# Characterisation of Luminescent Down-Shifting Materials for the Enhancement of Solar Cell Efficiency

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## Abstract

In this investigation commercially available semiconductor quantum dots (QDs) with emission peak at wavelength of 490nm and 450nm and Lumogen F organic dyes (Violet 570 and Yellow 083) were investigated for their use as luminescent down-shifting (LDS) layers. Their luminescent quantum yield (LQY) was measured by the comparative method technique. The measured LQY for 490nm-QDs, Violet 570 and Yellow 083 is >73%.

## 1. Introduction

The limited spectral response of solar cells is one of the main limiting factors to the possible efficiency achievable by the cell. Low energy photons are not absorbed by the solar cell, while high energy photons are not used efficiently and energy is lost via thermalization. Luminescent Down-Shifting (LDS) is an optical approach to increase a solar cell's spectral response by using luminescent materials to convert high energy photons to lower energy before the interaction with the solar cells occurs. [Hovel et al., 1979, Cheng et al., 2001, Strumpel et al., 2007, Klampaftis et al., 2009, McIntosh et al., 2009, van der Ende et al., 2009, Rothemund et al., 2011, Klampaftis et al., 2012].

## 2. Experimental

Two QDs with an emission peak at wavelength of 450nm and 490nm were investigated in this study. The QDs were purchased from Cytodiagnostics in solution (5mg/ml in toluene solvent). They were Trilite nanocrystals (approximately 6nm in size) with a CdS<sub>x</sub>Se<sub>1-x</sub> core encased in an inner shell of CdS and outer shell of ZnS. The absorption and emission spectra of the QDs are shown in Figure 1 and 2. Absorption spectra were recorded in a Perking Elmer Lambda 900 UV/VIS/NIR spectrometer and the emission spectra were measured in a Perkin Elmer Lambda LS55B luminescence spectrometer.

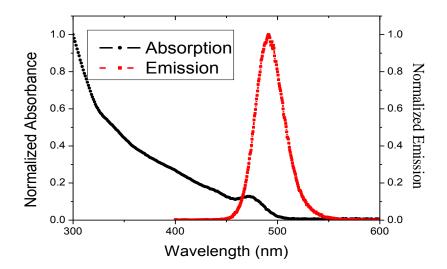


Figure 1: Normalized absorption (circles) and emission (squares) spectra of 490-QDs CdSeS/ZnS in toluene (0.15mg/ml).

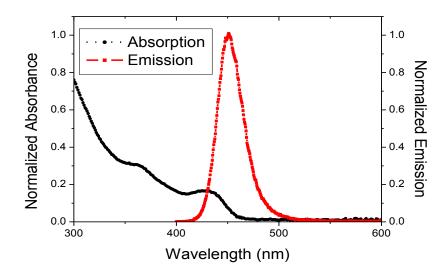


Figure 2: Normalized absorption (circles) and emission (squares) spectra of 450-QDs CdSeS/ZnS in toluene (0.15mg/ml).

Naphtalimide based Lumogen F Violet 570 and Perylene based Lumogen F Yellow 083 organic dyes from [BASF] were also investigated in this study. The absorption and emission of the dyes are shown in Figure 3 and 4.

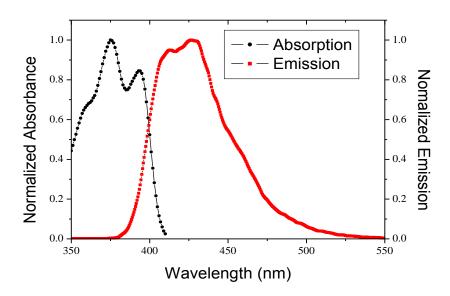


Figure 3: Normalised absorption (circles) and emission (squares) spectra of Naphtalimide Lumogen F Violet 570 dye in toluene (0.1mg/ml).

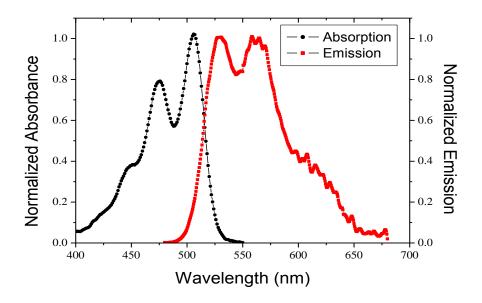


Figure 4: Normalised absorption (circles) and emission (squares) spectra of Perylene Lumogen F Yellow 083 dye in toluene (0.1mg/ml).

It is observed from the absorption and emission measurements the 490-QDs and 450-QDs downshift photons from 300 nm (Absorption peak) to 490 nm (Emission peak) and from 300 nm to 450 nm, respectively. The Violet 570 downshifts photons from 378 nm to 413 nm while the Yellow 083 downshifts photons from 478 nm to 525 nm. Absorption and emission measurements of QDs and Violet dye showed they have suitable spectral properties for transfer photons from ultra-violet/blue range to visible range. The Yellow dye has strong absorption across a wide range of the visible spectrum which limits its efficiency as LDS layer. It is important however to determine the luminescent quantum yield of these materials which is the ratio of photons emitted through luminescence to photons absorbed [Lakowicz, 2006]. The "comparative method" technique was used in this study to measure the luminescent quantum yield of the materials.

#### 2.1. Comparative method technique

The comparative method of Williams *et al.* involves the use of a standard fluorescent dye to compare with the test luminescent sample [Lakowicz, 2006]. 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 [Lakowicz, 2006, Jobin Yvon Ltd, Fluorescence Quantum Yield Standards]. 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.

$$QY_{x} = QY_{st} \left(\frac{slope_{x}}{slope_{st}}\right) \left(\frac{\eta_{x}^{2}}{\eta_{st}^{2}}\right)$$
(1)

where "x" and "st" denote the test and standard samples, "slope" is the calculated slope of integrated emission against absorbance and  $\eta$  is the refractive index of the solution.

The comparative method technique was validated using standard samples i.e. crosscalibrating the standard samples with each other and allowing their LQY values to be used for quantifying the test samples LQY. The LQY of Quinine Sulphate, Harmane and Harmine standard dyes were measured and their values are listed in table 1, along with the accepted LQY values reported in the literature [Jobin Yvon Ltd, Fluorescence Quantum Yield Standards]. The LQY measurements are, within the experimental error, in agreement with those reported. It is concluded, therefore, that the comparative method technique can be used to analyse the LQY of test luminescent samples.

	Standard	Solvent	Excitation	QY measured	Literature	
	dye			Values	values	
	,		(nm)			
Known	Harmane	0.1M H <sub>2</sub> SO <sub>4</sub>	380		0.83	
Standard						
Test A	Harmine	0.1M H <sub>2</sub> SO <sub>4</sub>	380	0.43 ±0.07	0.45	
Test B	Quinine	0.1M H <sub>2</sub> SO <sub>4</sub>	380	0.61 ±0.08	0.54	
	Sulphate					
	-					
Known	Harmine	0.1M H <sub>2</sub> SO <sub>4</sub>	380		0.45	
Standard						
Test C	Harmane	0.1M H <sub>2</sub> SO <sub>4</sub>	380	0.86 ±0.06	0.83	

Table 1: For validation of LQY "comparative method" measurement technique, LQY of standard dyes were determined.

## 3. Results

The luminescent quantum yield values of QDs-490 and QDs-450 were obtained. The integrated fluorescent emission of both QDs compared with Quinine Sulphate dye is

shown in Figure 5. From the slope of the integrated emission and using equation 1, the LQY of QDs-490 and QDs-450 in toluene solution was determined to be 0.81  $\pm$ 0.07 and 0.51  $\pm$ 0.05 respectively.

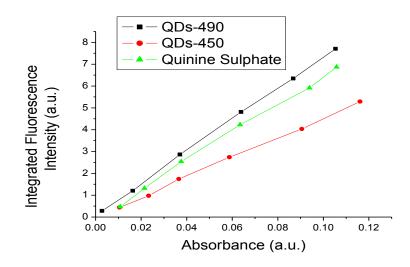


Figure 5: Integrated fluorescence intensity for QDs-490, QDs-450 and reference Quinine Sulphate dye. The gradient for each is proportional for their relative fluorescence quantum yield.

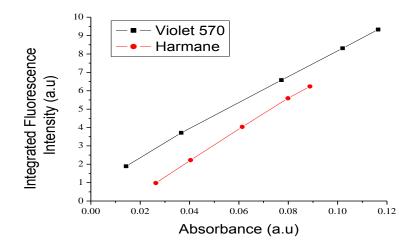


Figure 6: Integrated fluorescence intensity for Lumogen Violet 570 and reference Harmane dye. The gradient for each is proportional for their relative fluorescence quantum yield.

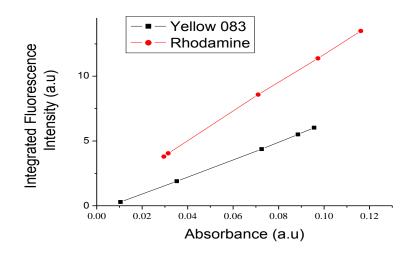


Figure 7: Integrated fluorescence intensity for Lumogen Yellow 083 and reference Rhodamine dye. The gradient for each is proportional for their relative fluorescence quantum yield.

The luminescent quantum yield values of Violet 570 and Yellow 083 were calculated. The integrated fluorescent emission of Violet 570 was compared with Harmane dye, and for Yellow 083 was compared with Rhodamine dye and they are shown in Figure 6 and 7. From the slope of the integrated emission and using equation 1, the LQY values of Violet 570 and Yellow 083 in toluene solution were determined to be 0.99  $\pm$ 0.08 and 0.78  $\pm$ 0.05 respectively. The quantum yield results are presented in table 2, along with the excitation wavelength and the comparative standard dyes used for each material.

Table 2: LQY of QDs and Organic dyes

	Solvent	Standard dye	Excitation (nm)	QY measured Values
490-QDs	toluene	Quinine Sulphate	365	0.81 ±0.07
450-QDs	toluene	Quinine Sulphate	365	0.51 ±0.05
Violet 570	toluene	Harmane	405	0.99 ±0.08
Yellow 083	toluene	Rhodamine	526	0.78 ±0.05

## 5. Conclusion

It is important to use materials which have high quantum yield for making LDS layers. The LQY obtained for QDs-490, Violet 570 and Yellow 083 in toluene solutions were found to be high >73%. This suggested that they are suitable candidates for processing into solid thin films to make LDS layers. The quantum yield value for QDs-450 was found low to result in efficient LDS layer. Organic dyes observed to have narrow absorption bands compared to QDs which exhibit broad absorption spectra. An overlaps between absorption and emission spectra was observed in both i.e. QDs and organic dyes, which will results in possible loss mechanism due to re-absorption.

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