Temperature-Responsive Luminescent Solar Concentrators: Tuning Energy Transfer in a Liquid Crystalline Matrix

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Abstract: *Temperature-responsive luminescent solar concentrators (LSCs) have been fabricated in which the Förster resonance energy transfer (FRET) between a donor–acceptor pair in a liquid crystalline solvent can be tuned. At room temperatures, the perylene bisimide (PBI) acceptor is aggregated and FRET is inactive; while after heating to a temperature above the isotropic phase of the liquid crystal solvent, the acceptor PBI completely dissolves and FRET is activated. This unusual temperature control over FRET was used to design a color-tunable LSC. The device has been shown to be highly stable towards consecutive heating and cooling cycles, making it an appealing device for harvesting otherwise unused solar energy.*

Materials that can change color in response to external stimuli, which can be found both in nature[1,2] and artificial devices, are currently receiving much attention.[3–5] Alongside stimuli-responsive optics, a particularly heavily studied topic in contemporary chemistry is Förster resonance energy transfer (FRET), the through-space migration of energy from an excited donor to an acceptor molecule that subsequently emits this energy as light.[6,7] FRET plays an important role in energy harvesting systems, for instance in collecting panchromatic light in a narrow waveband[8] or directing energy to specific reaction centers in the case of photosynthesis.[9] Artificial temperature-responsive FRET systems in supramolecular assemblies have been reported, in which aggregation of the donor and acceptor monomers takes place at lower temperatures resulting in FRET,[10–12]

while at higher temperatures, emission is blue-shifted as the thermal disruption of the co-assemblies results in spatial separation of the donor/acceptor pair, causing emission from the donor to be observable.[11,13,14] However, considerable research into supramolecular FRET for energy-harvesting purposes is still needed[9] because controlling and directing light in stimuli-responsive optical materials and devices remains a challenge.

LSCs are translucent devices containing fluorescent dyes that absorb sunlight and re-emit this light at longer wavelengths.[15,16] A fraction of the emitted light is channeled by the high refractive index lightguide to the edges, on which long, thin photovoltaic (PV) cells are attached. FRET between a donor–acceptor fluorescent dye pair has been used to reduce one of the primary LSC loss mechanisms, reabsorption, if the acceptor molecules emit light outside the absorption band of the donor.[17]

In this work, we use a liquid crystal (LC) as host for a coumarin-derivative donor (**Cou**)/perylene bisimide acceptor (**PBI**) pair. By using an LC as solvent, the device performs differently from conventional solution-based supramolecular FRET systems. At low temperatures, directed emission from only the aligned donor is visible because of the aggregation of the acceptor dye in the LC solvent; while in the isotropic phase at higher temperatures, the acceptor is molecularly dissolved, generating a FRET pair with the embedded donor with a redshift in emission (see Scheme 1). This construction is interesting since it allows for simultaneous control over absorption and luminescence through a single trigger, temperature.

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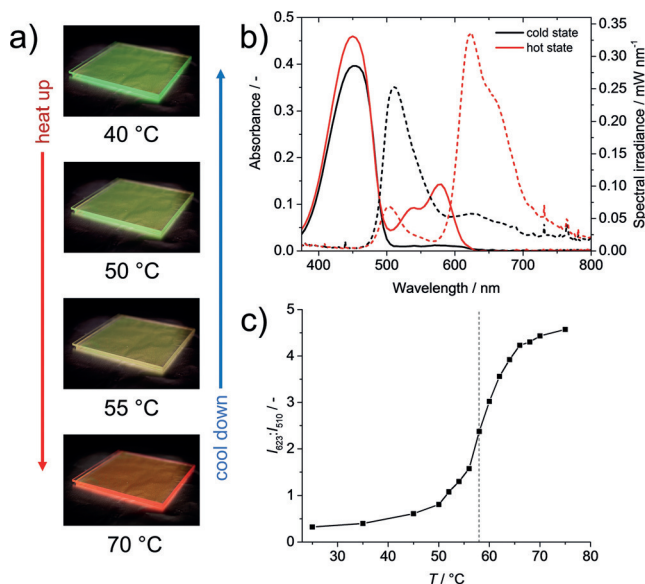Supporting information for this article can be found under:
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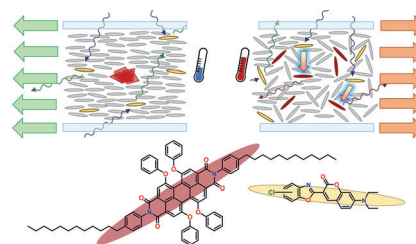
Scheme 1. Proposed interaction mechanism of the **C12-PBI** (red)/**Cou** (yellow) molecules in the LC E7. At lower temperatures at which the LC is in its nematic phase (top left), the **C12-PBI** is in the non-active aggregated state, so all visible emissions (large green arrows) derive from the donor dye **Cou**, which does not aggregate in the host LC. At higher temperatures (top right), **C12-PBI** is more soluble, acting as acceptor for the donor in a FRET interaction, resulting primarily in visible emission from the acceptor (large orange arrows). The two molecules used in this FRET pair are the perylene bisimide **C12-PBI** and the coumarin derivative **Cou**, respectively (bottom).

In order to study FRET in a liquid crystalline host, a green fluorescent dye (**Cou**) with favorable optical characteristics to facilitate FRET ($\lambda_{abs} = 450$ nm, $\lambda_{em} = 530$ nm) was used as dichroic donor dye. Nematic LC E7, which is often used in electro-optical devices, was chosen as the liquid crystalline host solvent (with a nematic–isotropic transition at 58°C, see Figures S1 and S2 in the Supporting Information for details). **C12-PBI** was synthesized as dichroic acceptor; because it is a tetraphenoxy-substituted perylene bisimide dye, it exhibits outstanding absorption and efficient emission ($\lambda_{max} = 573$ nm, $\lambda_{em} = 606$ nm; Supporting Information, Figure S3).[18,19] The dodecyl chains utilized herein impart a high degree of molecular order in the LC matrix.

By placing the resulting solution in an LC alignment cell, a device is obtained that fluoresces bright green if left at room temperature (RT) for a few hours, displaying only emission from the donor **Cou**, indicating that **C12-PBI** luminescence has been deactivated; there is only a weak emission between 600 and 700 nm (see Figure 1). Remarkably, almost no
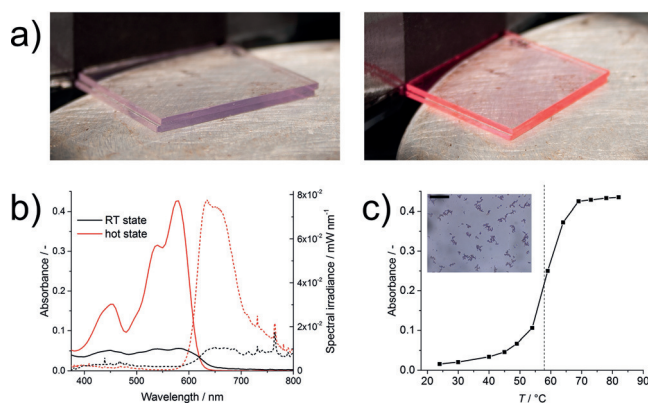
ried out. Time-correlated single-photon counting confirms that energy is transferred from **Cou** to the **C12-PBI** dye molecule. The fluorescence lifetime, τ_F, of **Cou** in the hot, "red" state decreases by 29% (to 2.4 ns) compared to the "green" RT state. Concomitantly, when monitoring acceptor **C12-PBI** at elevated temperature, a delay of about 2.5 ns is seen before maximum counts are reached, strongly suggesting that energy is transferred to this molecule (see the Supporting Information, Figure S5 and Table S2 for further details). The photoluminescence excitation spectrum ($\lambda_{em} = 700$ nm) supports this conclusion, as acceptor **C12-PBI** emission is detected at wavelengths in which normally only **Cou** is strongly excited (see the Supporting Information, Figure S6). From comparing the absorbance and excitation spectra, we estimate a FRET efficiency of 54%.

To unravel the mechanism responsible for the disappearance of the absorption and emission of **C12-PBI** at low temperatures, the optical properties of 0.25 wt% of the dye in nematic LC host E7 (**C12-PBI**/LC) as a function of temperature were investigated. As in the donor/acceptor blend system, the **C12-PBI**/LC mixture displays a weak and rather featureless absorption band, accompanied by very weak, redshifted emission from the edge of the device at RT; see Figure 2b. This featureless absorption band, together with the

Figure 1. a) Photographs of a **C12-PBI**/**Cou** cell demonstrating the color change as the surrounding temperature is increased from 40 to 70°C. b) Absorbance (solid lines) and edge emission (dotted lines) spectra of a cell filled with the two-dye mixture before (black lines) and after heating to 80°C (red lines). c) Ratio between edge emission intensities at 623 nm (**C12-PBI**) and 510 nm (**Cou**), clearly showing that the extent of FRET increases strongly above E7's clearing point of 58°C (vertical dotted line).

Figure 2. a) Photographs of a cell filled with LC/**C12-PBI** mixture left at room temperature (left) and after heating to 85°C (right). b) Absorption and emission spectra of the cell in the two states shown. c) Absorbance monitored at 578 nm shows a strong sensitivity towards temperature, the dashed grey line represents the clearing point of nematic host E7. Inset: Dye aggregates seen in the mixture at RT (scale bar = 100 μm).

absorbance by **C12-PBI** is measured at RT owing to dye aggregation. Upon heating, the green emission (from both the surface and edges of the cell) is gradually replaced by a red emission (see Figures 1 and the Supporting Information, Figure S4 and Video 1). The appearance of the absorption spectrum suggests that **C12-PBI** dissolves into the LC matrix. This most likely results in increased energy transfer from the **Cou** to **C12-PBI**, leading to the red emission.

To verify that energy transfer takes place at higher temperatures, fluorescence lifetime measurements were car-

redshifted edge emission (likely a result of the absorption band broadening), is indicative of *H*-type aggregates (see the Supporting Information, Figure S7).[20–22] Leaving the **C12-PBI**/LC mixture at RT for 2 to 3 h leads to the formation of amorphous aggregates, as confirmed by polarized optical microscopy. After heating to the isotropic phase of E7 at 58°C, the aggregates quickly dissolve and the cell adopts a more defined and stronger absorption typical of a molecularly dissolved state, and a strong red fluorescence is readily visible in minutes, reaching a maximum in about 15 min (see the Supporting Information, Figure S8). Therefore, both the transparency and luminescence of the **C12-PBI**/LC device are

temperature-dependent. Concentration-dependent measurements show the absorbance and fluorescence increase always takes place around 58 °C, independent of the dye concentration (tested from 0.12 up to 0.5 wt %).

This remarkable behavior is different from common supramolecular systems in which the degree of aggregation depends on the concentration and reveals that the aggregation of **C12-PBI** is determined by the phase transition of the LC solvent. In the nematic LC state, E7 is a poor solvent for the dye, while in the isotropic state, it is a good solvent. The thermal stability of **C12-PBI** in the LC host and its ability to reversibly form emissive and non-emissive states was tested by placing the cell in an oven in which the temperature was cycled between 30 °C and 75 °C, each cycle taking 7 h to complete. After 44 consecutive cycles, the measured absorbance of the samples only changed by circa 10 %, indicating the system was quite robust. The integrated power output at the edge parallel to the alignment direction decreased by 8 % (see the Supporting Information, Figure S9).

From edge emission measurements, it was found that the two-dye mixture in a 5×5 cm^2 20 μm cell gap LSC exposed to light from a solar simulator generates a total light power output of 25 mW (optical efficiency $\eta_{opt} = 2.4\%$) in the cold state and 34 mW ($\eta_{opt} = 3.2\%$) when warmed. Furthermore, as E7 is a positive dielectric, applying a voltage across the cell allows for electrical switching of the host LC between a planar (light absorbing) and homeotropic (light transmissive) orientations.[23] This leads to a dual-responsive device, as temperature can be used to control the absorption and emissive colors, while the applied voltage affects the overall absorbance by the incorporated dichroic dyes (see Figure 3 a and the Supporting Information, Figure S10).

Applied as a window, the **C12-PBI** dye alone could allow for a temperature-sensitive aperture. Adding a second dye

such as **Cou** offers the advantages of tuning both absorption and emission colors and providing extensive aesthetic potential to the presented device, including local coloration of the window by selective area heating (with a soldering iron, for instance; see Figure 3 b). The coloration effects can be expanded by adding different secondary dyes, yielding unique optical effects. As examples, we have combined the novel **C12-PBI** dye with an orange emitter, a blue UV dye, and a NIR-emitting pigment (see Figure 3 and the Supporting Information, Figures S11, S12, and S13).[24] These dyes do not show liquid crystal-induced aggregation and the UV/Vis absorbance and edge emission spectra can be found in the Supporting Information (Figure S13).

To conclude, we report on a new mechanism for controlling and directing light in an optical material. A thermochromic system has been fabricated in which the overall absorbance and fluorescence as well as the degree of FRET can be tuned and controlled by a liquid crystalline host. The use of an LC in this system allows for additional benefits over conventional organic solvents, in that we not only obtain specific solubility and alignment of the fluorescent dye molecule[25] but can also extend the device response to a dual-trigger system, utilizing either thermal and/or electric stimuli,[26] affecting both the absorbance and emission spectra of the device. The color change is reversible with minimal loss in fluorescence. Such temperature responsive optical materials and devices will find applications as aesthetically appealing smart devices for harvesting otherwise unused solar energy, be it in the form of electricity-generating responsive shading materials for greenhouses[27] or a photocatalytic microreactor, sending photons to designated reaction centers.[28]
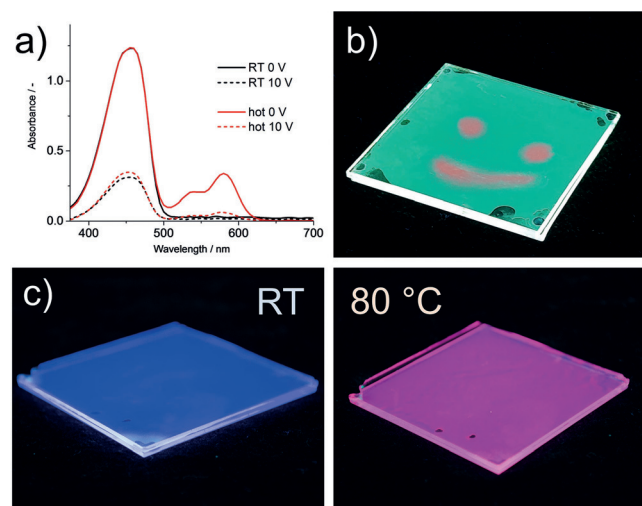
Experimental Section

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Figure 3. a) UV/Vis absorbance measurements of an E7 LC cell containing **C12-PBI** and **Cou**, showing dual-responsive behavior by switching thermally and electrically. b) The device can function as a writeable LSC by heating locally with a soldering iron, strengthening the aesthetic possibilities of the device. c) A cell in which the second dye is BASF Lumogen® F Violet 570. At RT (left), only this emission ($\lambda_{max} = 436$ nm) is visible. After heating to 80 °C, a pink mixture of **C12-PBI** and Violet 570 emissions is evident.

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