



Alternative and fully experimental procedure for characterizing downshifters placed on photovoltaic devices



Ricardo Guerrero-Lemus^{a,*}, Joaquín Sanchiz^b, Marta Sierra^b, Inocencio R. Martín^a, Cecilio Hernández-Rodríguez^a, Dietmar Borchert^c

^a Departamento de Física, Instituto de Materiales y Nanotecnología (IMN). Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez, 38206 La Laguna, Tenerife, Spain

^b Departamento de Química, Instituto de Materiales y Nanotecnología (IMN). Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez, 38206 La Laguna, Tenerife, Spain

^c Fraunhofer Institute for Solar Energy Systems, Laboratory, and Servicecenter Gelsenkirchen, Auf der Reihe 2, 45884 Gelsenkirchen, Germany

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ABSTRACT

In this work, we propose an alternative and fully experimental procedure based only on external quantum efficiency (EQE) measurements for characterizing the efficiency and transmittance of downshifters placed on photovoltaic (PV) devices. The experimental setup requires two PV devices as references, one of them showing a zero EQE in the downshifting spectral range. Therefore, the results obtained are independent of the quantum efficiency of the device, easing the analysis and comparison between experimental results. Also, this method avoids complex theoretical modeling proposed in other works. Those theoretical models are usually based on approximations and/or that require some input parameters difficult to determine without a wide range of experimental equipment in the lab.

1. Introduction

Downshifting is an attractive strategy to increase the efficiency of solar cells [1]. This is due to the capacity of the downshifter (DS) to shift the wavelengths of incoming solar UV photons to higher values where the external quantum efficiency of the device is also higher [2].

It is commonly considered that the DS applied to a PV device should be evaluated by comparing the external quantum efficiency (EQE) and/or short-circuit current (I_{sc}) of the device with the DS to a similar device with a non-DS layer of the same material and using the established AM1.5 G spectrum [3,4]. However, variations in EQE and I_{sc} due to the integration of the DS are dramatically dependent on the specific EQE characteristics of the used PV device, as it will be shown in this paper. Not considering this dependency can produce some inconsistent results like reporting: (i) relative increases in EQE (and IQE) [5] that are not reproducible in solar cells with EQE characteristics that differ from the ones used in the reported experiment; (ii) a partial decrease [6] or total cancellation of PV conversion efficiency when the DS is applied to the PV device and when the DC concentration increases [7,8]; (iii) increases or decreases in EQE depending on the geometry of the experiment [8]; and, mainly, (iv) results that are not reproducible in solar cells showing different EQE but using the same downshifter (e.g. [Eu

(bphen)(tta)₃] in [9–11]).

Recently, many authors have defined different theoretical models for describing the relationship between downshifting and increases in solar cells efficiency. Alonso-Álvarez et al. [12] published an exhaustive work based on two previous studies of Batchelder et al. [13,14], simulating and modeling experimental EQE results for luminescent organic dyes placed on top of CdTe, CIS and mc-Si solar cells. However, we consider that the huge amount of computational capacity and information required as input to simulate accurately, and the amount of information required as input to build the models are not desired, as these make the model difficult to apply. A simplification of the model could be an alternative, but this introduces errors and might make the model not valid. Also, additional difficulties are added when comparing results because of the permanent lamination of any sample in a PV device, and variations in PV characteristics between the devices, as the authors recognize.

Motivated by the content of these previous works and the need to expose a simplified, comparable and fully experimental procedure, our work is based on the work of Rothemund [15] to determine the main parameters of DSs placed on PV devices. In fact, our work proposes a more simplified model to explain the experimental results, defining a figure of merit called the *DS efficiency*, η_{DS} , determining the

* Corresponding author.

E-mail address: rglemus@ull.edu.es (R. Guerrero-Lemus).

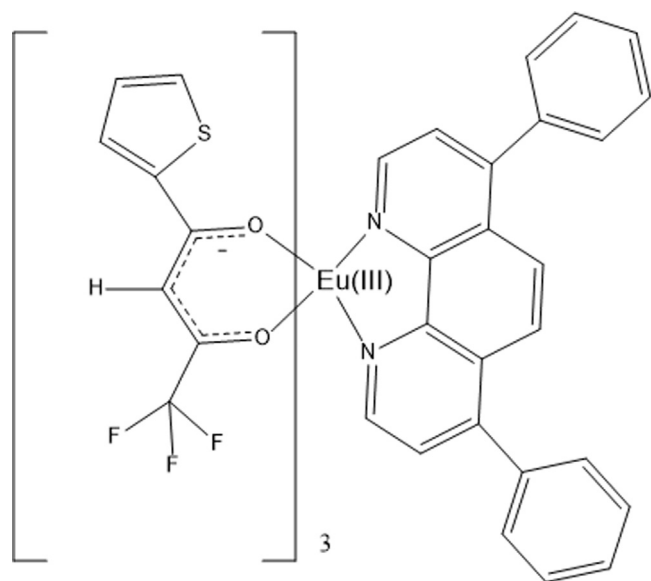


Fig. 1. Schematic view of the molecular structure of $[\text{Eu}(\text{bphen})(\text{tta})_3]$.

transmittance of the downshifting layer and exposing new experimental results for designing an optimal PV device with an integrated DS.

2. Materials and methods

The downshifter $[\text{Eu}(\text{bphen})(\text{tta})_3]$ active species (Fig. 1) was obtained by the reaction of stoichiometric quantities of europium (III) nitrate pentahydrate (99.99%), 4,7-biphenyl-1,10-phenanthroline (bphen, 97%), 2-thenyltrifluoroacetone (Htta, 99%), and triethylamine (99%). 2-thenyltrifluoroacetone (668 mg, 3 mmol) was dissolved in 40 ml of ethanol and the solution was heated at 65 °C under stirring in an erlenmeyer flask. Triethylamine (416 μL , 3 mmol) was added under stirring. Subsequently, a solution of bath (332 mg, 1 mmol) in ethanol (40 ml) was added. In a different beaker, $\text{Eu}(\text{NO}_3)_3$ (425 mg, 1 mmol) was dissolved in ethanol (10 ml). Finally, both solutions were mixed and stirred for 2 h. After that time, 50 ml of water was added and a white product was obtained that was filtered, washed with water and dried in an oven at 60 °C overnight (yield 1.059 g, 92%). Elemental analysis calculated (%) for $\text{C}_{48}\text{H}_{28}\text{N}_2\text{Eu}_1\text{O}_6\text{F}_9\text{S}_3$: C, 50.23; H, 2.46; N, 2.44; S, 8.38. obtained: C, 50.47; H, 2.47; N, 2.69; S, 8.51.

In a typical experiment for the preparation of the films, a $20 \times 20 \times 2$ mm bare glass is washed with an aqueous solution of soap, rinsed with deionized water, dried with a dinitrogen current and placed in the holder of a spin-coater. The desired amount of sample (in our experiments in the 0.26–7.90 mg range) is dissolved in 1500 μL of CH_2Cl_2 . Subsequently, 26.25 mg of poly(methylmethacrylate) (PMMA, average Mw 996,000 from Aldrich, ref. 182265) are added. Then, the solution is poured on the glass and spin-coated at 800 rpm for 10 s. The solvent is allowed to evaporate at room temperature. We have found that this solvent amount is enough to obtain a film that completely covers the glass. The PPMA/ CH_2Cl_2 ratio and spin coating conditions gives film thicknesses in the 350–450 nm range which are optimum for the EQE experiments.

The glasses have been alternatively placed on two different PV devices: a reference cell (Rcell) or a mc-Si mini module (M), and illuminated for obtaining different EQE spectra. The M and Rcell devices have been selected in order to offer almost zero EQE ($\text{EQE}_{\text{Rcell}}$) and significant EQE (EQE_{M}), respectively, in the spectral range where downshifting is produced (280–360 nm) (Fig. 2). M is based on a single p-type mc-Si solar cell (non-textured and with a SiN_x antireflection coating optimized at 600 nm) encapsulated in a standard solar glass and showing a 16% conversion efficiency. Rcell is a 20×20 mm Fz-Si solar

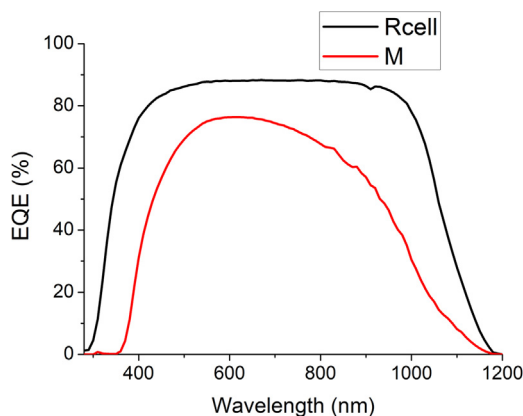


Fig. 2. EQE of the reference cell ($\text{EQE}_{\text{Rcell}}$) and the mini module (EQE_{M}).

cell fabricated and encapsulated in the Fraunhofer ISE.

An air gap exists between the glass and the PV device, which introduces an additional optical loss. However, this configuration has been selected because it eases the EQE characterization with different DSs and PV devices and, consequently, the comparison and reproducibility of results. Other authors add a refractive index matching oil carefully chosen to avoid the air gap and prevent reflection losses between the downshifter and the solar cell [16]. However, this procedure can produce some inconveniences (e.g., poor polymer adherence to the solar cell despite the application of the matching oil). As our experiments are carried out only for comparative purposes, avoiding the matching oil eases the experimental procedure.

Luminescent spectra were obtained exciting the samples using a 400 W Xe arc lamp passed through a 0.25 m Spex 1680 double monochromator. Fluorescence was detected using a 0.25 m Spex 1681 monochromator with photomultiplier. The active specie was selected showing a large Stokes shift, avoiding overlap of emission and absorption spectra and, consequently, reemission processes in the downshifter.

A standard EQE setup based on a 100 W Xe arc lamp, double monochromator and a digital lock-in amplifier integrated in the SPECLAB commercial setup at Fraunhofer ISE Lab (Germany) has been used. A spectroscopic ellipsometer model HORIBA UVISSEL 2 – UV – NIR with a thickness range 1 nm to 20 μm , 190–2100 nm spectral range, minimum spot diameter 34 $\mu\text{m} \times 34 \mu\text{m}$, 35–90° incidence, 200 \times 200 mm scanning area, and prepared for measurements on textured substrates has been used for characterizing the thickness and refractive index of the DS-PMMA layer.

We can calculate the increase in efficiency of M by placing the DS on top, measuring its EQE ($[\text{EQE}_{\text{DS}}]_{\text{M}}$) and considering the open circuit voltage (V_{oc}) and fill factor (FF) constant.

3. Results and discussion

3.1. EQE

The DS layers are characterized by spectroscopic ellipsometry, showing average thicknesses of about 380 nm and refraction indexes about 1.54. As the DS is deposited on $20 \times 20 \times 2$ mm standard glass substrates and an air gap exists between the PV device and the glass substrate, an edge loss of about a 5% of the downshifted photons can be considered [3].

Experimentally it is observed that the EQE_{M} increases from zero with increasing the concentration of DSs embedded in the thin PMMA film deposited on the glass (Fig. 3). This increase in EQE_{M} is completely attributed to the DS process.

However, when the EQE of the PV device is higher than zero at a particular wavelength where downshifting is produced, the EQE values

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