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Title:

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Date:

2017-04-01

Citation:

Breukers, R. D., Smith, G. J., Stirrat, H. L., Swanson, A. J., Smith, T. A., Higgino, K. P. G., Raymond, S. G., Winch, N. M., Clarke, D. J. & Kay, A. J. (2017). Light losses from scattering in luminescent solar concentrator waveguides. *Applied Optics*, 56 (10), pp.2630-2635.
<https://doi.org/10.1364/AO.56.002630>.

Persistent Link:

<https://hdl.handle.net/11343/345180>

ACCEPTED MANUSCRIPT

PUBLISHED IN APPLIED OPTICS, VOLUME 56, ISSUE 10, pp 2630-2635 (2017)

<https://doi.org/10.1364/AO.56.002630>

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Light losses from scattering in luminescent solar concentrator waveguides,

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Received XX Month XXXX; revised XX Month, XXXX; accepted XX Month XXXX; posted XX Month XXXX (Doc. ID XXXXX); published XX Month XXXX

The reductions in the transmission of emission originating from a fluorophore dissolved in a polymer matrix due to light scattering were compared in two forms of planar waveguides used as luminescent solar concentrators; a thin film of poly(methylmethacrylate) spin-coated on a glass plate and a solid poly(methylmethacrylate) plate of the same dimensions. The losses attributable to light scattering encountered in the waveguide consisting of the thin film of polymer coated on a glass plate were not detectable within experimental uncertainty whereas the losses in the solid polymer plate were significant. The losses in the solid plate are interpreted as arising from light-scattering centres comprising minute bubbles of vapour/gas, incomplete polymerization or water clusters that are introduced during or after the thermally-induced polymerization process.

OCIS codes:

<http://dx.doi.org>

1. Introduction

Organic compounds with high fluorescence quantum yields such as perylene-based fluorophores have attracted interest as a means of “harvesting” sunlight incident over a wide surface area [1-5]. In this application, a widely-used design involves a fluorophore dissolved in a suitable polymer coated on a planar waveguide. This polymer film collects/ absorbs solar energy over the surface of the waveguide and the fluorescence it emits is conveyed by total internal reflection to the thin edges of the waveguide where photovoltaic cells are located. In a variant on this approach, with commercial/practical potential, dispersing the fluorophores in a plate of the solid polymer matrix could be deployed as the windows and/or cladding panels on the facade of buildings [4]. Fluorophores in such systems result in an increase in the number of photons per unit area incident on the active surface of the photovoltaic cells. These devices are known as “luminescent solar concentrators”, LSCs [4,6], and in this regard, they mimic the light-harvesting molecular apparatus in photosynthesis that effectively concentrates the spatially diffuse solar energy reaching the earth’s surface. Such an approach to the concentration of solar energy is less expensive and requires less maintenance than the alternative of deploying arrays of mirrors that focus sunlight on an energy converter. They also operate well in collecting diffuse solar radiation on non-

horizontal surfaces where the performance of conventional photovoltaic cells is less effective than when they are under direct light and normal to the insolation [7,8].

However, LSCs are subject to a number of losses that contribute to a reduction in the efficiency of conversion of solar to electrical energy. These have been previously identified as the light emitted at angles less than the critical angle for total internal reflection that escapes the waveguide, reabsorption or scattering of light within the waveguide and fluorescence quenching resulting in a low intrinsic fluorescence quantum yield [6].

To improve the performance of luminescent solar concentrator devices, many organic fluorophores have been photophysically characterised in a variety of molecular environments to optimise their fluorescence quantum yields, broaden the wavelength range over which they absorb solar energy and minimise energy wastage by non-radiative relaxation, fluorescence self-absorption and quenching [2,5,6,9-18]. Efforts have been made to reduce the losses associated with self-absorption of emitted fluorescence directed at diminishing the overlap of the absorption and fluorescence spectra. In this regard, a number of luminescent semiconductor quantum dots/ nanocrystals have been also investigated [19,20].

A related loss of light encountered as a result of fluorescence travelling through the waveguide to the edge of the plate is light scattering by the waveguide material/s. In the research described in this report the light scattering occurring in a polymer-coated glass

waveguide was compared with that in a solid polymer waveguide of the same dimensions. This was accomplished by doping the polymer film/matrix with a fluorophore to serve as an internal light source. The fluorophore chosen for this study was Lumogen Red 305, LR 305, which has been studied previously as a highly fluorescent organic compound for use in LSC devices [6,21,22]. Although it is subject to self-quenching at the high concentrations used in thin polymer films coated on glass waveguide systems examined in this study [23], its fluorescence yield was sufficient to allow measurement of light scattering losses in the waveguide.

2. Experimental details

Materials

All solvents used were of HPLC or spectroscopic grade supplied by Sigma - Aldrich and were used without further purification. The poly(methylmethacrylate), PMMA, supplied by Aldrich had an average MW of $\sim 350,000$. The perylene diimide derivative with four phenoxy substituent groups attached to the core perylene moiety, LR 305, with the structure shown in Fig. 1 was supplied by Kremer Pigmente (as 94720 Fluoreszenzrot) and used without further purification.

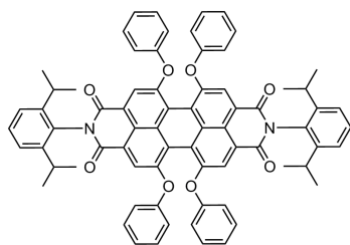


Fig. 1. Structure of perylene-based, Lumogen Red 305, LR 305.

Solutions of the PMMA in 1,1,2-trichloroethane, TCE, at a concentration of 2 g/10 ml (14% w/w) and containing the different concentrations of LR 305 were prepared and passed through a 0.45 μm Millipore filter to remove particulates before spin-coating on clean 25 x 25 x 1 mm glass plates at 1250 rpm for 12 seconds. The spun films and substrates were then dried in a vacuum oven at 80°C for at least 48 hours to ensure all traces of solvent had been removed. The thickness (8 μm) and refractive index (1.498) of these PMMA films, as well as the refractive index of the glass plate substrates (1.52), were measured using a Metricon 2010M at 633 nm.

The other type of waveguide studied in this work was in the form of 1 mm thick plates (25 X 25 mm) of solid PMMA containing the fluorophore at a concentration to give an absorbance (transverse) of ~ 0.3 . These waveguides were fabricated by dissolving the fluorophore in methylmethacrylate monomer and polymerizing the solution in a 1 mm thick (internal dimension) mould consisting of two parallel glass plates separated by a silicone gasket for 72 hours at 50°C using 1% w/w azoisobutyronitrile, AIBN, supplied by Aldrich as the thermal initiator. To facilitate removal of the solid PMMA plates after the polymerization is completed, the internal surfaces of the glass mould were sprayed with silicone prior to the introduction of the fluid solution of fluorophore in methylmethacrylate monomer.

Light scattering losses

The decrease in fluorescence intensity encountered as a result of light scattering within the two forms of waveguide described above were determined in the following way.

Light with a wavelength of 514 nm emitted by a Melles Griot 43 Series argon ion laser with a Gaussian beam profile and a diameter of 1.5 mm was used to excite the LR 305 fluorescence within the

waveguides. The 514 nm light was conveyed via a 400 μm silica fibre optic and microscope objective lens and directed downwards onto the top surface of the waveguide normal to the plane of the waveguide. This optical assembly for the excitation was held by an XY micro-positioning translational stage that allowed positioning of the excitation light beam at 2 mm intervals across the waveguide along the axis of the detection optics aligned at right angles to the front edge of the waveguide at its midpoint as shown in Fig. 2. The fluorescence emerging from this edge was coupled to a 1 mm diameter polymer optical fibre in contact with the front edge using glycerol as a refractive index matching fluid and the intensity and relative spectral distribution was recorded using a Avanter spectrophotometer (AvaSpec – 2048L).

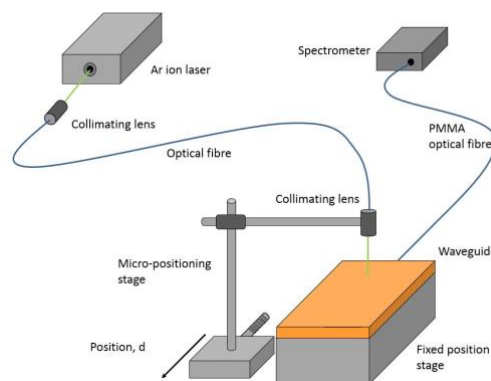


Fig. 2. Schematic diagram of the experimental assembly for determining the decrease in fluorescence intensity and spectral shape resulting from light scattering and self-absorption as a function of light pathlength through the waveguides.

Absorption and steady state fluorescence spectra

The absorption spectra were recorded using a Shimadzu UV-2100 double beam or a Perkin Elmer Lambda 1050 UV-Visible absorption spectrophotometer. The fluorescence spectra were recorded with a Horiba Jobin Yvon Fluorolog3 spectrofluorometer.

The spectra of the total fluorescence emitted in all directions by the thin films on 25 x 25 x 1 mm glass plates were determined by positioning the plate at the centre of a 10cm diameter Labsphere integrating sphere with a central holder for the spin-coated glass plates made from Spectralon, which has > 99% reflectance over the wavelength range 400 – 1500 nm. The coated plates were oriented at an angle of 22.5° to the excitation beam and 112.5° to the detection port to avoid specular reflections into the emission detection optics. The fluorescence spectra recorded inside the integrating sphere are distorted at shorter wavelengths by self-absorption by the fluorophore. The spectrum of the fluorescence of LR 305 not affected by self-absorption was also recorded using front-face excitation (without the integrating sphere) with the coated surface positioned normal to the excitation beam and collecting emission at an angle of 18 degrees to the front surface.

The fluorescence decay profiles were acquired using the time correlated single photon counting method inducing the fluorescence with the output of a frequency doubled, mode-locked and cavity dumped titanium: sapphire laser (Mira 900f/APE PulseSwitch) operating at 400 nm, with a pulse duration of ~ 120 fs at 5.4 MHz. Fluorescence decay times were determined by analysis of the decay profiles by iterative reconvolution methods (FAST, Edinburgh Instruments).

The losses due to fluorescence self-absorption in thin polymer films integrated over the entire fluorescence spectrum that are evident as a diminution in the fluorescence intensities at shorter wavelengths in the

fluorescence spectrum (absorption-fluorescence spectral overlap region) were evaluated using the method described by Bradshaw et al. [19]. This involves calculating the probability, $R(l)$, of an emitted photon being reabsorbed over a reduced pathlength, $l = L \cdot OD/t$ (where t is the film thickness) from [24]:

$$R(l) = \int F_n(\lambda) [1 - 10^{-A_n(\lambda)l}] d\lambda$$

where, $F_n(\lambda)$ and $A_n(\lambda)$ are the fluorescence and absorption spectral distributions normalised by the area of the fluorescence spectrum and at the maximum of the longest wavelength absorption band.

3. Results and discussion

Fluorescence emitted within a planar waveguide follows a random walk and the rays have been traced using a Monte Carlo simulation [8,20,25]. These rays are subject to total internal reflection when they are incident on the waveguide – air interface at an angle greater than the critical angle [6]. The light is attenuated by two mechanisms as it passes through the waveguide. Both types of attenuation result in an exponential reduction in transmitted intensity with increasing lateral pathlength, i.e. self-absorption by the fluorophore (Beer's law) and light scattering by small localized centres of refractive index discontinuity [26]. Self-absorption is evident as a distortion of the fluorescence spectrum of the fluorophore as shown in Fig. 3 for LR 305 dispersed in a PMMA film spin-coated on a 1mm thick glass substrate. The front-face fluorescence recorded without an integrating sphere (i.e. no self-absorption) is overlaid with the total fluorescence emitted in all directions from the waveguide determined with an integrating sphere and scaled to match the longer wavelength section of the front-face fluorescence spectrum beyond the absorption spectrum of LR 305 where there is no self-absorption at wavelengths longer than ~ 640 nm.

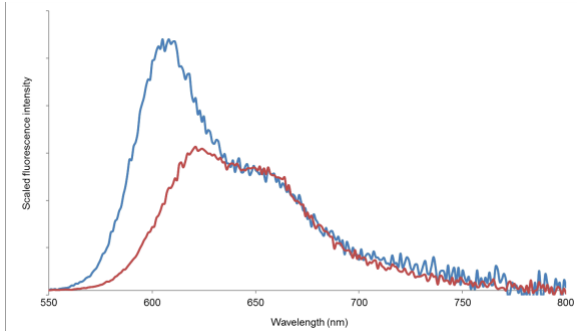


Fig. 3. Fluorescence spectrum of LR 305 dispersed in a thin PMMA film coated on a glass plate showing the effect of fluorescence self-absorption. The blue line is the spectrum of the fluorescence recorded from the front-face with no integrating sphere and negligible self-absorption. The red line is the spectrum of fluorescence emitted in all directions from the coated planar waveguide recorded using an integrating sphere and scaled to match the long wavelength front-face emission where there is no self-absorption.

Fluorescence self-absorption and scattering

Using the method proposed by Bradshaw et al. [19] and outlined in the Experimental section, the probability of an emitted photon of fluorescence being reabsorbed by passage through LR 305 fluorophores dispersed in a thin film of PMMA spin-coated on a glass substrate as a function of reduced pathlength was calculated and is shown in Fig. 4. However, this takes no account of light scattering encountered in passage through the waveguide material; in this case a PMMA film on glass. The change in shape of the fluorescence spectrum

resulting from self-absorption observed at the front edge of the waveguide plate as a function of distance from the point of excitation of fluorescence to the point of exit from the mid-point of the front edge of the waveguide plate is shown in Fig. 5 for a PMMA film spin-coated on a glass plate and for solid PMMA matrix respectively. Similar changes in the spectral distribution of the fluorescence emerging from a solid PMMA waveguide were observed (results not shown). It is apparent from Fig. 3 that LR 305 fluorescence at wavelengths longer than ~ 640 nm is not subject to self-absorption and any attenuation in intensity is therefore attributable solely to light scattering within the waveguide material/s.

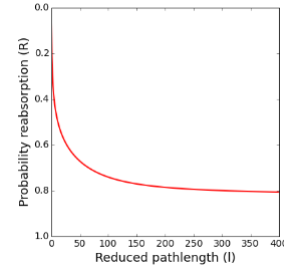


Fig. 4. The probability of fluorescence self-absorption by LR 305 dispersed in a thin film of PMMA on a glass plate as a function of "reduced" pathlength.

The extinction of light by scattering is given by equation 1

$$I/I_0 = \exp(-\alpha d) \quad (1)$$

where d is the pathlength, α is the linear scattering coefficient, I is the transmitted irradiance and I_0 is initial irradiance. With the experimental arrangement used in this work, depicted in Fig. 2, the irradiance of fluorescence, I_e , exiting over a small segment of the front edge is given by

$$I_e = 1/2\pi d \cdot I_0 \exp(-\alpha d)$$

hence

$$I_e d = 1/2\pi \cdot I_0 \exp(-\alpha d) \quad (2)$$

This assumes an isotropic radial 2-dimensional distribution of fluorescence emanating from the point of excitation and no contribution from total internal reflections from the side edges of the waveguide.

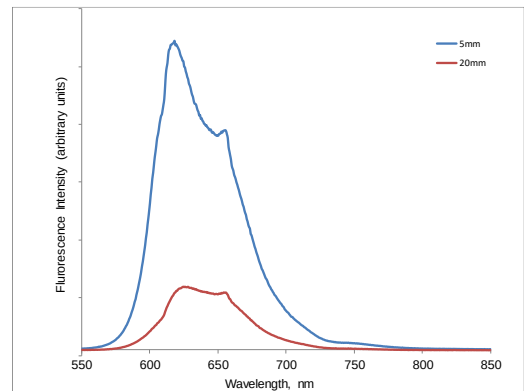


Fig. 5. The variation in fluorescence spectra resulting from self-absorption by passage through 5 mm (blue) and 20 mm (red) pathlengths of a thin film of PMMA on a glass plate (total thickness of 1 mm)

The dependence of the product of the irradiance, I_e , at 640 nm and the pathlength, d , on d , given by equation (2) from the point of excitation to the point of exit of the fluorescence from the front edge of

the waveguide plates is shown in Figs. 6 (a) and (b) for the PMMA film spin-coated on glass and for the solid PMMA matrix respectively. Within experimental error, there are no apparent losses of fluorescence intensity at 640 nm due to light scattering in the waveguide consisting of a thin film of spin-coated PMMA on a glass substrate, as shown in Fig. 6 (a). By contrast, there is an exponential attenuation of the long wavelength fluorescence with distance in the 1 mm thick planar PMMA waveguide made by thermally-initiated polymerization of the monomer using the method outlined in the Experimental section (attenuation coefficient 0.1 mm^{-1}) as shown in Fig. 6 (b).

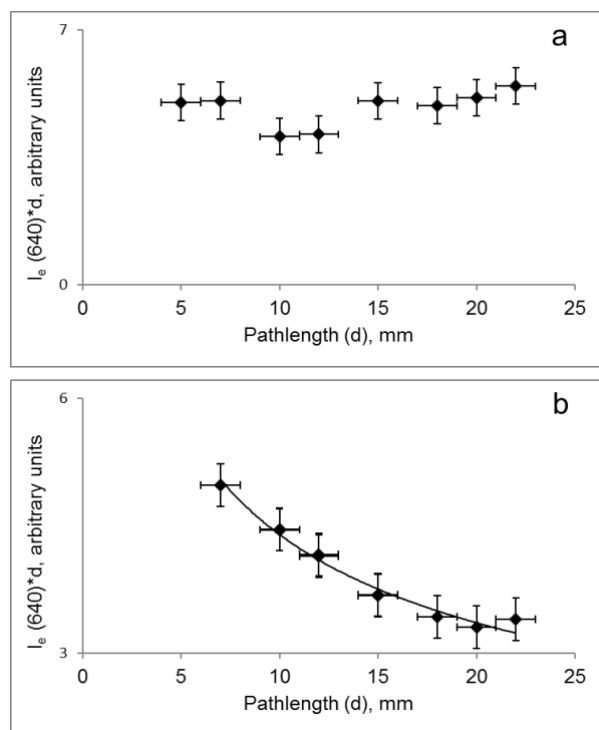


Fig. 6. The dependence of the product of the fluorescence intensity, I_e , at 640 nm and the pathlength through the waveguide, d , on d for (a) a thin film of PMMA on a glass plate (total thickness 1 mm) and, (b) a 1 mm thick solid PMMA plate of the same dimensions.

Light scattering arises from small particles (or voids) within a medium that have different refractive indices from that of the surrounding medium. As well as depending on the ratio of the refractive indices of the medium and the particles or voids, light scattering also depends on the size and shape of the scattering centres. Small centres with dimensions < 0.1 of the wavelength of scattered light exhibit Rayleigh scattering while larger centres with dimensions comparable to the wavelength of light exhibit scattering with a complex periodic (damped sinusoidal) dependence on the ratio of the size of the particle and the wavelength of light [26]. Light scattering centres in solid polymer matrices are often caused by minute bubbles liberated by volatile impurities in the monomer or dissolved gasses released as the monomer polymerizes/solidifies with concomitant decreases in the solubilities of the dissolved gasses. Residual monomer and/or incomplete polymerization products can also act as scattering centres [27]. PMMA absorbs significant amounts of water depending on the ambient relative humidity and it has been found that this water undergoes molecular association in a hydrophobic polymer matrix such as PMMA to form water clusters capable of Rayleigh scattering [28].

Fluorescence attenuation, excimer formation and self-quenching

The attenuation of fluorescence intensity exiting the front edge of the waveguide due to light scattering was substantially less in the case of the thin film of LR 305 coated on a glass substrate because the light being transmitted through the waveguide travels principally through the non-scattering glass substrate. However, the effect of the fluorescence yield of the fluorophore used in LSCs needs to be considered to assess the overall performance of the LSC device. Even with high absorption coefficients, many organic fluorophores, when dispersed in thin ($\sim 10\text{--}50 \text{ }\mu\text{m}$) polymer films coated on glass waveguides, require very high concentrations to achieve absorption of a high fraction of the incident light over such short pathlengths. The problem is exemplified by planar aromatic fluorophores such as those based on perylene that have a propensity to form π -stacked aggregates and excimers [29–32] at high concentrations. This behaviour substantially reduces the fluorescence yield because of the relatively low quantum yield of these excimers as exemplified by an end-substituted perylene diimide compound, N' -(di-2,5-tert-butylphenyl)- N -(4-tert-butylphenyl), perylene diimide [25] or by concentration (self-)quenching. Such ground state aggregation and excimer formation are apparent as changes to the positions and profiles of the absorption and fluorescence spectra respectively. In this work, the absorption and fluorescence spectra observed for LR 305 spin-coated films in PMMA at concentrations up to $20 \times 10^{-3} \text{ mol dm}^{-3}$ were identical to those of the monomer spectra as was found in the previous research of Al-Kaysi et al. [23]. They reported that the fluorescence spectrum of LR 305 in thin films with concentrations up to $100 \times 10^{-3} \text{ mol dm}^{-3}$ corresponded to that of the monomer. Further, in this concentration range, the fluorescence decay kinetics was adequately described by a single exponential with a lifetime only slightly shorter than that of the monomer at low concentrations [23]. Similarly, the average fluorescence lifetime we determined at a concentration of $20 \times 10^{-3} \text{ mol dm}^{-3}$ was 6.17 ns with more than 90% of the decay described by a single exponential. This is similar to the lifetime of 5.7 ns reported previously for a $1 \times 10^{-3} \text{ mol dm}^{-3}$ solution of LR 305 in a solid PMMA matrix [23]. Al-Kaysi et al. recognise that in the very high concentration regime, LR 305 could be subject to some self-quenching. Specifically, in “neat” films ($\sim 1 \text{ mol dm}^{-3}$) they found that the fluorescence decay exhibits 64% of a component with a lifetime 50 times shorter than that of the monomer and the other component, an order of magnitude shorter (0.41 ns) [23]. However, in the present work, at a concentration of $20 \times 10^{-3} \text{ mol dm}^{-3}$, no sub-nanosecond decay component could be discerned to the temporal resolution of $\sim 120 \text{ ps}$ of our lifetime measurement system. This indicates there is little or no concentration self-quenching in this time domain. Al-Kaysi et al. also reported the fluorescence depolarization kinetics of a related fluorophore at a concentration of $100 \times 10^{-3} \text{ mol dm}^{-3}$ demonstrating the existence of facile electronic energy transfer between the fluorophores [23].

Conclusion

If the waveguide for an LSC is to be in the form of fluorophores dispersed in a plate of solid polymer, the present work highlights the merit of refinements to the polymerization procedure to minimize the formation of pores, voids and the ingress of water into the polymer matrix that act as light scattering centres. For example, the “modified cell-casting bulk polymerization” described by Meinardi et al. [20] may prove beneficial.

Although the fluorescence associated with a spin-coated film of a fluorophore in PMMA on a glass waveguide experiences lower losses associated with light scattering, there is however, the potential for a reduction in the efficiency of conveying light to photovoltaic cells

located at the edges of the LSC waveguide. This is a result of self-quenching resulting from the high concentrations of fluorophores required to achieve absorption of a high fraction of the incident light over a short pathlength. To minimize reductions in fluorescence yields resulting from excimer formation or self-quenching, various refinements to the structure of the fluorophore and/or refinements to the spin-coating procedure may be of value. For example, Al-Kaysi et al's procedure of "locking" in place a homogeneous distribution of fluorophores by cooling the film immediately after spin-coating prior to removal of the solvent carrier under vacuum at low temperature [23] may be a viable approach. Another useful strategy for reducing the frequency of close, nearest-neighbour encounters or contacts between the fluorophores (molecular aggregation) may be to replace the phenoxy groups substituted on the perylene core of LR 305 with more bulky substituents.

Funding Information. Ministry for Business, Innovation and Employment (New Zealand) VICX1202

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