Towards an aligned luminophore solar concentrator

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Abstract: Luminescent solar concentrators promise to reduce the cost of solar energy, but are hindered by a number of losses. Escape of luminescence through the large waveguide-air interfaces can be attenuated through alignment of the optical transition dipole of the luminophore along the waveguide surface normal, directing the maximum possible proportion of luminescence into waveguide modes. We demonstrate such alignment using a guest-host dye-doped liquid crystal sandwiched between conductive glass slides. Application of a potential while illuminating through a narrow edge caused a drop in the intensity of luminescence escaping the large surfaces, and an increase in the intensity of light escaping the narrow edges of the system. This is explained in terms of alignment of the transition dipoles of the dye. We discuss implementation in a luminescent solar concentrator.

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1. Introduction

Luminescent solar concentrators (LSCs) have the potential to dramatically reduce the price of electricity generated by photovoltaic (PV) systems [1]. In a simple LSC, a transparent, planar substrate has a plurality of luminescent particles (luminophores) embedded within it, or dispersed across one of the large area faces, which is directed towards the sun. Light incident on the *sunlight face* is absorbed by the luminophores, and a large majority of the photons are reemitted in the form of luminescence. Those photons which impact the substrate-air interface at greater than the critical angle, avoiding loss through the *escape cones*, become trapped within the substrate by total internal reflection. Waveguiding then directs the photons to one of the narrow edges of the substrate where they are optically coupled to a narrow strip of PV cells, leading to the possibility of a dramatic reduction in the material cost per peak Watt of photovoltaic systems.

The performance of an LSC depends on how much incident flux is absorbed, and the efficiency of guiding luminescence to the edge of the LSC. The internal optical efficiency, \( \phi_{oi} \), is the probability that the absorption of one solar photon will result in the emission of one photon from a narrow edge of the substrate. Maximising \( \phi_{oi} \) by impeding various loss mechanisms is a requirement for achieving a highly efficient LSC.

The first generation of LSCs, developed in the late 1970s [12], were plagued with the problems of reabsorption and luminophore photostability [3456345634563456]. Activity in the field fell away steeply in the late 1980s, largely due to these problems. Reabsorption occurs when a photon emitted by one luminophore is absorbed by another, due to overlap between their emission and absorption spectra. Reabsorption does not equate to immediate loss of the photon’s energy from the system, since the absorbing luminophore can re-emit a new photon. Rather, with each reabsorption, there is a certain probability that the photon will be lost through nonradiative decay (dependent on the luminophore’s luminescence quantum yield, \( \phi_L \)) or the escape cones. Thus, reabsorption pumps the two main loss mechanisms in the LSC, and as such is often responsible for severe reductions in \( \phi_{oi} \).

Two complimentary approaches to increasing \( \phi_{oi} \) are to reduce the rate of reabsorption by employing new luminophores with a larger Stokes shift, or to reduce the impact of reabsorption by using luminophores with \( \phi_L \) approaching unity, effectively closing the nonradiative decay loss channel. These approaches have been boosted by the development of new species of organic luminophores and semiconductor nanocrystals with novel photophysical properties and enhanced photostability. Although these new materials have found growing success within LSCs, improvements are still required before LSCs will find widespread deployment. A review of recent results is given in [7]. A third approach to increasing \( \phi_{oi} \) which, when combined with the previous two strategies, should be sufficient to produce high efficiency LSCs, is to control the direction of light emission from luminophores. This may be achieved by aligning them with a certain orientation within or atop the substrate. In this paper we report a demonstration of aligning fluorescent organic molecule in such a manner.

2. Homeotropic transition dipole alignment

Employing the dipole approximation for luminescence, the intensity distribution of emitted light is proportional to \( \sin^2 \theta \), where \( \theta \) is the zenith angle, formed between the propagation
vector \( \mathbf{k} \) and the optical transition dipole \( \mathbf{\mu} \). The intensity is isotropic with the azimuthal angle.

To maximise the proportion of emitted photons that enter waveguide modes, the disc describing the maximum emission intensity, at \( \theta = \pi/2 \), is made coplanar with the substrate, with \( \mathbf{\mu} \) perpendicular to the substrate. The configuration where rod-like liquid crystals align in this manner is known as *homeotropic alignment*. For homeotropic alignment of luminophores to optimise the direction of light emission and thus minimise escape cone losses, the luminophore must emit from a single nondegenerate excited state with a transition dipole moment approximately coaxial to the long axis of the species.

The loss fraction, \( f_\perp \), denotes the proportion of luminescence emitted by a single luminophore that will be lost through the escape cones, in the absence of scattering or reabsorption. For a transition dipole in perfect homeotropic alignment, assuming the substrate surfaces are optically flat and unmirrored, and the particle is not near a narrow edge, the loss fraction \( f_\perp \) is given by:

\[
f_\perp = \frac{2}{4\pi r^2} \left( \int_0^{\theta_c} \sin^2(\theta) 2\pi r^2 \sin(\theta) \, d\theta \right) = \frac{1}{12} \left( \cos(3\theta_c) - 9\cos(\theta_c) + 8 \right)
\]

where \( \theta_c \) is the critical angle of the substrate from Snell's law. For a substrate with refractive index \( \eta = 1.5 \), \( f_\perp \approx 0.06 \). Comparison to \( f_0 \), the equivalent quantity for an LSC employing isotropically aligned luminophores, requires caution. As the luminescent species are oriented randomly, averaging across a large ensemble is necessary to produce a meaningful metric. It is sometimes assumed that the direction of photon emission in such a case is therefore isotropic, such that the analogue of Eq. 1 gives \( f_0 = 0.25 \). However, symmetry between the absorption and emission angular dependence of an individual transition dipole means \( f_0 \) may be larger, as the exact loss fraction for isotropically aligned luminophores is dependent on the angle of incidence. \( f_0 = 0.25 \) is thus a lower bound to the actual value when excitation is largely from a shallow angle of incidence. See Ref. [8] for a detailed discussion of escape cone losses.

Comparison of \( f_\perp \) to \( f_0 \) shows that homeotropic \( \mu \)-alignment can significantly increase \( \phi_o \) compared to standard random alignment. This advantage becomes especially pronounced when reabsorption is considered, as the probability of a photon remaining in a waveguide mode after \( n \) reabsorptions and emissions is given by \( (1 - f)^n \). It is important to note that bulk homeotropic \( \mu \)-alignment of like luminophores will increase the rate of reabsorption, by optimally orienting the luminophores to absorb waveguided light. Thus, in systems with very small Stokes shifts and high optical densities, homeotropic \( \mu \)-alignment may not actually increase \( \phi_o \). However, in more reasonable systems, homeotropic alignment will significantly boost \( \phi_o \) compared to random alignment.

The benefits of homeotropic \( \mu \)-alignment of luminophores have never been experimentally demonstrated. Debije et al. reported a study using dye-doped liquid crystals, where a decrease in solar absorption and top surface losses was observed, but there was no corresponding increase in the light emission from the edges [9]. As we discuss later, excitation through the top surface is ambiguous in demonstrating the benefits of homeotropic alignment, and should be used alongside other measurements. Debije et al. successfully demonstrated a different type of luminophore alignment in an LSC, where dye molecules were aligned with the transition dipole in the plane of the substrate, parallel to one pair of narrow edges [10]. This led to anisotropy in the edge emissions, the parallel pair of edges being favoured over the perpendicular, but by the reasoning advanced earlier must necessarily have enhanced the proportion of photons lost through the surface. Thus, such an alignment scheme is ultimately unsuitable for a high efficiency LSC unless accompanied by a cholesteric mirror coating or another coating with wavelength dependent reflectivity.
3. Experimental

As a proof-of-principle luminophore, N-N′-Bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic diimide (PDI), was chosen for a near-unity \( \phi_L \) from a single optical transition, good solubility, high photostability [11] and, crucially, emission anisotropy along the long molecular axis [12]. The main shortcoming of PDI is a small Stokes shift. However, the experiment took place on small physical dimensions at low optical density, so reabsorption was not overly severe.

To demonstrate homeotropic alignment in a model LSC, guest-host dye-doped liquid crystals (LC) were used, in which PDI was dissolved in the liquid crystal 4-pentylphenyl 4-methoxybenzoate (Nematal 105), to an approximate concentration of \( 10^{-5} \) M. Nematal 105 has a nematic phase at slightly above room temperature. Two drops of the LC-PDI solution were deposited from a transfer pipette onto a postage stamp-sized, 4 mm thick glass slide coated on the wetted side with the transparent conducting compound indium-doped tin oxide (ITO). The slide had been cleaned by sonication in analytic-grade 2-propanol. Another clean, identically proportioned slide was placed on top of the first with the ITO face downwards, trapping a thin layer of the LC-PDI solution between the slides. Two parallel edges of the slides were aligned; a slight offset was left between the other pair to allow the attachment of electrical contacts to the inner faces of both slides. Gentle pressure was applied along with warming by a heat gun to disperse the solution evenly. The high viscosity of the LC at room temperature largely prevented seepage or evaporation from between the slides, and the layer prevented electrical contact between the two slides. The device was illuminated by a xenon lamp emitting a collimated white beam, which was loosely focused to have a consistent beam width of 4 mm across the experiment. All emission spectra from the device were obtained using an Ocean Optics HR4000 spectrometer with a fibre optic probe head.

4. Results and discussion

In the nematic phase, the LC molecules align locally, but the orientation of alignment varies throughout the sample. Bulk homeotropic alignment was observed to occur when a potential of 10 V or higher was applied across the two slides. A potential of 50 V was used routinely in the experiment, but no change in the observed effects was detected above the 10 V threshold. The temperature of the device was monitored using a heat probe; ambient heat from the nearby xenon lamp was sufficient to keep the LC in the nematic phase. The guest-host system ensured...
that PDI was forced cooperatively into a similar alignment to the LC, with the long axis of the molecule along the field lines, due to the similarity in size and structure to the LC molecules. The expected effects of homeotropic alignment on light emission from the various faces of the device are shown in Fig. 1.

Initially the device was illuminated from above, with the xenon lamp beam directed through the centre of the glass slide normal to the top surface (Fig. 1 position T). It was clear to the naked eye that applying the potential caused an increase in the proportion of irradiance that was transmitted through the device, and that this change was reversible when the potential was switched off, occurring more quickly when accompanied by gentle heating of the device. This corresponded with the expectation that absorbance of normal incidence light should decrease when the PDI was oriented parallel to the direction of light propagation. The subsequent drop in emission intensity from all faces of the device meant this configuration was not optimal for determining whether homeotropic alignment had been achieved, and whether it reduced escape cone losses relative to the absorbed flux. Therefore the lamp beam was redirected to enter the device through the middle of the face of one of the non-staggered narrow edges (Fig. 1 position S). This configuration made the various effects of homeotropic alignment much clearer to observe.

For measurement of the top surface losses, a probe was fixed in position directly above the path of the illuminating beam, in the middle of the device, facing directly downwards at a height of 1 cm. The spectrum was recorded before and after the potential was applied, which caused a change that occurred in a fraction of a second. The emission from the top surface corresponded closely to the emission spectrum of PDI in toluene. Upon applying the potential, the intensity of the emission decreased by approximately one third, whilst the band shape was unchanged (Fig. 2A). The intensity change in top surface emission was dependent on two competing effects. Lamp absorption was increased by rotation of the PDI transition dipoles into an orientation well suited to absorbing the beam, leading to increased emission intensity from all surfaces. Escape cone losses, on the other hand, were decreased by rotation of the PDI into homeotropic alignment. Perfect homeotropic alignment would produce a factor of 3/2 increase in the absorption, and hence emission, since the lamp beam is unpolarised, and a factor 25/6 decrease in top surface losses, yielding a total intensity reduction of approximately two thirds. The measured one third reduction suggests non-ideal luminophore alignment within the liquid crystal.

Measurement of top surface losses with the excitation beam directed through a narrow edge, as described, was the most reliable indication of homeotropic alignment. The path length of emitted photons within the dye layer was very short, giving little opportunity for reabsorption to occur, and the direction of propagation normal to the LC layer meant there was no chance for trapping of the emission within the LC layer due to the refractive index mismatch, which would lead to high reabsorption losses. However, spectra recorded with the probe facing one of the staggered narrow edges, normal to the direction of the xenon lamp beam, suggest that trapping within the dye layer was not overly severe. Applying the potential in this configuration produced an increase in the intensity of emission from the narrow edges, noticeable both with the spectrograph and the naked eye (Fig. 2B). The exact extent of this increase derived from a host of experimental factors, such as the refractive indices, surface imperfections, dye concentration and beam position, and the proportion of the increase that resulted from increased absorption as opposed to decreased surface losses is not readily determinable. However, both effects are cooperative and indicative of homeotropic alignment.

Another result that suggested homeotropic alignment had been achieved was an enhanced reabsorption shift in the emission from the narrow edges. A reabsorption shift occurs when an emission spectral distribution shifts towards the red as a result of increased reabsorption of the bluer portions of the spectrum. A small reabsorption shift was seen in the narrow edge emission...
Fig. 2. Emission from the top surface of the narrow-edge illuminated device (A) and a narrow edge parallel to the lamp beam (B) before and after application of 50 V across the layer. The solid lines are fits to the data. Inset: Fits to the emission spectra from B normalised about the bluer emission peak at 553 nm, showing a clear reabsorption shift when the potential is applied.

when the potential was applied (Fig. 2B inset) which supports the thesis that reabsorption had been increased in the device by aligning the PDI luminophores in the manner best suited to reabsorbing waveguided emission.

After this manuscript was completed, Mulder et al. reported homeotropically aligned fluorophores using a polymerizable liquid crystal host as a scaffold [13]. However, aligning the luminophores in a homeotropic configuration in itself is not enough to generate a highly efficient LSC. Alignment of the luminophores in this way minimizes their interaction with sunlight incident on the LSC along the surface normal. Mulder et al. suggest the use of an external light diffuser to overcome this shortcoming. However, even photons entering the device at the shallowest angles are refracted along the escape cones and thus do not optimally interact with the aligned luminophores. In order to maintain the benefits of alignment while also maintaining optical density, the roles of absorption and emission can be separated. In this scenario, only the emitter need be aligned homeotropically. Solar radiation is absorbed by sensitizer chromophores, which are either unaligned, or which also align with the emitters but possess a transition dipole orthogonal to the alignment axis, which may interact with sunlight incident along the surface normal. Electronic energy is then efficiently transferred to the aligned emitter fluorophores by non-radiative processes which are known to exhibit efficiencies approaching unity [12]. Construction of an LSC in this manner should lead to an increased efficiency of solar energy collection.

5. Conclusion

PDI molecules were successfully aligned within a nematic liquid crystal. Homeotropic alignment resulted in decreased surface losses, despite increased absorption when illuminated through the narrow edges. Emission from the waveguide edges is enhanced, strongly suggesting that luminophore alignment will be a key feature of the next generation of high efficiency LSCs.

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