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The role of FRET in solar concentrator efficiency and color tunability

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ABSTRACT

We demonstrate concentration-dependent Förster-type energy transfer in a luminescent solar concentrator (LSC) material containing two high quantum yield laser dyes in a PMMA matrix. FRET heterotransfer is shown to be approximately 50% efficient in the regime of 2×10^{-3}molal acceptor dye by weight in the host polymer. The two dyes used have been well studied for solar concentrator applications: BASF's Lumogen Red 305, and Exciton Chemical Company's DCM both demonstrate desirable stability, quantum yield, and complementary absorption spectra. We demonstrate how multiple-dye LSC devices employing FRET increase the absorption of air mass 1.5 solar irradiance without affecting the self-absorption properties of the film. Color tunability may be achieved through the addition of additional absorbers while minimizing the impact on waveguide efficiency.

1. Introduction

Luminescent solar concentrators (LSCs) offer low cost improvements to building-integrated photovoltaics. An LSC generally consists of an optically transparent material with an index of refraction similar to that of glass doped or coated with a fluorescent downconversion material which absorbs solar radiation and isotropically reemits it at longer wavelengths with a high quantum yield. Thus, a certain percentage of the reemitted light is subject to total internal reflection and trapped in the waveguide. The trapped photons are then absorbed by strips of active PV material optically coupled into the waveguide in a variety of potential geometries.

The history of the LSC can be traced back at least 50 years, stemming from the development of scintillation detectors [1]. Although this work is noted for its pioneering consideration of the “fluorescent solar collector” concept in the publications of Seybold and Wagenblast [2], who later developed highly soluble and relatively stable perylene dyes specifically for solar concentrator applications, the 1976 conceptual publication of Weber and Lambe [3] is variously cited as the first published LSC concept, while several review articles [4,5]] note from the work of Batchelder et al. [6] that a 1973 NSF proposal by R.M. Lerner is considered to be the concept's unpublished introduction. In the proposal of the LSC concept by Weber and Lambe [3], the overall efficiency of an LSC device was defined as the product of three efficiencies:

$$E = Q_a \eta Q_c$$

with Q_a and η representing initial absorption of solar photon flux and fluorescence quantum yield, respectively. Thus Q_c was defined as the “collection efficiency,” which takes into account geometric losses from both the initial re-emission and subsequent re-absorption and emission events, as well as losses from reflection when light travels from a relatively low refractive index waveguide into a semiconductor photovoltaic material. Given approximately equal quantum yields of all dyes, the main benefit should come from reducing the number of re-emission and absorption events and thus total escape cone and quantum yield losses.

While dye stability still remains an issue for many LSC-suitable dyes [5], some progress has been made within the past several decades with dyes such as Rhodamine [7] and Perylene dyes with the work of Seybold and Wagenblast at BASF [2]. Still, LSCs have been inherently limited in power efficiency by low absorption of the solar spectrum, self-absorption of the emitted light, and waveguide losses. While attempts have been made to improve efficiency and maintain stability by increasing absorption using quantum dots [8,9]], broadening absorption and tuning emission through dye interaction with the host environment [10], or using dipole alignment to reduce escape cone losses [11,12], the largest single loss is often the narrow absorption spectra of many proposed LSC materials [13]. Shortly after Weber and Lambe's 1976 publication, the idea of constructing multiple-dye LSC films to increase absorption was studied [14]. While the prospect of exciton transfer through resonance between a donor's fluorescence transition dipole and a corresponding transition of an

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acceptor (Förster-type nonradiative transfer) was immediately considered, it was estimated to play a small role in the experiments carried out by Swartz et al. [14], owing to the low concentrations used. More recent undertakings have studied the overall efficiency in an LSC system where FRET was shown to be the dominant transfer mechanism between three chromophores [15], but no discussion was made of the concentration regime at which FRET began to occur in a PMMA matrix.

Average donor–acceptor pair distance calculation can be less straightforward than what a cursory glance at Förster's well known relations suggests (Eqs. (1)–(3)). While the relations are generally used to estimate Förster-type transfer efficiency between fluorophores in fixed positions, such as those bound to specific sites on proteins and used for biolabeling [16], in a polymer matrix a distribution of distances must be considered. A further complicating matter is that a polymer LSC host matrix does not guarantee a uniform distribution of dopants, leading to quenching-pair distance relations which are nontrivial to calculate numerically [17]. Specifically, mathematical models relating dopant distributions to FRET quenching in a two-dye system have been proposed as a means of gaining insight into the morphology of porous materials such as polymers, among other things [18]. Such models require time-resolved fluorescence measurements and, in the case of [18], neglect homotransfer and consider transfers only between isolated donor–acceptor pairs – a very low concentration situation that is of limited utility when considering solar concentrator applications.

The self-absorption characteristics of planar LSC films have similarly been well studied for DCM and Lumogen F dyes specifically [13,19–21]. For any given LSC geometry, there is a tradeoff between increasing AM1.5 photon capture and the associated geometric losses from self-absorption and lowered quantum yield due to possible aggregate formation and other quenching effects. Thus, for LSC devices containing multiple fluorescent species, a knowledge of the concentration regimes at which FRET begins to occur is important to consider when optimizing dye concentrations against geometric gains.

Initial interest in solar concentrator devices was sparked in the mid- to late 1970s [4]. Oil supply shock coupled with an inflation adjusted cost per watt of PV modules around two orders of magnitude higher than today [22] motivated a search for cost effective concentration mechanisms allowing for maximal PV power output from a minimal amount of area. The considerably lower cost per watt of solar in today's market has led to a re-evaluation of the economics of LSC schemes, with recent potential application focused on cells which receive both direct and waveguide illumination and close attention is paid to installed cost per watt [23]. In these types of layouts, self-absorption of the LSC will determine the optimal arrangement of face mounted photovoltaic cells [13,23], and building integrated PV will generally require higher transparency and thus push low concentration limits for esthetic purposes. We frame our study with these considerations, and quantify concentration depending FRET experimentally in a PMMA-host planar LSC setup with a spectroscopic study of a two dye system.

2. Experimental procedure

DCM ([2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H pyran-4-ylidene]-propanedinitrile; Exciton) and Lumogen Red 305 (BASF) were used as obtained (structures are shown in Fig. 1). Luminescent inks were prepared from a mixture of the as-received powdered dyes, polymethylmethacrylate (Spectrum Chemical Co., 350k molecular weight), and toluene. To achieve global film uniformity across a range of dye to host polymer concentrations, a standard 13.3% PMMA:toluene weight ratio was established for all inks. The film deposition was performed using an Industry Tech Auto Draw III automatic drawdown machine. The machine draws a rod across a slide at constant pressure and velocity to produce a film. Film thickness was set using a single layer of Scotch 810 magic tape, in a process commonly referred to as “doctor-blading”. The films were deposited on 3 in. × 1 in. quartz glass microscope slides. The films themselves were determined to be approximately 5 μm in thickness.

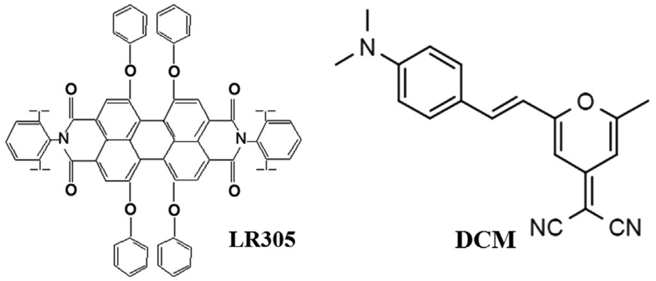

Fig. 1. Chemical structures of BASF Lumogen F Red 305, a perylene diimide and Exicton DCM, a merocyanine.

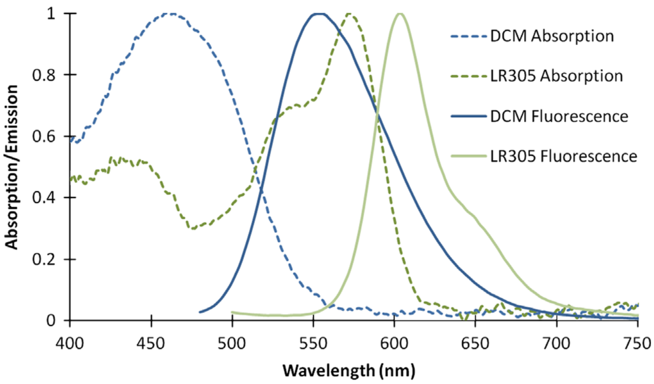

Fig. 2. Normalized absorption and emission spectra of LR305 and DCM dyes in PMMA.

A Stellar Net Thin Film Measurement System, including an SL-1 Filter, a CXR-SR-25 BW-16 Spectrometer, and a Wave NIR-25 InGaAs BW Spectrometer, was used to measure absorption spectra. A Perkin-Elmer Instruments LS45 Luminescence Spectrometer was used to measure the surface emission of the films, by placing the samples in the spectrometer's “front surface” accessory. The excitation beam strikes at 60° to the film's normal, and emission is collected at 30° relative to the film normal. Film thickness measurements were determined by a Dektak profilometer and found to be in agreement with the known molar absorption coefficient from literature [21].

3. Results and discussion

BASF Lumogen Red 305 and DCM dyes fluoresce in the yellow–red visible range, with emission peaks around 604 nm and 555 nm, respectively, when embedded in a PMMA polymer matrix. Both have been considered for use in LSC applications because of their broad Stokes shifts and high quantum yields. In addition to its promising spectroscopic properties, DCM was investigated as a companion dye to Lumogen Red 305 because its absorption peak complements a dip in the absorption spectrum of LR305 (Fig. 2).

It is worth noting that DCM, like other merocyanines, is prone to solvatochromatic effects; its emission peak redshifts from approximately 550 nm to 600 nm or more, generally varying with the polarity of its host environment; the effect was noted in the