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

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

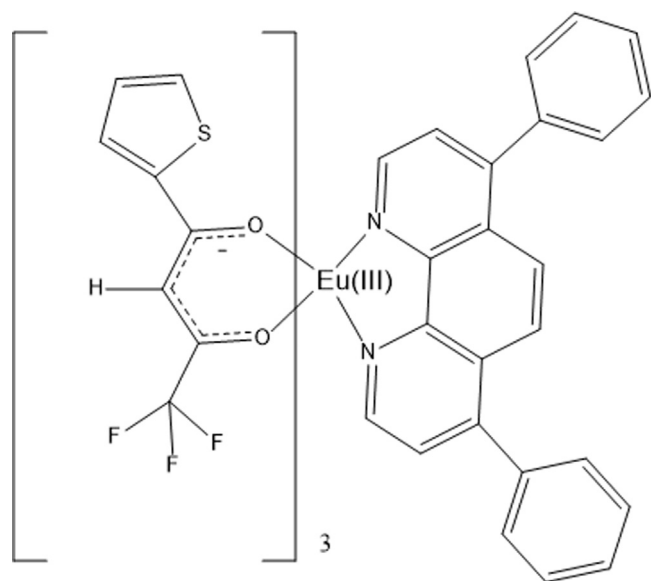**Fig. 1.** Schematic view of the molecular structure of [Eu(bphen)(tta)$_3$].

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 [Eu(bphen)(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-phenantroline (bphen, 97%), 2-thenoltrifluoroacetone (Htta, 99%), and triethylamine (99%). 2-thenoyltrifluoroacetone (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, Eu(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 C$_{48}$H$_{28}$N$_2$Eu$_1$O$_6$F$_9$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 × 20 × 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$_2$Cl$_2$. 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$_2$Cl$_2$ 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 (EQE$_{Rcell}$) 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
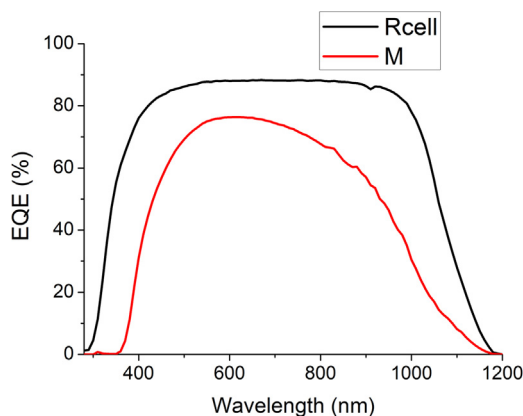

Fig. 2. EQE of the reference cell (EQE$_{Rcell}$) and the mini module (EQE$_M$).

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 UVISEL 2 – UV – NIR with a thickness range 1 nm to 20 µm, 190–2100 nm spectral range, minimum spot diameter 34 µm × 34 µm, 35–90° incidence, 200 × 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 ($[EQE_{DS}]_M$) 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 × 20 × 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
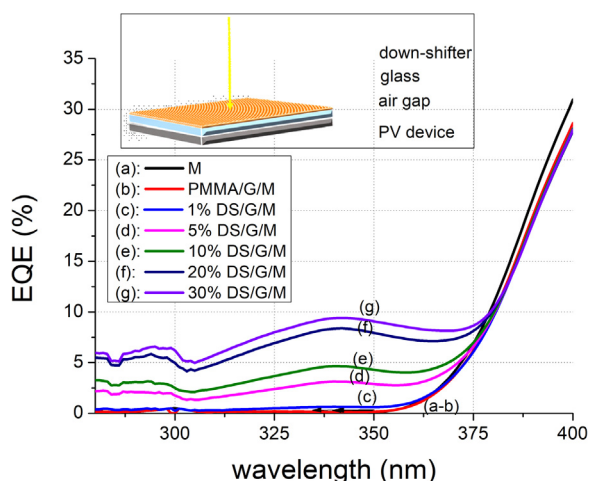
Fig. 3. EQE of (a) the mini module (EQE_M); (b) M below the glass substrate (G) with the thin PMMA film deposited on top; and (c - g) M below G with [Eu (bphen)(tta)$_3$] DSs at different concentrations (1–30%) embedded in the thin PMMA film deposited on top ([EQE$_{DS}$]$_M$). Inset: scheme of the DS/glass/PV structure.

Table 1
EQE values for the reference cell (EQE_{Rcell}) and the mini module (EQE_M) at 340 nm when a thin PMMA film embedded with [Eu(bphen)(tta)$_3$] at different concentrations is deposited on glass and placed on the PV device.

[Eu(bphen)(tta)$_3$] concentration (%)	EQER$_{cell}$ (%) (340 nm)	EQE$_M$ (%) (340 nm)
0	39.6	0.1
1	32.5	0.6
5	27.2	3.1
10	23.6	4.6
20	15.0	8.4
30	11.4	9.4

produced, the [EQE_{DS}]$_M$ increases with the [Eu(bphen)(tta)$_3$] concentration, as the DS conversion process has no other conversion mechanism competing at the same wavelength. The evolution of [EQE_{DS}]$_{Rcell}$ and [EQE_{DS}]$_M$ shown in Figs. 3 and 4, respectively, is listed in Table 1 for the 340 nm wavelength, where the highest conversion of downshifted photons is detected.

3.2. DS efficiency and transmittance

The amount of incident photons that reach the solar cell without downshifting is directly related to the transmittance of the thin PMMA film and glass. These transmittance values are difficult to be directly measured by conventional methods as: (i) standard spectrophotometers, because they measure any transmitted photon independently of its wavelength value; (ii) standard spectrofluorimeters, because they are not capable of simultaneously measuring photons with different wavelengths and, also, because they do not offer direct quantitative analysis in terms of transmittance percentages; and (iii) spectroscopic ellipsometers, because this technique is not capable for modeling in a spectral range where incident and downshifted photons are being simultaneously detected, and because this technique requires some input parameters (e.g., PMMA thickness) that are difficult to obtain for defining an accurate model.

However, the transmittance of the thin converter film can be directly obtained combining the Rcell and M devices, and the EQE values in the spectral range of the incident and downshifted photons. Thus, for [Eu(bphen)(tta)$_3$] embedded in PMMA the emission $E_m(\lambda)$ spectrum when the sample is excited at 340 nm is exposed in Fig. 5.

The $EQE_{DS340nm}$, that is the contribution to EQE of a PV device due to the downshifting of incident photons at 340 nm, can be calculated by the following equation:
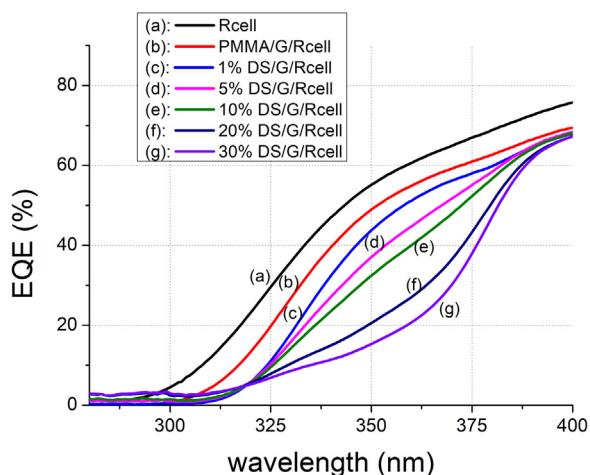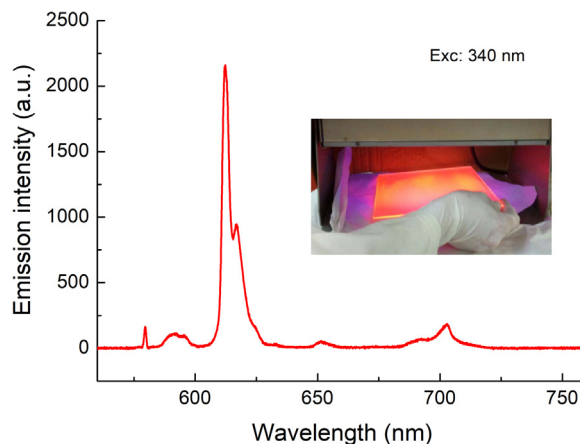

Fig. 4. EQE of (a) the reference cell (EQE_{Rcell}); (b) Rcell below the glass substrate (G) with the thin PMMA film deposited on top; and (c - g) Rcell below G with [Eu(bphen)(tta)$_3$] DSs at different concentrations (1–30%) embedded in the thin PMMA film deposited on top ([EQE$_{DS}$]$_{Rcell}$).

with DS (e.g., [EQE$_{DS}$]$_{Rcell}$) are due to a combination of photons shifted to higher wavelengths where the PV device can convert photons to photocurrent and photons transmitted through the DS to the PV device and converted to photocurrent. Thus: (i) some photons are firstly converted by the DS and, subsequently, some of these photons reach the solar cells and are converted to charge carriers; (ii) other photons do not provide charge carriers because the downshifting efficiency is usually below 100%, and the downshifting is based on spontaneous isotropic emission such that a part of the downshifted photons is emitted out of the solar cell (mainly, through back-reflections and edge losses); and (iii) some other incident photons are directly transmitted to the solar cell without being previously downshifted. Then, the EQE of a PV device with the DS placed on top can decrease if the efficiency of the downshifting process (including back-reflections and edge losses) is lower than the efficiency of the PV device at a defined wavelength as shown in Fig. 4, when the Rcell is placed under the same set of thin film DSs.

Consequently, $EQE_{Rcell(DS)}$ decreases as the [Eu(bphen)(tta)$_3$] concentration in the thin PMMA film increases. On the contrary, for the almost zero EQE_M in the spectral range where downshifting is

Fig. 5. Emission spectrum of the [Eu(bphen)(tta)$_3$] embedded in PMMA and excited at 340 nm. Inset: image of the downshifter embedded in PMMA, deposited on bare glass and under UV radiation.

Table 2
DS efficiency (η_{DS}) and DS/glass/air transmittance (T) at 340 nm and different [Eu(bphen)(tta)$_3$] concentrations.

[Eu(bphen)(tta)$_3$] conc. (%)	η_{DS}	$T_{340\,nm}$(%)
–	–	100
1	0.1	80.5
5	3.7	60.8
10	5.5	47.8
20	10.1	16.8
30	11.3	5.1

$$EQE_{DS340nm} = \frac{\int_{1200}^{280} E_{em340nm}(\lambda) \cdot EQE_{PV}(\lambda) \cdot d\lambda}{\int_{1200}^{280} E_{em340nm}(\lambda) \cdot d\lambda} \tag{1}$$

Where $E_{em340nm}(\lambda)$ is the emission spectrum obtained exciting at 340 nm and EQE_{PV} is the EQE of the PV device without the DS.

Considering the experimental data from Figs. 3, 4 and 5, in this case, the EQE for the photons emitted by the DS and captured by the reference cell, $[EQE_{DS340nm}]_{Rcell}$, is 87.6%; and for the mini module, $[EQE_{PV340nm}]_M$, is 83.2%.

Then, for calculating the value of the DS efficiency at 340 nm, $\eta_{DS340nm}$, we used the 9.4% total EQE measured at 340 nm, $[EQE_{T340nm}]_M$, and given in Table 1 for the 30% Eu(bath tta)$_3$ thin PMMA film on M, and take into account that the M device has negligibly small EQE at 340 nm, as shown in Fig. 2:

$$\eta_{DS340nm} = \frac{[EQE_{T(30\%)340nm}]_M}{[EQE_{DS(30\%)340nm}]_M} = 11.3\% \tag{2}$$

Similarly, DS efficiencies can be calculated for all the PMMA/glass substrates with different [Eu(bphen)(tta)$_3$] concentrations (Table 2).

In our opinion, reporting EQE efficiencies of the PV device with the DS, which varies depending on the EQE efficiency of the PV device used, is not satisfactory. Instead, the DS efficiency, η_{DS}, defined in this work is the parameter that should be reported in any research paper because it is independent of the EQE of the PV device used. Then, comparing the η_{DS} reported for any DS and the EQE of a PV device, at a defined spectral range, a quick estimation about the capacity of the downshifter to increase the efficiency of the PV device can be directly obtained.

We consider that similar procedures should be also used for characterizing solar cell efficiencies where up- or down-converters are integrated in the device. Of course, up-conversion processes are nonlinear with irradiation intensity [4], but this is not relevant for non-concentration PV cells and modules, where irradiations of only 1 sun or less are reached.

Now we consider the 11.4% total EQE measured at 340 nm, for the 30% [Eu(bphen)(tta)$_3$] thin PMMA film deposited on glass and placed on Rcell, $[EQE_{T(30\%)340nm}]_{Rcell}$. This EQE value corresponds to: (i) the 340 nm photons downshifted and emitted to Rcell, $[EQE_{DS(30\%)340nm}]_{Rcell}$, and (ii) the 340 nm photons directly transmitted to Rcell, $[EQE_{Tr(30\%)340nm}]_{Rcell}$. We also know that for the 30% [Eu(bphen)(tta)$_3$] thin PMMA film (Table 2):

$$\begin{aligned}[EQE_{Tr(30\%)340nm}]_{Rcell} &= [EQE_{T(30\%)340nm}]_{Rcell} - [EQE_{T(30\%)340nm}]_M \\ &= 11.4\% - 9.4\% = 2.0\% \end{aligned} \tag{3}$$

is the share of EQE due to the 340 nm photons directly transmitted to Rcell. Then, as the glass/PMMA (undoped) placed on Rcell shows a 39.6% EQE (Table 1), the percentage of photons transmitted (transmittance) to the solar cell at 340 nm is:

$$T_{(30\%,340nm)} = \frac{[EQE_{Tr(30\%)340nm}]_{Rcell}}{[EQE_{Tr(0\%)340nm}]_{Rcell}} = 5.1\% \tag{4}$$

Similarly, we can obtain the transmittance values for the DS/glass/air structures at different [Eu(bphen)(tta)$_3$] concentrations and same

wavelength (Table 2):

3.3. Alternative equation proposed

As we mentioned in the introduction, the theoretical model that we consider as a first approach for describing the experimental results has recently been proposed by Rothemund [15]. This model presents an equation (adapted to this work notation) for describing the total EQE of a PV device, EQE_T, with a luminescent DS on top and described by an intrinsic *luminescent downshifting efficiency*, η_{LDS}:

$$EQE_T(\lambda) = f_{abs}(\lambda) \cdot \eta_{LDS} \cdot EQE_{DS}(\lambda) + f_{trans}(\lambda) \cdot EQE_{PV}(\lambda) \tag{5}$$

where f_{abs} is the fraction of photons absorbed by the DS, and f_{trans} is the fraction of photons transmitted to the PV cell. These parameters are defined as:

$$f_{abs}(\lambda) = (1 - \Delta R_{LDS}) \cdot (1 - \exp[\Lambda_{abs} \cdot A(\lambda)]) \tag{6}$$

$$f_{trans}(\lambda) = 1 - \Delta R_{LDS} - f_{abs}(\lambda) \tag{7}$$

where A is the absorbance, Λ_{abs} is the absorbance scaling factor, and ΔR_{LDS} is the additional reflectance due to the incorporation of the DS.

However, we consider that there are some difficulties to develop this model, as (i) η_{LDS}, Λ_{abs}, and ΔR_{LDS} should be dependent on the wavelength; (ii) in some cases ΔR_{LDS} should not be neglected; (iii) there is a fraction of photons, f_{loss}, [3,17] (e.g., edge losses, parasitic absorption from the DS host material, increased reflectance at the interfaces between layers, overestimation of luminescent quantum yield, reabsorption from the luminescent species due to partial overlapping of its absorption and emission bands, and/or idealistic isotropic emission) that should be introduced in this model; and (iv) the need of computational procedures to adjust the experimental results to the parameters of the model. Then, we propose an alternative and simplified equation where all parameters are wavelength dependent:

$$EQE_T(\lambda) = \eta_{DS}(\lambda) \cdot EQE_{DS}(\lambda) + T(\lambda) \cdot EQE_{PV}(\lambda) \tag{8}$$

Eq. (10) represents the general expression used for determining the values of η_{DS} and the transmittance, T, exposed in Table 2, and it also has the advantage compared to Eq. (7) that it is fully based on experimental results obtained with EQE measurements using two PV devices, one of them showing near zero EQE in the downshifting spectral range.

3.4. Location of the DS

Additional information about the transmittance of the [Eu(bphen)(tta)$_3$]-PMMA/glass structure can be obtained by comparing the EQE values locating the thin [Eu(bphen)(tta)$_3$]-PMMA film on top of the PV device or between the glass and the PV device.

The glass and PMMA/glass transmittance spectra are very similar, decreasing sharply from 85% at 370 nm to below 10% for wavelengths below 316 nm (Fig. 6). Then, as the EQE of M is close to zero at wavelengths below 360 nm, it is expected a larger increase in EQE in the 280–360 nm spectral range when the DS is placed in the configuration [Eu(bphen)(tta)$_3$]-PMMA/glass/air/PV-mini module compared to the configuration glass/[Eu(bphen)(tta)$_3$]-PMMA/air/M. This is expected because many photons can avoid high absorption by the glass when they are previously downshifted. Also, the EQE between 280 and 360 nm increases with the [Eu(bphen)(tta)$_3$] concentration either when the DS is placed on top or between glass and the PV mini module.

However, it can be observed in Fig. 7 that the EQE value is larger for highly [Eu(bphen)(tta)$_3$] DS concentrations in PMMA when the DS is placed between the glass and M compared to the DS placed on top of the device. This result can be attributed to the effect of the total internal reflection for the glass/[Eu(bphen)(tta)$_3$]-PMMA/air/M when many of the photons downshifted are reflected down to M. Thus, only about 12.5% of emitted photons from the DS escape from a top glass (escape
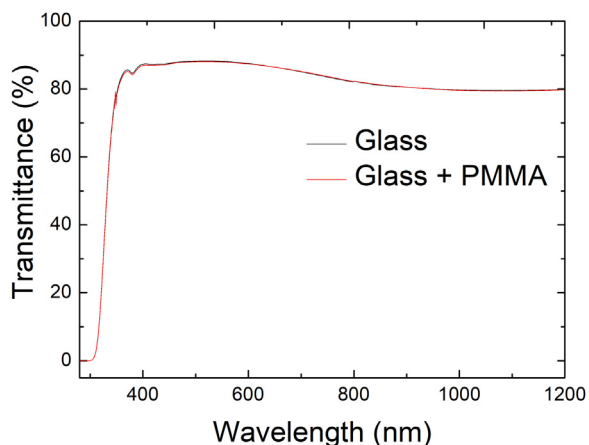
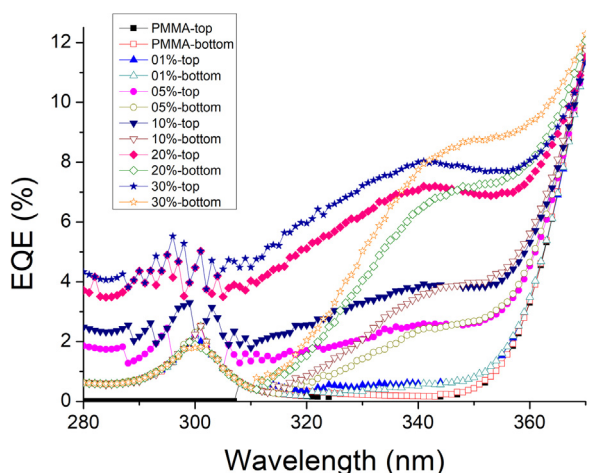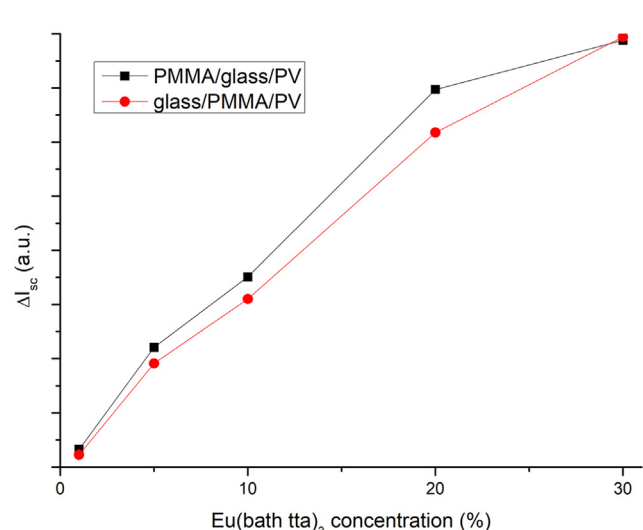**Fig. 6.** Transmittance of the glass substrate and the PMMA/glass structure used in this work.
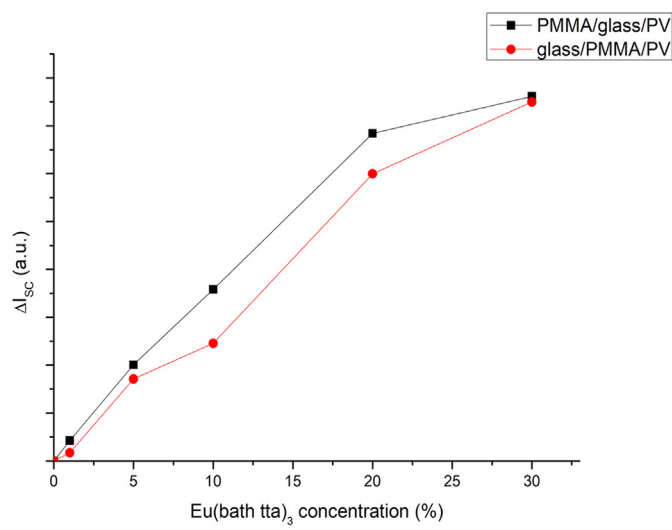

Fig. 7. Normalized EQE values for M when the DS with different [Eu(bphen)(tta)$_3$] concentrations is placed on top of the structure or between the glass and M.

cone) with a 1.5 refractive index [18,19]. Then, at larger wavelengths in the 280–360 nm spectral range, the combination of total internal reflection and photon conversion in the DS-glass structure when the DS is placed between the glass and M produces a larger EQE than for a photon conversion in the DS placed on top of the device. This is attributed to the fact that the transmittance throughout the glass sharply increases for larger wavelengths and, thus, a larger share of incident photons reach the DS when it is placed between the glass and M. Then, as the solar irradiation is larger at longer wavelengths in this spectral range, the increase in EQE can be larger for the DS placed between the glass and M compared to the DS placed on top of the glass.

Thus, if we consider the increase in I_{sc} for these configurations, we can observe that at the highest [Eu(bphen)(tta)$_3$] concentration (30%), close to the solubility limit, the value for the DS placed between the glass and the PV mini module is slightly higher than for the DS placed on top of the glass (Fig. 8a). Then, at high [Eu(bphen)(tta)$_3$]concentrations it is more convenient in terms of conversion efficiency to add the DS between the glass and M. This result is very convenient, as the DS placed between glass and M will be also encapsulated in a standard manufacturing process of PV modules and, consequently, protected from the ambient conditions.

The I_{sc} values derived from the use an aluminum hemispherical reflector are also exposed. This reflector is placed on top of the DS/glass structure for redirecting many of the photons back-reflected from the DS to the solar cell. We observed that at the highest [Eu(bphen)(tta)$_3$] concentration (30%) the ΔI_{sc} value for the DS placed between the glass and the PV mini module is slightly lower than for the DS placed on top of the glass (Fig. 8b). For lower [Eu(bphen)(tta)$_3$] concentrations, the gap between ΔI_{sc} for the DS placed on top of the glass and between the glass and the PV mini module is slightly larger than without the use of the hemispherical reflector. This is attributed to a slight increase in redirecting photons from the reflector to the solar cell when the DS is on top than when it is between the glass and the PV device.

4. Conclusions

An alternative and fully experimental procedure based only on EQE measurements for characterizing the efficiency and transmittance of downshifters placed on PV devices is proposed. The experimental setup also requires two PV devices, one of them showing zero EQE values in the downshifting spectral range. This method is simple and allows

Fig. 8. Increase in I_{sc} for M when (a) the DS at different [Eu(bphen)(tta)$_3$] concentrations and deposited on glass is placed on top or between the glass and M; and (b) an aluminum hemispherical reflector is placed on the DS/glass structure to redirect photons to M.

obtaining downshifting efficiency values independent of the quantum efficiency of the solar cell considered on the device, therefore, improving comparison between experimental results. Also, this method avoids the use of theoretical models that have been proposed by other authors usually based in many approximations and requiring some input parameters difficult to determine without a wide range of experimental equipment in the lab.

Experimental results also shows that for the high-concentration downshifters embedded in PMMA and deposited on standard glass it is slightly more efficient to place the downshifter between the glass and the PV device instead of on top of the glass. This result has technological implications because placing the DS between the glass and the PV device increases the protection of the DS from ambient conditions and, consequently, enlarge its lifetime. Finally, the use of a hemispherical reflector shows quite similar results, offering only a small improvement in photon collection when the downshifter is on top of the device.

Acknowledgements

References

[1] T. Trupke, M.A. Green, P. Würfel, Improving solar cell efficiencies by down-conversion of high-energy photons, J. Appl. Phys. 92 (2002) 1668–1674, http://dx.doi.org/10.1063/1.1492021.

[2] B.S. Richards, Luminescent layers for enhanced silicon solar cell performance: down-conversion, Sol. Energy Mater. Sol. Cells 90 (2006) 1189–1207, http://dx.doi.org/10.1016/j.solmat.2005.07.001.

[3] E. Klampaftis, D. Ross, K.R. McIntosh, B.S. Richards, Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: a review, Sol. Energy Mater. Sol. Cells 93 (2009) 1182–1194, http://dx.doi.org/10.1016/j.solmat.2009.02.020.

[4] B. McKenna, R.C. Evans, Towards efficient spectral converters through materials design for luminescent solar devices, Adv. Mater. 29 (2017) 1–23, http://dx.doi.org/10.1002/adma.201606491.

[5] L. Dumont, P. Benzo, J. Cardin, I.S. Yu, C. Labbé, P. Marie, C. Dufour, G. Zatryb, A. Podhorodecki, F. Gourbilleau, Down-shifting Si-based layer for Si solar applications, Sol. Energy Mater. Sol. Cells (2017), http://dx.doi.org/10.1016/j.solmat.2017.05.011.

[6] J. Kettle, N. Bristow, D.T. Gethin, Z. Tehrani, O. Moudam, B. Li, E.A. Katz, G.A. Dos Reis Benatto, F.C. Krebs, Printable luminescent down shifter for enhancing efficiency and stability of organic photovoltaics, Sol. Energy Mater. Sol. Cells 144

[7] G.J.J. Draaisma, D. Reardon, A.P.H.J. Schenning, S.C.J. Meskers, C.W.M. Bastiaansen, Ligand exchange as a tool to improve quantum dot miscibility in polymer composite layers used as luminescent down-shifting layers for photovoltaic applications, J. Mater. Chem. C 4 (2016) 5747–5754, http://dx.doi.org/10.1039/C6TC01261B.

[8] S.D. Hodgson, W.S.M. Brooks, A.J. Clayton, G. Kartopu, D.A. Lamb, V. Barrioz, S.J.C. Irvine, Increased conversion efficiency in cadmium telluride photovoltaics by luminescent downshifting with quantum dot/poly(methyl methacrylate) films, Prog. Photovolt. Res. Appl. 23 (2015) 150–159, http://dx.doi.org/10.1002/pip.2408.

[9] T. Fix, A. Nonat, D. Imbert, S. Di Pietro, M. Mazzanti, A. Slaoui, L.J. Charbonnière, Enhancement of silicon solar cells by downshifting with Eu and Tb coordination complexes, Prog. Photovolt. Res. Appl. 24 (2016) 1251–1260, http://dx.doi.org/10.1002/pip.2785.

[10] T. Fukuda, S. Kato, E. Kin, K. Okaniwa, H. Morikawa, Z. Honda, N. Kamata, Wavelength conversion film with glass coated Eu chelate for enhanced silicon-photovoltaic cell performance, Opt. Mater. 32 (2009) 22–25, http://dx.doi.org/10.1016/j.optmat.2009.05.016.

[11] J. Liu, K. Wang, W. Zheng, W. Huang, C.-H. Li, X.-Z. You, Improving spectral response of monocrystalline silicon photovoltaic modules using high efficient luminescent down-shifting Eu3+ complexes, Prog. Photovolt. Res. Appl. 21 (2012), http://dx.doi.org/10.1002/pip.1251.

[12] D. Alonso-Álvarez, D. Ross, B.S. Richards, Luminescent down-shifting for CdTe solar cells: A review of dyes and simulation of performance, Conference Rec. IEEE Photovolt. Spec. Conference. doi:10.1109/PVSC.2012.6317557, 2012, pp. 9–14.

[13] J.S. Batchelder, A.H. Zewai, T. Cole, Luminescent solar concentrators 1: theory of operation and techniques for performance evaluation, Appl. Opt. 18 (1979) 3090, http://dx.doi.org/10.1364/AO.18.003090.

[14] J.S. Batchelder, A.H. Zewail, T. Cole, Luminescent solar concentrators 2: experimental and theoretical analysis of their possible efficiencies, Appl. Opt. 20 (1981) 3733, http://dx.doi.org/10.1364/AO.20.003733.

[15] R. Rothemund, Optical modelling of the external quantum efficiency of solar cells with luminescent down-shifting layers, Sol. Energy Mater. Sol. Cells 120 (2014) 616–621, http://dx.doi.org/10.1016/j.solmat.2013.10.004.

[16] T. Uekert, A. Solodovnyk, S. Ponomarenko, A. Osvet, I. Levchuk, J. Gast, M. Batentschuk, K. Forberich, E. Stern, H.J. Egelhaaf, C.J. Brabec, Nanostructured organosilicon luminophores in highly efficient luminescent down-shifting layers for thin film photovoltaics, Sol. Energy Mater. Sol. Cells 155 (2016) 1–8, http://dx.doi.org/10.1016/j.solmat.2016.04.019.

[17] M. Kennedy, H. Ahmed, J. Doran, B. Norton, P. Bosch-Jimenez, M. Della Pirriera, E. Torralba-Calleja, D.G. Tauste, L. Aubouy, S. Daren, F. Solomon-Tsvetkov, S. Galindo, C. Voz, J. Puigdollers, Large Stokes shift downshifting Eu(III) films as efficiency enhancing UV blocking layers for dye sensitized solar cells, Phys. Status Solidi 212 (2015) 203–210, http://dx.doi.org/10.1002/pssa.201431683.

[18] H.J. Hovel, R.T. Hodgson, J.M. Woodall, The effect of fluorescent wavelength shifting on solar cell spectral response, Sol. Energy Mater. 2 (1979) 19–29, http://dx.doi.org/10.1016/0165-1633(79)90027-3.

[19] W. Viehmann, Thin-film scintillators for extended ultraviolet (UV) response silicon detectors, in: H.P. Field, E.F. Zalewski, F.M. Zweibaum (Eds.), International Society for Optics and Photonics, 1979, pp. 90–95, , http://dx.doi.org/10.1117/12.957960.