Combining Positive and Negative Dichroic Fluorophores for Advanced Light Management in Luminescent Solar Concentrators

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This work describes the unexpected alignment of a common perylene bisimide fluorescent dye (Lumogen Red305) in a host liquid crystal matrix. The negative dichroic fluorophore orients with the primary absorption/emission dipole, corresponding to the physical long axis of the perylene bisimide core, perpendicular to the director of a host liquid crystal. A second absorption dipole, which lies perpendicular to the primary dipole and corresponding to the physical short axis of the perylene core, lies parallel to the host liquid crystal. Individual illumination of the two absorbing optical transition dipole moments of the Red305 dye results in a single linearly polarized emission. When Red305 is combined with a second positive dichroic Coumarin-type fluorophore that aligns in the conventional manner in a liquid crystal host, that is, with an absorption dipole along the physical long axis of the fluorophore and the director of the host liquid crystal, advanced light management is possible, such as electrically switchable colors and directing emission light to different edges in a luminescent solar concentrator device.

1. Introduction

Bringing solar energy systems to the urban areas has proven to be a challenge. Traditional silicon-based photovoltaic (PV) panels have been difficult to deploy in these settings due to their reduced performance in shaded situations and to their limited visual appeal and generally inflexible geometries. A promising device for use in the built environment as, for example, a façade element, window or decorative feature is the luminescent solar concentrator (or LSC), first suggested in the late 1970s.[1,2] The LSC is very basic in concept: incoming sunlight penetrates the top surface of a plastic lightguide containing fluorophores. The fluorophores absorb some of the sunlight and re-emit it at longer wavelengths. A significant fraction of the emitted light is trapped in the high refractive index lightguide by total internal reflection, and becomes concentrated along the edges where one places small PV cells to convert the light into electrical current. The LSC is very flexible in its implementation, as they may be of almost any color or shape and perform well under sub-optimal lighting conditions.[3,4]

Recent work has focused on improving the light in/light out management in LSCs. Organic, generally rod-shaped dyes orient in liquid crystal (LC) hosts in such a way as to place the primary absorption and emission axes of the dichroic dye parallel to the alignment direction of the LC, since in most dyes the main optical transition moment is in the same direction as the long axis of the chromophore. Planar alignment of fluorescent dichroic dyes in LSCs improved light concentration along two sides by directing light to specific waveguide edges.[5–7] As the degree of dye alignment increases, the anisotropy of edge emission also increases.[5] In such LSCs the use of high performance solar cells that operate at specific wavelengths becomes interesting as the size of such expensive cells can be significantly reduced. Dyes have also been aligned homeotropically, which has the advantage of reducing light losses through the lightguide surfaces.[8–10]

Alignment of dyes in LC hosts has also been applied in dynamic devices: switchable electricity-generating ‘windows' based on dye guest/liquid crystal host systems.[11,12] A variety of window designs capable of switching their transparency have been described,[13–18] as well as static windows capable of generating electricity from sunlight.[19–24] The LC/fluorescent dye windows in this work are unique in combining both light control and electricity generation, accomplished by applying a voltage across two transparent metal coated lightguide panels which reorients a liquid crystal sandwiched between the plates. By manipulating the orientation of the liquid crystals, the orientation of dye molecules embedded in the LC host is also altered. Since the dye molecules are dichroic in both absorption and emission, reorienting the dyes parallel and perpendicular to the waveguide surfaces (or any intermediate position) can rapidly alter the transparency of the windows between ‘dark' and ‘light' states while simultaneously generating electrical current via edge-attached PV cells.[11]

One of the most commonly-encountered fluorophores used in LSC studies has been the perylene-based dye Lumogen

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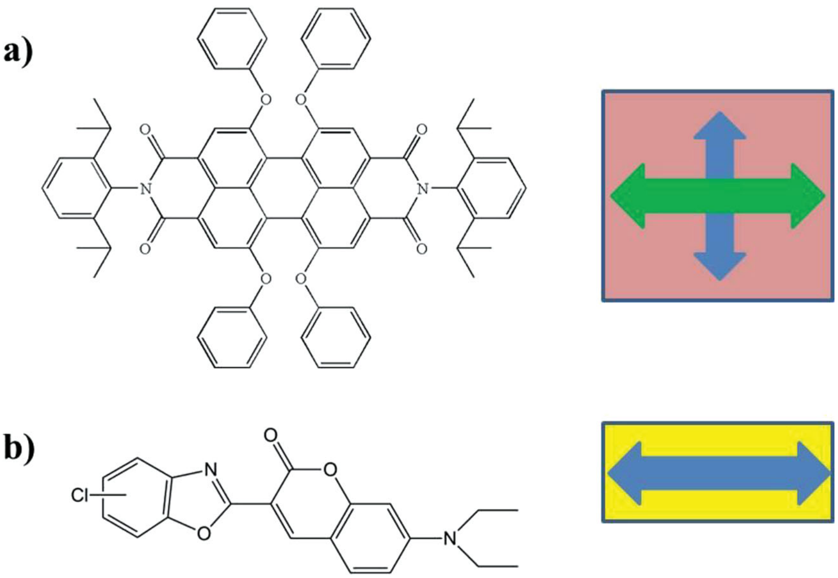

Figure 1. Chemical structures of a) Lumogen Red305 and b) coumarin derivative used in these experiments. To the right of the structures is depicted the direction of the main absorption dipoles: the arrow colors roughly correspond to the wavelength regions absorbed by the dipole. The surrounding box is a visual representation of the physical shape assumed by the dye.[33]

Red305 (**Figure 1**) from BASF because of its near unity fluorescence quantum yield and high photostability.[4,25–27] In this work, we will demonstrate that Red305 aligns with the main optical absorption axis of the perylene core perpendicular to the alignment direction of the host liquid crystal molecules, resulting in a negative dichroism of the system in absorption and emission. While several dyes have been described to display negative dichroism in absorption,[28,29] few have been described to do so in fluorescence,[30,31] and none have been employed in aligned systems for LSCs. By taking the design a step further, combining Red305 with, for instance, a coumarin dye having positive dichroism, one could direct emissions towards two different orthogonal edge mounted PV cells, each tuned to perform optimally at the specific wavelengths emitted by each dye, or daylighting systems where each edge emits light of a different color into an optical fiber.[32] In addition, by electrically switching the orientation of the dyes in an LSC 'window' device, many new possiblities for advanced light management become accessible including color switching depending on the applied voltage.

2. Results and Discussion

2.1. Single Dye Solid Films

To determine the orientation of Red305 (Figure 1a) in planar aligned host, we incorporated Red305 fluorescent dye in a polymerizable LC host by spin coating from solution onto a PMMA lightguide coated with a rubbed polyvinyl alcohol (PVA) alignment layer, which was subsequently crosslinked and formed a solid anisotropic polymer film after exposure to ultraviolet light.

Absorbance measurements showed two main peaks for perylenebisimide derivatives, one at 584 nm and the other at 445 nm, each responding differently to changes in the polarization of the incident light. To characterize the alignment, we calculated the order parameter in absorption, R_a:

$$R_a = \frac{A_{par} - A_{per}}{A_{par} + 2A_{per}} \tag{1}$$

where A_{par} and A_{per} are the peak absorbance with the incident light polarized parallel and perpendicular to the rubbing direction of the PVA, respectively. A totally random sample would have an $R_a = 0$. Perfect alignment of the dye with absorption axis completely parallel to the incident light would be $R_a = 1$. A negative R_a indicates an absorption axis perpendicular to the main alignment axis. Measurements of the 1.4 wt% Red305 film in the LC host on PMMA resulted in two values for R_a, –0.13 at 584 nm and 0.19 at 445 nm (see **Figure 2**a).[34] The remarkable negative order parameter at $\lambda = 584$ nm strongly suggests the perylene core is oriented perpendicular to the direction of the LC alignment since the main optical axis is parallel to the long axis of the chromophore (vide infra). The positive order parameter at $\lambda = 445$ nm suggest that this optical transition is perpendicular to the long axis of this dye. To determine the relative orientation of the two absorbing dipoles, the aligned Red305 polymer film was placed on an adjustable stage and again exposed to polarized light. The substrate was rotated in the beam, and absorption spectra recorded for every 5° rotation. The results are depicted as the inset in Figure 2a and indeed reveal that the two dipoles of absorption are orthogonal, with the dipole responsible for absorption at 584 nm situated parallel to the long axis of the core perylene molecule (the green arrow in Figure 1a) which lies perpendicular to the host liquid crystal director, and the 445 nm dipole direction corresponding to the short axis (the blue arrow in Figure 1a) lies parallel to the liquid crystal director. This alignment is unusual, and contrary to other perylenebisimides[12,35,36] and to the alignment of dyes such as 4-dicyanomethyl-6-dimethylaminostiryl-4H-pyran (DCM) and the coumarin derivative described in earlier work.[5,7,11] The order parameters of Red305 are lower than many of the fluorescent dyes previously described[5,12] which is most likely due to the square shape of the dye.

As mentioned in the introduction, emission from aligned dichroic dyes also tends to be anisotropic.[37–39] To confirm the polarization of the light emitted by the dipole, time integrated photoluminescence (PL) measurements of aligned 0.2 wt% Red305 in LC host solid films on glass substrates were performed, with a schematic depicting the experimental setups given in Figure 2b. The time integrated PL observed when the fluorophore is excited at 450 nm has an emission at 650 nm and shares the same vibrational structure as the 584 nm absorption peaks and is assigned to Stokes shifted emission from this same state, consistent with previous work.[40] The PL

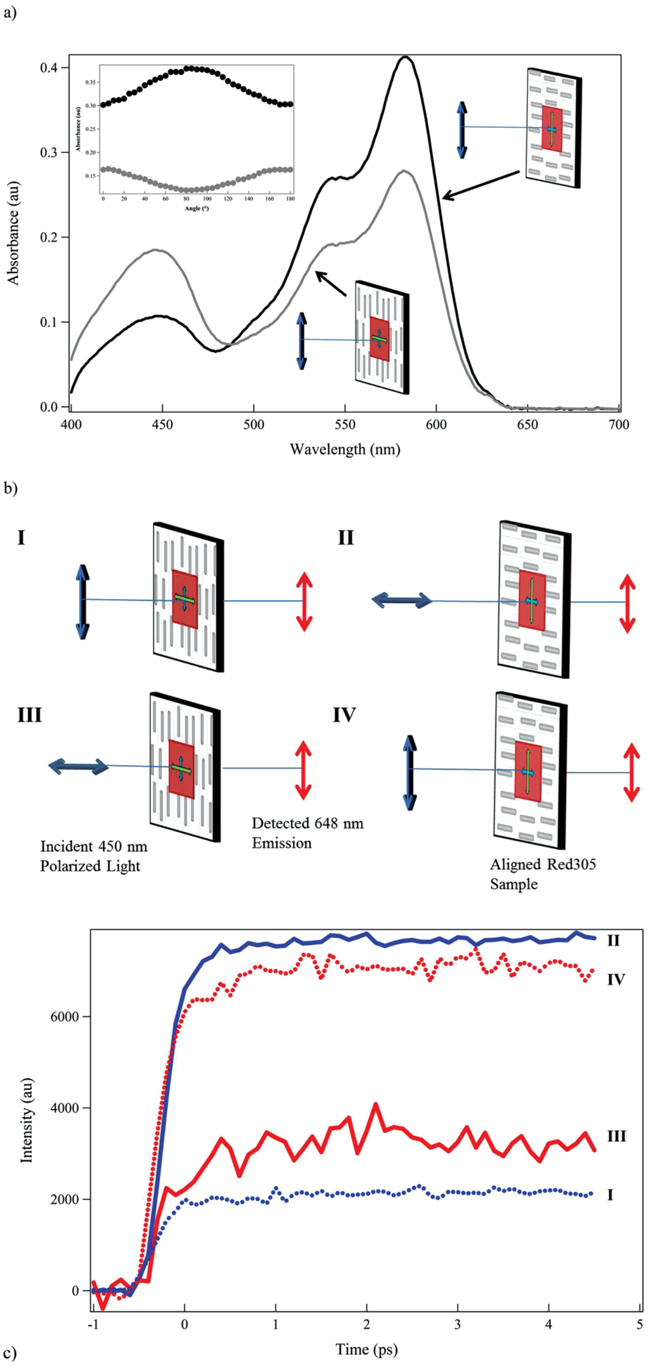

Figure 2. a) Absorbance spectra of 1.4 wt% Red305 in a polymerized LC host on PMMA substrate coated with PVA exposed to light polarized parallel (gray) and perpendicular (black) to the rubbing direction of the PVA alignment layer with accompanying depictions of the light/sample orientations. (Inset) Peak absorbance of light at 584 nm (black) and 445 nm (gray) as a function of angle between the alignment direction of the LC host and the polarization of the incident light. b) Schematic setup for time integrated photoluminescence measurements depicting relative orientations of aligned dye samples, polarization of the 450 nm incident light, and polarization of detected 648 nm emission. c) Photoluminescence emitted from a sample of Red305 embedded in the solid LC host as a function of time after excitation, for the four different absorption/emission polarization geometries shown in (b). The sample was excited at a wavelength of 450 nm with 10 mW average power, and the PL detected at 648 nm.

intensity transients were measured with excitation polarization both parallel and perpendicular to the rubbing direction (Figure 2c). The emission signal is greatest when the polarizer is oriented perpendicular to the alignment direction of the liquid crystals.

The time dependence of the emission anisotropy, the PL polarization anisotropy R_e was calculated from the PL transients using its definition:

$$R_e = \frac{I_{par} - I_{per}}{I_{par} - 2I_{per}} \tag{2}$$

where I_{par} is the PL intensity component polarized parallel to the excitation polarization (I and IV, in Figure 2b), and I_{per} when polarized perpendicular (II and III). Two different excitation geometries were examined, one for which the polarization of the excitation pulse is parallel to the alignment direction of the LC, yielding R_e^{par} (I and II in Figure 2b), and another in which it is perpendicular, yielding R_e^{per} (II and III). When measuring the time dependent polarized PL a rapid rise in intensity is seen within the first 0.5 ps, followed by emission of constant intensity over the first 4.5 ps, continuing so for over 100 ps. Values of $R_e^{par} = -0.30$ and $R_e^{per} = 0.29$ were measured (see Supporting Information Figure S2), and are constant over the first 100 ps after excitation with all PL intensity transients having very similar shapes over this time scale. The strong negative anisotropy found when the higher energy state is excited (450 nm) parallel to the rubbing direction is indicative of a high degree of molecular alignment, coupled with phenomenally rapid (the PL anisotropy assumes its final value within the 200 fs time-resolution of our system) and efficient rotation of the PL polarization through 90° on relaxation from the higher energy state to the emitting state, as would be expected for reorientation of an intramolecular dipole moment. The origin of the positive anisotropy observed when exciting at 450 nm with polarization perpendicular to the rubbing direction may be a consequence of direct excitation into the 584 nm absorption band, if higher vibrational modes have non-zero absorption down to 450 nm. However, based on a Gaussian peak fitting of the UV-Vis absorption spectrum, it is unlikely that this is the case (See Supporting Figure S1). More likely is that the two states are decoupled, such that the majority of emitted PL is polarized perpendicular to the rubbing direction, irrespective of the polarization of the exciting radiation. In such a situation, the magnitude of the anisotropy observed would be related primarily to the degree of molecular alignment within the polymer film.

All our results suggest the Red305 dye is lying with the long axis of the perylene core (the green arrow in Figure 1) oriented perpendicular to the direction of the host liquid crystal (Figure 2b). Considering the structure of the dye, we assume the more square-like shape frustrates the normal alignment. The entities extending from the bay positions of the perylene core better align with the host LCs, causing the unusual alignment:[41] we plan to investigate this behavior in future work. Furthermore, excitation of the two independent absorbing perpendicular optical transition dipole moments of the Red305 dye resulted in a single polarized emission that is parallel to the rubbing direction of the polymer sample.

2.2. Single Dye Switchable Systems

In order to make responsive LSC windows, we studied the electrical switching behavior of Red305, so the dye was mixed in the nematic liquid crystal E7 and the solution used to fill a 20 μm Indium Tin Oxide (ITO) coated glass cell with alignment layers. In E7, the order parameter of Red305 in the cell at 0 V in absorption is lower than in the solid films: R_a at 445 nm was 0.11 and at 584 nm was –0.07. The E7 host itself has an alignment with an order parameter (S_2) of around 0.6;[42] the reduced effective alignment of Red305 suggests the square shaped fluorophore in E7 is effectively disordered. However, as demonstrated by **Figure 3**, the emission from the edges perpendicular to the alignment direction of the host liquid crystal is slightly greater than that parallel (compare the pink and red curves in Figure 3). Since the dipole for absorption at 584 nm is also responsible for the emission (vide supra), these results support the hypothesis that the long axis of the perylene core is aligned perpendicular to the director of the LC host.

In previous devices, at no applied voltage the LC lies planar in the cell, and the dyes absorb incident light forming the 'dark' state.

When voltage is applied across the cell, the LCs stand homeotropically which also reorients the embedded fluorophores, resulting in the fluorophores absorbing much less incident light, forming the 'light' state. However, when Red305 is used in a cell configuration, the absorbance of light around 584 nm actually increases slightly upon application of a voltage, meaning the window would appear somewhat darker when switched on, opposite to the switching seen in other dye systems studied (Figure 3).[11,12] In contrast, the absorption of the short wavlength component at 450 nm decreases, but less than one might expect if the axis is aligned parallel to the LC. However, it is likely that the bay area constituents do not sit in the plane, but rather are twisted, projecting above and below this plane (similar to other substituted perylene bisimides.[43] In this situation, the two dipoles would appear orthogonal at no applied voltage, but upon switching at 10 V the out-of-plane dipole would assume roughly the same projection into the horizontal plane, and thus absorb approximately the same amount of light to be indistinguishable from the state where the dye lies planar to the surface. Finally, we believe at least one factor contributing to the slight increase in absorption of the longer wavelength component upon applying a voltage is a degree of increased order of the dye in the homeotropic state, an alignment probably more uniform than the natural planar alignment in the LC host E7.

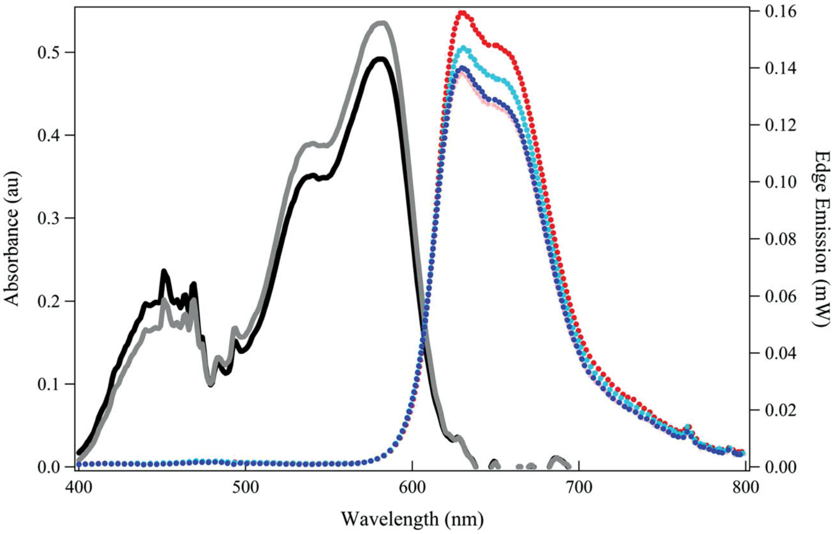

Figure 3. Absorption spectra at 0 V (black solid line) and 10 V (gray solid line) of 0.75% Red305 in E7 in 20 μm cell exposed to isotropic light from a solar simulator, and emission spectra at 0 V from the edge parallel (pink) and perpendicular (red) to the alignment direction of the host liquid crystals, and emission from the edge parallel (dark blue) and perpendicular (light blue) to the alignment direction of the host liquid crystals at 10 V.

2.3. Two Dyes Switchable Systems

The alternate alignment of Red305 opens the possibility of advanced light management: by combining the Red305 with a second dye that aligns in a regular manner, light emitted from the two dyes could be directed to orthogonal edges of the waveguide. The coumarin derivative shown in Figure 1b was chosen as the second dye. This coumarin aligns quite well in LCs with an $R_a \sim 0.5$ (Figure S3). Four cells containing 0.4 wt% Red305 and 0.14 wt% of the coumarin derivative in E7 were produced, and the polarized absorption spectra and emission spectra from the two different edges for one cell is shown in **Figure 4**a: all four samples gave esentially identical results, demonstrating the results were very reproducible. The coumarin has an absorption peak that overlaps the short wavelength absorption peak of Red305. Upon rotation of the transmission axis of the polarizer from parallel to perpendicular to the alignment direction of the host LC molecules, the absorption dramatically reduced as expected, a dramatic reduction of absorption from the coumarin, but an increase in absorption of the Red305 at the 584 nm peak. The apparent color of the cell also changes as seen in the photographs inset in Figure 4a. Using dichroic dyes to affect perceived color has been described,[44] but not with the use of luminescent species. The coumarin derivative emits light (the emission is at ~510 nm) predominantly from the edge parallel to the alignment direction, while the Red305 dye (emission > 600 nm) preferentially to the edge perpendicular to the alignment direction of the host LCs, demonstrating the possibility of selectively directing light to different locations (see Figure 4b).

The appearance of the cell containing Red 305 and coumarin under polarized light changes depending on the voltage applied across the cell (see **Figure 5**). We investigated the cell under various conditions: with polarizers oriented either parallel or perpendicular to the LC alignment direction, with and without applied voltage (in the planar and homeotropic states). By rotating a polarizer from parallel to perpendicular, the sample in the planar state is observed to transition from deep yellow to red (Figures 5a and c). At 10 V

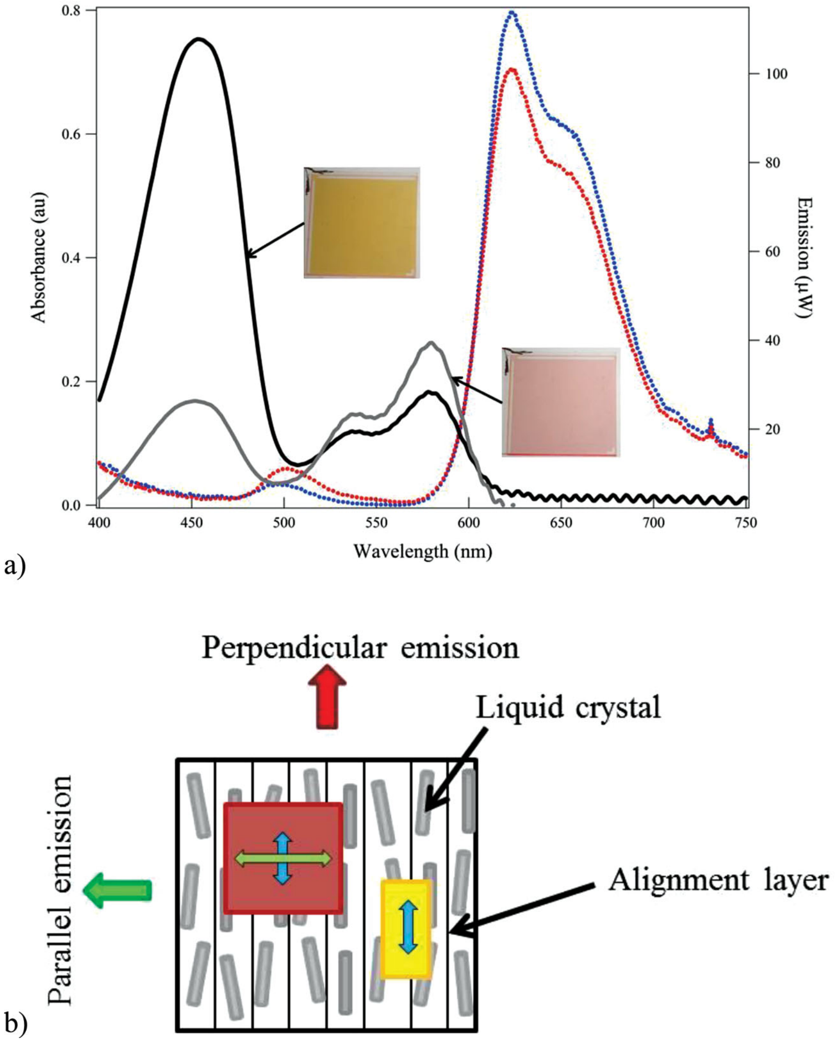

Figure 4. a) Absorption spectra of cell containing 0.4 wt% Red305 and 0.14 wt% coumarin derivative (solid lines) for incident light polarized parallel (black) and perpendicular (gray) to the alignment direction of the host liquid crystal, and emission (dotted lines) from the edge parallel (red) and edge perpendicular (blue) to the alignment direction of the host liquid crystals. Photographs of the cell under polarized light are included to give an impression of the appearance of the cells. b) Schematic representation of the performance of the cell at 0 V. the emission arrows roughly correspond to the light color emitted from each edge. The dyes are represented as shown in Figure 1 above.

in the homeotropic orientation, the cell is not obviously different in color upon viewing under different polarizerizations (Figures 5b and d). Figure 5e depicts the quantities being measured as well as our conjecture as to the relative alignments of the dyes during the switching process. The cells could be switched many times with no observable change in performance. As seen in Figure 3, 5b, and 5d, there is only a small change in the absorbance of Red305 upon applying voltage. Under the same conditions, it is obvious the coumarin derivative displays a much larger anisotropy in absorption states between planar and homeotropic orientation (0 V and 10 V), common to almost all other dichroic dyes we have tested in this architecture.[11,12] Because the Red305 dye actually becomes slightly darker after applying voltage, obtaining a more neutral appearance for the windows cannot easily be accomplished using the Red305 dye without compromising the bright/dark ratios of the windows.

3. Conclusions

We have demonstrated that the Lumogen Red305 dye, commonly used in LSC-type devices, aligns in a liquid crystal host in such a way as to present its emission dipole perpendicular to the director of the host LC molecules, exhibiting a negative dichroism. Employing positive and negative dichroic dyes in this way allows novel changes of appearance of a window as a function of applied voltage, while simultaneously generating electricity from edge mounted solar cells. We introduce an opposite aligning negative dichroic dye to an LSC control emitted light to direct emissions from multi-dye LSCs to specific, tuned photovoltaics for enhanced performance while allowing switchable color 'windows'. The performance of the dual-dye system with color switching upon application of voltage and directing light to different waveguide edges opens intriguing possibilities for advanced light control. One example could be a 'window' configuration that allows alternating bright/dark states for visual light, but a constant absorbance of either ultraviolet or infrared light under both alignment conditions. For higher performance spectral separation to be realized, improved alignments of the dyes will be achieved via synthesis of new molecules and more appropriate host LC materials will need to be employed. Our concept of using combined positive and negative dichroic fluorescent dyes can be extended to include dyes that could process ultraviolet or infrared light separately to visible light, for example. Such systems could also find use in other application ranging from thin emissive polarizers to security features. In an LSC configuration, it could be both more practical and less expensive to attach different PV cells on orthogonal edges tuned to the specific wavelengths ranges emitted by each dye rather than trying to employ a tandem PV cell, for example, to manage a broad emission spectra from a multi-dye system.

4. Experimental Section

For solid polymer film samples, a mix of 0.2 wt% Lumogen Red305 (BASF) (structure given in Figure 1), 1 wt% surfactant 2-(*N*-Ethylperfluorooctanesulfamido) ethyl acrylate (ABCR GmBH), 1 wt% photoinitiator Irgacure 184 (Ciba) and host liquid crystal LC242 (BASF) were dissolved at a ratio of roughly 1:1 by weight in xylene and allowed to thoroughly mix at 80 °C before spinning on 30 × 30 mm^2

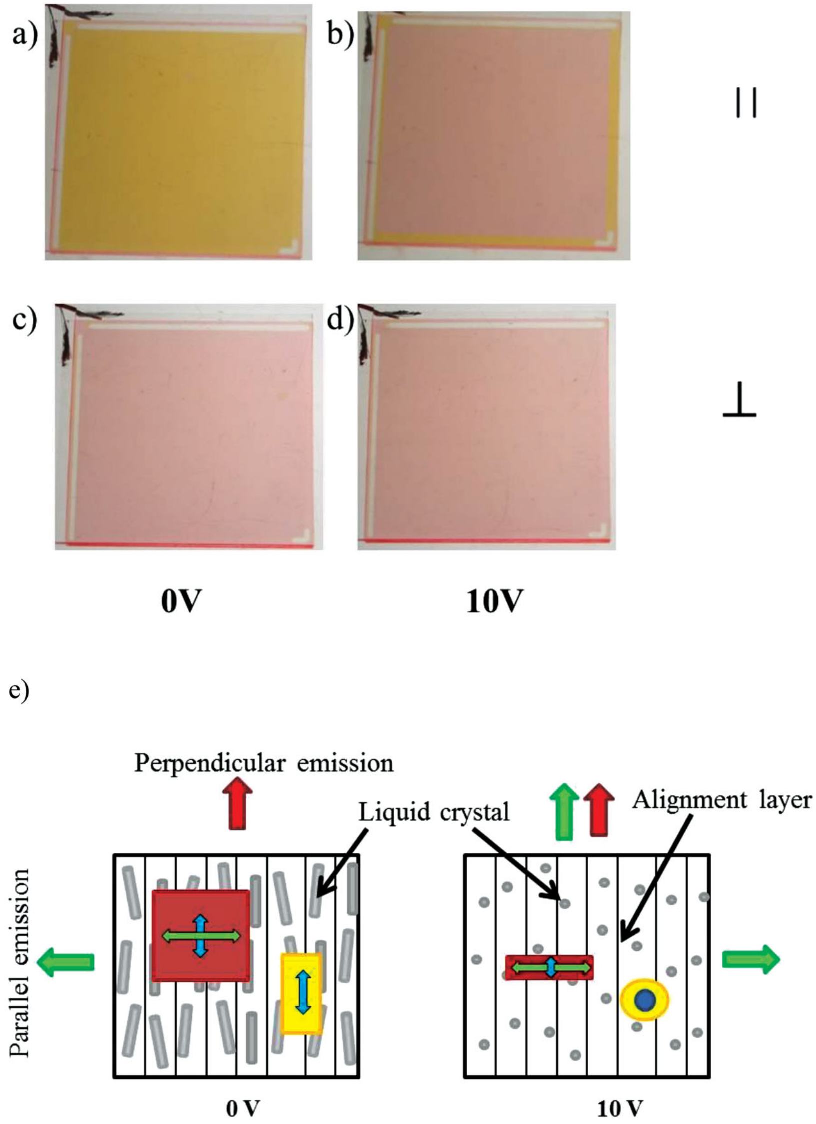

Figure 5. Photographs of cell containing a mix of 0.4% Red305 and 0.14% coumarin dye in the LC host E7 at 0 V (a,c) and 10 V (b,d) through polarizer placed parallel (a,b) and perpendicular (c,d) to the LC alignment direction. e) Schematic displaying postulated dye and relative dipole orientations and predominant emission directions of the dyes at both 0 V (left) and 10 V (right).

glass slides previously coated with a 5 wt% polyvinyl alcohol (PVA) solution in water and rubbed on a velvet cloth which induces planar alignment of the LCs. A second sample using 1.4 wt% Red305 was spin cast in a similar way on a 50 × 50 × 5 mm^3 PMMA plate with similar rubbed PVA aligning layer. After spin coating at 1000 rpm for 30 s, the samples were exposed to ultraviolet light in a nitrogen environment to form a crosslinked, solid polymer film.

Absorption spectra of all the waveguides were recorded on a Shimadzu UV-3102 PC spectrometer with polarized light directed both parallel and perpendicular to the rubbing direction of the alignment layer.

Time-resolved photoluminescence (PL) emitted from the samples was measured with the photoluminescence up-conversion (PLUC) technique. Information about the evolution of the PL polarization was extracted by separately detecting the intensity components polarized parallel and perpendicular to the excitation polarization. The sample could be rotated in order to allow excitation with polarization either parallel or perpendicular to the rubbing direction of the samples. In this experiment, the 900 nm output from a MaiTai Ti:Sapphire laser with 100 fs pulse duration and 80 MHz repetition rate is split into two beams, one of which is frequency doubled to 450 nm and used to excite the sample with polarization selected by passing the beam through a half wavelength plate and a Glan-Thompson polarizer. Photoluminescence from the sample is collected and focused onto a β-Barium Borate crystal by a pair of off-axis parabolic mirrors. A 900 nm gate beam was used to up-convert the collected vertically polarized photoluminescence, with the relative delay between the two varied by means of a delay stage. Up-converted photons with 3.41 eV energy (converted from 648 nm) are selected by a monochromator (Jobin Ivon Triax 190) and detected by a liquid nitrogen cooled CCD.

The setup for edge emission for the lightguide edges has been described previously.[5] Emission was measured by an SLMS 1050 integrating sphere (Labsphere) equipped with a diode array detector (RPS900, International Light). The LSC samples were placed in a custom-made sample holder with a black background with the rubbing direction of the alignment layer both parallel and perpendicular to the entry port of the sphere and exposed to a collimated light source from a 300 W solar simulator with filters to approximate the 1.5 AM (global) solar spectrum (Lot-Oriel), located at a distance of about 15 cm. Light output spectra and intensity from the emission edge of the sample were recorded. Total output was determined by integrating the recorded spectra over the range of 350–750 nm. A correction for the small (~10%) polarization anisotropy in the solar simulator emission was made for the edge outputs of the samples.

For the switchable samples, customized 1.1 mm thick ITO coated glass cells with 20.0 µm cell gap coated with rubbed polyimide layers with 5 × 5 cm^2 active areas (LCTec) were used to make the 'windows'. These cells allowed measurement from 2 orthogonal edges that were different only in their position relative to the alignment layer. The cells were filled with the liquid crystal solution by capillary action with a solution of 0.75 wt% Lumogen Red305 dye in the LC host E7 (Merck), and four two-component cells were made by filling the cells with a mix containing 0.4 wt% Lumogen Red305 and 0.14 wt% of a commercial coumarin derivative shown in Figure 1. Peak absorbance for the four two component cells differed by <3% and the integrated edge measurements from the four cells different by <4%, demonstrating reproducibility of the system. Measured resistance accross filled cells was typically greater than 10 MΩ.

Transmission spectra for incident light polarized parallel and perpendicular to the rubbing direction of the polyimide as a function of applied voltage for the cells were recorded on a Shimadzu UV-3102 spectrophotometer. The peak-to-peak voltage across the cell was regulated by a waveform generator (Agilent 33220A) set with a square wave driving signal at 1 kHz, as described in [11]. The emissions from the two perpendicular cell edges were determined in the same way as for the solid film samples described earlier.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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