High-efficiency dyes for Luminescent Solar Concentrators – photostability and modelling

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ABSTRACT: In luminescent solar concentrators, photostability of the luminescent dyes is a major factor in their development. Here, photostability measurements on the BASF Lumogen F series of visible fluorescent dyes are presented. All exhibit degradation, with Violett 570 degrading most and Rot 305 the least. Ray-tracing simulations indicate the optimum dye mixture contains Rot 305 and Violett 570 dyes alone. A 10cm x 10cm x 3mm LSC module is constructed and its efficiency measured at 2.4% under a simulated AM1.5g solar spectrum.
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1 INTRODUCTION

Luminescent solar concentrators (LSCs)[1-4] provide a means of reducing the silicon requirements for an electricity-generating solar panel. Although the principle was demonstrated more than 30 years ago, development has been hindered by the poor quantum yield and photostability of the fluorescent dyes used in the concentrator sheet. A range of visible fluorescent dyes (Lumogen F) has been developed by BASF specifically for LSC use [5]. The five dyes cover a wide range of absorption and emission wavelengths and have high quantum yields. Here, the photostabilty properties of the range of dyes are studied and the results of ray-tracing simulations to determine the optimum dye mixture are presented.

2 DYE PROPERTIES

The optical properties of the Lumogen dyes (absorption spectrum, emission spectrum and quantum yield) have been extensively studied previously[5, 6]. They all exhibit high (>95%) quantum yield and have wide absorption spectra, making it possible to absorb all of the solar radiation from 300-600nm using either one or a combination of the dyes. Some of the dyes can be used at high (~1000ppm) concentrations without quenching occurring[6]. The properties are summarised in Table 1 below for reference. Although these dyes certainly have the desirable optical properties for an LSC, they must also obviously survive many years' exposure to solar radiation, in particular UV. Photostability testing has been conducted and some preliminary results will be presented.

Table 1: Summary of Lumogen F dye properties[6]

Dye	Peak abs. λ (nm)	Peak abs. coeff. (ppm^{-1} cm^{-1})	Peak em. λ (nm)	Ave. em. λ (nm)	FQY(%) (±2%)
Violett 570	376	0.1125	425	434	~100
Gelb 083	475	0.2395	483	513	~96
Gelb 170	502	0.1981	516	551	~98
Orange 240	527	0.2291	534	561	~100
Rot 305	574	0.1024	597	622	~100

3 PHOTOSTABILITY

Samples of each of the five Lumogen dyes in PMMA were illuminated in a QUV exposure machine (Lucite International) for periods of up to five weeks. This machine not only illuminates the samples with UV light but also exposes them to heat and humidity. The exposure cycle consisted of 4 hours UV exposure at 50°C with no humidity) and then 4 hours in darkness at 50°C with a water spray. The irradiance at the samples is around 0.74W/m^2 at 340nm. The samples were, on average, around 3.5mm thick, with some variation due to non-uniformities in the larger sheets from which they were cut. It is important to note that none of the samples contained UV stabiliser, as this made absorption measurements of the violet dye impossible because of the UV stabiliser absorption.

The absorption spectrum of each of the samples was measured at each exposure time. To gain an understanding of the relative stability of the dyes, the peak absorption coefficient was used. Fig. 1 shows how the peak absorption coefficient for each of the dyes changes as the exposure time is increased. The absorption coefficients of each sample have been normalised to 100% at zero exposure time. The graph then shows the relative percentage change in absorption coefficient.

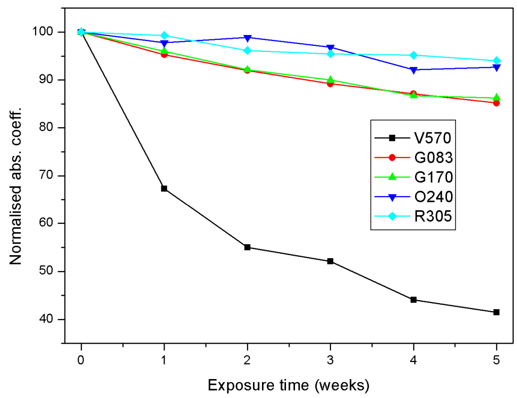

Fig. 1: Normalised absorption coefficient vs. exposure time

The worst-performing dye is clearly Violett 570, showing almost a halving in absorption coefficient after only 2 weeks' exposure. These samples, which normally appear clear, turned visibly brown after only 1 week. The exponential decrease in absorption coefficient is expected – as the dye degrades, less UV is absorbed by the dye and hence the rate of degradation will decrease. The two best dyes, are Orange 240 and Rot 305. However, while the peak absorption of Orange 240 may not decrease appreciably, additional absorption peaks appear at longer wavelengths as the dye degrades. These are shown (magnified) in Fig. 2.

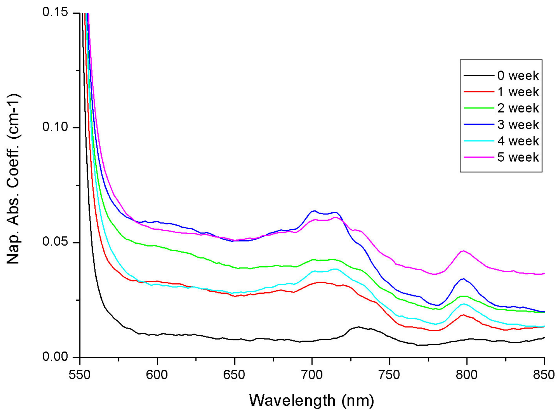

Fig. 2: Increasing long-wavelength absorption of orange dye

Before exposure, absorption stops at around 600nm. However, as the dye is degraded, the absorption in the region 600-850nm increases. The absorption here must be from the breakdown products of the orange dye, as no such increase in absorption at this wavelength was observed with clear PMMA. This increased absorption will have a detrimental effect on LSC performance as not only is there less orange dye present to absorb light but the breakdown products will actually absorb the orange fluorescence emission. Since it is highly unlikely that the breakdown products are also fluorescent, this will result in a reduction in overall efficiency.

By contrast, the Rot 305 dye shows no such increased absorption at longer wavelengths. This, combined with its large absorption bandwidth, makes it the best candidate for LSC applications. By simply increasing the concentration of the red dye alone, we can avoid the need for other dyes in the mixture to “fill in” the absorption spectrum.

It should be pointed out that the above photostability results for the single dyes will only apply when the dyes exist on their own. If there is more than one dye in the same sample, the results may be different. For example, in a mixture containing both the violet and the red dye, the violet dye will not degrade as quickly because the red dye has good absorption in the UV region 300-350 and this will “protect” the violet dye, preventing its degradation.

We might conclude from this that the optimum combination of dyes would be a high concentration of red (to achieve good absorption over most of the visible spectrum) and a lower concentration of violet (to “fill in” the region 350-400nm where the red absorption is poor). As is turns out, this is confirmed by simulation results which will be presented next.

4 RAY-TRACING SIMULATION RESULTS

A Monte-Carlo ray-tracing simulator[7] has been developed in-house specifically for modelling luminescent solar concentrators. Both single dyes and mixtures of dyes in the PMMA sheet are catered for. The model can calculate the overall solar-to-electric efficiency of an LSC module. Simulations were run on all possible combinations of the five dyes in concentrations up to and including an optical density of 12 (around 390 different combinations). The module efficiency was calculated for each combination and the results then sorted in order of decreasing efficiency to determine which dye mixture was best. The dimensions of the LSC were 20cm square and 3mm thick. Multicrystalline silicon cells were simulated attached to the edges of the sheet, as data for the laser-grooved back-contact (LGBC) cells used in the module were not available at that time. With 100,000 rays, the error in calculated cell efficiency is ±0.02%. As might be expected, the best dye mixture was that containing a high concentration of red (OD ~9) and a low concentration of violet (OD ~2), giving an expected module efficiency of 3.8%. Fig. 3 shows the decrease in module efficiency as the module dimension is increased. The mixture used here was optimal.

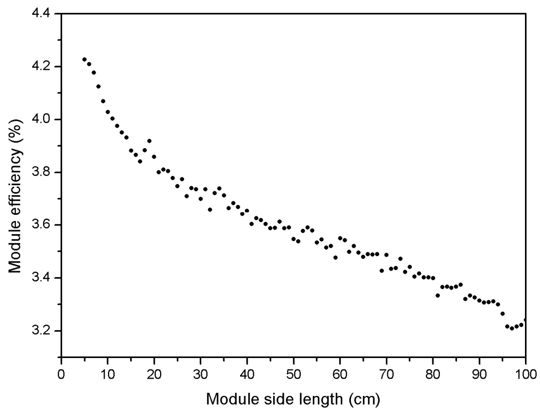

Fig. 3: Module efficiency vs. module dimension

The decrease in efficiency is caused by both self-absorption and host absorption. Although the efficiency drops, it decreases approximately linearly. Since the power output will scale with the area of the module but the amount of cells required will scale with the perimeter, the net result is that less silicon will be needed per watt produced for a large module compared with a small one. This obviously has implications for the embodied energy content of the module. Work is currently underway to analyse this and compare with current figures for conventional panels.

5 LSC MODULE RESULTS

A small (10x10cm) LSC module was constructed using a mixture of the red and violet dyes (~900ppm red, ~200ppm violet) with laser-grooved back-contact (LGBC) solar cells (NaREC) affixed to the edges. Its efficiency was measured under 1-sun AM1.5 illumination as 2.4%, considerably less than predicted from the model. However, there were several constructional factors which could lead to this decrease. The cells used were optimised for around 4-5x concentration. On such a small module, there will be little, if any, concentration of the edge-emitted light and the extra fingers required on the cells will lead to a reduction in power output. Also, electrical connection was made to the cells using silver conductive paint (soldering caused the cells to distort and make edge attachment difficult) and this led to poor connections as the device heated and expanded under illumination.

6 CONCLUSIONS

The Lumogen F series of fluorescent organic dyes have been shown to exhibit high quantum yield and a wide range of absorption spectra. Photostability tests indicate the suitability of the Rot 305 dye for LSC use and modelling confirms that this is the best dye to use. Performance of an actual module is less than predicted but this may be explained by several experimental factors.

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