Photochemical Phase Transition versus Photochemical Phase Separation

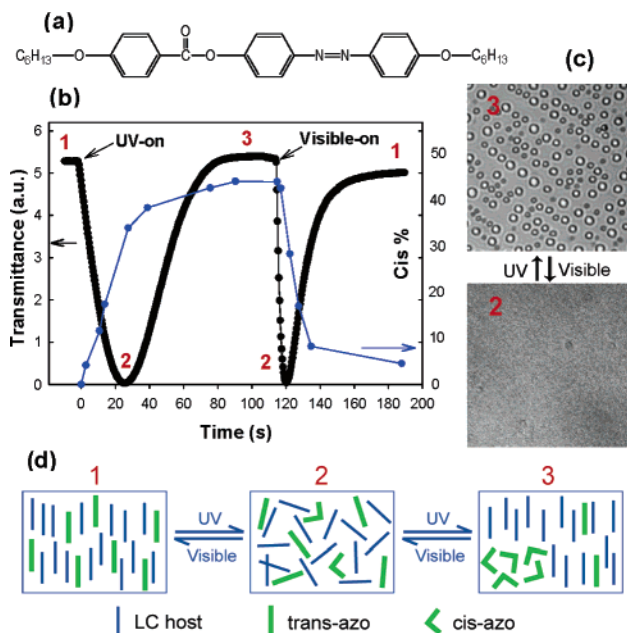Xia Tong, Guang Wang, and Yue Zhao*

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Azobenzene derivatives are among the most studied chromophores in developing new photoactive materials. When used as dopants in liquid crystals (LCs), the reversible trans−cis photoisomerization of azobenzene can exert large effects on the properties of LCs.[1] The most salient effect is arguably the destabilization of LC phases by the conversion of azo guest molecules from the trans form to the cis form. The rod-like shape of the trans isomer is compatible with LC phases, while the bent shape of the cis isomer is incompatible with them, which, in the case of nematic LCs, can give rise to an isothermal photochemical nematic−isotropic phase transition.[1] This property has been largely explored for possible optical device applications.[2] Generally, the concentration of azo dopants is kept low (≤5 wt %) due to their limited solubility in LCs.[3] Recently, we have synthesized a LC azo compound (chemical structure in Figure 1a) that has high solubility in LCs due to its own LC nature, having a broad nematic phase between 110 and 227 °C (Supporting Information). Here, we report the discovery of a new phenomenon in LCs doped with a *high* concentration of LC azo dopant (≥10 wt %), namely, the interconversion between a reversible photochemical phase transition and a reversible photochemical phase separation at the micrometer scale. These two processes are controlled by the amount of cis isomer of azo dopant in the mixture and allow for two (normal and reverse) modes of photocontrolled switching of transmittance (optical shutters) with the same doped LC. We believe that the richer photochemical effects in the regime of high concentrations of azo dopants, revealed for the first time to our knowledge, are of fundamental interest and may offer new possibilities for applications of azo dye-doped LCs.
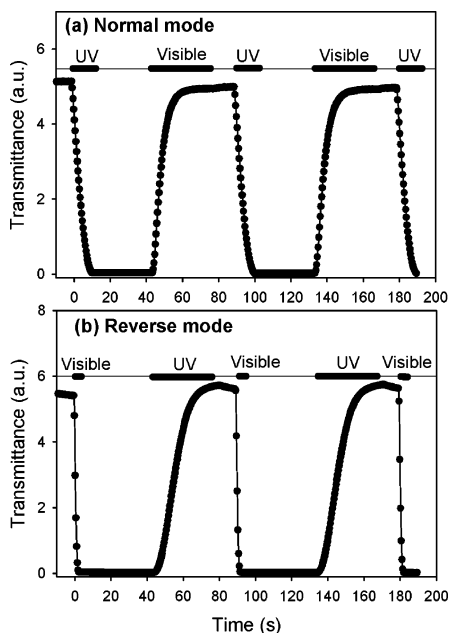
The nematic LC host used was BL006 (Merck), which is a eutectic mixture of several LC compounds (T_{ni} = 116 °C). As much as 25 wt % of our LC azo compound can readily be solubilized in BL006. Above this concentration, phase separation was observed. The homogeneous mixtures were filled into a parallel-rubbed and indium−tin-oxide (ITO)-coated cell with a gap of 5 μm. Their photochemical responses to UV or visible light exposure were monitored by measuring the optical transmittance of a probe light (λ = 633 nm from a He−Ne laser) through the cell placed between crossed polarizers setting at 45° to the rubbing (LC orientation) direction.[1] The example of results in Figure 1b, obtained at room temperature, shows the interconvertible photochemical phase transition and phase separation in the LC doped with 15% of the LC azo compound. When UV light (λ = 365 nm, 6.5 mW cm^{-2}) was applied to the mixture, the transmittance dropped as a result the trans−cis isomerization-induced destabilization of aligned LC molecules. However, instead of a stable low transmittance (disordered) state under UV irradiation, as observed for mixtures with a low concentration of dopant (≤5%), the transmittance rose again at longer times to reach a new high transmittance state *under UV irradiation*. When visible light (λ = 440 nm, 4.5 mW cm^{-2}) was turned on (UV turned off) to induce the reverse cis−trans isomerization, the transmittance dropped first and then went up

Figure 1. (a) Chemical structure of the liquid crystalline azo dopant. (b) Change in transmittance of BL006/dopant (15%) exposed to UV (6.5 mW cm^{-2}) and visible light (4.5 mW cm^{-2}), and variation of the amount of cis azobenzene in the mixture. (c) Photomicrographs of the mixture in states 2 and 3 marked in (b) (image area: 50 × 50 μm^2). (d) Schematic illustration of the reversible and interconvertible photochemical phase transition and photochemical phase separation.

again. The numbers marked in Figure 1b refer to the different states in the mixture as discussed below.

The new high transmittance state under UV irradiation (state 3) resulted from a photochemical phase separation process. The examples of photomicrographs in Figure 1c show the appearance of two phases at state 3 (most droplets have a diameter around 1.5−2 μm). On visible light irradiation, the mixture was quickly homogenized, returning to state 2. Careful UV−vis measurements were performed to determine the amount of azo dopant molecules in the cis form under the same sequence of irradiation. The results, also given in Figure 1b, support the mechanism sketched in Figure 1d. Before UV irradiation, LC azo dopant molecules and the LC host in their miscible mixture are aligned by rubbed surfaces (state 1). On UV irradiation, the increase in the amount of cis azo molecules disorders the aligned LC phase, leading to the photochemical phase transition (state 2) at about 35% of cis azo dopant. However, as the amount of cis azo dopant continues to increase under UV light, they start to phase separate from the LC host (recall that the initial high concentration solubility stems from the LC nature of azo dopant in the trans form). The phase separation should reduce the destabilization on LC molecules and allow their realignment by rubbed surfaces. This ordered state was observable on a polarizing optical microscope (Supporting Information). The two processes compete to see that the photochemical phase

Figure 2. Two modes of photocontrolled switching of transmittance of BL006/dopant (15%): (a) normal mode based on transition between states 1 and 2; (b) reverse mode based on transition between states 2 and 3 indicated in Figure 1 (UV = 10.6 mW cm^{-2}; visible = 10.4 mW cm^{-2}).

separation predominates the photochemical phase transition when the amount of cis azo dopant reaches about 46%, which is the photostationary state under the conditions used. At this point, state 3, the realignment of LC molecules separating from cis azo dopant should account for the reappearance of high transmittance. Since the two processes are controlled by the amount of cis azo dopant in the mixture, upon subsequent visible irradiation, which decreases the amount of cis azo dopant due to the reverse cis−trans isomerization, it is no surprise to see that the photochemical phase transition dominates again (back to state 2) as the mixture is rehomogenized when the amount of cis azo dopant is reduced to around 30%. As the amount is further diminished, the perturbation becomes no longer enough to destabilize the aligned LC, and the initial state 1 can then be recovered. These two processes are reversible and interconvertible through the control of the amount of cis azo dopant in the mixture. With a low concentration of azo dopant (≤5%), only reversible changes between states 1 and 2 can be observed (Supporting Information). This is because the smaller amount of cis azo molecules at the photostationary state can remain solubilized in the disordered LC (state 2). For the system studied, significant photochemical phase separation at the micrometer scale was observed from about 10% of azo dopant. Note that the phenomenon reported here is different from the photoinduced phase separation in azobenzene-containing Langmuir monolayers[4] and is different from the nanophase segregation of an azo dopant from within the layers to locations between the layers of a smectic LC upon the trans−cis isomerization.[5]

The richer photochemical effects in the regime of high concentrations of azo dopant can be exploited for new applications. Figure 2 shows two modes of reversible photocontrolled switching of transmittance realized using the same mixture with 15% azo dopant at room temperature. In the normal mode, which is the switching between states 1 and 2, UV light (10.6 mW cm^{-2}) was applied to induce the photochemical phase transition, but turned off after the transmittance dropped to the minimum level (state 2). In this way, the amount of cis azo dopant did not continue to increase, so that

no photochemical phase separation occurred. On visible irradiation (10.4 mW cm^{-2}), the transmittance was recovered as the mixture returned to state 1. In the reverse mode, which is the switching between states 2 and 3, the high transmittance state was first obtained with the phase-separated state (state 3). The transmittance dropped on visible light irradiation that turned the mixture to state 2. As the visible irradiation was turned off after the transmittance reached the minimum level, the amount of cis azo dopant did not continue to decrease, so that state 2 remained stable, while state 3 was recovered upon UV irradiation. We measured the transmittance fall-time and rise-time under various UV and visible irradiation intensities (Supporting Information). In this study, the reverse cis−trans isomerization was activated using visible light irradiation. Without it, the thermal relaxation of cis azo dopant is slow. For instance, in the normal mode of switching, after UV irradiation was turned off, the transmittance was recovered to about 20% of the high transmittance state after 7 h. By contrast, for the reverse mode, after turning off UV irradiation, the high transmittance state was less stable; it dropped by about 50% after 3 h. This observation can be related to the results in Figure 1b that a difference of only about 10% of cis azo dopant controls the transition between states 2 and 3, while the difference is about 30% for the transition between states 1 and 2. We mention that, at high temperatures close to T_{ni} of the mixture, no photochemical phase separation was observed with 15% of azo dopant, even though complete photochemical phase transition was faster. This is because at high temperatures the fast thermal relaxation of cis azo dopant prevents the formation of a large amount of cis azo molecules under UV irradiation.

To summarize, we report that LCs doped with a large amount of LC azo compound can display reversible and interconvertible photochemical phase transition and photochemical phase separation at the micrometer scale. We show that the amount of azo dopant molecules in the cis form under UV or visible light irradiation controls the two processes. We demonstrate that making use of the two processes, both normal and reverse mode of photocontrolled switching of transmittance, can be realized using the same doped LC mixture. Studies are underway in our laboratory to further explore the use of the discovered rich photochemical effects in the regime of high concentrations of azo dopants in LCs.

Supporting Information Available: Liquid crystalline azo dopant synthesis and characterization, and more data on photocontrolled switching. This material is available free of charge via the Internet at http://pubs.acs.org.

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