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Using “Internal Free Volume” to Increase Chromophore Alignment

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Received November 9, 2001

The control of the orientation of molecules is of fundamental importance for the efficient production of efficient optical materials.[1] From dichroic polarizers to holographic data storage, the anisotropic orientation of molecules is a key to their success. The greater the alignment of solutes in a host media, be it liquid crystals (LC) or polymers, the greater the polarization, and therefore, the higher data content that is possible.

In a LC host, this alignment of guest molecules is called the guest–host effect.[2] Nearly all anisotropic materials incorporating dyes or polymers depend on the aspect ratio of the molecules to guide alignment with an alignment axis. While, theoretically, the dichroic ratio can be increased by continually increasing the molecular aspect ratio, response times and solubilities become limiting factors when used in optical devices.[3] It has been suggested that other shapes could overcome this limitation.[4] However, until recently, no real-world physical examples had been demonstrated.

We have very recently shown, that when incorporated into a triptycene molecule, anthracene can be aligned with its aspect ratio perpendicular to the director of a nematic LC or stretching direction of a stretch-aligned polymer.[5] We believe that this alignment is governed by the minimization of free volume of the system. By threading LC molecules through the void spaces defined by the aromatic faces of the triptycene moieties, the volume is most efficiently filled. These void spaces can be considered the “internal free volume” of the triptycenes.

In this communication, we illustrate that triptycenes have general applicability for increasing the alignment of commonly used fluorescent and dichroic dyes in LC hosts. Building upon what we learned from our previous investigations, we synthesized fluorescent blue dyes $\mathbf{1_{0-3}}$ (Chart 1) to study the effect of free-volume alignment of triptycenes on the alignment of dyes. These dyes were designed such that multiple triptycenes could be incorporated, and the triptycene free-volume is coincident to the aspect ratio of the dye. This design (as illustrated in Figure 1) allows for a cooperative effect on alignment of the dyes to increase their overall average alignment. Notice how the LC molecules in Figure 1 occupy the convex space defined by the triptycene.

Fluorescent dyes $\mathbf{1_{0-3}}$ were dissolved in a common LC host (1 wt % in 4-*trans*-(4-pentylcyclohexyl)benzonitrile) and homogeneously aligned in a rubbed polyimide-coated test cell (10 μm thick, ITO glass). Polarized UV–vis spectra, parallel and perpendicular to the LC alignment, were recorded and their observed order parameters calculated according to eq 1.[6]

$$S_{\mathrm{ob}} = (A_{\|} - A_{\perp})/(A_{\|} + 2A_{\perp}) \qquad (1)$$

These results are summarized in Table 1. The polarized UV–vis spectra for $\mathbf{1_{0-3}}$ are shown in Figure 2, with all 90° polarized spectra normalized to illustrate the trend in the data. A stepwise, nearly linear, increase in the alignment parameters of each dye was seen within the series. With each additional triptycene incorporation into the dye, their alignment increases incrementally, to ultimately 23% with respect to dye $\mathbf{1_0}$.

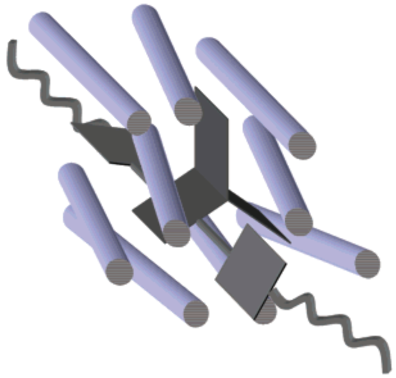

Figure 1. Schematic Representation of $\mathbf{1_1}$ in a LC host (cylinders represent the LC).

Chart 1. Model Compounds $\mathbf{1_{0-3}}$–**2**

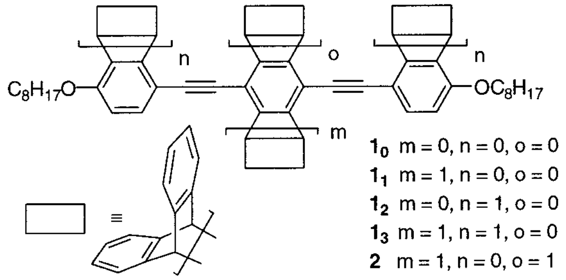

Table 1. Order Parameters (S_{Ob}) and Switching Times (T_{off}) for $\mathbf{1_{0-3}}$–**4**

cmpd	S_{ob}	T_{off} (ms)
blank LC	–	2.8 (0.2)
1_0	0.62 (0.01)	2.5 (0.1)
1_1	0.68 (0.01)	2.7 (0.1)
1_2	0.73 (0.01)	6.7 (0.1)
$\mathbf{1}_3$	0.76 (0.01)	4.6 (0.2)
2	0.61 (0.01)	-
3	0.62 (0.01)	5.0 (0.2)
4	0.68 (0.01)	8.0 (0.1)

Dye number **2** was designed under the assumption that pentiptycene would give a greater increase in alignment with respect to triptycene, due to its greater internal free volume. Interestingly, compound **2** did not have increased alignment, but rather had decreased alignment with respect to dye $\mathbf{1_0}$. This can be attributed to the restricted environment around the central ring of the pentiptycene moiety. Only one LC molecule can occupy either face

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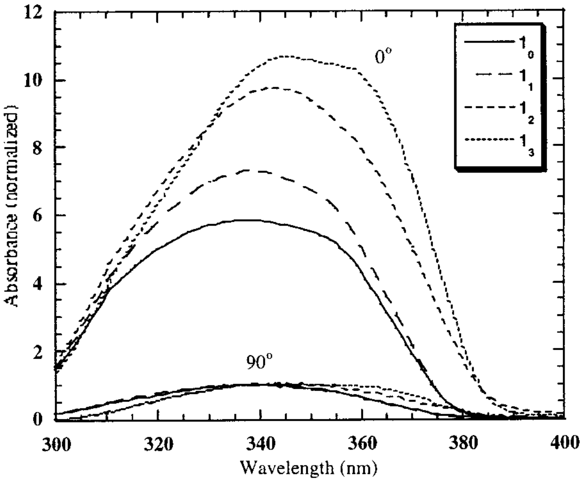
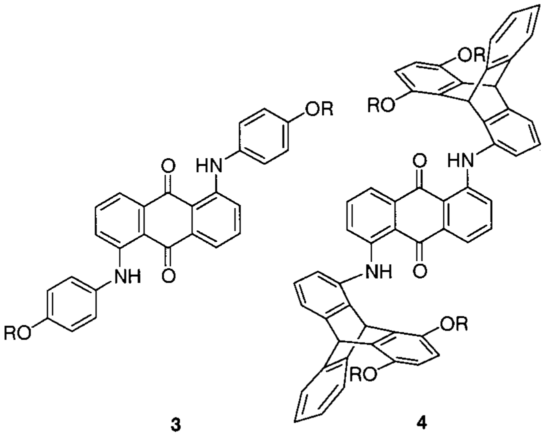


Figure 2. Polarized UV−vis spectra of $\mathbf{1}_{0-3}$ with 90° spectra normalized.

Chart 2. Structures of Dyes **3** and **4** (R = n-C_8H_{17})



3 **4**

of the pentiptycene. In a solvated state, this occupation is very unlikely and results in a large disruption of the local order of the LC host. Triptycenes, on the other hand, allow for more rotational and positional entropy in the nematic LC. These triptycenes can sense the director of the LC and act as a stabilizer wing to average out the local motions of the host LC.

We further wished to demonstrate the generality of the effect of the triptycenes on more complex dyes. Aminoanthraquinone dyes are popular for use in LCDs due to their vivid colors, high extinction coefficients, and longevity.[7] We synthesized dichroic dyes **3** and **4** (Chart 2) to see if triptycenes gave the same alignment enhancement in these dichroic dyes as in the bis(phenylethynyl)benzene cases. These 1,5-diaminoanthraquinones have greater flexibility and greater rotational freedom, and their transition dipoles are slightly off the long axis of the anthraquinone.

The switching response times of $\mathbf{1}_{0-3}$ and **3**−**4** were compared to determine the effect that attachment of triptycenes has on their switching times. Generally, the elongation of dichroic dyes, to increase their alignment, has the detrimental effect of slowing the response time. The same 1 wt % solutions were used, and the LC mixture was switched from homogeneous to homoeotropic while viewed through crossed polarizers (with the director 45° to both polarizers). The voltage was applied such that the "OFF" state was 0 V and transparent; the "ON" state was at −40 V and dark.

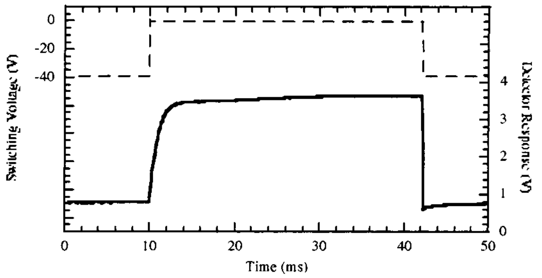


Figure 3. Optical switching response of $\mathbf{1}_1$.

Response times herein are defined as the time it takes to see a 90% optical response.[8] In both cases $T_{\text{on}} < 0.2$ ms. T_{Off} times are listed in Table 1, and a representative switching response for $\mathbf{1}_1$ is shown in Figure 3.[9] The attachment of one triptycene group has a negligible effect on switching time ($\mathbf{1}_0$ vs $\mathbf{1}_1$) while two triptycenes have a detectable effect ($\mathbf{1}_2$ and **4**). Interestingly, $\mathbf{1}_3$, which has three triptycenes attached, switches faster than $\mathbf{1}_2$. We believe this is due to the cylindrical shape of $\mathbf{1}_3$, versus the dumbbell shape of $\mathbf{1}_2$, which should require less reorganization to return to its original state.

As previously stated, increasing the aspect ratio of a dye has been known to increase the order parameter of a dye, be it fluorescent or dichroic. This is most often achieved by attachment of longer alkyl groups or by extension of the size of the chromophore.[7a] By extending the dye design into an additional dimension, new design principles can be elucidated. In this study, we are able to maintain the overall length of the triptycene-containing dye molecules while increasing the alignment. We believe this can be a very powerful tool for designing dichroic and fluorescent dyes with higher alignments for a variety of applications including guest−host reflective LCDs and holographic data storage.

Acknowledgment. We thank the National Science Foundation (NSF) and the Army Research Office (ARO), through a MURI Grant, for funding.

Supporting Information Available: Detailed descriptions of experimental procedures and synthetic preparations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The voltage used in this study is the same as in ref 2a. The voltage dependence on switching times of $\mathbf{1}_0$−$\mathbf{1}_3$ is listed in Supporting Information.

JA017499X