of photovoltaic (PV) cells. They are comprised of polymer sheets or thin films doped with fluorophores such as organic dyes or quantum dots. Incident light is focused onto PV cells situated at the edges of the device by total internal reflection (TIR) at the plastic to air interface. By decreasing the amount of PV material required, production costs are reduced. In addition, the systems are well suited for building integrated photovoltaics.

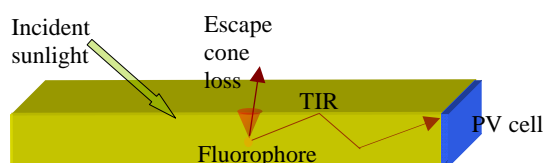


Figure 1: Schematic of a LSC

An ideal fluorophore for LSCs with silicon PV cells attached would have (i) a broad absorption range to utilize the solar spectrum most efficiently (ii) 100% FQY so that all light absorbed results in emission (iii) large Stokes shift to minimize overlap of the absorption and emission spectra thereby reducing re-absorption losses (iv) emission in the near infrared (NIR) and (v) long term stability. While organic dyes and quantum dots offer some of these features, they both suffer from re-absorption losses. When a fluorophore has an FQY of 100%, re-absorption might not seem to be too much of a problem but in LSCs each re-emitted photon could be lost through the escape cone. For an LSC with a refractive index of 1.5 approximately 25% of light is lost this way.

The Ln complexes described in this paper have large Stokes shifts (>200 nm), therefore re-absorption does not occur, making them attractive for use in LSC systems. This paper presents improved FQY values compared to previous results [1] using fluorinated and deuterated

solvents to reduce the effects of C-H and O-H bond vibrations which can lead to quenching of Ln emission.

2 MATERIALS AND METHODS

2.1 Lanthanide Complexes

Ln complexes display intense, narrow emission peaks in the visible or NIR region but have extremely low absorption coefficients due to their f-f transitions being only weakly allowed [2]. For this reason, highly absorbing organic ligands are co-ordinated to the Ln ions to transfer energy, resulting in Ln emission.

Upon excitation of the ligand, the energy transfer process, as shown in figure 1, involves transfer from the singlet state of the organic ligand to its triplet state via intersystem crossing (ISC). ISC is enhanced by the presence of the Ln ion, the heavy atom effect, and by close proximity between the ligand and ion [3].

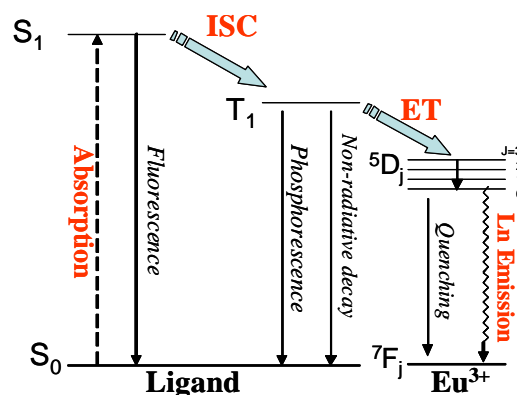


Figure 2: Energy transfer from ligand to Ln ion. Successful Ln emission results from transfer from S_1 , ligand singlet state, to T_1 , ligand triplet state via ISC, intersystem crossing, and finally ET, energy transfer to the 5D_j energy states of the Ln and relaxation to the ground states 7F_j .

As shown in Figure 1, there are numerous processes competing with energy transfer to the Ln ion such as ligand fluorescence, phosphorescence from the triplet state and triplet quenching due to the presence of molecular oxygen. Once the Ln ion is excited, this energy can be lost to vibrational modes in the surrounding ligand or solvent molecules such as C-H or O-H bonds [2].

2.2 Europium Complex

Recently, the authors synthesised a Eu^{3+} complex (EuhD) with the structure $\text{Eu}(\text{hfac})_3(\text{DPEPO})$ where hfac= Hexafluoroacetylacetonate and DPEPO= bis(2-(diphenylphosphino)phenyl)ether oxide [4]. Eu^{3+} displays several emission peaks with the most intense being at 613 nm. A FQY of $86\% \pm 10\%$ relative was measured in a polymethylmethacrylate (PMMA) host. Figure 3 shows the absorption and emission spectra of EuhD while Figure 4 shows a photograph of a EuhD PMMA sheet under UV illumination.

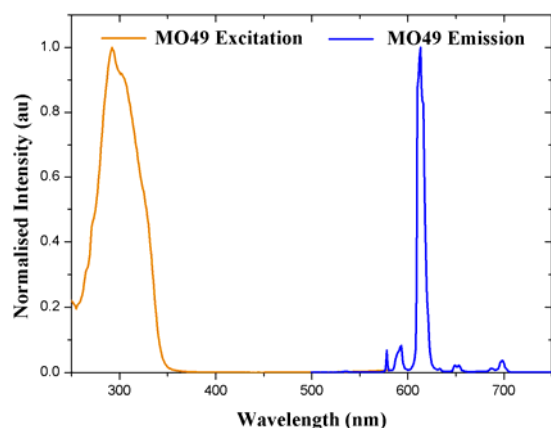


Figure 3: Excitation and emission of EuhD complex

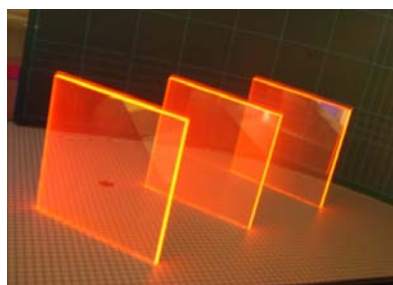


Figure 4: EuhD Ln complex in PMMA under UV light

While this complex displays a very impressive FQY for such complexes, its absorption range is not broad enough to justify its incorporation into LSC devices.

It has been suggested that the longest wavelength that Eu^{3+} can be excited at is 385 nm as any wavelength longer than this will not have sufficient triplet energy to transfer to the Ln ion [5]. In addition to this, the gap between the ligand triplet state and the accepting state of the Ln ion must be about $1000\text{--}2000\text{cm}^{-1}$ to avoid energy back transfer [3]. These limitations to the absorption properties of Eu^{3+} complexes mean that they are not suitable for use as single fluorophores in LSC devices. EuhD demonstrates what can be achieved by Ln complexes such as these and also provides a fluorophore with high FQY void of re-absorption losses.

2.3 NIR emitting Lanthanide complexes

NIR emitting ions such Nd^{3+} and Yb^{3+} can be excited in the visible region [4] and fluoresce in the range best suited to silicon solar cells. Yb^{3+} exhibits a single peak centered at 980 nm while Nd^{3+} has its main peaks at 880, 1064 and 1300 nm.

As described previously, once energy has been transferred to the Ln ion, it is susceptible to de-activation to surrounding vibrational states such as those presented by O-H, N-H and C-H bonds in the surrounding environment. Hydrogen (H) bonds become increasingly problematic in the NIR region where their vibronic levels are close to those of the Ln excited. For this reason, FQY values for NIR emitting Ln complexes are generally lower than visibly emitting Ln complexes [3].

Improved FQY values are expected when the number of H-bonds is decreased through deuteration or fluorination of the secondary co-ordinating sphere, that is, the replacement of H atoms in the surrounding solvent environment with deuterium (D) or fluorine (F). Absorption due to C-D or C-F bonds occur at lower energies and therefore longer wavelengths thereby reducing or removing the non-radiative pathway presented by C-H or O-H bonds.

A Yb^{3+} complex $\text{Yb}(\text{hfac})_3(\text{DPEPO})$ (MO65) (see fig. 4) with the same ligand configuration as the EuhD complex previously described was used in this paper to demonstrate what improvement can be achieved using deuterated and fluorinated solvents.

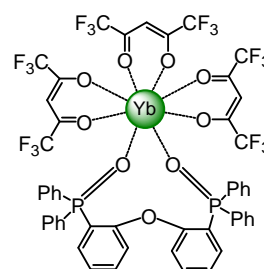


Figure 5: Molecular diagram of MO65

2.4 Spectroscopic Characterisation

An Edinburgh Instruments FS920 UV/vis/NIR fluorescence spectrometer was used to measure the excitation and emission spectra of the MO65 solutions. Excitation light from a 450 W Xenon lamp was delivered via double monochromators to the sample chamber and emission was detected either by a Peltier cooled R2658P Hamamatsu photomultiplier or a liquid nitrogen cooled Hamamatsu R5509-72 NIR photomultiplier.

To measure the FQY, a Horiba Jobin Yvon integrating sphere was placed inside the sample chamber of the FS920 spectrometer. With the excitation range being in the UV and the emission peak in the NIR, it was necessary to use separate detectors to complete the FQY measurement. It was then necessary to scale the spectra accordingly by measuring one sample with both detectors that emits in the overlap region of the detectors.

3 EXPERIMENTAL

3.1 Spectroscopy of MO65 in range of solvents

The emission spectrum of MO65 in a range of solvents at a concentration of 131 ppm was measured and the intensities compared. The solvents used were Dichloromethane (DCM) (CH_2Cl_2), Chloroform (CHCl_3), Deuterated Chloroform (CdCl_3) and a fluorinated solvent Perfluoromethylcyclohexane (PFMC) (C_7F_{14}). Throughout the measurement series, all conditions were identical such as slit width, step size and dwell time. Excitation was at 320 nm and the emission was scanned from 900-1100 nm.

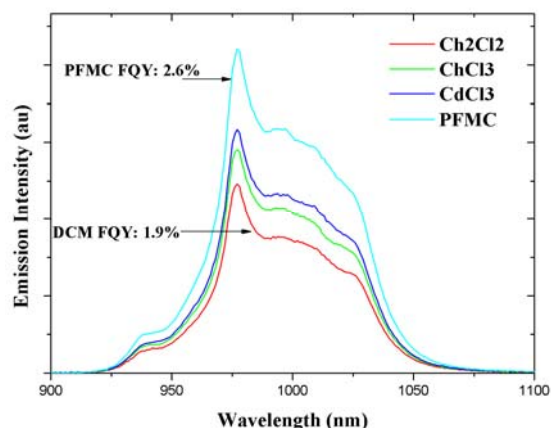


Figure 6: Emission spectra of MO65 (131 ppm) in DCM (CH_2Cl_2), Chloroform (CHCl_3), Deuterated Chloroform (CdCl_3) and PFMC (C_7F_{14}).

It can be seen in figure 6 that as the amount of H atoms are reduced, the emission intensity increases e.g. comparing DCM (CH_2Cl_2) to chloroform (CHCl_3). Replacement of H with D in deuterated chloroform (CdCl_3) results in further improvement, indicating that a reduction in vibrational quenching due to C-H and O-H bonds has occurred. Finally, the complete removal of hydrogen from the secondary co-ordinating sphere of the complex in PFMC (C_7F_{14}) results in the greatest improvement in emission intensity. This is explained by the relative weights of F and D as F (19 atomic mass unit (amu)) is significantly heavier than D (2 amu) and therefore the vibrations occur at lower energy levels. FQY measurements were carried out on the lowest and highest intensity samples DCM and PFMC and the values were 1.9 and 2.6% respectively.

4 RAY TRACE SIMULATIONS

To demonstrate the effect that overlap of absorption and emission spectra has on the amount of light trapped in a LSC device, ray trace simulations were performed using an in-house ray trace software package, RAYLENE. LSCs containing an organic dye that exhibits re-absorption losses was compared to one containing a NIR emitting Ln complex. Red305, an organic dye from the Lumogen series of BASF has a FQY of 100% and peak emission at 597nm [6]. The absorption spectrum of Red305 was added to an Yb^{3+} emission spectrum to simulate a visibly excited Ln complex. It has been shown recently [7] that Red305 displays a long tail of

absorption that extends out to 750 nm (see Figure 7). This means that re-absorption occurs across the whole emission spectrum. To demonstrate the effect that this tail has on re-absorption losses, an LSC with the tail of absorption removed was included in the simulations.

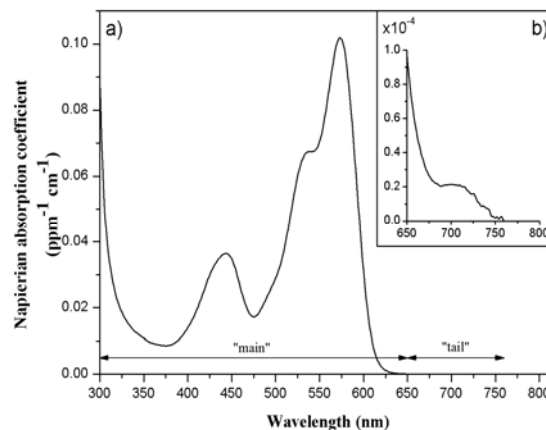


Figure 7 (a) absorption spectrum of Red305 (b) close up of absorption tail [7].

Since re-absorption losses become more problematic as LSC size increases, a series of simulations for Red305 and the Yb^{3+} complex in LSCs increasing in size from 30 x 30 x 0.3 cm up to 100 x 100 x 0.3 cm was carried out. The results in figure 8 show the escape cone losses (ECL) that occur following interaction with a dye molecule. It can be seen that they are highest for the Red305 dye with the absorption tail and are seen to increase significantly with increasing module size. A maximum of 48% ECL is reached for a 1 m² module of Red305 while the ECL for the Yb^{3+} complex increases only slightly due to longer pathlengths.

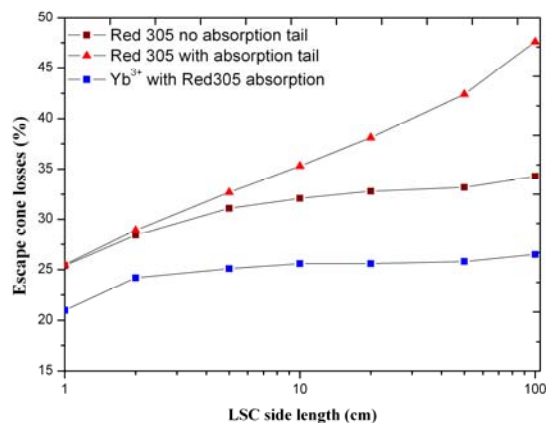


Figure 8: Escape cone losses for 3 LSCs of increasing size containing Red305 dye with and without tail absorption and a Yb^{3+} complex with Red305 absorption.

These results highlight the extent to which re-absorption losses can reduce the emission intensity reaching the PV cells in a LSC device. Ln complexes offer a potential solution to this problem if sufficiently high FQYs can be reached.

5 CONCLUSIONS

An improvement in emission intensity and FQY has been achieved for the NIR emitting Ln complex, Yb(hfac)₃(DPEPO) by using deuterated and fluorinated solvents. The best results were achieved with the fluorinated solvent PFMC.

Further improvement in FQY can be expected when the primary co-ordination sphere of the complexes is deuterated or fluorinated, that is, the H-atoms of the ligand are replaced with D or F atoms.

In addition to improving FQY, it is necessary to broaden and extend the absorption spectrum of Ln complexes to facilitate maximum utilization of the solar spectrum. This will be investigated by co-ordinating ruthenium or organic dyes to Ln ions.

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