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Photostimulated and Photosuppressed Phase Transitions in Liquid Crystals

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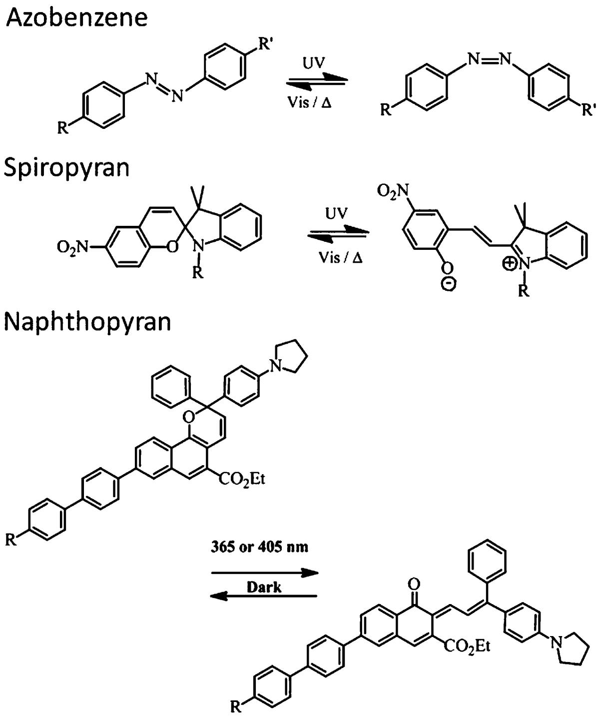
The temperature and concentration of the solvent are the traditional parameters, the variation of which brings about liquid crystal (LC) phase transitions. While the class of LCs affected by temperature is known as thermotropic, the latter is termed lyotropic.[1] In recent years a new parameter has been added to this list, namely light,[2] and LC phases obtained in this manner are dubbed phototropic.[3] The ability of light to alter or stabilize a particular thermodynamic phase through the photoisomerization of the constituent molecules is an interesting tool for investigating condensed matter from a new dimension. An illustration of nature utilizing photoinduced effects is that of the biological photochrome bacteriorhodopsin found in the eye.[4] Over the last couple of decades, a number of photostimulated isothermal phase transitions have been reported in LCs with respect to the reversible change in the molecular shape anisotropy of the photoresponsive component(s) as driven by actinic light. Some of the molecules which have been exploited as photoresponsive components are given in Scheme 1.[5] Of these, the most often used are the azobenzenes, not only because of their ability to exhibit fast, efficient, and fully reversible photoisomerization, but also because of their isomerization being one of the cleanest photoreactions ever known in that side products are not formed, even with innumerable isomerization cycles.[6] Although photoisomerization-related effects are large if the entire material is photoactive, from an operational point of view it is obviously better to dope small quantities of a guest photoactive material onto a host LC system which has been optimized for temperature range, viscosity, etc.



Scheme 1. Representative molecular structures of some popular photoresponsive molecules in their equilibrium form and the form resulting from irradiation.

In Figure 1 we illustrate the phenomenon behind the photoinduced transformation from the nematic (N) phase, which is an orientationally ordered fluid, to an isotropic (Iso) fluid in an azobenzene-doped LC system with nonphotoactive host molecules. Illuminating a thin film of such a guest/host mixture brings about photoisomerization of the azobenzene from its rodlike *trans* isomer to a bent *cis* form. The dissimilarity of the molecular shapes of the guest and host molecules after isomerization destabilizes the equilibrium N phase, even to the point of bringing about an isothermal phase transition to the otherwise higher temperature Iso phase. The resulting structural differences yield spectacular changes in many physical properties including birefringence of the medium.

Over the years, diverse photoinduced phase transitions in LC systems covering a large number of the forty or so LC structures involving achiral as well as chiral materials, nematic, smectic, columnar, and Blue phases have been reported (for a review see Ref. [2b]). With very few exceptions, photoisomerization of the photoactive material results in the melting of the phase, or in other words, transformation to a less ordered state. The first report of a photodriven ordering in a system comprising an azobenzene derivate involved a re-entrant nematic transforming into a more ordered smectic phase;[7] this transformation was explained using a nanophase segregation model.[8] An even more exotic dynamic self-assembly occurs for a composite not exhibiting

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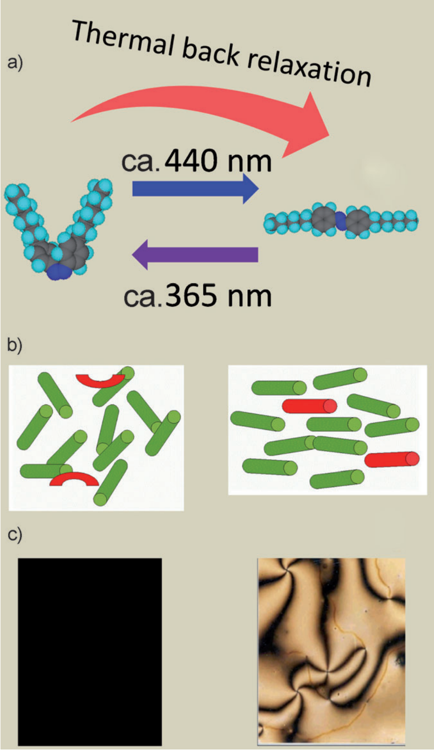

Figure 1. Diagram illustrating the effect of photoisomerization with $\lambda = 365$ nm light on the a) shape of the photoresponsive azobenzene molecule changing from the straight to bent form, and reversing it with $\lambda = 440$ nm light or heat, b) structural change from the N phase (right) to the Iso phase (left), and c) the corresponding birefringent (right) and dark (left) fields of view as seen using a microscope.

the smectic phase in the absence of UV radiation. In this case, aggregation to a layered phase occurred with UV light acting as a stimulant and existed only as long as the radiation was present. Two different ways of suppressing the effects induced by photoisomerization have also been discovered in recent times, that is, the application of pressure[2a] and an electric field.[9]

Kosa et al.[10] have recently published interesting work in which the reverse transformation, namely the light-driven transformation of the Iso phase to the N phase, is observed in a system composed of naphthopyran guest molecules. The mechanism exploited is well known in a certain class of compounds such as spiropyrans and naphthopyrans wherein the molecule can be switched from a colorless closed form to a colored open form upon irradiation with UV light, and returned to the original form by irradiation with visible light. The advantage in these molecules is that the form resulting from UV irradiation is more rodlike than the equilibrium form. Consequently, the stability of the LC phase can be expected to be greater upon illumination with light, a feature opposite to that of azobenzene systems. Indeed, years ago, Kurihara et al.[11] had shown that in a spiropyran-doped LC, UV illumination can drive the Iso phase to the N phase. Kosa et al.[10] suggest that the underlying mechanism could have an impact on a number of applications such as telecommunications, energy conversion, and protection against radiation. For instance, exploiting the photoswitchable chromaticity of the system to yield an equilibrium transparent state, and a photoswitched dark state. In this context, it may be recalled that recently photochromic spiropyran molecules embedded in electrospun polymer microfibers were employed to realize photoswitchable displays.[12] Hypsochromic shifts in the selective reflection wavelength of the cholesteric phase when exposed to UV light has been used to fabricate a rewritable full color image recorder.[13] A very attractive features of the studies by Kosa et al.[10] is that the back relaxation process—the return of the photoinduced state to the original one—is very fast and uncommon in azobenzene-based systems. This obviates the need for other measures such as illuminating the material with a different wavelength of light or applying electric fields, thereby greatly simplifying device fabrication, and also usage of naphthopyran-based materials such as photoaligning layers.[14]

The work by Kosa et al.[10] is significant in that it brings together various photoinduced effects explored earlier in a cohesive manner and emphatically demonstrates how such photodriven transitions are interesting not only from an academic point of view, but has potential for important technological applications for holographic recording and as soft actuators[6,15] utilizing the change in shape and chromaticity of the system. The point that one of the naphtopyran derivates employed by Kosa et al.[10] exhibits a very large order parameter adds to the importance of the work.

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