

Characterization of Luminescent Down-Shifting Materials and Applications for PV Devices

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Abstract

Enhancement in the performance of Silicon solar cell can be achieved via luminescent down-shifting (LDS) of the incident light. Lumogen Violet dye and Tb(ant)₃.2H₂O complex were characterized to determine their suitability for inclusion in LDS layers. LDS layer characterization techniques are discussed and preliminary results from PV cell/LDS layer devices are presented.

1. Introduction

Losses due to the limited spectral response of solar cells represent a fundamental limit to the maximum efficiency achievable by the cell. The potential exists to increase cell efficiency by making better use of short wavelength light. One way to do that is to improve the electric properties of the solar cell but the processes involved can be expensive in production and difficult to implement [1]. Another potential solution is to use luminescent materials to convert high energy photons to lower energy before the interaction with the solar cells occurs, a process referred to as Luminescent Down-Shifting (LDS) [2-6]. The downshifted photons have wavelength which may better match the photosensitivity spectral response of the solar cell.

1. Experimental

In this investigation, Naphtalimide based Lumogen Violet organic dye [BASF] and rare-earth ion complex Tb(ant)₃.2H₂O are characterized for inclusion in LDS layers. The Tb(ant)₃.2H₂O complex was synthesized at Leitat Technologies by adding a solution containing KOH (2.0 mmol) and anthranilic acid (2.0 mmol) which results in an aqueous solution of Tb(NO₃)₃.6H₂O (0.5 mmol) from where the Tb(ant)₃.2H₂O precipitated. The solution is finally filtered and washed with water, resulting in white powder.

It is important to determine the luminescent quantum yield (LQY) which is the ratio of photons emitted through luminescence to photons absorbed [7]. Two techniques considered to determine the LQY are the

“comparative method” and the “integrating sphere method”. Both are discussed in the following sections 2.1 and 2.2.

2.1 Comparative method technique

The comparative method¹ of Williams *et al.* involves the use of a standard fluorescent dye to compare with the test luminescent sample [8]. This requires solutions of standard and test samples to be prepared with equivalent absorbance ranges (by varying the concentrations) at the same particular excitation wavelength [8]. The respective ratio of the integrated luminescent intensities of the two solutions yields the ratio of the quantum yield values. Since LQY for the standard sample is known, the LQY can be calculated for the test sample from equation 1.

$$QY_x = QY_{st} \left(\frac{\text{slope}_x}{\text{slope}_{st}} \right) \left(\frac{\eta_x^2}{\eta_{st}^2} \right) \quad (1)$$

where “x” and “st” denote the test and standard samples, “slope” is the calculated slope of integrated emission against absorbance and η is the refractive index of the solution.

2.2 The integrating sphere technique

LQY of Lumogen Violet is determined in two distinct host materials (PMMA and Epoxy resin). Some difficulties arise in using the comparative method technique for evaluating the LQY of solid thin films. The wave-guiding effects modify the angular distribution of the emission, and the test sample and the reference sample films may differ in morphology. Therefore, the LQY in thin films was determined by using the integrating sphere technique [9, 10] illustrated in Fig 1. The number of photons emitted is quantified relative to the total excitation photons absorbed by the sample. Filtered light from a metal-halide discharge lamp (Griven lighting) is coupled into an integrating sphere via optical

¹ The method was tested first by comparing QY of known standard dyes (Harmin, Harmane and Quinine Sulphate with literature values.

fiber. A CCD spectrometer (AVASPEC 2048-USB2, Anglia Instruments UK) is used to monitor the photon count rate exiting at the measurement port of the integrating sphere. All measured emission spectra are corrected for the spectral response of the detector system in totality, which was determined from comparison of a measured deuterium-halogen light source with that of the known calibrated spectrum. Photon count readings are taken with the sphere empty and again with the sample inserted. LQY is calculated as follows;

$$LQY = \frac{\text{relative number of photons emitted}}{\text{relative number of photons absorbed}} \quad (2)$$

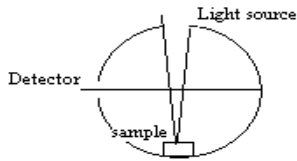


Fig 1: Schematic diagram of integrated sphere setup for LQY measurement.

To account for reabsorption of emitted light by the sample within the sphere a correction factor "a" given in equation 3 is applied. The value of "a" is determined by comparison of the detected emission profile with that of the true emission measured from a very low concentration sample [9].

$$QY_{\text{Corr}} = \frac{QY_{\text{obs}}}{1 - a + aQY_{\text{obs}}} \quad (3)$$

2.3 LDS layers and device fabrication

The LDS layers were prepared by dissolving the Violet dye in PMMA (Carl Roth GmbH+Co.KG) and Epoxy resin (ABL Resin & Glass, UK) solutions (1mg/ml in each case). The dye was first dissolved in 0.5g Toluene, added to the PMMA and Epoxy solution, and stirred for 45 minutes resulting in homogeneous solutions. Uniform thicknesses were achieved by drop casting the solutions onto glass plates. The Lumogen Violet dye was selected as it has a high absorption coefficient, is relatively easy to process with polymers, and was expected to have high LQY according to suppliers. PMMA and Epoxy resin LDS layers of 0.26mm and 1.81mm thickness, respectively, were obtained. Absorption and emission spectra of the LDS layers were measured using a UV/VIS spectrometer (Perkin Elmer Lambda 900) and Luminescence spectrometer (Perkin Elmer Lambda LS55B). Mono-crystalline silicon cells (2x2 cm, Sunrydz, Germany) were used for assessing

the downshifting effect of the Lumogen Violet in the PMMA and Epoxy host material.

2.4 I-V measurements

The electrical measurements on LDS layer/PV cell devices are performed with a Keithly 2400 SMU (Source Meter Unit) with Labview interface. The light source is a metal Halide lamp (Griven, GR0262). The lamp spectral irradiance was compared against the standard ASTM G173-03 air-mass 1.5G solar spectrum. Table 1 shows the percentage of the spectral irradiance within six defined wavelength regions over the range 400-1100nm. The spectral component below 400 nm is not explicitly considered by the solar simulator standard. However, the percentage irradiance within 350-400 nm is 3.9% (relative to that over 400-1100 nm range). The Griven lamp light source used has only 1.9% of the spectral irradiance within this range. An additional, low intensity UV lamp (0.49 mW/cm²), is introduced so that spectral mismatch is minimized (see Table 1) in the region 350-400nm where the LDS material absorption is most significant.

Table 1. Percentage of spectral irradiance within six defined wavelength bands according to ASTM G173-03 standard. Corresponding % values for solar simulator lamp with and without additional UV lamp.

		% of irradiance within specific band range relative to total within 400-1100 range.		
	Wavelength range (nm)	"White" light lamp (Griven lamp, GR062)	ASTM G173-03 standard +/- 25% relative	"White" light lamp and UV lamp
"0"	350-400	1.5%	3.9%	4.4%
1	400-500	13.8%	18.4%	13.7%
2	500-600	18.0%	19.9%	17.9%
3	600-700	18.7%	18.4%	18.7%
4	700-800	12.6%	14.9%	12.7%
5	800-900	14.6%	12.5%	14.6%
6	900-1100	18.0%	15.9%	18.0%

2.5 Photo-stability study on PMMA and Epoxy films

PMMA and Epoxy LDS layers containing the Lumogen Violet dye were inserted in an accelerated ageing simulation chamber (Q-sun, XE-1, Q-Labs) to measure the respective photostability. Half of each sheet

was covered with a UV blocker with 380 nm cut off. Exposure time was 72 hours in total. The irradiance was $0.28 \text{ W/m}^2/\text{nm}$ at 340 nm (total irradiance ~ 2.2 suns). The absorption of the films was measured every 24 hours.

3. Results

3.1 Luminescent quantum yields

3.1.1 LQY measurement in solution

Fig 2 shows the absorption and emission for Lumogen Violet in PMMA and Epoxy host materials.

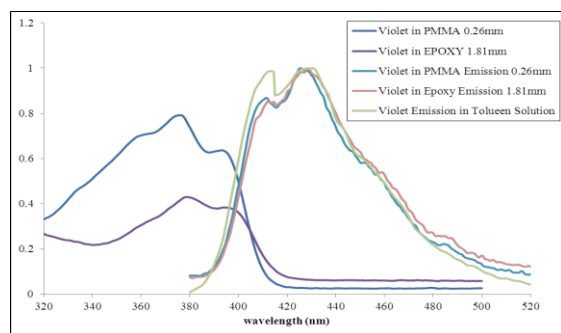


Fig 2: Absorption and emission for Lumogen Violet dye in PMMA and Epoxy layers. Violet emission in toluene solution is also shown.

The same absorbance features are observed for Lumogen Violet dye dissolved in solution and in polymeric layers (see Fig 3) indicating that the Violet dye is well dissolved and uniformly doped in the PMMA and Epoxy sheets.

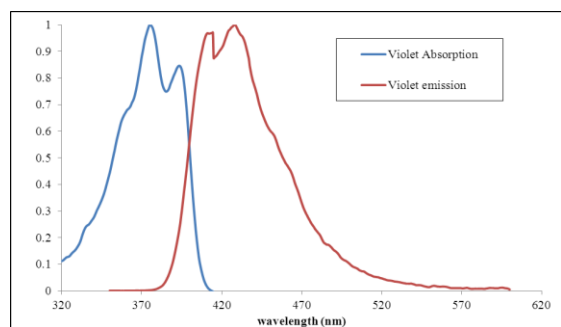


Fig 3: Absorption and emission of Lumogen Violet dye solution of 0.12mg in 10ML of Toluene.

Fig 4 shows the integrated fluorescent emission of Violet when compared with the standard dye Harmane. The LQY of Lumogen Violet dye in toluene solution is hence determined to be 0.99 ± 0.08 .

Fig 5 shows the absorption and emission of $\text{Tb}(\text{ant})_3 \cdot 2\text{H}_2\text{O}$ dissolved in DMSO solution

while the integrated luminescent emission of the complex is shown in Fig 6.

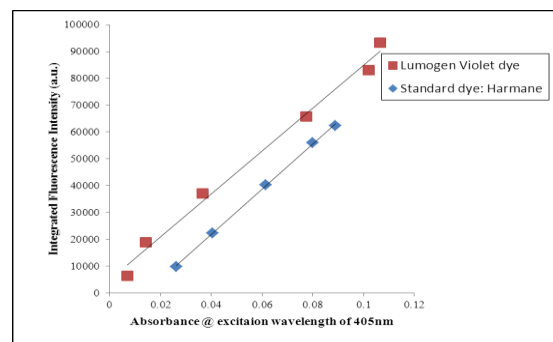


Fig 4: Integrated fluorescent intensity for Lumogen Violet dye and standard dye Harmane. The gradient for each is proportional to their fluorescence quantum yields.

Quinine Sulphate is used as standard dye. The LQY of $\text{Tb}(\text{ant})_3 \cdot 2\text{H}_2\text{O}$ is hence determined to be 0.72 ± 0.07 .

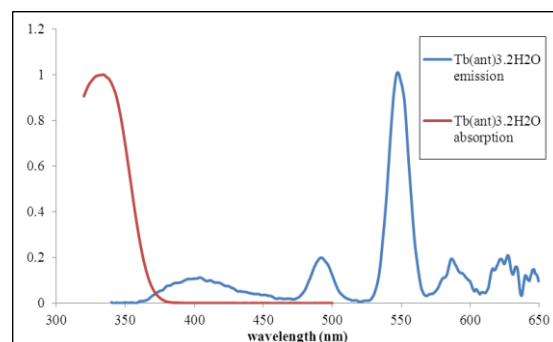


Fig 5: Absorption and emission of $\text{Tb}(\text{ant})_3 \cdot 2\text{H}_2\text{O}$ solution of 10^{-4} M in DMSO.

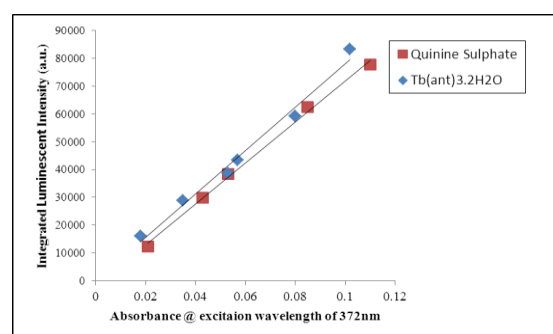


Fig 6: Integrated luminescent intensity for $\text{Tb}(\text{ant})_3 \cdot 2\text{H}_2\text{O}$ and standard dye Quinine Sulphate. The gradient for each is proportional to their luminescent quantum yields.

3.1.2 LQY measurement in thin film

The LQY of Lumogen Violet in PMMA film is determined to be 0.83 ± 0.03 (absorption and emission shown in Fig 7). In the Epoxy film the

LQY is 0.50 ± 0.04 . From the LQY measurements in thin film, the PMMA appears to be the more suitable host material for the Violet dye.

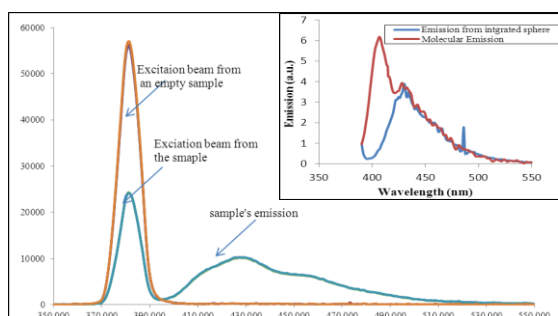


Fig 7: Absorption and emission of Lumogen Violet/PMMA film with the correction factor “a” calculated to be 0.42 ± 0.01 .

3.2 Electrical characterization

From initial electrical characterization tests, we observe that the measured short circuit current of the solar cell device with PMMA LDS layer (Violet dye) is 9% higher than that of the Epoxy resin LDS layer. This is most likely due to the higher LQY of Lumogen Violet in the PMMA host material compared to that in the epoxy host layer.²

3.3 Photostability

Fig 8 presents the results of degradation studies in Lumogen Violet /PMMA LDS layer which shows a rapid decrease in absorption. When a UV blocking layer is used the degradation was observed to be slower. The same trend was observed for Violet dye in the Epoxy resin host.

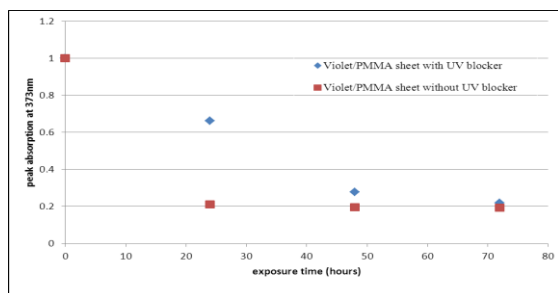


Fig 8: Violet/PMMA photo-degradation over 72 hours exposure time.

The PMMA and Epoxy degradation is caused by light in the blue/UV region of the spectrum

² Although differences in optical densities (and hence re-absorption losses) may partially account for difference in electrical output.

as this region has sufficient energy to cause damage to the structures of the polymers or the Violet dye [11].

5. Conclusion

Initial results characterising the LDS materials are presented. The LQY of Lumogen Violet is determined in solution (0.99 ± 0.08), in PMMA (0.83 ± 0.03), and in Epoxy resin (0.50 ± 0.04) thin films. Results indicate that the PMMA is the more suitable host material. PMMA LDS layer on c-Si solar cells demonstrate 9% higher I_{sc} relative to devices with Epoxy resin LDS layer. It is proposed to incorporate large Stokes shift rare-earth Tb(ant)₃.2H₂O complex in luminescent downshifting layers for enhanced c-Si cell efficiency. The LQY of the complex is determined in solution (0.72 ± 0.07). Polymer films containing the complex are in progress. Gains in conversion efficiency using Tb complex LDS film will be compared with that of LDS films containing Lumogen Violet organic fluorescent dye.

Acknowledgements

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Reference

- [1] H. J. Hovel, R.T. Hodgson, and J.M. Woodall, *Solar Energy Materials*, 19-29, 2, 1979.
- [2] E. Klmpaftis, et al., *Sol. Energy Mater. Sol. Cells.*, 2009.
- [3] C. Strumpel, et al., *Sol. Energy Mater. Sol. Cells.*, 238-249, 91, 2007.
- [4] E. Klmpaftis and B. S. Richards, *Prog. Photovolt: Res. Appl.*, 2010.
- [5] B. M. van der Ende, L. Aarts and A. Meijerink, *Phys. Chem. Chem. Phys.*, 11081–11095, 11 2009.
- [6] K. R. McIntosh and B. S. Richards, 1-4244, *IEEE.*, 2006.
- [7] J. R. Lakowicz, Kluwer Academic/Plenum Press, New York, Second Edition., 1999.
- [8] A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst.*, 108-1067, 1983.
- [9] L. R. Wilson, B. S. Richards, *Appl. Opt.*, 212-220, 48, 2009.
- [10] T.S. Ahn, R.O. Al-Kaysi, A.M. M Mueller, K.M. Wentz, C.J. Bardeen, *Rev. Sci. Instrum.*, 086105-1-086105-3, 78, 2007.
- [11] P. F. Conforti and B. J. Garrison. *Chem. Phys. Lett.*, 294-299, 406, 2005.