# Enhanced Luminescent Solar Concentrator Efficiency by Foster Resonance Energy Transfer in a tunable six-dye absorber

J.M. Delgado-Sanchez *[a], I. Lillo-Bravo [b], A. Menendez-Velazquez [c]

[a] Department of Applied Physics, University of Seville. Avda Reina Mercedes s/n, 41012 Seville (Spain)

[b] Department of Energy Engineering, University of Seville. Avda Camino de los descubrimientos s/n, 41092 Seville (Spain)

[c] IDONIAL, C/ Calafates Parcela L-3.4, 33417 Aviles, Asturias (Spain)

## ABSTRACT

Luminescent solar concentrators (LSCs) collect and concentrate the solar irradiation to generate electricity through the photovoltaic effect. LSCs have attracted attention due to their concentration factors, their ability to provide wavelength-to-bandgap matched photons, and because they can work well under both diffuse and direct illumination. This paper assesses luminescent solar concentrators, in which the inclusion of a tunable photoluminescence optical layer is analyzed. Three main goals are achieved. First of all, we achieved for the first time an optical window based on a randomly oriented six-dye system that exchanges energy sequentially between them (Förster Resonance Energy Transfer, FRET). This is interesting from a scientific point of view. Secondly, the present work achieved a broad absorption spectrum by combining six dyes, which is interesting from a practical point of view. Thirdly, although we can achieve a similar broad absorption with a reduced number of dyes, this strategy allows to tune both the absorption of the optical window and the emission with high selectivity (by removing dyes) in order to match the emission of the luminescent system to the bandgap of the PV technology used in the LSC, whose efficiency is increased by 26.9% with respect to the reference prototype.

**Keywords:** Luminescent Solar Concentrator, FRET, dye, photovoltaic

## 1. Introduction

Power energy technologies are changing worldwide. There has been a profound transformation from carbon sources toward a renewable market. In examining the different renewable alternatives, solar photovoltaic technology has a potential to shape clean, reliable, scalable features for the future. Indeed, photovoltaic is one of the easiest renewable technologies to hybridize with others like wind or thermal solar energy.[1-3]

The main drivers to get this high penetration on the current electrical market are derived from the intense R&D programs that lead the research on new absorbing semiconductors to simultaneously reduce the price of the semiconductor and the installation cost. Complementary research relating to how managing the solar radiation for a better matching with the band gap of the solar cell is also under investigation. Solar spectrum offers a broad photon energy range, that goes from the UV to far infrared. One proposed solution is to develop tandem solar cells, but nowadays this technology is not cost-competitive against silicon ones. [4] Moreover, the photovoltaic efficiency depends on the solar spectral energy distribution, as it changes during the day, through the season and with the location. [5]

A promising alternative proposed in the early 1970's was the Luminescent Solar Concentrator (LSC), with the incorporation of the luminescent optical window acting as light absorber. The basic design consists in a flat and transparent material (host) doped with fluorophores to absorb the incoming radiation and to emit photons with a high energy. [6-9] This active material is placed on top of a glass or a transparent substrate or between a glass sandwich structure to act as a waveguide; based on the total internal reflection, emitted photons are trapped and guided on top of the solar cells located on the edge of the glass.

The main advantage [10] to develop an LSC device is to replace the solar cell required for a conventional photovoltaic module by a low-cost polymeric material acting as optical window, and thus, reducing Level Cost of Energy (LCOE) of photovoltaic generation. For this purpose, the LSC concentrates the incoming radiation, but opposite to the conventional Concentrator Photovoltaics (CPV) technologies, neither the tracker system nor the specific lens is required (again, another cost reduction input). Moreover, LSC is also able to operate under both direct and diffuse radiation [11], which open the market to new locations where conventional CPV cannot be installed due to the radiation existing: CPV needs direct radiation and mechanical trackers to follow the sun position, and both requirements are suppressed in the LSC technology. LSC also offers advantages derived from their esthetic capabilities: transparency and tunable color, which makes it suitable for building integrated photovoltaic (BIPV) applications. [12-15]

Therefore, ideally, dyes employed for LSCs design must fit the following four specifications: (a) broad absorption range at lower wavelengths of the LSC, narrower than the absorption wavelengths of the solar cell technology used; (b) emitted photons by the LSC have to be aligned energetically with the optimal band gap of the solar cell; (c) large Stokes shift to minimize the overlapping between absorption and emission spectrum and thus, to reduce the self-absorption in the dye; (d) high photoluminescence quantum yield of the terminal dye to minimize thermal losses.

Despite their potential, LSCs have two main limitations: [16-19] (1) most commercial dyes offer a narrow Stokes shift, which means that absorption and emission peaks overlap in a certain energy range and thus, potential photons emitted in that energy range will be reabsorbed and not useful for the solar cell; (2) absorption spectral range for individual dyes is not as large as desired, so only a small amount of incoming photons can be converted into the desired energy range for the solar cell.

To achieve a wider absorption spectrum in the optical window, and thus to increase the photon’s wavelength shift, alternative strategies have been suggested by several authors. Two approaches are emphasized: (1) to stack different dyes vertically as it works as a tandem solar cell [20,21] (Figure 1a): the benefit of this proposal is that each dye is able to transform a different interval of the solar spectrum and all reemitted photons are collected simultaneously in the solar cell active area; however, the disadvantage of this solution is that manufacturing cost impact is high (longer manufacturing time and specific solar cells spectrally matched to each dye are needed, which at the end, represents a drawback in terms of cost). Also, the effect of illuminating partially the solar cell with different photons distribution energy has not been fully understood; in the worst scenario, each dye will require a specific band gap solar cells; (2) to mix multiple types of dyes at the correct concentration to induce the Förster Resonance Energy Transfer (FRET) mechanism [22] (Figure 1b); the correct concentration is needed to ensure that the different dyes are close so as to facilitate the FRET development, without quenching the luminescence by an excess of dye molecules.

Several mechanisms can result in energy transfer between fluorescent dye molecules. In 1948 Förster published his quantum-mechanical treatment of the transfer of electronic excitation energy between similar molecules, [23] which he considered as oscillating dipoles with an energy transfer governed by their Coulomb interaction. In a host of multichromophore materials, FRET represents a non-radiative energy transfer mechanism which can be used to shift the spectrum. This process takes place when the emission spectrum of a fluorophore (called donor), overlaps with the absorption spectrum of another dye (called acceptor). A key concept is that FRET does not imply emission of light by the donor, so there are not intermediate photons in the dyes-chain that define FRET. Both molecules (donor and acceptor) are coupled by dipole-dipole interactions. [24] The three principal determinants of the FRET transfer efficiency are the separation, mutual orientation and spectral overlap of the donor-acceptor pair.

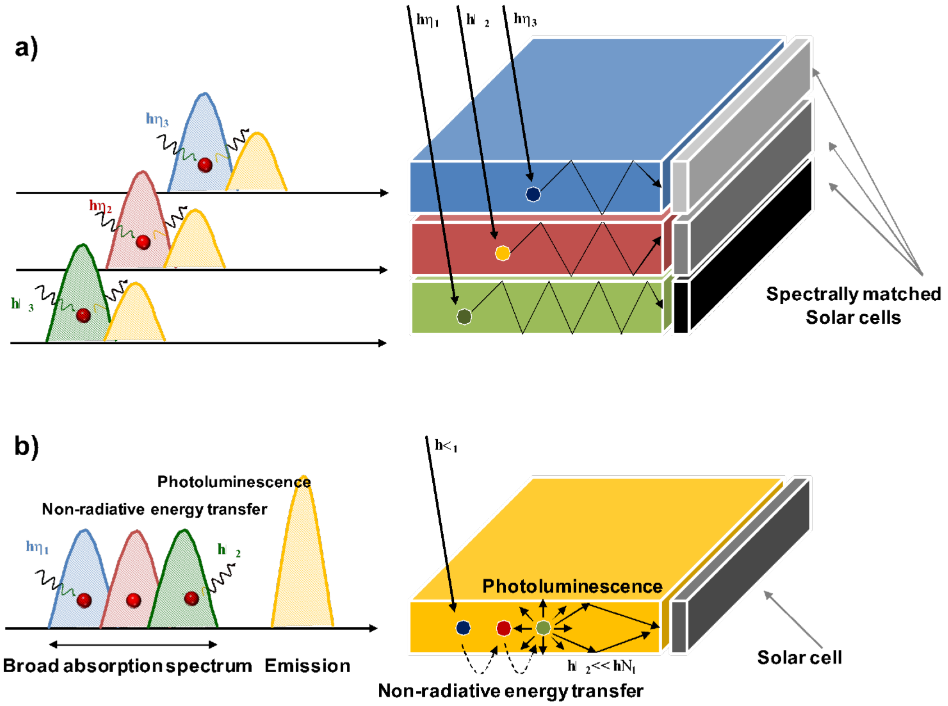

**Figure 1.** a) Schematic mechanism proposed for an optical window based on dye stack and specific spectral matched solar cells. b) FRET example using 3-dyes, with the advantage of a wider absorption spectrum

Banal *et al* [25] introduced one modification in the basic concept of the optical window of LSCs. They used the excitation energy transfer (EET) strategy with a donor chromophore to enhance the efficiency of LSCs to achieve large Stokes shift to reduce reabsorption of the emitted photons.

Swartz *et al* [26], studied the design of a solid LSC considering two dyes and a liquid LSC with three dyes in a FRET combination, with unsuccessful results due to the concentration of the selected; despite the results these authors established a new approach to improve the LSC design. Later, C. Tummeltshammer *et al* [22] fabricated one LSC considering the FRET concept and using a quantum dot acting as a donor, mixed with an organic dye as acceptor. They demonstrated that a fluorophore with a lower quantum yield and a small Stokes shift might be used in LSCs devices. This report shows how a single dye absorbs less than 1% of the incoming wavelength, while the FRET combination of quantum dots and organic dyes increases this absorption factor until 13.5%.

Balaban *et al* [27] demonstrated the FRET mechanism applied to LSC optical windows but using only two dyes: DCM and LR305. They observed that the absorption spectrum of the mixed dye was increased against the LR305 situation. They also claim a secondary advantage: the capability of color tunability. However, they advised that, on one hand, results should be improved in terms of waveguide of the emitted light into the solar cells when dye concentration was too low; on the other hand, when they increased dye concentration, the reabsorption was higher than expected.

In a similar line of research, Bailey *et al* [28] optimized the previous LSC design considering three-dyes connected in a FRET network. They found an increase of the absorption of the solar light compared with the single-dye case. These authors also pointed out that the challenge in making an efficient multiple-dye LSC were to find dyes that have suitable properties for better LSC performance, and again, their concentration in the host material was the critical parameter.

Zhang *et al* [18] recently created a FRET-based optical window considering only two perylene dyes and with the novelty of designing the LSC prototype with three types of solar cells. They observed that the same optical windows reported significatively different performance upon the bandgap of the solar cell, so, in our opinion, FRET might be crucial to provide tunability properties to the LSC concept.

Menendez *et al* [29,30] developed an absorber based on FRET system working as a polarized luminescent solar concentrator. However, to facilitate the non-radiative energy transfer between the dyes embedded in the host material, it was required to use liquid crystals as matrix, which represented an expensive design, not aligned with the photovoltaic market constraints. So, based on the existing literature, all these previous research works reported lower LSC efficiency, and FRET configuration selected was limited to a lower number of dyes (a maximum of three).

Present work demonstrates that it is possible to reach a FRET transfer efficiency using a randomly oriented six-dye system of interconnected dyes. We postulate that in this case it is possible for each dye to find another dye at the right orientation and distance in order to have a full energy transfer. This provides an easy way for the design of efficient down-shifting systems avoiding liquid crystals, molecular alignment, etc. We are, to the best of our knowledge, the first to show experimentally the linking of six dyes randomly oriented and connected in FRET configuration, using LSC front-face with CIGS solar cells technology.

## 2. Materials and methods

The LSCs fabricated in the present work are based in dye-doped PMMA thin films. Selected dyes are combined to achieve FRET, so the optical window is based on a single layer. For molecules in a dye to be highly absorptive, they must fulfill the following specifications:

i. The dyes must be highly fluorescent. This is particularly important for multiple layer LSCs, where accurate dye tuning is required for an efficient cascading energy transfer. In a monolayer configuration, high quantum yield maximizes the Förster radii but is not strictly mandatory since FRET can out-compete non-radiative losses.
ii. The final emissive dye of the stack should show a large spectral shift (Stokes shift) between absorption and emission to minimize self-absorption of the waveguided light.
iii. Dyes should exhibit a broad absorption in the visible spectrum in order to minimize the number of dyes in the stack.

We combined six dyes to cover the UV-VIS absorption spectrum from 325 nm to 650 nm. The selected dyes were Lumogen Violet, Coumarin 6, DCM, PM567, PM597 and PM650, first of them supplied by the company BASF, and the rest obtained from the company Exciton. The dyes form a near field energy transfer cascade to the terminal PM650 dye, which emits in the 650nm approx. It is possible to sequentially remove (or to add) final dyes to modify the optical properties of the luminescent layer in order to match the photoluminescent wavelengths to the semiconductor bandgap used in the solar cell.

Luminescent solutions were prepared from a mixture of the as-received powdered dyes, polymethyl methacrylate (PMMA) and chloroform, both from Sigma Aldrich. 300 mg of PMMA and 4 ml of chloroform were stirred during 48h to ensure a homogeneous solution. Then the dyes were added to the PMMA solutions, acting PMMA as the host polymer of the dyes. Dye concentration was 1% w/w for every dye (with respect to the PMMA). Then, a solution containing the six dyes was deposited on glass by spin-coating (Laurell, WS-650Mz-8NPP). Finally, the solvent was evaporated by a hot-plate at 50ºC in a covered Petri dish to increase the vapour pressure of the solvent and to avoid dust particles deposition on the coated film. At the end of the process the thickness of the optical window is 150 μm approx.

The prototypes consider CIGS thin film solar cells instead of conventional silicon solar cells. Typical thickness for luminescent coatings is in the range of 5-50 µm, while silicon solar cell thickness is around 300 µm and CIGS solar cells thickness is close to 5 µm. Then, the use of CIGS solar cells minimizes the emission of the light from the LSC into the lateral side of the solar cell (inactive area), which will induce a lower performance of the device. Thus, CIGS technology, against conventional silicon solar cells, ensures a better guide light coupling between the LSC and the front active area of the solar cell in a front-face LSC configuration. Moreover, handling and preparation of the CIGS solar cells is easier than silicon ones for this purpose, with a similar spectral response. [31]

CIGS solar cells (210x100 mm$^2$) from Global Solar were prepared to the required geometry of the Luminescent Solar Concentrator (100x100 mm$^2$) by means of laser scribing. First, solar cells were cut in the desired dimensions (50x10 mm$^2$) using an IR 1064nm scanner. Second, edge isolation was performed with a picosecond laser source of 532 nm. To ensure a suitable performance of the solar cells, they were characterized with an electron microscope FESEM Hitachi S-3000N and a solar simulator ABET 3000 AAA.

Fabrication of LSC samples consists in placing CIGS solar cells (50x10 mm$^2$) in a front-face configuration on top of a glass in square geometry, connected in series. Inside this area, the organic dyes are deposited forming the optical window (Figure 2). [31] Using this configuration, solar cells benefit from two irradiation sources: a direct one from the sun, and a that photoemitted by chromopheres in the optical window. With the design proposed in this paper, both light sources are collaborative

Finally, components were encapsulated with commercial EVA and a front glass (2mm thickness) using a laminator manufactured by the company P Energy (model L036LAB). Samples had 100x100 mm$^2$ in order to ensure scalability and reproducibility of the results.

Total concentration factor ($C_x$) of the device is calculated as the product of the optical efficiency ($\eta_{opt}$) and the geometrical concentration factor (G); Moreover, the geometrical concentration factor (G) is defined at the ratio of the optical window of the LSC surface ($S_1$) and the solar cells surface ($S_2$). Thus, this results in a geometrical concentration factor (G) of 2.5x:

$$C_x = G \cdot \eta_{opt} = \frac{S_1}{S_2} \cdot \eta_{opt} \tag{1}$$

Each prototype was replicated 5 times, to provide consistent statistics results.

Transmittance and reflectance measurements were carried out to characterize the optical response of the dyes used. Other experiments provided the internal quantum efficiency and the optical efficiency of the luminescent coating. In addition, the characteristics I-V curve and the spectral response were measured to characterize the performance of the LSC prototype. To quantify the enhancement effect of the luminescent material, results were compared with a reference sample that did not have any dye incorporated in the optical window.

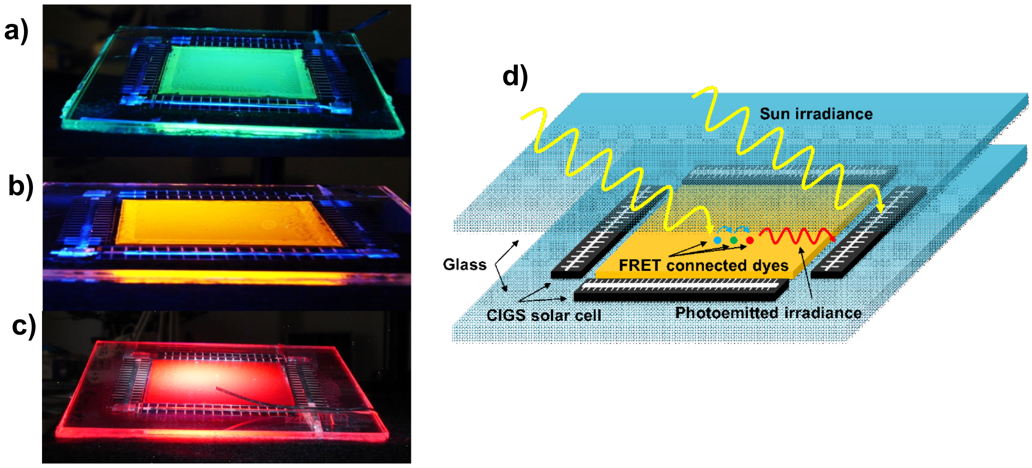

**Figure 2.** LSC fabricated with different combinations of dyes. From a) to c): C6, C6+DCM and LUV+C6+DCM+PM657+PM597+PM650. d) schematic design of the LSC using front face CIGS solar cells encapsulated in glass-glass.

Thus, the experimental setup to evaluate this LSC characteristic consisted in a white halogen lamp (Newport), with the corresponding optical filter to ensure AM1.5G spectrum, coupled to a monochromator (Oriel Cornestone 260). The sample was located inside an integrating sphere (Labsphere) with different ports: one for the incoming light, the second one located in the opposite side for the transmitted light, and a third port located at 30° with respect to the normal incoming light, to measure the reflected light. Light was modulated with a mechanical chopper (Stanford Research Systems Inc) and monitored with a silicon detector (Newport model 7610). Recorded signals were amplified with a Lock-In Amplifier (Stanford Research Systems SR830 dual phase). This procedure was proposed by Baldo *et al* from MIT [32] and provides similar results to those obtained according to the procedure described by Goldschmit *et al* [33] from Fraunhofer Institute.

A fluorimeter (Edinburgh Instrument FLSP920) was used to measure the surface emission of the films. To analyze the opto-electronic performance (I-V curve) of the LSC prototypes, a solar simulator (Abet 3000 AAA) and a quantum efficiency system (PVE300 Bentham) were used.

## 3. Results and discussion

### 3.1. Luminescent coating characterization

There is extending literature on a variety of dyes explored for LSC design. [34,35] Dyes selected for this research work were from the coumarins and pyrromethene families, except the first one that was dye from the naphtalimide family. The whole system, with six dyes, results in higher luminescence than that of individual dyes. Another specific advantage for Coumarin dyes was that they exhibit large Stokes shifts by using intramolecular charge transfer and rarely, excited state intramolecular proton transfer mechanisms. This large Stokes shifts feature reduced reabsorption phenomena in the LSC optical window. An advantage of the Pyrromethene family is its high yields of fluorescence due to their planar structure. In terms of photostability, the less vulnerable dyes were those selected for this research work: PM567, PM597 and PM650. [36] In a FRET system, photoluminescence quantum yield mainly matters at the terminal dye. But we have tried to design a tunable molecular system. In this system dyes can be removed and then any dye could be the terminal dye. Having this in mind, we have tried to find dyes with large Stokes shift and high photoluminescence quantum yield, in case they should be the terminal dyes. An extra advantage of these dyes and polymer host material selection was that all of them were soluble in the same solvent. Dyes remained as monomers in the concentration required for FRET combination in the solid PMMA to prevent the quenching of excited states by the formation of aggregates.

The absorption peak measured for each individual dye is summarized in Table 1. It should be remarked that the absorption spectral range increases when single dyes were mixed to obtain the FRET system.

| Dye | Family | Absorption ($\lambda_{max}$) | Emission ($\lambda_{max}$) |
|---|---|---|---|
| LUV | Naphtalimide | 375 | 420 |
| C6 | Coumarin | 447 | 464 |
| DCM | Coumarin | 467 | 534 |
| PM567 | Pyrromethene | 520 | 567 |
| PM597 | Pyrromethene | 532 | 597 |
| PM650 | Pyrromethene | 590 | 650 |
| FRET |  | 375-590 | 650 |

**Table 1.** Characteristics of luminescent dyes used in this paper. The experimental absorption and emission peak wavelengths are indicated

Figure 3 shows spectral properties of the dyes selected for this research work embedded in a PMMA host material: absorption and emission. For each individual dye, the absorption spectrum revealed a large primary peak and some small secondary peaks at shorter wavelength with non-significant intensity compared with the principal signal. They were compared with the absorption obtained for the set of dyes embedded together in the host material. To ensure the proper FRET energy transfer mechanism, the concentration of each dye was fixed at 1% w/w. The optical performance of the LSC was clearly improved with the FRET design, as the absorption spectrum was 4 times broader than the individual dye spectrum, as shown in figure 3.

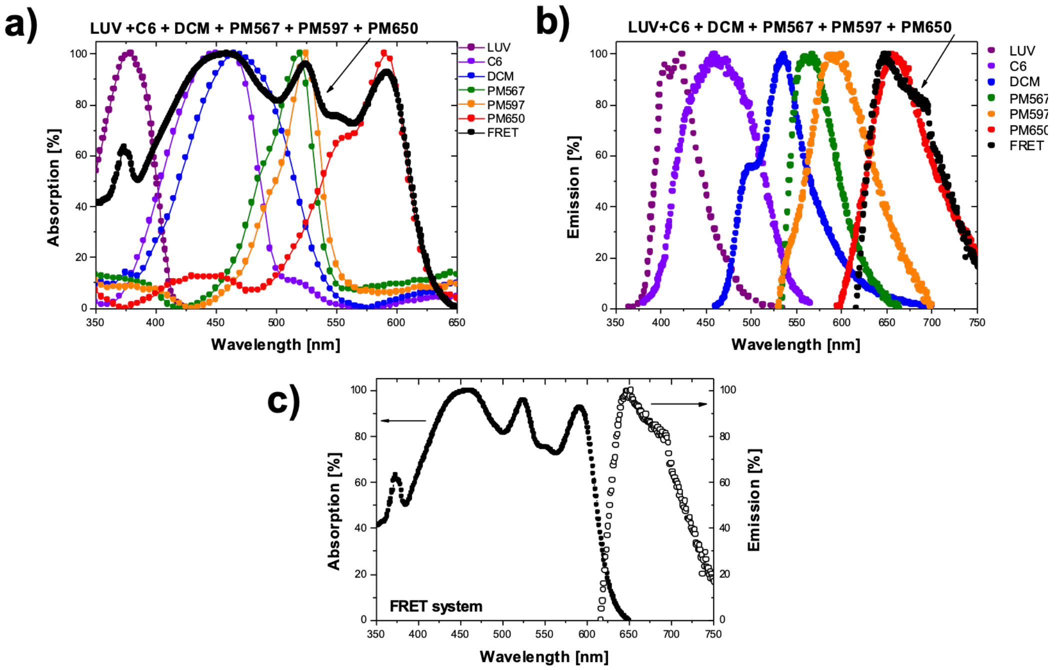

**Figure 3.** a) Absorption spectrum of individual dyes and combined proposal to enhance optical window performance by FRET configuration (black line). b) Normalized photoemission exhibit by each dye used and FRET response (black line). **c) C**omparison of the absorption and photoemission spectra of sequential incorporation of terminal dye to FRET network in the LSC optical window (FRET photoluminescence measurements resulting from excitation at 380 nm).

Measurements of the fluorescence intensity of the acceptor in the presence of donor molecules with a fluorimeter were carried out to analyze the potential irradiance on the solar cells, and the right match of the photoemitted photons according to the photovoltaic spectral response. The fluorescence of the last dye was observed in the yellow-red visible range, with a photoemission peak at 650 nm approx., corresponding to the first excited single state ($s_0 \rightarrow s_1$) of the dye.

Energy transfer between fluorescent dye molecules in the optical window might have occurred through different mechanisms: non-radiative energy transfer (FRET) to the smallest band gap dye, or the emission of a photon by a donor chromophore and its reabsorption by the acceptor. Furthermore, figure 3c illustrates the absorption and emission spectrum of the FRET system, when the sample was excited using a monochromatic light associated to the corresponding excitation energy of the first dye employed (Lumogen UV). When the LSC is based on a single dye, and the selected dye is Lumogen UV,the emission is located at 420 nm (Figure 3a and 3b). For the rest of dyes, the emission is null. However, when the sample is based on the previous combination of dyes, the emission is located at 650 nm, using the same excitation wavelength (Figure 3c), and unlike the single-dye samples, the absorption spectra was wider. This result proved that FRET energy transfer mechanism had been achieved for the six dyes. To our best knowledge, this achievement shows for the first time a FRET mechanism combining six dyes with isotropic orientation, with the advantage that the selected dyes had a random orientation in the host material: no additional sophisticate technique, such as the employment of liquid crystal matrix, [30] is needed during the manufacturing to induce any preferential orientation.

Once the FRET mechanism was proved, we analyzed the impact of this optical window on the LSC device. For that, the optical quantum efficiency (OQE) was characterized, defined as the fraction between the number of photons that reach the LSC's edge and the photons absorbed by a dye in the front surface. For that purpose, the sample was located inside an integrating sphere, and excited with white light coupled to a monochromator. This characterization provides information about the density of photons emitted by the device, and which is the spectral range of the excitation spectrum useful for the LSC (Figure 4).

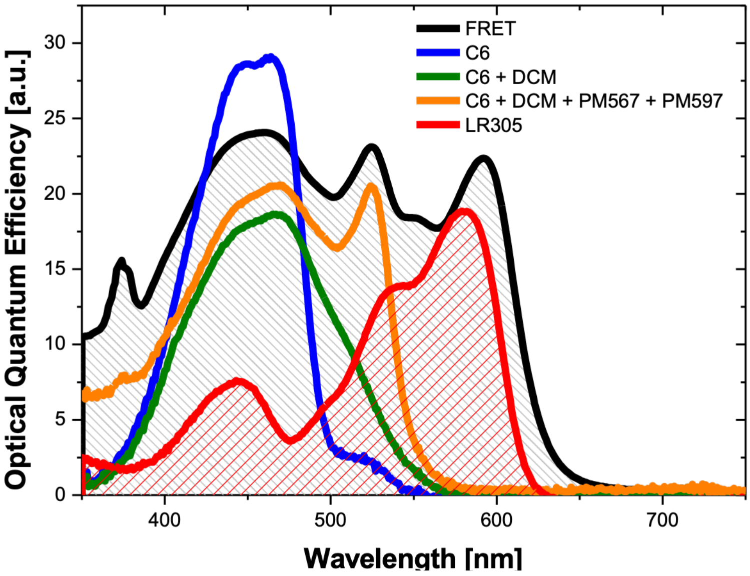

**Figure 4.** Optical Quantum Efficiency (OQE) measurements of the different optical window designs proposed. The samples shown are four different combinations of dyes: C6 as single dye, and three alternative acting as FRET systems. The recorded signals demonstrate how the design might be tunable according the solar cell spectral response required. Red dots shown the OQE of the reference sample (Lumogen LR305), with lower OQE than our FRET based proposal in terms of absorption width spectra and photons density emitted.

It was observed that close to an average of 20% of the incident photons were absorbed. The most relevant result observed was that the optical quantum efficiency ranged from

350 nm to 600 nm, which represents a broader spectrum when compared to any other combination of dyes or single dyes used. Figure 4 also shows the characterization of an optical window based on Lumogen Red LR305, one of the most extended dyes to manufacture LSC devices. It was observed that this FRET system improved its optical performance, either in terms of density, and absorption spectral range.

Results obtained are also compared with previous published results (Table 2). The most optimum performance in terms of OQE was obtained with the sample with six-dyes combined as a FRET mechanism. This sample was able to extend its absorption spectrum to wider values than the rest of samples without any detrimental effect on the photon intensity. Thus, we demonstrate that the FRET concept offers a wider absorption spectrum than conventional designs that use a single dye, or dyes combined in pilled stacks, with the additional advantage that a multiple-dye chain is tunable to ensure the emission in a specific and desirable range of the spectrum.

| Ref – Year | Luminescent material | LSC size | Absorption range | $\eta_{opt}$ |
|---|---|---|---|---|
| [37] - 2019 | Tandem dye - FRET & QDs | 50x25 mm$^2$ | 400 – 500 nm | 11.97% |
| [38] - 2018 | Tandem dye - QDs | 20x20 mm2 | 500 – 700 nm | 6.4 % |
| [39] - 2017 | $CuInS_2$ / ZnS QDs | 100x100 mm$^2$ | 400 – 800 nm | 8.1% |
| [34] - 2013 | Lumogen Red 305 dye | 50x50 mm$^2$ | 500 – 600 nm | 7.2% |

**Table 2.** Optical efficiency obtained in previous related works.

The main objective of the optical window design is to enhance the LSC efficiency. To achieve this goal, three requirements need to be met: a) the solar irradiation must be concentrated; b) the dye emission must match that of the solar cell semiconductor bandgap; c) the width of the absorption spectrum must be maximal, according to the solar irradiation profile.

Our results show that the 6-dye prototype ansorbs in the range of 350 to 650 nm, and the maximum photoluminescence peak is located at 650 nm approx.., which is the optimal value to match the CIGS solar cell bandgap (1.3 eV in the solar cells used in these experiments), but also compatible with conventional and mature silicon technology. In addition, this wavelength range between 350 and 650 nm coincides exactly with the available range of the solar spectrum with the higher amount of photons.

An additional advantage of this proposal consists on its tuneability: if the cell bandgap were different, as would happen with the CdTe and perovskites technologies, it would be enough to remove the terminal dye to optimize the system, while keeping the efficiency of the solar concentrator.

Once the optical quantum efficiency had been determined, the optical efficiency ($\eta_{opt}$) could be calculated. Optical efficiency is a key parameter that measures the ratio between the output photons arising from the solar cell at the edge of the LSC and the incoming photons from the external irradiation source. [20]

$$\eta_{opt} = \frac{\int OQE(\lambda) \cdot G_{AM\ 1.5G}(\lambda) d\lambda}{\int G_{AM\ 1.5G}(\lambda) d\lambda} \qquad (2)$$

Thus, the optical quantum efficiency (OQE) is independent on the irradiation spectrum, while the optical efficiency considers which is the spectrum distribution of the light ($G_{AM\ 1.5G}$) and how those photons are absorbed at the luminescent material. Results obtained (Table 3) show a) the benefit of luminescent coatings, b) the proposed FRET design exhibited the highest optical efficiency, and c) the optical efficiency obtained for this FRET set of dyes was higher than that previously reported for other design approaches (Table 2). Moreover, FRET offered the advantage of easy tuneability to ensure the optimum matching between the solar cell bandgap and the optical window of the LSC.

| C6 | C6+DCM+PM567 | C6+DCM+PM567+ PM597+PM650 | LUV+C6+DCM+ PM567+PM597+PM650 |
|---|---|---|---|
| 3.3 % | 6.7 % | 9.1 % | 16.2 % |

**Table 3.** Optical efficiency calculated for 4 types of optical windows

### 3.2. Luminescent Solar Concentrator characterization

In the previous section, the first hypothesis of this research work was validated: the FRET system, connecting six nonaligned dyes, showed a better performance in terms of absorption and emission when compared with previously reported similar optical windows. In this section, the coupling of this new optical window with the solar cell to build the LSC device is characterized and analyzed.

First, we attempted to demonstrate that the FRET dye-emitted photons at the right wavelengh, according to the solar cell technology used: thin-film CIGS solar cells. This is evidenced in Figure 4: the photoemission peak was centered at 650 nm, where CIGS technology had its maximum spectral response. Furthermore, the spectral response of the LSC prototype using six dyes as optical window, was compared with a reference sample, consisting in a CIGS solar cell without any luminescent material (Figure 5). The spectral response improved in the spectral range where the luminescent dyes act: the flux of photons that were absorbed by the solar cell is enhanced, which had positive consequences for the LSC performance. Employing the combination of six dyes in FRET configuration, there was a rise in the spectral response at wavelengths shorter than 650 nm, which corresponded to the contribution of the dyes and the photoemission spectrum of the terminal dye (PM650).

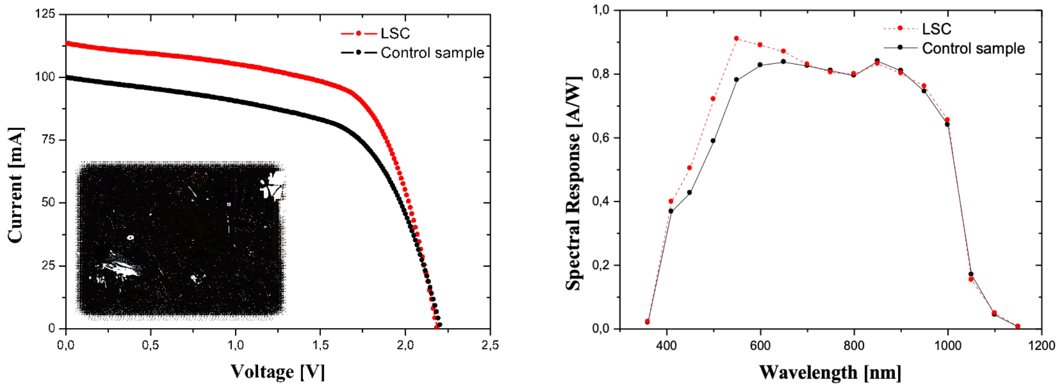

**Figure 5.** a) I-V characteristics of the LSC prototype with six dyes in FRET configuration. b) Spectral response of the LSC. In both cases the LSC performance measured is compared against one control sample.

| | | |
|---|---|---|
| Voc (V) | 2.348 | 2.394 |
| FF (%) | 60.86 | 66.94 |
| G (W/cm$^2$) | 0.1 | 0.1 |
| PV Efficiency (%) | 1.44 | 1.82 |

| | |
|---|---|
| Current Enhancement | 13.17 % |
| PV Efficiency Enhancement | 26.92 % |

**Table 4.** Optoelectronics characterization of the LSC device

Second, we observed that the luminescent coating was responsible for the increase in the density of incoming photons to the solar cells, with respect to the control sample. As a consequence, the photocurrent increased (>13%), while the open-circuit voltage ($V_{oc}$) remained approximately invariant. Therefore, the improvement of the efficiency of the photovoltaic device with the luminescent layer (LSC) was as high as a 26.9% (Figure 5). Thus, the incorporation of dye coatings improved the device efficiency.

To compare the proposed FRET dye system against conventional dyes, another prototype was manufactured (reference sample) with the same geometry specifications using a well-known chromophore: Lumogen LR305 [34,35,36] but with different absorption spectrum. The enhancement factor ($\Gamma_{LSC}$) was calculated for both prototypes:

$$\Gamma_{LSC} = \frac{P_{LSC} - P_{PV}}{P_{PV}} = \frac{V_{LSC}^{pp} \cdot I_{LSC}^{pp} - V_{PV}^{pp} \cdot I_{PV}^{pp}}{V_{PV}^{pp} \cdot I_{PV}^{pp}} \quad (3)$$

where superscript “pp” represents maximum voltage and current at power point, and subscript “LSC” and “PV” are the terms associated to the contribution due to the photons emitted by the organic dye and solar spectrum, respectively. Results are summarized on Table 4. As can be observed in Table 5, the FRET system proposed on this work offered a higher performance when compared with previously reported designs based on conventional dye Lumogen Red 305.

| Dye | $\Gamma_{LSC}$ | Absorption range | Emission ($\lambda_{max}$) |
|---|---|---|---|
| Lumogen Red | 25% | 500-600 nm | 650 [18] |
| This work | 78% | 350-600 nm | 650 |

**Table 5.** Absorption performance of the optical window for FRET and more extended used dye (Lumogen Red)

## 4. Conclusions

The multiple-dyes selected and used for this experimental research work demonstrate the original idea suggested for Swartz *et al.* [26], who studied the design of a solid LSC considering two dyes in a FRET combination, with unsuccessful results due to the concentration of the selection. Here we have demonstrated that this original idea is feasible and, what is more challenging, we have proved for first time that it can be extended to six dyes in a randomly oriented configuration, with the advantage of the tuneability, and which improves significantly the LSC optical efficiency: 16.2%.

Our optimum configuration to design LSC based on FRET energy transfer between dyes consisted in the sequential multiple-dyes: LUV + C6 + DCM + PM567 + PM597 + PM650. This set of dyes was able to absorb the solar irradiation in a wide spectral interval and reemit photons in the 650 to 800 nm wavelength range.

The key parameters of this design are to ensure:

a) Broad absorption range.
b) Reduction of reabsorption losses.
c) Narrow photoemission peak centered at the maximum spectral response of the solar cell.
d) Color tunability upon dyes to provide aesthetic features to the device, which might be interesting for building integrated photovoltaic market.

To further improve the performance of our design, an advanced design of LSC might be analyzed by considering geometry and optical coatings (photonic crystals and plasmonic effects) on the front/back faces to minimize cone scape photons distribution. Future research should consider the potential degradation mechanism of the proposed dyes and their impact in the performance of the device. Accelerated-degradation and outdoor tests will test the optical coupling between all dyes used, and to demonstrate the industrial feasibility of this design.

## Acknowledgments

We would like to acknowledge L. Griffin for fruitful discussions, suggestions, and careful reading of the manuscript.

## Data availability statement

Raw data of this research study are available upon request.

## 5. References

[1] Energy World (2015) Renewable Energy: “What Does 2015 Holds for Bioenergy in the UK?” Energy Institute. London: Geerings Print Ltd.

[2] Tyag V.V., Rahim Nurul A.A., Rahim N.A. Selvaraj J.A.L., “Progress in solar PV technology: Research and achievement”, *Renewable and Sustainable Energy Reviews* **20** (2013) pp. 443–461

[3] Gul M., Kotak Y., Muneer T., “Review on recent trend of solar photovoltaic technology”, *Energy, Exploration & Exploitation* **34**(4) (2016) pp. 485-526

[4] Peters I.M., Sofia S., Mailoa J., Buonassisi T., “Techno-economic analysis of tandem photovoltaic systems*”, The Royal Society of Chemistry* **6** (2016) pp. 66911-66923

[5] Guitas A.E., “Studying the effect of spectral variations intensity of the incident solar radiation on the Si solar cells performance”; *Journal of Astronomy and Geophysics*; (2012) pp. 165-171

[6] Keil G., “Radiance Amplification by a Fluorescence Radiation Converter”, *Journal of Applied Physics* **40**(9) (1969) pp. 3544-3547

[7] Seybold G., Wagenblast G., “New perylene and violanthrone dyestuffs for fluorescent collectors” *Dyes and Pigments*; **11** (1989) pp. 303-317

[8] Webert W.H., Lambe J., “Materials for luminescent greenhouse solar collectors” *Applied Optics* **16**(10) (1977) pp. 2684-2689

[9] Rafiee M., Chandra S., Ahmed H., McCormack S.J., “An overview of various configurations of Luminescent Solar Concentrators for photovoltaic applications” *Optical Materials* **91** (2019) pp. 212-227

[10] Moratis P., Schropp R.E.I., van Sark W.G.J.H.M., “Nanoparticles for luminescent solar concentrators – A review”, *Optical Materials* **84** (2018) pp. 636-645

[11] Debije M.G., Verbunt P.P., “Thirty years of luminescent solar concentrator research: solar energy for the built environment” *Advanced Energy Materials* **2**(1) (2011) pp. 12-35

[12] de la Mora M.B., Amelines-Sarria O., Monroy B.M., Hernandez-Perez C.D., Lugo J.E., “Materials for downconversion in solar cells: perspectives and challenges” *Solar Energy Materials & Solar Cells* **165** (2017) pp. 59-71

[13] Meinardi F., Bruni F., Brovelli S. “Luminescent solar concentrators for building-integrated photovoltaics*” Nature Reviews* **2** (2017) pp. 17072-17081

[14] Currie M. J., Mapel J. K., Heidel T. D., Goffri S., Baldo M. A., "High-efficiency organic solar concentrators for photovoltaics"*, Science* **321** (2008) pp. 226–228.

[15] Schiphorst J., Cheng M.L.M.K.Y.K., Heijden M., Hageman R.L., Bugg E.L., Wagenaar T.J.L., Debije M.G., “Printed luminescent solar concentrators: artistic renewable energy” *Energy & Buildings* **207** (2020) pp. 1-6

[16] McKenna B., Evans R.C., “Towards efficient spectral converters through materials design for luminescent solar devices”, *Advanced Materials* **29**(28) (2017) pp. 160691(1-23)

[17] Reinders A., Kishore R., Sloof L., Eggink W., “Luminescent solar concentrator photovoltaic designs”, *Japanese Journal of Applied Physics* **57** (2018) 8S3

[18] Zhang., Zhao P., Wilson L.J., Subbiah J., Yang H., Mulvaney P., Jones D.J., Ghiggino K.P., Wong W.W.H., “High performance large-area luminescence solar concentrator incorporating a donor-emitter fluorophore system”, *Energy Letters* **4**(8) (2019) pp. 1839-1844

[19] Sanguineti A., Sassi M., Turrisi R., Ruffo R., Vaccaro G., Meinardi F., Beverina L., “High stokes shift perylene dyes for luminescent solar concentrators”, *Chemical Communications* **16** (2013) pp. 1618-1620

[20] Rowan B.C., Wilson L.R., Richards B.S., “Advanced Material Concepts for Luminescent Solar Concentrators” *IEEE Journal of Selected Topics in Quantum Electronics* **14**(5) (2008) pp. 1312-1322

[21] Yang C., Lunt R.R. “Limits of visibly transparent luminescent solar concentrators”, *Advanced Optical Materials* **5** (2017) pp. 1600851(1)-1600851(10)

[22] Tummeltshammer C., Portnoi M., Mitchell S.A., Lee A.-T. Kenyon A.J., Tabor A.B., Papakponstantinou I., “On the ability of Föster resonance energy transfer to enhance luminescent solar concentrator efficiency” *Nano Energy* **32** (2017) pp. 263-270

[23] Föster V.T., “Zwischenmolekulare Energiewanderung und Fluoreszenz*” Annalen der Physik* **6** (1948) pp. 55-75

[24] Lakowicz J.R., *“Principles of Fluorescence Spectroscopy”* (2006) 3rd Ed. Singapore, Springer

[25] Banal J.L., Ghiggino K.P., Wong W.W.H., “Efficient light harvesting of a luminescent solar concentrator using exciton energy transfer from an aggregation-induced emitter” *Physical Chemistry Chemical Physics* **46** (2014) pp. 25358-25363

[26] Swartz B.A., Cole T., Zewail A.H., “Photon trapping and energy transfer in multiple-dye plastic matrices: an efficient solar-energy concentrator” *Optics Letters* **1** (1973) pp. 73-75

[27] Balaban B., Doshay S., Osborn M., Rodriguez Y., Carter S.A., “The role of FRET in solar concentrator efficiency and color tenability” *Journal of Luminescence* **146** (2014) pp. 256-262

[28] Bailey S.T., Lokey G.E. Hanes M.S., Shearer J.D.M., McLafferty J.B., Beaumont G.T., Baseler T.T., Layhue J.M., Broussard D.R., Zhang Y.-Z., Wittmerhaus B.P., “Optimized excitation energy transfer in a three-dye luminescent solar concentrator” *Solar Energy Materials & Solar Cells* **91** (2007) pp. 67-75

[29] Menéndez-Velázquez A., Mulder C.L., Thompson N.J., Andrew T.L., Reusswig P.D., Rotschild C., Baldo M.A. “Light-recycling within electronic displays using deep red and near infrared photoluminescent polarizers” *Energy & Environmental Science* **6** (2013) pp. 72-75.

[30] Mulder C. L., Reusswig P. D., Velazquez A. M., Kim H., Rotschild C., Baldo M. A., "Dye alignment in luminescent solar concentrators: I. Vertical alignment for improved waveguide coupling" *Optics Express* **18** (2010) pp. A79– A90.

[31] Jimenez-Solano A., Delgado-Sanchez J.M., Calvo M.E., Miranda-Muñoz J.M., Lozano G., Sancho D., Sanchez-Cortezon E., Miguez H., “Design and realization of transparent solar modules based on luminescent solar concentrators integrating nanostructured photonic crystals” *Progress in Photovoltaics: Research & Applications* **23**(12) (2015) pp. 1785-1792

[32] Mulder C.L., Theogarajan L.S. Currie M. Mapel J.K., Baldo M.A., Vaughn M., Willard P., Bruce B.D. Moss M.W., McLain C.E., Morseman J.P., “Luminescent solar concentrators employing phycobilisomes” *Advanced Materials* **21**(31) (2009) pp. 3181-3185

[33] Goldschmidt J.C., Peters M., Hermle M., Glunz S.W., “Characterizing the light guiding of fluorescent concentrators” *Journal of Applied Physics* **105**(11) (2009) pp. 1194111-1194119

[34] Maggioni G., Campagnaro A., Carturan S., Quaranta A., “Dye-doped parylene-based thin film materials: application to luminescent solar concentrator” *Solar Energy Materials and Solar Cells* **108** (2013), pp.108, 27-37

[35] Renders A.H.M.E., Debije M.G., Rosemann A., “Measured efficiency of a Luminescent Solar Concentrator PV module called Leaf Roof”, *IEEE Journal of Photovoltaics* (2017), **7**(6), pp. 1663-1666

[36] Jones G., Klueva O., Kumar S., Pacheco D., “Photochemical and lasing properties of pyrromethane dyes”, *Proceedings of SPIE - The International Society for Optical Engineering* **4267** (2001) pp. 24-35

[37] Mateen F., Ali M., Oh H., Hong S.-K., “Nitrogen-doped carbon quantum dot based luminescent solar concentrator coupled with polymer dispersed liquid crystal device for smart management of solar spectrum”, *Solar Energy* **178** (2019) pp 48-55

[38] Bergren M.R., Makarov N.S., Ramasamy K., Jackson A., Guglielmetti R., McDaniel H., “High performance $CuInS_2$ quantum dot laminated glass luminescent solar concentrators for windows”, *Energy Letters* **3** (2018), pp. 520-525

[39] Wilson L.R., Klampaftis E., Richards B.S. “Enhancement of power output from a large area luminescent solar concentrator with 4.8x concentration via solar cell current matching”, *IEEE Journal of Photovoltaics* **7**(3) (2017), pp. 802-809