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Solar Cell Efficiency Enhancement Through Down-Shifting and Up-Converting Layers: the Ephocell Project: Luminescent Downshifting Quantum Yield Measurements

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SOLAR CELL EFFICIENCY ENHANCEMENT THROUGH DOWN-SHIFTING AND UP-CONVERTING LAYERS. – THE EPHOCELL PROJECT; LUMINESCENT DOWNSHIFTING QUANTUM YIELD MEASUREMENTS

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ABSTRACT: Organic cells and dye-sensitized cells developed to-date have a narrow active absorption range, relative to the spectral range of the available solar resource. Their efficiency could be significantly enhanced through a process of down-shifting (DS) and up-conversion of non-absorbable photons converting them to photons better matching the spectral response of the particular solar cell. The DS molecules must exhibit a large Stokes shift and high luminescent quantum yield when incorporated in the downshifting polymer layer. In this paper, the QY of a downshifting Europium (III) complex in solution is determined using two distinct experimental techniques. The QY is measured for varying concentration and at varying excitation wavelength.
Keywords: Down-shifting layer, spectral response, photoluminescence.

1 INTRODUCTION

Organic cells and dye-sensitized cells developed to-date have a narrow active absorption range, relative to the spectral range of the available solar resource. Their efficiency could be significantly enhanced through a process of down-shifting (DS) and up-conversion (UC) of non-absorbable photons, converting them to photons better matching the spectral response of the particular solar cell (see Fig. 1). The EPHOCELL project focuses on the development of a new advanced DS and UC molecular system based on organic and metal complexes. In the DS process, the DS antenna molecule transfers the absorbed energy (UV photons) to an emitter, which emits a photon in the absorption band of the cell. In the UC process, the sensitizer molecules transfer the absorbed infra-red energy (700 nm – 840 nm) to the emitter. Ultimately, it is envisaged that the molecular system will comprise of a single, unique emitter for both UC and DS. The alternative approach, to use distinct emitters, is also being developed for comparison of results. The developed molecular system will be included in a transparent polymeric matrix, ensuring impermeability to Oxygen and water. Within the EPHOCELL project, a novel triplet-triplet annihilation up-conversion system has been developed, demonstrating UC independent on the coherence of the excitation light and, moreover, at low incident light intensities (~ 20 mWcm^{-2}) [1].

The *DS* molecules must exhibit a large effective "Stokes shift", and also high luminescent quantum yield (QY) when incorporated in the polymer host matrix. Lanthanide complexes have been demonstrated as effective molecules for use in downshifting layers [2, 3]. Luminescence processes in these compounds occurs in three steps: light absorption by the ligand, followed by highly efficient intraenergy conversion from the ligand singlet state to the triplet state by intersystem crossing, and energy transfer from ligand triplet state to the excited state of lanthanide ions.
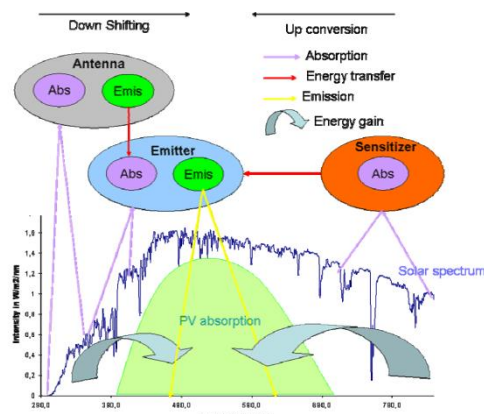

Figure 1. Incident photons not within PV absorption range are modified through down-shifting and up-conversion processes, enhancing the solar cell efficiency.

The Europium (III) complex, Eu(tta)$_3$phen, has been synthesized - demonstrating an effective large "Stokes shift" (LSS), as shown in Fig. 2. Two techniques have been used to quantify the luminescent QY of Eu(tta)$_3$phen at varying concentrations in solution, and at varying excitation wavelengths.

2 EXPERIMENTAL

2.1 Synthesis of Europium(III) complex:

Eu(tta)$_3$phen complex has been prepared by adding a quantity of thenoyltrifluoroacetate ligand to a solution of EuCl$_3$.6H$_2$O dissolved in methanol. The pH was kept at pH=8, by adding NaOH saturated methanol solution. After, a suitable amount of phenanthroline ligand was added and the Eu(tta)$_3$phen precipitates. The complex is recovered using a Büchner funnel, and cleaning with methanol and drying in vacuum. An 80% yield was obtained. The absorption and emission spectrum of 10^{-5}M Eu(tta)$_3$phen in CH$_2$Cl$_2$ are shown in Fig 2.
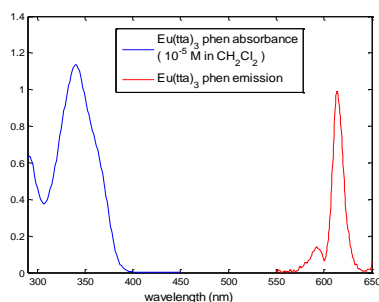
Figure 2. Absorbance and emission (a.u.) spectra of 10^{-5}M Eu(tta)$_3$phen in CH$_2$Cl$_2$

2.2 Quantum yield measurements – Comparative Technique:

The absolute luminescent QY was determined by comparison with that of a known reference standard dye from;

$$QY = QY_{ref}\left(\frac{m}{m_{ref}}\right)\left(\frac{n^2}{n_{ref}^2}\right) \qquad (1)$$

where, n and n_{ref} are the refractive indices of the test and reference solutions, and m and m_{ref} are the corresponding slopes obtained from a graph of the integrated emission spectra against the absorbance of the sample at the excitation wavelength [7]. The absorbance is measured on a Perkin Elmer UV/VIS 900 spectrometer, correcting for the absorbance of the solvent and for background absorption. Luminescence is measured on a Perkin Elmer LS55 luminescence spectrometer fitted with Hamamatsu R6925 photomultiplier tube (PMT). The excitation wavelength is not varied when exciting both reference and test dye samples. PMT gate times are set to 10ms to detect the Europium complex luminescence, which have long luminescent lifetimes of the order of 1 ms. A set of five 10-mm pathlength cuvette solutions were prepared, corresponding to absorbance values ranging from 0.02 to 0.1 at the excitation wavelength. Low absorbance values in this range are required in order to minimise inner filter effects on excitation photons [7].

The reference dye, Quinine Sulphate, emits over a different spectral region (peak ~ 460 nm) to that of the Europium complex (peak 612 nm). Therefore, the spectral response of the detector must be known. The overall wavelength dependence of the detector system (i.e. collection optics, filters, monochromator, and photomultiplier tube) was determined by comparing the uncorrected in-situ *measured spectra* of four standard dyes with their respective accepted *corrected spectra* [7]. The four dyes used were Harmine, Harmane, Quinine

Sulphate, and 3-Aminophthalimide providing emission ranging across the visible spectrum. The generated response and manufacturer spectral response data of the instrument are shown in Fig. 3. The mean of the two response curves was taken for spectral correction of measured luminescence spectra.
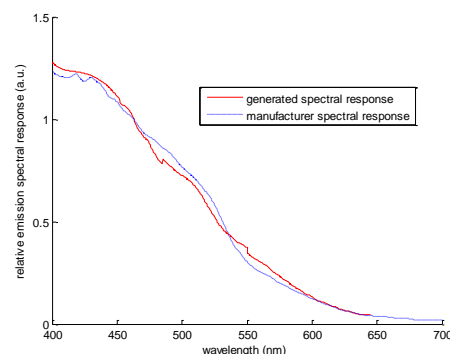
Figure 3. Manufacturer specified spectral response and generated spectral response of Perkin-Elmer LS-55 luminescence spectrometer detector.

2.3 Quantum yield measurements – Integrating Sphere Method:

Quantum yields were also determined using an integrating sphere method [4, 5, 6]. The luminescent sample is placed inside the integrating sphere (Avantes, AvaSphere-50-REFL), as indicated in Fig. 4, so that the excitation beam is incident at an 8° angle. A 160μL quartz cuvette (with all sides and base polished) is used to hold liquid test solutions. The number of photons emitted by the sample is quantified relative to the total excitation photons absorbed by the sample and, thereby, the QY can be obtained. Excitation is provided by a pulsed Xenon discharge lamp with excitation wavelength tunable over the range 360-800nm. Excitation light is coupled into the integrating sphere (IS) via optical fibre. A CCD spectrometer (AVASPEC 2048-USB2-UA) is used to detect the photon count rate of emitted and excitation light. All measured spectra are corrected for the spectral response of the CCD/fibre optic/IS detector system, which was determined from comparison of a measured spectrum of a calibrated quartz-halogen light source with that of its known spectrum. Uncertainty in the spectral response of the IS/CCD detector increases in the UV (see Fig. 5). In addition, the intensity of the Xenon lamp light source drops off significantly at wavelengths below 360 nm. The shortest excitation wavelength possible with the setup described is ~360 nm.
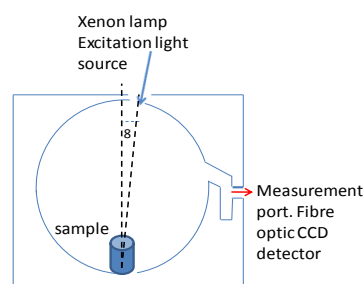
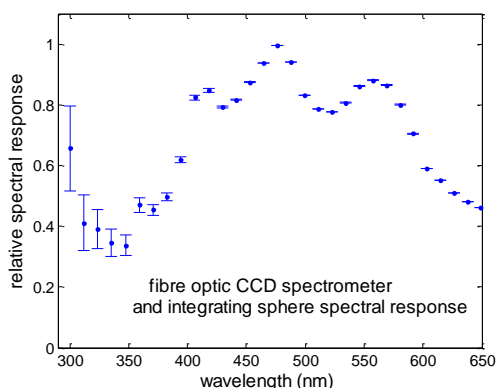Figure 4. Schematic of integrating sphere setup for QY measurement.

Figure 5. Relative overall spectral response of fibre optic CCD and integrating sphere.

Photons absorbed within the sphere but not by the luminescent species, i.e. by the host polymer matrix / quartz micro-cuvette, must be accounted for[1]. To do so, a second "blank" sample containing no active luminescent molecules is required. In the case of solid thin-films, the blank sample should be fabricated by the same method, and be of the same cross-sectional area and thickness, as the test luminescent sample. To account for possible minor differences in dimensions between blank and luminescent sample thin-films, both are excited at a longer wavelength (beyond the absorption range of the DS molecules). The ratio of excitation intensities detected can then be used to correct for any discrepancies.

To calculate the QY, the photon count intensity from the measurement port is detected for i) the empty IS, ii) the IS containing test sample, iii) the IS containing the "blank" sample, using two distinct excitation wavelengths for each of the three cases; 1) excitation at a wavelength within absorption range of LSS-DS molecules, and 2) excitation at a longer wavelength within the emission spectral range where, ideally, the DS molecules do not absorb light. The QY is given by the ratio of photons absorbed by LSS-DS molecules to photons emitted;

$$QY = \frac{\text{phot emitted}}{\text{phot absorbed}} \qquad (2)$$

The total number of excitation photons *emitted* by the DS molecules is given by;

$$\text{photons emitted} = \sum E_{s1}(\lambda)d\lambda \left(\frac{\sum L_{n2}(\lambda)d\lambda}{\sum L_{s2}(\lambda)d\lambda} \right) \qquad (3)$$

where, *E* and *L* are the measured emission and excitation spectra, respectively. The subscripts "s", "b", and "n" refer to whether the integrating sphere contains the sample, the blank, or is empty, respectively. Subscripts "1" and "2" refer to the two excitation wavelengths alluded to above. Emitted photons may be absorbed by the host polymer/cuvette. The final term in eqn. 3

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[1] This is particularly important for UV excitation wavelengths, as host polymer/cuvette absorption may be significantly higher in the UV spectral region compared to that at the visible. Also, this is particularly important in the case of liquid tests using the micro-cuvette, which absorbs ~8% of photons emitted at 612nm.

corrects for the fraction of emitted photons which are absorbed by the host polymer/cuvette within the sphere.

The total number of excitation photons *absorbed* by the DS molecules is given by;

$$\text{phot absorbed} = \sum L_{b1} \ \lambda \ d\lambda \left(\frac{L_{s2}}{L_{b2}} \right) - \sum L_{s1} \ \lambda \ d\lambda \qquad (4)$$

The first term in eqn 4 includes the factor L_{s2}/L_{b2} to correct for differences in dimensions between the blank and test luminescent samples, as discussed above (L_{s2}/L_{b2} was in the range 0.98 to 1.02 for the thin-film samples measured). The terms referred to in eqns. 1 to 4 are illustrated in Fig. 5.

If molecular absorption and emission bands overlap, self-absorption of emitted light will attenuate E_{s1}, thereby underestimating the true QY of the LSS-DS molecules. By comparing the detected emission signal E_{s1} with that obtained from a very low concentration sample (free from self-absorption effects), a self-absorption correction factor may be applied, as proposed by Ahn et al. [5]. It is noted that the observed emission spectra of the Europium(III) complex does not overlap with the UV absorption bands. Therefore, the self-absorption correction is not required in this case.
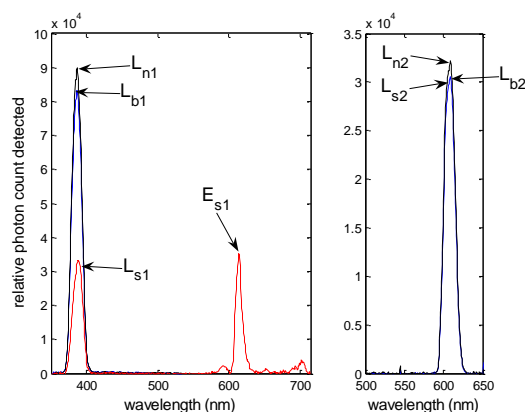

Figure 5. *E* and *L* are the measured emission and excitation light source spectra. The subscripts "s", "b", and "n" refer to whether the integrating sphere contains the sample, the blank, or is empty, respectively. The subscripts "1" and "2" refer to excitation wavelengths of 380nm and 612 nm, respectively.

3. RESULTS

3.1 "Comparative technique", QY measurements in solution:

The absolute QY for a range of concentrations of Eu(tta)3phen, determined relative to that of a Quinine Sulphate standard dye are given in Table I (column A). The QY of each concentration of Eu(tta)3phen relative to other concentrations can be evaluated omitting the experimental uncertainty arising from detector spectral correction error (column B), as all Eu(tta)3phen samples emit at the same wavelengths and, therefore, are subject to same over/under estimation in QY. The results in column B demonstarte an increase in QY with concentration.

Test Solution (solvent)	Conc.	Excitation (nm)	A: Absolute QY including spectral correction error	B: QY relative to other concentrations
Eu(tta)$_3$phen, (CH$_2$Cl$_2$)	10^{-3}M	405	0.60± 0.05	0.60± 0.03
	10^{-4}M	395	0.56± 0.05	0.56± 0.03
	10^{-5}M	383	0.53± 0.05	0.53± 0.03
	10^{-6}M	355	0.50± 0.05	0.50± 0.03

Table I. Absolute QY of Eu(tta)$_3$phen at varying concentration determined using "comparative technique".

To minimise experimental uncertainty arising from inner filter effects on excitation light, samples should be excited at a wavelength where the absorbance is < 0.1 [7]. A drawback of this technique therefore is that, for high concentrations, choice of excitation wavelength is limited the absorption tail of the luminescent material.

3.2 Integrating Sphere QY measurements in solution:

The QY determined using the integrating sphere setup is given in Table II. The QY of Rhodamine 101 (lit. QY =1.0) dye was determined to be 0.96 ± 0.10 and 0.94 ± 0.04 for excitation wavelengths of 370 and 570 nm. The consistent result obtained for varying excitation wavelength demonstrates the spectral calibration of detector system is accurate for excitation wavelengths over this range. In the Europium(III) complex, the measured QY increases at excitation wavelengths closer to the absorption peak of the complex. For example, the QY of Eu(tta)$_3$phen (10^{-4}M) was 0.71 ± 0.06 and 0.51± 0.05 for excitation wavelengths of 360 and 390 nm, respectively. 10^{-5}M was the lowest concentration of Eu(tta)$_3$phen from which reliable signal intensity was detectable using the IS setup described in section 2.

Test Solution	Conc.	Excitation (nm)	Absolute QY
Rhodamine 101 (ethanol)	10^{-5}M	370	0.96 ± 0.10
		570	0.94 ± 0.04
Eu(tta)$_3$phen (CH$_2$Cl$_2$)	10^{-3}M	360	0.81 ± 0.08
		370	0.68 ± 0.08
		390	0.71 ± 0.06
		400	0.64 ± 0.06
Eu(tta)$_3$phen (CH$_2$Cl$_2$)	10^{-4}M	360	0.71 ± 0.06
		370	0.56 ± 0.07
		390	0.51 ± 0.05
Eu(tta)$_3$phen (CH$_2$Cl$_2$)	10^{-5}M	360	0.64± 0.08
		370	0.61± 0.07

Table II. Absolute QY of Eu(tta)$_3$phen at varying concentration and excitation wavelength measured using integrating sphere (IS) setup. An increase in QY at wavelengths closer to the absorption peak of the Europium complex (III) is observed. An increase with concentration is also observed.

3.3 QY measurements of Eu(tta)$_3$phen in solid thin films:

An increase in QY with concentration has been reported for Eu(tta)$_3$phen in thin film samples [3]. A strong quenching of the energy transfer from the organic antenna to the lanthanide ion has also, however, been observed by LeDonne et al [8] at high concentrations.

QY of DS molecules in polymer thin films can be evaluated using the IS measurement technique. Eu(tta)$_3$phen was incorporated in polyvinyl acetate and in polyvinyl butyral (Butvar) thin films. QYs of 0.41 ± 0.05, and 0.66 ± 0.08 were determined, respectively, at an excitation wavelength of 360nm. Further studies are required to evaluate the effect on luminescent QY of varying concentration in thin films.

4. CONCLUSIONS

A lanthanide Europium (III) complex, Eu(tta)$_3$phen, has been synthesised, absorbing in the UV and emitting in the "red". The large Stokes shift molecules are potential candidates for inclusion in down-shifting (DS) layers to increase the efficiency of solar cells which do not efficiently utilize the UV part of the solar spectrum. In this paper, two techniques have been used to determine the QY of Eu(tta)$_3$phen in solution and in solid thin films. The integrating sphere (IS) technique is advantageous as it allows a wider range of excitation wavelengths to be used. The analysis presented on the IS technique allows a correction to be made for QY error arising from emitted photons absorbed within the IS by the host polymer/cuvette. Also, a corrective technique accounting for error arising from inhomogeneities between "blank" and test luminescent samples is included.

The QY of the Eu(tta)$_3$phen complex has been determined at varying concentration and excitation wavelengths. The QY was found to increase marginally at wavelengths closer to the absorption peak of the complex, and also to increase at higher concentrations in solution. QY was found to be higher in PVB thin film compared to that in PVAc thin film. Further study will investigate the effect of varying concentration on QY in different thin-film polymer hosts.

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