

Advanced Material Concepts for Luminescent Solar Concentrators

Brenda C. Rowan, Lindsay R. Wilson, and Bryce S. Richards, *Member, IEEE*

(Invited Paper)

Abstract—Sunlight that is incident on the front surface of a luminescent solar concentrator (LSC) is absorbed and subsequently re-emitted by luminescent materials. The resulting luminescence is transported to the edge of the LSC sheet and concentrated onto photovoltaic devices. Despite its potential for generating low-cost solar power, LSC development faces numerous challenges, the majority of which are related to the luminescent materials used in their design. Earlier LSC research focused on organic dyes, and while several of the shortcomings with these materials have been solved over time, some major challenges remain. This paper outlines the loss mechanisms that limit conversion efficiency of the LSC and highlights the role that advanced materials can play. Losses include nonunity fluorescence quantum yield (FQY), reabsorption losses, incomplete utilization of the solar spectrum, and escape cone losses. Long-term photostability is also discussed as it is essential for commercial feasibility of any solar technology. Past and current techniques, designed to reduce these losses, are described and their experimental achievements are discussed.

Index Terms—Fluorescent, luminescent, photovoltaic (PV), quantum yield, solar concentrator.

I. INTRODUCTION

THE APPLICATION of organic and inorganic luminescent materials to the field of photovoltaics (PVs) involves many interesting challenges for scientists and engineers. The LSC [1], [2] is a unique nonimaging optical device that can be used to concentrate sunlight onto a small area of solar cells. A typical design consists of a polymer plate doped with a luminescent material, such as a fluorescent organic dye, with solar cells optically matched to the plate edges. Fig. 1 shows a cross-sectional diagram of an LSC and illustrates the operation of the device.

The main motivation for implementing an LSC is to replace the large area of expensive solar cells required in a standard flat-plate PV panel, with an inexpensive polymeric collector, thereby, reducing the cost of the module (in dollars per watt) and also of the solar power (in dollars per kilowatt-hour). A key advantage of LSC technology compared to other concentrating systems is that it can collect both direct and diffuse

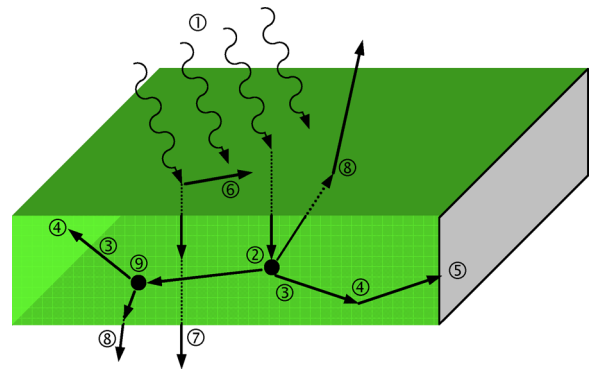


Fig. 1. Cross-sectional diagram of an LSC. Ideally, sunlight (①) incident on the front surface of the LSC is absorbed by a fluorescent organic dye molecule (②). Light is subsequently re-emitted at a longer wavelength at a high fluorescent quantum yield (FQY) (③) and is transported to the edge by total internal reflection (④). Solar cells (⑤) mounted to the perimeter of the LSC convert the concentrated luminescence to electricity. Common loss mechanisms include front surface reflection (⑥), transparency to long-wavelength incident light (⑦), and escape cone losses for light emitted within the Brewster angle (⑧). Additionally, luminescence may be reabsorbed by dye molecules that have an overlapping absorption and emission spectra (⑨), which can again result in luminescence being emitted at a certain LQE (③) and transported to the edge (④) or passing out the front or rear escape cones (⑧). Loss mechanisms that are not illustrated here include parasitic absorption in the host matrix, and scattering of light from within the bulk and at surfaces.

solar radiation. This means that tracking of the sun is not required—enhancing further potential cost reductions and making LSCs excellent candidates for building integrated photovoltaics (BIPV)—as well as making them the ideal PV technology for cloudier northern European climates. Similarly to electricity conversion, LSCs also have applications in daylighting [3], thermal conversion, and hybrid thermal–photovoltaic systems that could generate electricity and extract the heat generated by the LSC plate [4].

II. LUMINESCENT SOLAR CONCENTRATOR DEVELOPMENT

A. History of LSCs

The first publications on LSCs first appeared in the late 1970s [1], [2], and the technology was studied intensely through the early 1980s until limitations of fluorescent organic dyes hindered further development [5], [6]. The highest conversion efficiency achieved for a large-area LSC (40 cm × 40 cm × 0.3 cm) was $\eta_{\text{LSC}} = 4.0\%$ with a two-stack system consisting of a shorter wavelength emitting plate coupled to gallium arsenide (GaAs) solar cells and below that, a longer wavelength emitting plate coupled to silicon (Si) solar cells [7]. Multilayered

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The authors are with the School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, U.K. (e-mail: b.c.rowan@hw.ac.uk; lrwl@hw.ac.uk; b.s.richards@hw.ac.uk).

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mixed-dye thin-film LSCs of smaller dimensions (14 cm \times 14 cm \times 0.3 cm) achieved $\eta_{\text{LSC}} = 3.2\%$ using Si solar cells and $\eta_{\text{LSC}} = 4.5\%$ using GaAs devices [8]. It was estimated that the maximum achievable conversion efficiency of LSCs that collected sunlight in the range 300–900 nm was $\eta_{\text{LSC}} = 8\text{--}12\%$ [8]. These limits were not reached due to problems that will be outlined in the following section.

In recent years, there has been a renewed interest in LSCs due to the availability of new luminescent materials, such as semiconductor quantum dots (QDs) [9], rare earth (RE) materials [10], and semiconducting polymers [11]. Second, materials such as photonic layers [12] and liquid crystals [13] have also been utilized to reduce losses within the devices. Developments in ray-trace [14]–[17] and thermodynamic [18] modeling software has also encouraged further research.

B. Future of LSCs

The challenges faced in LSC development will be described in detail throughout this paper, starting with a brief description of the main requirements of LSC materials. There are four main criteria that should be met in order for LSCs of greater than 10% efficiency to be achieved with Si solar cells.

- 1) Absorption of all wavelengths $\lambda < 950$ nm with high absorption coefficients and an emission peak ~ 1000 nm.
- 2) Minimum reabsorption losses due to overlap of absorption and emission spectra.
- 3) Near-unity fluorescence quantum yield (FQY).
- 4) Long-term outdoor stability (more than ten years)

Typically, organic and inorganic materials possess unique characteristics, both satisfying some but not all of the aforementioned criteria. This section will briefly show how, ultimately, it is most likely to be a combination of organic and inorganic materials that will provide a solution.

Organic luminescent materials such as perylene-based dyes exhibit near-unity FQY [19] and have been demonstrated to be stable for many years in a polymethylmethacrylate (PMMA) host incorporating a UV absorber [20], [21]. However, organic dyes exhibit narrow absorption bands, and dyes possessing high FQY with emission peaks in the near infrared response (NIR) are not yet available [22]. In addition, significant reabsorption losses occur with organic dyes, being lower in solution but increasing in solid host matrices [23].

RE materials and QDs are discussed as two separate inorganic materials due to greatly differing properties. Lead sulfide (PbS) based NIR-emitting QDs exhibit broad absorption spectra, high absorption coefficients, and emission peaks in the NIR region. However, commercially available PbS QDs exhibit low FQYs of $\sim 10\%$ and are very unstable and expensive [22]. On the other hand, RE materials such as neodymium (Nd^{3+}) and ytterbium (Yb^{3+}) in glassy hosts exhibit superior stability, emission peaks at $\lambda \sim 1000$ nm [24], and high FQY values of $\sim 90\%$ have been reported in phosphate glasses prepared in a nitrogen environment [25]. Unfortunately, they have narrow absorption peaks with low absorption coefficients; therefore, high concentrations are required leading to increased cost [26]. The characteristics

TABLE I
IDEAL CRITERIA FOR AN LSC COUPLED TO A SI SOLAR CELL SHOWING THE PROPERTIES OF ORGANIC AND INORGANIC MATERIALS

Desired property	Organic	Inorganic	Hybrid
(i) Absorb all $\lambda < 950$ nm	✗	✗ [†] / ✓ [‡]	✓
(ii) Minimal re-absorption	✗	✓ [†] / ✗ [‡]	✓
(iii) FQY > 90%	✓	✓ [†] / ✗ [‡]	✓
(iv) Stable for >10 yrs	✓*	✓ [†] / ✗ [‡]	✓

[†] RE materials; [‡] PbS QDs; *not all materials

of typical organic and inorganic luminescent materials are summarized in Table I.

The following sections contain further details on the shortcomings of organic and inorganic materials and past and present techniques that have been investigated to minimize these losses. It seems likely that all the criteria in Table I could be met by combining organic and inorganic materials into a hybrid device [26].

C. Challenges in LSC Design

The challenges faced in LSC development can be subdivided into those presented by the luminescent materials encapsulated into the devices and those of the matrix materials used to fabricate devices. The following section outlines the main challenges faced in each category.

Luminescent materials:

- 1) *Absorption range*: Narrow absorption ranges of luminescent species limit the amount of the solar spectrum that is utilized.
- 2) *Reabsorption*: Reabsorption of emitted light leads to increased escape cone losses (ECLs; see later) and decreased FQY.
- 3) *FQY*: Nonunity FQY of luminescent species.
- 4) *Stability*: Long-term stability (more than ten years) of LSC plates is necessary to make them commercially viable and competitive with existing PV modules, which are typically sold with a warranty of >20 years.

Matrix materials:

- 1) *ECLs*—light emitted from within the LSC at angles less than the critical (Brewster) angle—account for $\sim 25\%$ loss of luminescence from an LSC plate (assuming a refractive index of $n \sim 1.5$) [27].
- 2) *Matrix material*: A host matrix with an extremely low absorption coefficient over a very wide wavelength range (e.g., 350–1000 nm) is required to realize large-area LSC modules that may exhibit optical pathlengths up to 1 m.

Discussion of the effects of each of these challenges, past efforts to minimize these effects, and possibilities presented by new materials are outlined in the following sections. Since most of the earlier LSC work was carried out using organic dyes, they will be discussed primarily in each section with new materials being introduced as alternatives.

One of the greatest challenges for LSC development is achieving an accurate and absolute measurement of the FQY of

luminescent species within the chosen host matrix. It is useful for carrying out comparative studies to identify the most efficient luminescent material and to study the effects of polymerization on FQY. Accurate FQY values are also essential to obtain realistic outputs using ray-trace modeling, which, in turn, facilitate scale-up of the technology. Details of two techniques used to measure FQY are given later in the paper and the advantages and disadvantages of each are outlined.

III. LUMINESCENT MATERIALS

A. Absorption Range

When a LSC plate is used as a solar collector, it will absorb a smaller fraction of sunlight than a Si solar cell. This percentage of a LSC plate containing a single visible-emitting dye with a full-width at half-maximum (FWHM) of 80–100 nm will absorb about 20% of incident air mass 1.5 global (AM 1.5g) radiation.

For maximizing LSC performance with Si solar cells, the luminescent material would ideally absorb all wavelengths up to 950 nm and then possess a single intense emission peak in the 950–1000 nm range [22]. Emission in this range is desirable as it corresponds to the maximum spectral response of the Si PV device. Additionally, extending the absorption range from 300 to 600 nm out to the NIR (300–900 nm) would double the number of photons in the LSC [28]. Realizing this in the past has been problematic due to narrow absorption bands of luminescent dyes and low FQYs at wavelengths beyond the visible range [29]. The low FQY values of NIR dyes has been attributed to the increased nonradiative recombination occurring at longer wavelengths due to increasing molecular dimensions and the decreasing probability of radiative transitions with increasing wavelength [29]. Also, overlapping of the absorption and emission spectra is more severe in longer wavelengths dyes leading to increased reabsorption losses [29].

The use of multiple dyes or inorganic materials offers the opportunity of extending the absorption range of LSCs.

1) *Multidye LSC Plates:* Multidye systems consisting of several dyes in a single plate were suggested in the 1980s to increase the absorption range of LSCs [30]. It has been shown by Zewail [5] that up to 70% of the solar spectrum can be absorbed using a multidye system. Cascaded emission can occur in such mixtures where the emission of one molecule is absorbed and re-emitted by another molecule that has a longer emission wavelength. Through this process, photons absorbed at shorter wavelengths travel through the different luminescent dyes and are finally emitted by the longest wavelength dye [22].

The maximum efficiency of a multidye plate was calculated as 3.9% using a ray-tracing model (RAYLENE) for a mixture of visible-emitting dyes (BASF Lumogen Violet 570, Yellow 083, Orange 240, and Red 300 dyes) [22]. After the addition of NIR dyes with emission peaks $\lambda < 659$ nm and FQY < 62%, the LSC efficiency dropped significantly, indicating that a tradeoff exists between increasing the absorption range and reducing LSC efficiency by using low FQY dyes [22]. The overall efficiency of a multidye plate is strongly dependant on the FQY of the NIR dyes since they are the final dyes in the cascade sequence and nonunity FQY could lead to quenching of emission that could

otherwise reach the LSC edge. One possible solution to this would be to place a second LSC plate containing the NIR dyes below the plate containing visible dyes to convert the longer wavelength light without hindering the efficiency of the upper plate [22].

If the dye concentrations are sufficiently high, dye mixtures offer the possibility of cascading of emission via nonradiative Förster resonant energy transfer (FRET) rather than the more typical radiative recombination [30]. Recently, highly efficient FRET has been achieved with polystyrene spheres containing six dyes, with 95% of absorbed light being transferred to the lowest energy dye, resulting in a dominant emission peak at 718 nm [31]. Due to the high concentrations required for FRET to occur, multidye systems are most suited to thin-film devices. Thin-film devices consist of a thin layer of doped polymer cast onto a clear substrate. Light emitted in the fluorescent layer can be transported to the edge by TIR in the undoped layer. Recent studies on thin-film multidye LSCs showed that a LSC containing three dyes in one layer that between them absorb 70% of the available photons between 350 and 650 nm showed a 45% improvement in efficiency when compared to the best performing single-dye LSC [32].

2) *Inorganic Luminescent Species:* PbS and lead selenide (PbSe) QDs have broad absorption spectra with high absorption coefficients facilitating extensive utilization of the solar spectrum and emission peaks that can be tuned from 850 to 1900 nm [33]. NIR QDs with FQYs of up to ~80% have been produced in laboratories [34], [35] but such high efficiency QDs are not commercially available. PbS QDs with lower FQY values of around 10% can be purchased, but they lack long-term stability and are expensive [33].

QDs display unique properties such as spectral tunability, whereby the absorption and emission characteristics of QDs are controlled by altering the QD diameter [36]. Absorption and emission spectra of visible emitting Cadmium Selenide/Zinc Sulphide (CdSe/ZnS) QDs with a diameter of about 5 nm and PbS QDs with an estimated diameter of 8 nm are shown in Fig. 2(a). In addition, PbSe QDs offer the possibility of multiple exciton generation, when photons with energy two or three times the bandgap of the QDs can lead to the formation of multiple electron-hole pairs. This has been observed recently and resulted in FQY values up to 300% [37], [38]. Therefore, when photostable NIR QDs with high FQYs become commercially available, they will present great potential for use as NIR emitters in LSC devices.

RE materials such as Nd^{3+} and Yb^{3+} offer another alternative to NIR organic dyes, with excellent photostability and large Stokes shifts [8], [39]. The FQY of RE materials vary greatly depending on host materials and concentration but values >90% have been reported in glass substrates [40]. The two main drawbacks of RE materials are the following. First, since the luminescent transitions with the 4f electron shell are forbidden, RE materials exhibit extremely low absorption coefficients in the order of $1\text{--}5\text{ cm}^{-1}$. Thus, high concentrations are required to effectively harvest a significant fraction of sunlight. Second, they exhibit numerous narrow absorption bands resulting in limited utilization of the solar spectrum [41].

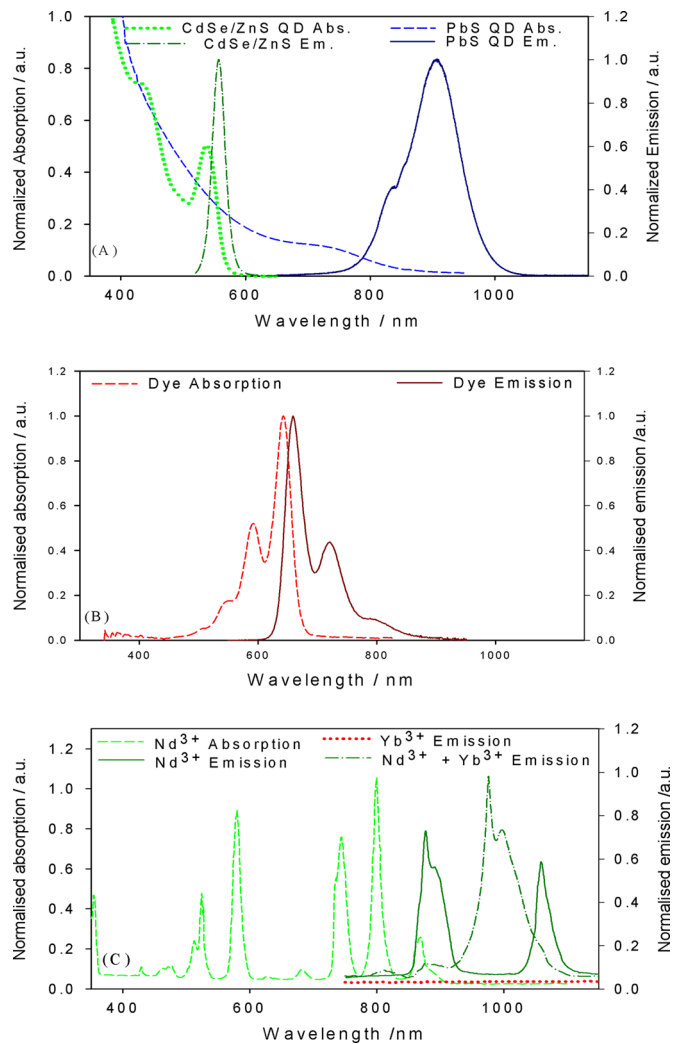


Fig. 2. Absorption and emission spectra. (a) CdSe/ZnS QDs and PbS QDs. (b) Lumogen red dye. (c) 2.0 wt% Nd^{3+} , 2.0 wt% Nd^{3+} + 3.0 wt% Yb^{3+} , and 3.0 wt% Yb^{3+} .

Due to its numerous absorption peaks spanning the solar spectrum, Nd^{3+} can be used as an absorber (sensitizer) combined with Yb^{3+} , which acts as a suitable emitter (activator) due to its single emission peak at 970 nm [39]. When implemented in a LSC, this combination of RE materials in glass host materials has been shown to absorb 20% of the solar spectrum in the 440–980 nm range [24]. The absorption and emission spectra of Nd^{3+} , the emission spectra of Yb^{3+} and a combination of Nd^{3+} and Yb^{3+} , are shown in Fig. 2(c). It can be seen how the Nd^{3+} and Yb^{3+} combination leads to a single emission peak close to 1000 nm, perfectly matched to the maximum spectral response of a Si solar cell. Fig. 2(b) shows the absorption and emission spectra of Lumogen red dye, indicating the limited range of the solar spectrum that can be utilized by a single organic dye.

Another option is the attachment of highly absorbing species to the emitting RE element facilitating broad absorption ranges coupled with emission peaks in the NIR region. This has been done using the transition metal chromium (Cr^{3+}), which displays two broad absorption bands covering most of the solar spectrum [24]. Energy transfer efficiencies of 92% with Nd^{3+}

and 88% with Yb^{3+} were observed, suggesting them as promising combinations for LSCs. Unfortunately, FQYs of Cr^{3+} in glasses exhibit a maximum of 23% in lithium lanthanum phosphate glass [24].

The high absorption coefficients of organic dyes can be combined with the long wavelength emission of RE materials to produce luminescent lanthanide complexes [10], [42]. The organic dye acts as a sensitizer, absorbing incident light and transferring it to the lanthanide where it may be emitted as light or heat, depending on the FQY.

Sensitization of Nd^{3+} and Yb^{3+} with fluorescein dye has been achieved for use in biological labeling [10] and overall quantum yields of up to 50% have been shown for Europium with fluorescein antennae [42]. Luminescent lanthanide chelates such as these could provide a suitable luminescent material for LSCs providing high absorption coefficients, NIR emission, stability, and reduced reabsorption losses. One limitation of these complexes is the absorption range of the organic dyes, so chelation of multiple dyes may be necessary.

With regards to utilization of the solar spectrum, it seems that maximum absorption could be achieved by combining organic and inorganic materials to produce hybrid systems to satisfy all the criteria necessary to utilize the solar spectrum most effectively [8], [26].

B. Reabsorption Losses

In the region where the absorption spectrum of a luminescent species overlaps with the emission spectrum, emitted light can be reabsorbed by another luminescent species. When this occurs, the light may be lost through the escape cone of the LSC, or if the luminescent species does not have 100% FQY, the light may not be re-emitted due to radiationless relaxation [43]. Reabsorption losses are represented by decreasing emission intensity and redshifts in emission spectra. The effects of reabsorption are intensified with increasing pathlength and with high concentrations of luminescent species [43]. Reabsorption can be minimized by using materials with a large Stokes shift. Calculation of the optimum concentration is also beneficial, balancing the need for sufficient absorption of incident light and minimum reabsorption.

1) *Thin-Film Devices*: Thin-film devices consist of a 0.15- to 1-mm-thick layer of luminescent material deposited onto a thicker transparent plate, ideally of the same refractive index [8]. They offer the possibility of reducing reabsorption effects by confining all the absorption and emission to the thin film while trapping and reflection events occur primarily in the clear matrix [8], [44]. Light emitted into the undoped layer will travel to the plate edges by TIR with a greatly reduced chance of being reabsorbed. Absorption by the host material can also be minimized since pure materials with high optical clarity can be used. The thin-film multidye system described in the previous section minimizes reabsorption losses since the energy transfer between molecules is nonradiative. In such systems, it is important to have minimal reabsorption by the final dye in the cascade sequence [32].

2) *Quantum Dots*: The overlap of QDs absorption and emission spectra remains too large, so reabsorption losses still present

a problem although there is potential of solving this problem in the future. The spread of QD sizes in a QD sample controls the width of the absorption and emission spectra, and therefore, the degree of overlap [45]. This means that, future improvements in QD fabrication techniques could potentially reduce the reabsorption losses in QD samples by producing samples with smaller size distributions [11].

3) *Semiconducting Polymers*: The use of semiconducting polymers synthesized for the light-emitting diode industry was recently investigated by Sholin *et al.* [11]. A range of liquid LSCs of approximately 1 in \times 3 in \times 0.2 in containing laser dyes, semiconducting polymers, and QDs were compared. Despite having a lower FQY than Rhodamine B dye, the semiconducting polymer (red polyfluorene) sample produced a higher optical efficiency ($\lambda_{\text{opt}} = 19.8\%$) due to reduced reabsorption losses (compared to $\lambda_{\text{opt}} = 15.3\%$ for Rhodamine B) [11]. The amount of reabsorption was quantified by measuring the red-shift in edge emission that resulted from excitation at increasing distances from the samples edge [11]. These results highlight the effect that reabsorption losses can have on system efficiency and also indicate that semiconducting polymers are possible candidates for use in LSCs.

4) *Rare Earth Materials*: Apart from providing broad absorption spectra, the combination of RE materials with absorbing species such as Cr^{3+} has the advantage of reducing reabsorption losses. This is because RE ions emit to energy levels above the ground state, thereby preventing reabsorption. This has also been demonstrated with uranyl (UO_2^{2+}) ions combined with Nd^{3+} in glasses [24]. This is a significant advantage for RE materials; combined with their photostability, this makes them excellent candidates for use in LSC devices.

C. Fluorescence Quantum Yield

One of the major factors that affect the overall efficiency of an LSC module is the FQY of the luminescent species used in its design. Many organic dyes exhibit FQY values close to 100% in certain solvents; however, it is their FQY within the LSC host matrix that is actually required to be near unity in value. The FQY of a luminescent species in a host matrix is strongly affected by the matrix material and the concentration of luminescent material used.

1) *Matrix Material*: PMMA is commonly used in LSC fabrication due to its high transparency, excellent photostability, and mechanical and chemical resistance [46], [47]. Drake *et al.* [48] found the FQY of two out of three types of dye in PMMA to be equal to or higher than their FQY in solution. The dyes investigated were coumarin 540 A, 4-dicyano-methylene-2-methyl-6-*p*-demethylaminostyryl-4 H-pyran (DCM) and Rhodamine 640, exhibiting FQY values in PMMA of 98%, 81%, and 75%, respectively. The improvements seen in FQY were thought to be due to increased molecular rigidity reducing nonradiative processes [48].

An early study of NIR dyes showed that solvent viscosity has an effect on the dyes FQY. FQY values of 30% in highly viscous solutions dropped to 0.6% in less viscous solutions [29]. A detailed study into the FQY of a range of dyes

in solution and in a polymer matrix revealed that many organic dyes including coumarin 6 and sulforhodamine-B showed improved FQY values when encapsulated into a solid matrix [6]. This was attributed to restriction of the torsional motion of the di-*n*-ethylamino groups leading to reduced nonradiative pathways [6]. These results indicate that the movement of molecules in liquid solutions can increase nonradiative recombination, and encapsulation of luminescent species can be beneficial and can lead to increased FQY.

2) *Concentration of Luminescent Materials*: The concentration of luminescent material can have a large impact on the FQY. A recent study showed FQY values for coumarin in a copolymer matrix drop from 78% at a concentration of 1×10^{-4} M to 45% at a concentration of 1×10^{-3} M. A similar trend was seen for perylene dye in the same circumstances with FQY values dropping from 96% to 75% [46]. This highlights the importance of identifying the optimum concentration of luminescent material being used.

Studies have also shown increases in FQY with increasing concentration up to a maximum at which point FQY values fall due to reabsorption losses caused by the large number of molecules present [49]. In addition to reabsorption, aggregation of molecules can occur and the clusters of material formed can induce scattering losses [20].

3) *Enhancing FQY*: The addition of silver particles has been investigated as a means of enhancing the FQY of LSC plates [50]. This occurs due to the interaction between the electric dipole of the dye molecules and the surface plasmons of the submicroscopic silver particles [50], [51]. An increase of 35% in fluorescent intensity has been achieved with coumarin dye in a sol-gel glass film [52]. Recently, the FQY of a Rhodamine monolayer was improved by over 20 times due to the deposition of silver nanoparticles. With improved techniques up to 50 times could be achieved [53]. This technique could be useful for enhancing the FQY of long-wavelength dyes that exhibit low FQY values.

D. Stability

The stability of luminescent species is one of the main challenges in LSC development. If high LSC efficiencies are achieved, it will not be commercially viable unless lifetimes greater than ten years are possible. In the initial period of study, stability of up to two years was measured [54], while more recently, dye stability of many years under sunlight has been reported [20], [21]. Techniques to improve the stability of LSC devices include choice of optimum matrix materials, use of specific casting and curing techniques, and use of inorganic materials.

1) *Matrix Materials*: The stability of luminescent materials in PMMA can be affected by additives that react negatively with luminescent species or by the presence of monomer residues due to incomplete polymerization [47]. A recent study [47] showed better stability was achieved by pure PMMA coatings on glass plates compared to bulk PMMA samples. This was thought to be caused by additives in the bulk PMMA samples but could also be due to UV curing of bulk PMMA causing photodegradation of the dyes. Alternatives such as the use of

copolymers of polystyrene and PMMA have produced samples with better stability than PMMA alone [46]. The half life for coumarin 6 in a copolymer matrix was 1964 min with exposure to unfiltered light compared to 361 min in a PMMA matrix [46].

The incorporation of BASF perylimide dyes into a sol-gel matrix (inorganic glass) was found to produce samples with improved stability. Thin-film samples exhibited 65% of their initial fluorescence after exposure to the equivalent of five years of outdoor weathering [55].

In earlier work, the stability of 61 different host systems doped with luminescent dyes were compared, 17 of these polymers including acrylates, esters, and silicates showed no visual signs of degradation after 50 kWh/m² (~14 days) [6]. These results highlight the dependence of sample stability on the choice of host matrix.

2) *Fabrication Techniques*: In addition to choosing the most suitable host material, the methods used to cast and cure the samples can have an effect on sample stability. A comparison of perylene-doped PMMA samples cured thermally and at room temperature showed that thermal polymerization reduces UV degradation effects and produces more stable samples [56]. Tanaka *et al.* determined that photooxidation was responsible for photodegradation of polymer-dispersed perylene dyes, while samples in anaerobic conditions underwent partially reversible photoreduction. The fabrication of devices in an oxygen-free environment to extend lifetime was recommended or the incorporation of O₂ quenchers and/or triplet perylene di-imide dye quenchers to suppress photooxidation [57].

3) *Inorganic Luminescent Species*: Core-shell QDs are expected to exhibit good photostability due to their inorganic nature and passivation of the QD cores with shells of higher bandgap material, for example, a cadmium selenide (CdS) core surrounded by a zinc sulfide (ZnS) shell [58]. However, this improved stability has not been observed in practice [59], and this has prompted the development of multishell QDs. Multishell QDs gradually change from the lower bandgap core to the higher bandgap shell material, reducing the strain of lattice mismatches, and therefore, preventing the formation of defect sites. This increases FQY and has been found to improve stability [60]. When high-FQY multishell QDs become commercially available, they will be excellent candidates for LSC devices.

IV. MATRIX MATERIALS

A. Escape Cone Losses

Total internal reflection will occur in a medium with refractive index n when light strikes the matrix to air boundary at angles greater than the critical angle. The critical angle θ_c is determined by

$$\theta_c = \sin^{-1} \left(\frac{1}{n} \right) \quad (1)$$

while the amount of light that will be totally internally reflected in an LSC plate (L) is given by

$$L = \frac{(n^2 - 1)^{1/2}}{n}. \quad (2)$$

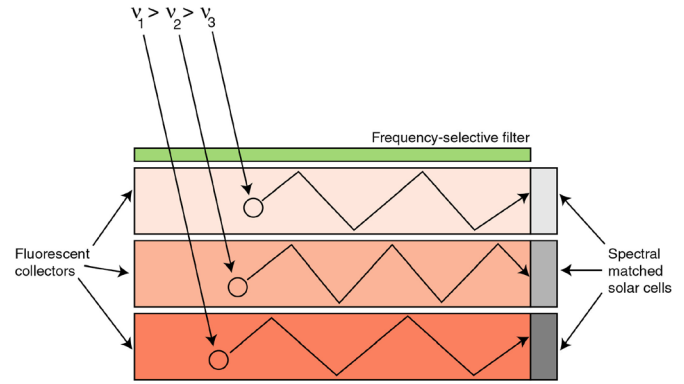


Fig. 3. Three-plate stacked LSC with spectrally matched solar cells and a frequency-selective filter.

For a material with $n = 1.5$, 74.5% of emitted light would be trapped inside the plate [4], leading to a significant loss of 25.5% of incident light.

1) *Frequency-Selective Filters*: Frequency-selective filters have been suggested as a means to prevent light from departing via the escape cone. Taking advantage of the emission red-shift, these layers act as spectrally selective reflectors allowing incident light of shorter wavelengths to be transmitted, while longer wavelength light is reflected. This allows for trapping of emission that would otherwise be lost through the escape cone [12], [26], [61].

Rau *et al.* [12] have demonstrated via ray-tracing simulations that a photonic bandpass filter is essential for LSCs to achieve their maximum possible efficiency. One-dimensional periodic dielectric structures were suggested as a means of fabricating such filters but reflection occurs in one direction only, filters that reflect in two or three directions are yet to be examined [12].

Advanced rugate filters and a three-dimensional photonic crystal, the opal, were compared with respect to their reflectance and angular dependence [62]. Rugate filters function best at perpendicular incidence, and are therefore, better suited to tracking systems while photonic crystals differ by showing low reflectance at polar angles close to 90°. Another advantage of photonic crystals is their ability to diffract light at higher angles, thereby reducing the number of reflections required before reaching the LSC edge [62].

Filters such as these are expensive and their angular dependence causes shifts in their reflective properties that can prevent necessary wavelengths of light from entering the device [26].

2) *Multiple Plates*: A stack of multiple plates containing different dyes can be used to recover light that is lost through the escape cone of upper plates. Stacking of the LSC plates doped with different dyes was first suggested by Goetzberger and Gruebel in 1977 [2]. This configuration also allows spectral matching of the LSC plates to different types of solar cell to optimize the output from each plate. A stacked LSC with a frequency-selective filter is shown in Fig. 3. Multiple plates such as these, separated by air gaps have been commercialized for daylighting applications [20], [63].

When stacked concentrators are being evaluated, it is important to determine whether the increase in cost is justified by an increase in efficiency [8]. Wittwer *et al.* [64] achieved

optical efficiencies of 15.8% for a three-stack system compared to 10% for a single-stack system [64]. Goetzberger [4] calculated theoretical efficiencies for stacked systems of one to four plates, each with a different solar cell attached. He calculated that a three-plate system with optimized solar cells attached had a theoretical efficiency of 23.3%. Adding a fourth plate with a germanium (Ge) cell attached led to a small increase in efficiency (23.7%), indicating that it would not be worth the extra cost [4].

A different configuration suggested by Friedman [8] is a multilayered thin-film LSC. This system consists of a thin-film dye layer sandwiched between two thin films of longer wavelength dye. These layers are then surrounded by two more layers of longer wavelength dye. This reduces ECL to the outer layers of the system while emission from the inner layers will be absorbed by the surrounding layers of longer wavelength dyes [8].

3) *Dye Alignment*: Alignment of dye molecules has been shown to cause an increase in the amount of light emitted at the edge of LSC plates by reducing the ECL [13]. Dye molecules were aligned on the surface of a clear PMMA waveguide in several orientations: isotropic, homeotropic, planar, and tilt-aligned using liquid crystals. A 15% increase in edge output was achieved using planar alignment of dyes compared to an isotropic sample [13]. Emission from the edge perpendicular to this alignment was 25% higher than the edge parallel. Homeotropic layers were found to reduce surface losses but did not improve output. The tilted layers are currently being investigated and have the potential to minimize reabsorption through the dye layer and maximize total internal reflection by controlling the orientation of the emitted light [13].

B. Host Matrix

Identification of the optimum host material for the chosen luminescent species is essential. As mentioned previously, the polymer used can have a significant effect on the samples FQY and stability. The host matrix should exhibit maximum transmission over a broad range of wavelengths and minimal scattering. PMMA is the most commonly used polymer; it is inexpensive, transparent, and stable [65]. Results by Cole [5] showed that PMMA remained stable under exposure to 17 years of desert sunlight.

One problem with polymers is the presence of C–H bond absorption at 750 nm [5]. When the energy gap of a luminescent species matches the vibrations of C–H or O–H bonds, non-radiative energy transfer by vibrational excitation can lead to quenching of luminescence [66]. The substitution of hydrogen with heavier elements such as deuterium (deuterated) or fluorine (fluorinated) decreases the vibrations of these bonds [67] and can lead to improved FQY.

The incorporation of organic dyes into sol–gel glasses was first introduced in 1984 [68], and more recently, they have been used to incorporate inorganic ions [69]. Sol–gel methods use low-temperature techniques to create solid glass in bulk or thin-film form [70]. Zirconia-based glass is mechanically and thermally stable and exhibits a high refractive index making it suitable for deposition onto glass substrates [71] and decreasing

the ECL. A hybrid material incorporating the properties of zirconium oxide mentioned earlier and the ease and flexibility of polymers was produced to incorporate a large range of dyes. This novel ORMOCER matrix and sol–gel glasses in general present a possible alternative to PMMA and other polymers [71].

A comparison of QD-doped matrix materials including PMMA, polyurethanes, and a nontoxic bio-resin found that a clear cast epoxy resin produced the most efficient samples. The epoxy sample produced 77.5% the efficiency of the QDs in toluene solution and maintained this efficiency over approximately six months [59]. Recently, a comparison of encapsulants for QDs found biphenyl-perfluorocyclobutyl polymer (BP-PFCB) to have no negative effect on the FQY of the QDs [72].

V. MEASUREMENT OF FLUORESCENCE QUANTUM YIELD

One of the most important characterization techniques for LSCs is measurement of the FQY of the luminescent species, as this is important in determining the overall efficiency of the module. Whatever measurement technique is chosen must be capable of measuring the dyes in the host material of the LSC (bulk or thin films). Two main techniques currently used involve the use of an integrating sphere [73]–[76] or a thermal lens system [67], [77]–[79]. Both these techniques will be described briefly, and then critically evaluated.

A. Integrating Sphere

An integrating sphere equipped with a variable-wavelength excitation source (such as a Xenon lamp and monochromator) can be used to measure FQY. Either a photodiode [74] or a spectrofluorometer [73], [75], [76] can be used as a detector. The detector can measure both the amount of light absorbed by the dye-doped sample and the amount of light emitted by the sample as fluorescence. A simple calculation [73], [75] enables the FQY of the sample to be determined.

The integrating sphere method is limited by the need for accurate calibration of the throughput of the sphere and the response of the detector. Generally, a fluorescence standard with known FQY and fluorescence spectrum is needed for calibration. Such standards are difficult to make repeatably, which limits the accuracy of this technique to around 10% [73], [75], [76], although some groups claim accuracies approaching 2% [80]–[82]. Reabsorption by the sample of the fluorescence light in the sphere can affect the obtained value of quantum yield, especially when the sample has a large surface area and small Stokes shift. However, it is possible to correct somewhat for this by making a separate measurement of fluorescence with the sample placed outside the sphere but still in the path of the excitation beam [81].

B. Thermal Lens

An alternate technique, which does not rely on a fluorescence standard, instead involves measuring the amount of light energy absorbed by the sample that is turned into heat instead of fluorescence. Since this is a calorimetric measurement, a fluorescent reference sample with known FQY is no longer required and it

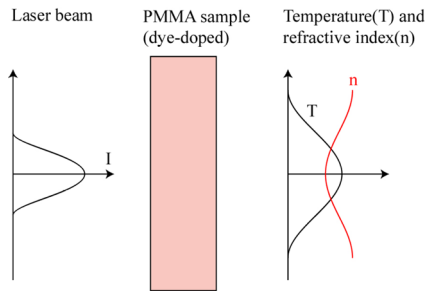


Fig. 4. Temperature and refractive index profiles in irradiated sample.

is possible to calculate the FQY of a sample by comparison with a nonfluorescent (FQY = 0%) reference standard.

The origin of the thermal lens technique dates back to the 1960s [67] [83]; however, Hu and Whinnery [32] were the first to point out that the formation of the thermal lens could be used to calculate the FQY of a sample containing fluorescent dye molecules. The technique has been used since then to measure the FQY of samples in both solid [77], [84]–[87] and liquid [78], [88]–[91] form. The advantages and limitations of the thermal lens technique are discussed in [92]–[94]. Several excellent reviews cover many aspects of thermal lens measurement methods including the experimental instrumentation and data analysis. The thermal lens technique is ideally suited for the LSC analysis because it can measure the FQY of the dye when it is actually in the LSC sheet.

When a Gaussian laser beam (the *pump beam*) of such a wavelength that it is absorbed by the dye molecules passes through an LSC sheet doped with a fluorescent dye, varying amounts of heat are deposited in the LSC host material at points across the laser beam front. An equilibrium temperature distribution will eventually be reached, and since the refractive index of most materials depends on temperature (dn/dT for PMMA is $1.1 \times 10^{-4} \text{ K}^{-1}$), a refractive index gradient forms inside the sheet (Fig. 5). This acts on the laser beam in much the same way as a conventional lens, giving rise to the term “thermal lens.” The rate of formation of the thermal lens, which is an indication of the amount of heat deposited in the sample, can be measured by recording the time decay of the on-axis intensity of the pump beam in the far-field.

From a fit of a theoretical equation to this intensity time-decay [77], a thermal lens (TL) coefficient θ can be determined that is related to the amount of heat deposited in the sample.

For highly absorbing samples, where little of the pump laser is transmitted, a probe laser (of such a wavelength that it is not absorbed by the dye) can be passed through the thermal lens to monitor its formation.

The FQY is calculated from the TL coefficients of both the fluorescent sample and the nonfluorescent reference [78], [88]–[91], see (3):

$$\text{LQE} = \frac{\nu_{\text{ex}}}{\langle \nu_{\text{em}} \rangle} \left(1 - \frac{A_{\text{p}}^{\text{ref}} \theta_{\text{sample}}}{A_{\text{p}}^{\text{sample}} \theta_{\text{ref}}} \right) \quad (3)$$

where $A_{\text{p}}^{\text{ref}}$ and $A_{\text{p}}^{\text{sample}}$ are the fractional absorbances of the nonfluorescent reference and fluorescent sample, respectively.

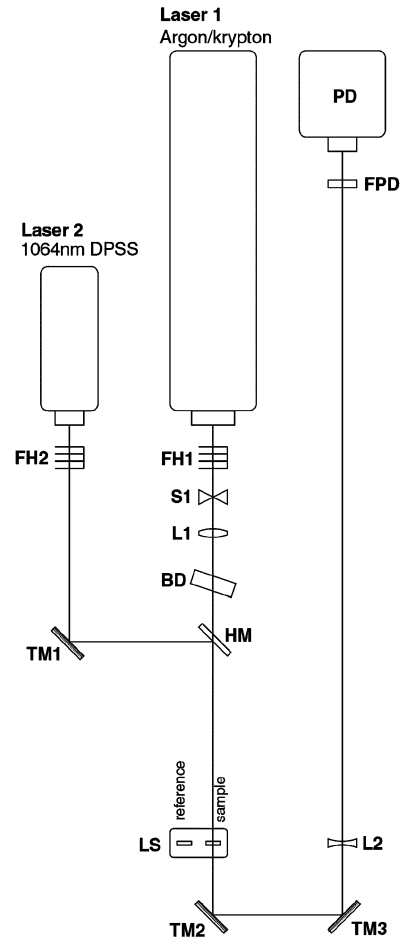


Fig. 5. Thermal lens system. FH1, FH2: filter holders; S1: shutter; L1: convex lens; BD: beam displacer; HM: hot mirror; LS: linear slide for sample & reference; L2: concave lens; FPD: photodiode filter; PD: photodiode; TM1, TM2, TM3: turning mirrors.

The ratio $\nu_{\text{ex}}/\langle \nu_{\text{em}} \rangle$ accounts for the heat generated by the Stokes shift in the fluorescence emission. For example, a dye with 100% FQY would still deposit some heat into the PMMA host because of the lower energy of the emitted photons.

A multiwavelength thermal lens system has been developed at Heriot-Watt University; it uses an argon/krypton ion laser as a pump and a diode-pumped solid-state Nd:YAG laser as the probe. Preliminary results on the BASF Lumogen F dyes confirm their high quantum efficiencies (>92%), and thus, their suitability for solar concentrators. The Lumogen Orange 240 dye was measured to have an efficiency of 100% with an error of $\pm 2\%$ over 10 repeated readings.

The thermal lens technique has a major advantage over the integrating sphere method in that it samples an extremely small area of the sample (no more than the diameter of the pump beam that may be only 0.5 mm). The effect of self-absorption over this distance scale is negligible, especially when working with high quantum efficiency dyes.

VI. CONCLUSION

The challenges in LSC development have been highlighted and various means to overcome them have been discussed.

One promising concept is the multidye thin-film device described earlier. It minimizes reabsorption and ECL losses and utilizes a broad section of the solar spectrum. Production costs are low compared to a stacked concentrator since all dyes are encapsulated into a single thin film. The luminescent species used in such a device should be chosen to maximize the absorption range while producing an efficient FRET network, they should also be soluble at high concentrations.

NIR emitting QDs could present excellent candidates for LSCs in the future when improvements lead to high FQY and long-term stability. The possibility of achieving multiple exciton generation is very promising.

It is unlikely that a solution will be provided by one single organic or inorganic material at this point in time, integration of the positive characteristics of each into a hybrid material or device could be necessary. NIR-emitting lanthanide complexes are one example of this, coupling the high absorption coefficients of organic dyes with the stability and efficient emission of RE materials.

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Brenda C. Rowan was born in Sligo, Ireland, in 1979. She received the B.Sc. degree in earth science from the National University of Ireland, Galway, Ireland, in 2001, and the Ph.D. degree in physics from the Dublin Institute of Technology, Dublin, Ireland, in 2007.

She is currently a Research Associate in the School of Engineering and Physical Sciences at Heriot-Watt University, Edinburgh, U.K. Her current research interests include photovoltaics, solar concentrator development, luminescent materials, and nanotechnology.

Dr. Rowan has been a member of the International Solar Energy Society since 2006 and was involved in the re-establishment of the Solar Energy Society of Ireland in 2007, serving a vice president of membership affairs for one year.



Lindsay R. Wilson was born in Edinburgh, U.K., in 1988. He received the B.Sc. degree (with first class) in physics from the University of Strathclyde, Strathclyde, U.K., in 2005. He is currently working toward the Ph.D. degree in the School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, U.K.

His current research interests include the field of luminescent solar concentrators.



Bryce S. Richards (M'00) received the B.Sc. degree in physics from Victoria University of Wellington, Wellington, New Zealand, in 1994, and the M.E.S. and Ph.D. degrees in photovoltaic engineering from the University of New South Wales, Sydney, Australia, in 1998 and 2002, respectively.

During 1995, he was a Visiting Scientist at Max Planck-Institut für Festkörperforschung, Stuttgart, Germany. In 2002, he was a Postdoctoral Fellow and a Lecturer at the University of New South Wales, Sydney, and then, at the Australian National University, Canberra, Australia. He is currently a Reader at Heriot-Watt University, Edinburgh, U.K., where he is engaged in investigations into the optical and electronic properties of dielectric thin films, the application of luminescent materials to photovoltaics, and the development of renewable energy powered desalination systems. He is currently the Managing Editor of the *Progress in Photovoltaics*. He is the author or coauthor of more than 35 articles published in international journals, and two book chapters, and 52 conference papers.