Light harvesting and energy transfer are critical to achieving high quantum yields in LSCs. The triad dye consists of two perylene bisimide donors and one perylene bisimide acceptor, which is substituted at the bay position with two phenoxy units (Figure 1c). Rotational constrained connections are present between the individual chromophores, resulting in orthogonal conformations. The triad has been synthesized according to a reported procedure and the individual monomer donor and acceptor dyes have also been synthesized as references. All dyes have been fully characterized by 1H NMR, 13C NMR, and MALDI-ToF mass analysis. Pure compounds were obtained by recycle GPC and confirmed by GPC analysis.

To confirm energy transfer from donor to acceptor, the triad was dissolved in chloroform and the UV/vis absorption and fluorescence spectra were recorded (Figure 2). The absorption at 533 nm originates from the two donor moieties, while the absorption at 556 nm is from the acceptor. The absorption spectrum of the triad is similar to the summation of the spectra of the individual compounds, with the acceptor absorbance in the triad being red-shifted relative to that of the free acceptor reference, indicating that some degree of electronic coupling.

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may be present$^{17,19}$ between the perylene bisimide chromophores, as reported recently in a series of similar molecules.$^{17,20,21}$ Fluorescence measurements of the individual donor and acceptor reference molecules show emission from the donor located around 540 nm, while the acceptor has a maximum at 588 nm.$^{16}$ The fluorescence spectrum of the triad revealed an emission peak at 588 nm, indicating efficient energy transfer as there is no residual fluorescence from the donor detected.$^{16}$ By monitoring an excitation spectrum at 630 nm, where the emission of the donor is negligible one achieves a spectrum that is identical in shape to the absorbance spectrum of the linear dye, suggesting energy transfer close to unity (Figure 2).

For the fabrication of switchable LSCs, the triad dye was incorporated in a commercial LC host mixture (MLC-6284-000, Merck licristal) having a nematic phase over a broad temperature range and used to fill an ITO coated alignment cell.$^{22}$ The polarized absorption spectra showed that the highest absorption is obtained when the light is polarized parallel to the director of the LC host (Figure 3). The order parameter of the dye ($S_\parallel$) was calculated using

$$S_\parallel = \frac{A(\lambda_{\max \parallel}) - A(\lambda_{\max \perp})}{A(\lambda_{\max \parallel}) + 2A(\lambda_{\max \perp})}$$

where $A(\lambda_{\max})$ is the maximum absorption for light polarized parallel (||) and perpendicular (\(\perp\)) to the alignment direction of the LC, respectively (Figure 3, inset). The triad has an order parameter of 0.8 at 536 nm, which is among the highest reported order parameters for a fluorescent dichroic dye in a nematic LC.$^{12}$ The edge emission spectrum of the cell only exhibits one maximum at 604 nm, indicating efficient energy transfer (Figure 3). As a control experiment, the edge emission of the reference dye mixture was also measured showing clear emission from both the acceptor and the donor molecules, as evidenced by two peaks, one from the donor at 586 nm and the other from the acceptor at 615 nm.$^{16}$ When measuring the emission spectrum from the sides parallel and perpendicular to the alignment of the liquid crystal, a clear difference in intensity was obtained. Coupling individual dyes increased the edge output ratio, defined as edge emission from side 1 divided by edge emission from side 2 (see inset cartoon in Figure 3). For the triad, this ratio is 1.55, among the highest values reported.$^{11}$

The switching of the LSC from an absorbing “off” state to a transparent “on” state was achieved by applying 10 Vp across the cell gap to reorient the molecules in a homeotropic orientation, perpendicular to the cell surface (Figure 1b). The switching behavior of both the triads as the reference mixture was investigated. The polarized absorption spectra are recorded in the “on” (10 V) and “off” (0 V) states (Figure 4). The contrast, $C_s$ of the switchable LSC is defined as the integrated nonpolarized absorbance from 450 to 600 nm of the LSC in the “off” state divided by the absorbance in the “on” state over the same range, resulting in a contrast for the multichromophoric dye of $C_{1,\text{triad}} = 2.83$, while the reference system has a contrast of $C_{1,\text{ref}} = 1.87$. When using the maximum absorption, a contrast $C_2$ of $C_{2,\text{triad}} = 2.69$ is reached, while the reference
system has a contrast of $C_{\text{ext}} = 1.83$ (Figure 4 and Supporting Information Figure S4b,c). The switching edge output ratio for the triad system, defined as the integrated edge emission from edge $I_{\text{on}}$ divided by edge $I_{\text{off}}$, is 2.02, while the reference mixture has an output ratio of 1.65, showing the anisotropy in emission direction can be improved upon coupling chromophores as a rigid system.

In conclusion, we have demonstrated that coupling multiple chromophores in a single triad dye results in highly anisotropic and high contrast switchable LSCs. These triads show light harvesting and energy transfer properties, while maintaining contrast in transmission between “on” and “off” states, which has not been possible using individual dye mixtures. Our results are not only relevant for LSCs but are also of importance for achieving efficient control over light distribution in optical devices.

* ASSOCIATED CONTENT

1 Supporting Information
Experimental methods, synthetic procedures, full characterization and optical analysis of the molecules and devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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