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Abstract

A visible light transmitting BODIPY derivative with an emission peak at 604 nm and quantum yield of 64% is incorporated into a PMMA matrix, resulting in an aesthetically pleasing luminescent solar concentrator (LSC), suitable for "power window" applications. A Monte Carlo modeling platform is shown to be useful firstly to tune device performance, but also to give direction to future synthetic efforts. From this an 4 mm thick LSC of (100 x 100 mm) is shown to have optical efficiency of $\approx 3.3\%$.

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Aesthetically Pleasing, Visible Light Transmissive, Luminescent Solar Concentrators Using a BODIPY Derivative

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Abstract

A visible light transmitting BODIPY derivative with an emission peak at 604 nm and quantum yield of 64% is incorporated into a PMMA matrix, resulting in an aesthetically pleasing luminescent solar concentrator (LSC), suitable for ‘power window’ applications. A Monte Carlo modelling platform is shown to be useful firstly to tune device performance, but also to give direction to future synthetic efforts. From this an 4mm thick LSC of (100 mm × 100 mm) was shown to have optical efficiency of ~ 3.3 %.

Luminescent Solar Concentrators (LSCs) were first introduced in the 1970’s, where it was envisioned that they could be produced with large form factors and coupled with a minimum of photovoltaic (PV) devices¹. This was particularly relevant at the time with the high price of PV devices, and offered an alternative to lensed or reflected (e.g. parabolic mirror) concentrators, meaning that they would be able to operate under diffuse lighting conditions, without the requirement of sun tracking and having a low profile (flat design). While one of the recurring aims of much of the early work was to increase the broadband absorption of LSCs, driven by the price of PV modules, recent decreases in Si PV cost (as well as thin film technologies such as CdTe) has largely nullified this motivation for creating LSCs (see the “Swanson effect”). LSCs can however fulfil other purposes, which conventional technologies cannot, including “power windows”, which incorporate (at least partially) visible light transmissive LSCs². Here the reduced cost of PV actually assists the viability of such systems. As such, LSCs have been touted as an attractive option for building-integrated photovoltaics (BIPV). A quick inspection of the AM1.5 spectrum showing almost as high of a photon flux in the 700 – 1000 nm as in the 350 – 700 nm regions, suggests an strong opportunities for visible light transparent systems³. Of course, with transmission of a certain amount of light a prerequisite for ‘power window’ applications, the attainable solar-to-electric efficiencies of such systems will be limited when compared to opaque PV panels⁴.

Ideal LSC operation involves photoexcitation and reemission (typically fluorescence) from a lumiphore, with the emitted photon waveguided to the edge where a photovoltaic device is attached¹. A number of factors limit the overall efficiency, such as transmission of incident photons (a factor to be balanced in power windows), non-radiative relaxation and photons not being successfully waveguided to the PV (failing to be internally reflected if they hit the surface at too shallow of an

angle, being absorbed by the matrix or scattered from defects). In addition, waveguided photons may be reabsorbed by another lumiphore at which point the photon is subject to all aforementioned obstacles (shown schematically in Figure S1). The extent to which light is downshifted through the process of absorption and reemission (*i.e.* the Stokes shift) has a strong influence on losses related to reabsorption. A number of reviews cover the basic operation of LSCs along with methods to mitigate the above loss channels. Complimentary to the development of new chromophores/fluorophores, engineering approaches undertaken in order to improve LSC device performance include the use of wavelength selective mirrors & filters⁵⁻⁶, lambertian back reflectors⁵, liquid crystal matrices⁷⁻⁸, multi-chromophore systems⁹ with Förster Resonance Energy Transfer (FRET)^{8, 10-11}, multilayer (with matched PV)^{5, 9, 12-13}, core-shell quantum dots for larger Stokes shift¹⁴⁻¹⁵, and bi-layer (dye + light guide)¹⁶⁻¹⁷. LSCs are typically composed of glass or glassy polymers, however liquid¹⁸ and flexible¹⁹ LSCs have also been realised.

Two metrics commonly used when evaluating LSC performance are the optical (η_{opt}) and overall solar-to-electric power conversion efficiencies (η_{PCE}). The former a ratio of the total photonic power out at the edges divided by that which is incident on the top face of the LSC and the latter term relying upon the PV devices used. The incident power (P_{in}) used is from the AM1.5 spectrum across the whole face of the LSC (although some authors also report η_{opt} as photonic power out divided by photonic power absorbed²⁰ or use other light sources²¹). For η_{opt} , as defined here (see SI for more detail), P_{out} is the luminous power at the edge, whereas η_{PCE} uses the electric power out of PV devices along the edges. Until recently the highest reported η_{PCE} was held by Slooff *et al.* with 7.1%, using an InGaP PV device to effectively utilise the light emitted from their commercially available chromophores⁹.

Crystalline silicon (c-Si) may not be ideal to be incorporated with an LSC. Other large band gap PVs, such as InGaP, have been reported to make more effective use of edge emitted photons; providing higher open circuit voltages (V_{oc})⁹. Methylammonium lead iodide (MALI) perovskite PV is of interest with demonstrated high V_{oc} s (>1.2V)²³⁻²⁴.

Despite being widely utilised in other applications due to their strong absorption and luminescence properties²⁵, along with synthetic adaptability²⁷, boron-dipyrrene (BODIPY) based dyes have only seen limited application in LSCs to date²⁸⁻³⁰. Bailey *et al.* mixed three BODIPY containing dyes, delivering energy to the red-most emitter through FRET²⁹, while Altan Bozdemir *et*

al. similarly used an energy cascade dendrimer system, resulting in panchromatic absorption and emission originating only from the terminal absorber²⁸. Although not quantified, this strategy appears to produce intense edge emission. Another, related, approach by Mirloup *et al.* involved producing dyes with multiple BODIPY moieties³⁰, while more recently Davis *et al.* showed BODIPY functional groups as part of a donor acceptor oligomer³¹. In most of these cases their aesthetic appeal and applicability as power windows is not a primary consideration. Indeed, the majority of high performance LSC-PV systems still utilise dyes which result in a reddish appearance of transmitted light, not dissimilar to what is seen for partially transparent amorphous silicon³², Ru-complex based dye-sensitised solar cells³³ or many of the polymers commonly used in OPVs³⁴⁻³⁵ (although it is noted that visible light transparent OPVs exist³⁶).

In recent years, a number of researchers have developed NIR absorbing chromophores and employed them in transparent LSCs. High performances, however, have been difficult to realise due to limited luminescence. Results achieved by Lunt's group harvesting NIR photons using a LSC based on fluorescent organic salts showed a η_{PCE} of 0.4%³⁷. While QD based LSCs were demonstrated by Meinardi *et al.* with an η_{opt} of 3.27 %³⁸ and further improved upon by Chen *et al.* (3.94%)³⁹ and Zhou *et al.* (6.1%)¹⁵. These tend to have a yellow/brown tint, which has been noted to be less aesthetically appealing⁴.

The BODIPY derivative reported here absorbs and emits in the red / near infrared part of the solar spectrum, and wide optical window in the blue, green and yellow parts. As mentioned, the PV device in the integrated system can be selected in order to make best use of the LSC output spectrum. In this work we model our LSC with a number of different PV technologies, in conjunction with the measured output. In the case of the dye presented here, the majority of light emitted at the edge is in the 600-750 nm range, making MALI and GaAs attractive options (where thermalisation losses will be less than for c-Si). This is discussed in more detail later. We also look to the future possibilities of BODIPY dyes, with simulated performances for LSCs made with larger Stokes shifts and/or higher photoluminescence quantum yields (PLQY).

Dye I was synthesised based on a previously reported material⁴⁰, via Knoevenagel condensation of tetramethyl BODIPY derivative with carbazole-3-carbaldehyde, with the full synthetic description reported elsewhere⁴¹. Optical properties of dye I were characterised for dilute solutions in MMA (Aldrich), with an absorption maximum at 586 nm (Shimadzu UV-1800), emission peak at 604 nm (Horiba Fluorohub), which translates to the Stokes shift of 509 cm^{-1} (18 nm, Figure 1). The dye exhibits high molar extinction coefficient of $\sim 110,000 \text{ M}^{-1} \text{ cm}^{-1}$ and a PLQY (measured with integrating sphere attachment) of $64 \pm 1 \%$. High PLQY values are particularly important for LSC applications as it drastically increases performance.

A PMMA:MMA (5:18 weight ratio) syrup was produced and dye added (to give 15 or 60 μM), based on the syrup mass and density of PMMA (1.18 g/cm^3). After the dye was thoroughly mixed through, an initiator, Azobisisobutyronitrile solution

(AIBN, 768375 Aldrich) was added at 3.4 $\mu\text{L/g}$ of syrup. The initiated syrup was then injected into a gap in the gasket of a mould comprised of two glass sheets, separated using low odour rubber (LST group, Australia). The gap in the gasket was then closed and left to settle before being immersed in a water bath at 50 $^{\circ}\text{C}$ for 72 hours, followed by annealed at 120 $^{\circ}\text{C}$ for 2 hours (2 $^{\circ}\text{C/hr}$ ramp each way) and the surfaces polished to < 3 μm surface flatness, using a rotary polishing system (Struers Tegramin-25) and diamond paste (Struers DP lubricant green). Polymerisation resulted in a slight red shift of both absorption and emission (also in Figure 1), with the peak absorbance and emission at 590 nm and 608 nm respectively (emission in PMMA was collected in front facing mode to minimise reabsorption effects). Preliminary empirical calculations suggested 60 μM was an optimal dye concentration for this slab thickness (although this was a broad maximum) and 15 μM was predicted to also produce an efficient LSC. The broad optimum concentration is promising for organic dye based LSCs, as it allows a greater degree of flexibility for aesthetic considerations.

The LSC was illuminated using simulated sunlight from a Xe lamp (Oriel), filtered to approximate the AM1.5 spectrum. Edge emission spectra were measured using an Ocean Optics HR4000 spectrometer, while the intensity was quantified using a calibrated Hamamatsu S1337-1010BR Si photodiode pressed against the edge of the LSC. Areal dependence of η_{opt} was measured (see in Figure S3) through the use of shadow masks. Digital photographs of the University of Wollongong are shown in Figures 2b-d without (b) and with either the 15 μM (c) or 60 μM (d) LSC in front of the camera. The transmission of visible light corresponds well with expectation, given the low extinction coefficients of Dye I in the 400 – 550 nm region of the spectrum seen in Figure 1. Again, this highlights the suitability for architectural purposes, particularly at lower concentrations. Furthermore, even under modest lighting conditions an intense deep red glow is seen at the edge of the LSC plate (Figure 2a). The CIE L*a*b* co-ordinates (D65 illuminant) for these LSCs were measured to be (83.06, 5.71, -18.6) and (52.93, 40.15, -48.15) for the low and high concentrations, leading to CCT values of 7759K and 7520K respectively⁴².

Figure 1. Absorption and emission spectra of dye I, measured as dilute in methyl methacrylate and in PMMA matrix. The chemical structure of dye I is shown as an inset.

The $100 \times 100 \times 4$ mm LSC was illuminated at the top face using simulated AM1.5 light while the spectrum of light outputted at the edges was measured using the HR4000 spectrometer. Edge emission was seen to be considerably red-shifted as compared to the emission of Dye I in dilute MMA, which was ascribed to significant reabsorption of emitted light on account of overlap between the emission and absorption spectra of the dyes. Figure 3a shows the measured output spectra from the LSC plate with the whole area exposed, along with when it is partially shaded and the dilute solution spectrum again for reference. The shift in the emission peak is ascribed to reabsorption effects. When the LSC slab is masked, it is seen that with higher dye concentrations the edge emission spectra are both more red-shifted and more size dependent.

Figure 2. Digital photographs of (a) the $15 \mu\text{M}$ LSC with the emissive edge angled towards the camera, (b) the UOW Innovation Campus, unfiltered, (c) UOW Innovation Campus through the $15 \mu\text{M}$ LSC “window” and (d) UOW Innovation Campus through the $60 \mu\text{M}$ LSC “window”. The camera settings for (b) - (d) were locked to ensure direct comparability - $1/320$ s exposure time, F7.1, ISO400 and autofocus on a Canon EOS 700D SLR camera. (e) Absorption spectra of the two LSCs along with a clear PMMA sheet for comparison. (f) Lab space representation of LSC slabs in transmission mode using HunterLab ColorQuest XE.

The optical efficiency (η_{opt}) was calculated, based on the measured emission and the observed intensity, to be around 2.7 % for illumination of the full plate of the lower dye loading, 3.3 % for the higher concentration, and up to 5.1 % for small areas and high concentrations (Figure 3b). It is interesting to again note the differences in size dependences for the two concentrations used here, as the lower loading is able to provide both similar efficiencies at 100×100 mm, while maintaining better transmission across the visible spectrum (seen by comparing Figures 2c and 2d). Although these are some of the highest reported η_{opt} values for visible light transparent systems, the geometric dependence suggests that ultimately this metric may have limited utility as a means of comparing dyes with no agreed upon standard dimensions. The high observed optical efficiencies for small (such as those

with 2 cm edge length) are not expected to be particularly practical for the stated purpose of power windows. We note here that this metric can also be gamed. For example, a $100 \times 100 \times 100$ mm block with have η_{opt} several times higher than the optimised $100 \times 100 \times 4$ mm plate. Fortunately, this practice does not seem to be happening at present, however, it suggests the need for better quantification approaches. Using the emission profiles and intensities reported above, in conjunction with reported Incident Photon to Charge Carrier Efficiencies (IPCE), Fill Factors (FF) and Open Circuit Voltages (V_{oc}), predicted PCEs were obtained. From Table 1, it can be seen that InGaP, used in other high voltage LSC + PV systems, will not be particularly useful here as its 1.88 eV bandgap means it cannot capture the bulk of the emission from the

Figure 3. (a) Output spectra of LSCs of different sizes and dye loadings. Edge emission spectra intensities were scaled based on Si diode responses. (b) Calculated optical efficiencies.

edge of the dye I based LSC. More so, in spite of the slightly higher η_{opt} for the $60 \mu\text{M}$ LSC, the redshifted emission results in a lower η_{PCE} for InGaP than for the $15 \mu\text{M}$ plate. Although the highest η_{PCE} values were observed when coupling with GaAs, it remains expensive. On the other hand, perovskites have been predicted to be a very cheap form of PV⁴³. Furthermore, the development of this technology suggests that a substantial amount of optimization may be carried out in the near future and the efficiencies used in this estimation will probably soon be improved upon – affording even higher performance power window systems.

Monte Carlo modelling was employed to predict the efficiencies of systems of hypothetical dyes consisting of modified optical properties of dye I. A computational model was developed, representing components of the physical LSC system. The AM1.5 spectrum was used to generate the proportions of photons. Individual photons were then traced through the internal volume of the simulated LSC, entering the LSC from the top face alike the experimental setup. Randomised absorption and emission events occurred based on the measured dye properties. Internal reflection also occurred if the photon reached a boundary at above a critical angle. Photons that reached a boundary edge were terminated and their contribution to the output power was recorded. This model is explained in further detail in the SI (S4), with code available at www.github.com/PhotonFiend/LSC.

Table 1. Predicted efficiencies based on state-of-the-art PV devices and the two LSCs described here.

Device	V_{oc} (V) [a]	FF	15 μM LSC		60 μM LSC	
			J_{sc} (mA/cm^2) ^[l]	η_{PCE} (%) ^[c]	J_{sc} (mA/cm^2)	η_{PCE} (%) ^[c]

	[a]		[b]		[b]	
Si	0.740 ⁴⁴	0.827 ⁴⁴	8.73 ⁴⁵	0.84	10.96 ⁴⁵	1.05
GaAs	1.122 ⁴⁴	0.865 ⁴⁴	8.56 ⁴⁶	1.31	10.69 ⁴⁶	1.63
InGaP	1.390 ⁴⁷	0.860 ⁴⁷	3.16 ⁴⁸	0.60	2.37 ⁴⁸	0.45
MALI	1.130 ⁴⁹	0.750 ⁴⁹	8.00 ⁴⁹	1.07	9.92 ⁴⁹	1.32

VOC and FF taken as 1 sun values from literature sources. JSC based on the integration of device EQE (literature) over emission spectra of the LSC (as per Figure 3). Pout is average power density out along edges, based on calculated JSC, while the overall efficiency takes into account the total illumination area. [a] Note that in calculating the efficiency, VOC is scaled in accordance with J_{SC} compared to reported 1 sun J_{SC} values (60 mV / decade of light intensity). [b] J_{SC} calculated for the attached PV strip.

Increased Stokes shifts of 10, 20 and 30 nm were modelled, along with PLQY values of 80 and 90 % (Table 2). In order to simulate an increased Stokes shift, the emission spectrum of

Table 2. Predicted enhancements to the optical efficiency of an LSC made with a dye similar to I, but with a larger stokes shift and/or enhanced emission yield.

A19m 'modification'	Relative increase (%) in η_{opt}
+5 nm stokes	+10.6
+10 nm stokes	+23.8
+20 nm stokes	+51.3
70% PLQY	+20.9
80% PLQY	+76.7
90% PLQY	+190.8
+20 nm stokes; 90% PLQY	+285.8

dye I was translated, with all other spectroscopic properties unaltered. The geometry is kept at 100 × 100 × 4 mm for these simulations.

As expected, modelling data, shown in Table 2 and Figure S3(c & d), indicates that increases in either Stokes shift or PLQY will give more efficient LSCs. An interesting observation here is that the magnitude of the predicted increase is strongly dependent upon the PLQY, and as such, more effort should be invested in synthetic strategies to raise this value. Even with most optimistic conditions modelled here, the enhancement will still only provide modest overall η_{PCE} values. As such, broadening the absorption range also appears to be a necessary goal (although not specifically modelled here). Further enhancement can be expected from optical management techniques, such as dichroic coatings, which were not incorporated here. It is also noteworthy that with enhanced PLQY and Stokes shifts, the optimal concentrations increase.

In summary, BODIPY containing Dye I, was demonstrated to be a promising dye for LSC applications, when incorporated in a PMMA matrix. This performance is attributed to a combination of PLQY (64 %) and a Stokes shift of 16 nm. A 100 × 100 × 4 mm slab, containing 60 μ M of Dye I was shown to have an optical efficiency in excess of 3.3 %, with a calculated η_{PCE} of 1.63 % when paired with GaAs, while a lower dye loading of 15 μ M gave only slightly lower efficiency and high visible light transmission. It was however seen that, in spite of this performance, there is still significant room for improvement.

Particularly through synthetic strategies aimed towards increasing the emission yield of the dye.

Conflicts of interest

The Authors declare no conflicts of interest.

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Supporting information for: Aesthetically Pleasing, Visible Light Transmissive, Luminescent Solar Concentrators Using a BODIPY Derivative

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S1. Overview of processes in LSC operation

The individual steps involved in LSC operation are outlined below in Figure S1. This was used to inform our Monte-Carlo modelling (below in section S4).

Figure S1 – Schematic of LSC operating principles

S2. Calculation of η_{opt}

The optical efficiency, that is the ratio of photonic power out (P_{out}) over the input (P_{in}), can be calculated based on the intensity and wavelength of light, as observed at the edges of the LSC panel.

$$\eta_{opt} = \frac{P_{out}}{P_{in}}, P_{in} = AM1.5$$

This involved measuring the wavelength distribution of photons, in accordance with an ocean optics spectrometer measured EQE for each corresponding wavelength, based on the assumption that all edge emitted light (from the 1 cm wide, 4 mm high section to which the diode was pressed) was absorbed by said diode. The energies of the emitted photons were then factored in and the total optical power out determined. This was then divided by the simulated AM1.5G light used as input (100 mW/cm² from a Xe arc lamp – Oriel).

- An Ocean Optics HR4000 spectrophotometer was used to measure the output spectrum in a semi-quantitative manner.
- The short circuit current density of the Si diode, placed against the edge of the LSC, along with its measured EQE (such that the sensitivity to light of any wavelength is known) and the spectral information mentioned above mean that the edge emission can be quantified.
- This was used, in conjunction with literature results of photovoltaic devices, to calculate the predicted short circuit current density (integrating the reported EQE over the LSC output spectra). In turn, this was used to calculate a predicted efficiency (η_{PCE}), again using literature values for fill factor and open circuit voltage. It should be noted here that the lower $J_{sc,OC}$ than the literature values. V_{oc} values have been adjusted in accordance with a typical 60 mV shift per decade of intensity. FF has not been adjusted, however it is anticipated that this only change slightly within the light intensity range observed here.

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S3 – Partial masking, examining small area responses

Although η_{opt} has been widely adopted as a metric for comparing LSCs, it does have a size dependence. To explore this, a series of masks were applied to our LSC testing apparatus (Fig S3(a) below). The two schematics on the right illustrate a larger and small exposed area.

Figure S2 – (a) edge emission testing (with both Si diode and optical fibre connected to ocean optics spectrophotometer) and (b, c) schematics of different tests for different illumination areas based on partial masking.

S4. Monte Carlo Modelling

Monte Carlo (MC) simulations have previously been employed [1, 2] in order to determine optimal dye concentrations for LSCs, on account of the trade-off between light harvesting and re-absorption (where either thermalisation or emission at steep angles result in losses). There is no 'optimal' length or width for an LSC, nor is there a thickness as increases in either of these leads to a greater total photonic output, albeit with diminishing returns. On the other hand, smaller cross-sectional areas will provide greater flux concentration factors (less light lost), however this requires more total PV area. Practically, economic and aesthetic considerations will play the major role in determining these values. MC modelling also allows us to readily 'forward plan' future dye development. For example, we can use it to see what could be achieved with a 10 nm larger stokes shift, or if the FQY was enhanced, giving researchers direction in terms of where further dye development efforts should be placed.

In this paper, we present a simple model (based upon Figure S1 above), along with its use in the optimisation of an LSC system for a BODIPY derivative and incorporation into a whole photovoltaic window. An area of 100 × 100 mm was selected as an exposed area.

Figure S3 – (a) relative power out calculated from MC model and measured η_{opt} . (b) Modelled versus experimentally obtained spectrally resolved output for three sizes of 15 μM LSCs. *Monte Carlo simulations of the relative optical efficiency expected for dyes similar to I but with (c) larger stokes shifts (simulated by red-shifting the emission), (d) enhanced fluorescence yields or both.*

S4. LAB colorspace measurements of LSCs

The LSCs were measured on both the Shimadzu 1800 spectrometer (Fig S4(a), with sequential wavelength probing) and using a HunterLab ColorQuest XE spectrophotometer (Fig S4(b)) with photodiode array). The transmission of the LSCs and a control of plain Perspex are shown, acquired from the two spectrometers respectively. It is clear that front/back face luminescence in the red/infrared part of the spectrum has an impact on the observed result (Figure S4(b)). Lab values, shown in the main text, are calculated from measurements performed on the ColorQuest XE.

Figure S4 – (a) transmission as measured using Shimadzu 1800 spectrophotometer and (b) apparent transmission as measured using a HunterLab ColorQuest XE, noting the > 100% values where the LSC emits.