



Supporting Information

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Supporting Information

Fast Cis-Trans Isomerization of An Azobenzene Derivative in Liquids and Liquid Crystals under A Low Electric Field

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1) Experimental Setup

Figure S1 shows a picture of the experimental setup used to record the UV-vis spectra of HHBAzo dissolved in liquids or liquid crystals while being subjected to an electric field. The different components are identified on the photo.

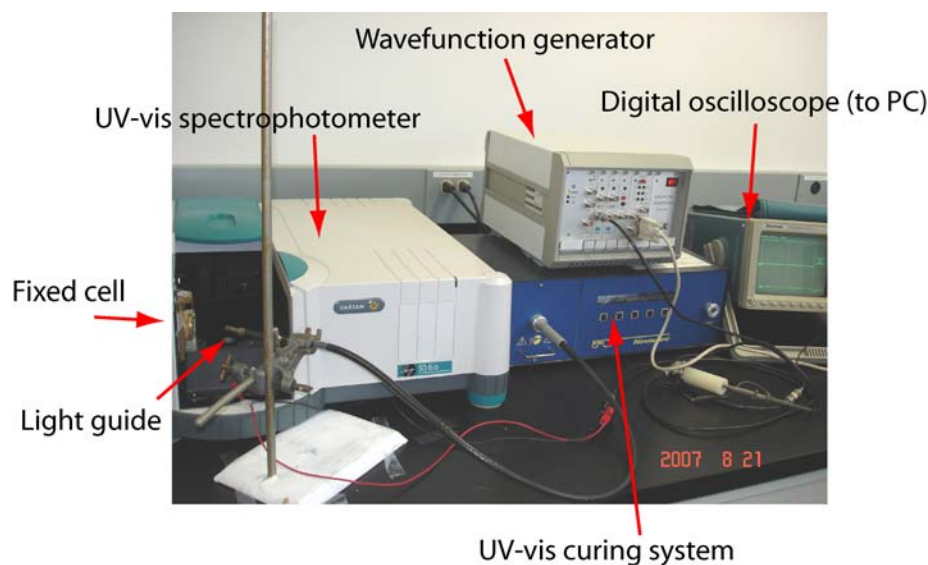


Figure S1

2) Azobenzene Derivative in Nematic Liquid Crystal BL006

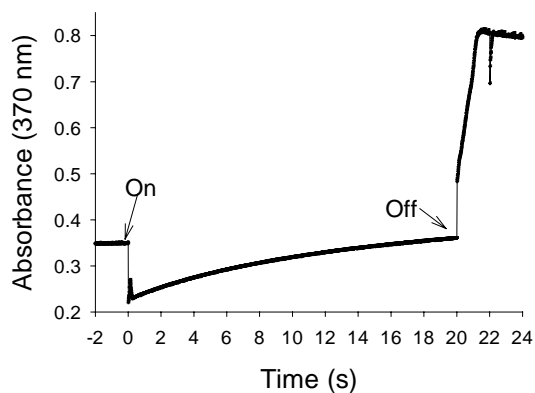
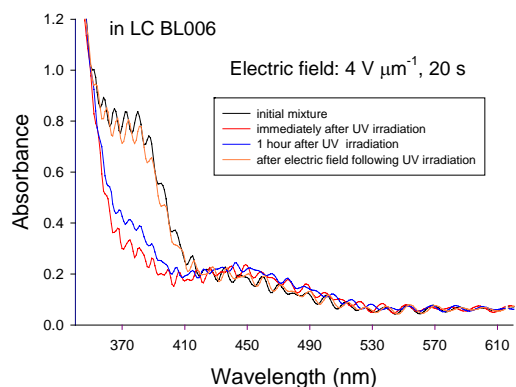
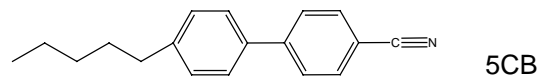


Figure S2

In addition to 5CB (structure shown below), the nematic BL006 (Merck, $T_{ni}=106\text{ }^{\circ}\text{C}$) was also used. BL006 is a eutectic mixture of several compounds (actual formulation is undisclosed by the company). Figure S2, shows the results obtained with HHBAzo dissolved in BL006. Similar observations can be made as in the case of 5CB, though relatively lower voltages are required for the cis-trans isomerization.



3) Comparison for Azobenzene Derivative Dissolved in Various Solvents

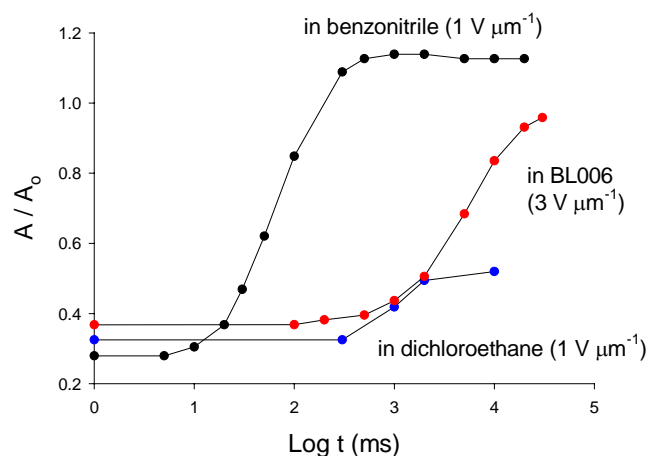


Figure S3

Figure S3 shows the plots of normalized absorbance of trans-azobenzene (356 nm in benzonitrile and dichloroethane, 370 nm in BL006) as a function of logarithmic time (in ms) over which the electric field was applied (the same strength of $1\text{ V } \mu\text{m}^{-1}$ for the two organic solvents and $3\text{ V } \mu\text{m}^{-1}$ for the nematic liquid crystal solvent). In benzonitrile, the electric field-induced cis-trans isomerization occurs under an electric pulse as short as 20 ms, while in dichloroethane and BL006, it takes longer time to observe the isomerization process. With $1\text{ V } \mu\text{m}^{-1}$, the electric field-induced isomerization is limited in dichloroethane.

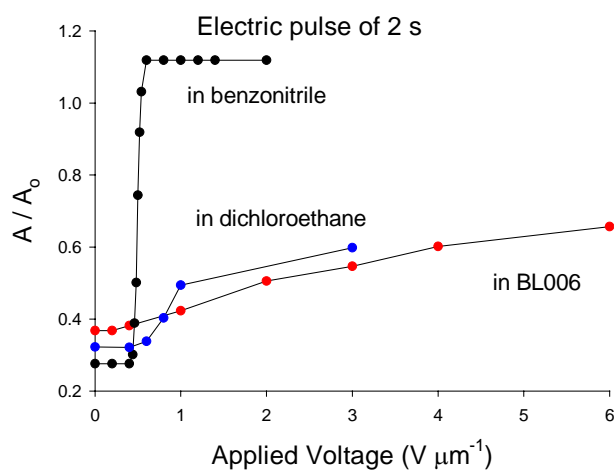


Figure S4

Figure S4 compares the electric field-induced cis-trans isomerization in the two organic solvents and the liquid crystal in a different way, showing the plots of normalized absorbance of trans-azobenzene as a function of applied voltage under an electric pulse of the same width of 2 s. The threshold voltage in all cases is below $1 \text{ V } \mu\text{m}^{-1}$. However, only in benzonitrile, the isomerization can be completed during the 2 s period.

In contrast to the cis-trans isomerization under an applied voltage, the different polarity has little effect on the thermally activated cis-trans isomerization of HHBAzo in the three solvents in the absence of electric field. Figure S5 compares the increase in trans-azobenzene (%) over 5 h after UV irradiation-induced trans-cis photoisomerization. The thermal isomerization is fastest in benzonitrile and slowest in dichloroethane. However, the difference after 5h is only about 4% of HHBAzo molecules in the trans form.

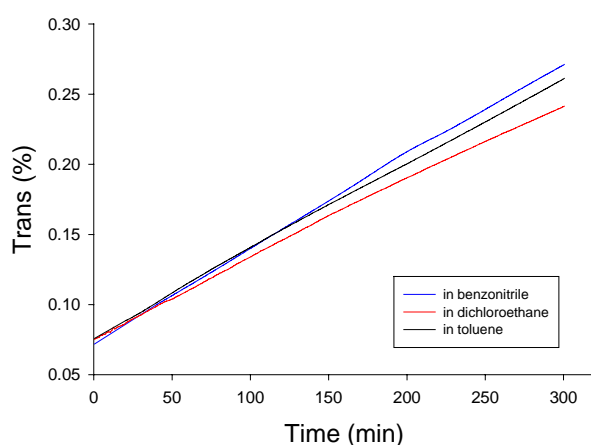


Figure S5

4) Electric Field-Induced Cis-Trans Isomerization in An Azobenzene Polymer Solution

The electric field-induced cis-trans isomerization was also observed for a polymer containing a different azobenzene moiety, poly{6-[4-(4-cyanophenylazo)phenoxy]hexyl methacrylate} (structure in Fig. S6) dissolved in benzonitrile. As can be seen, 1 h after the UV-induced trans-cis isomerization, only about 20% of cis-azobenzene was converted to the trans form through thermally activated relaxation. By contrast, when an electric field pulse of 2 s with amplitude of $1 \text{ V } \mu\text{m}^{-1}$ was applied across the polymer solution immediately after the UV irradiation, more than 80% of cis-azobenzene was recovered to the trans isomer.

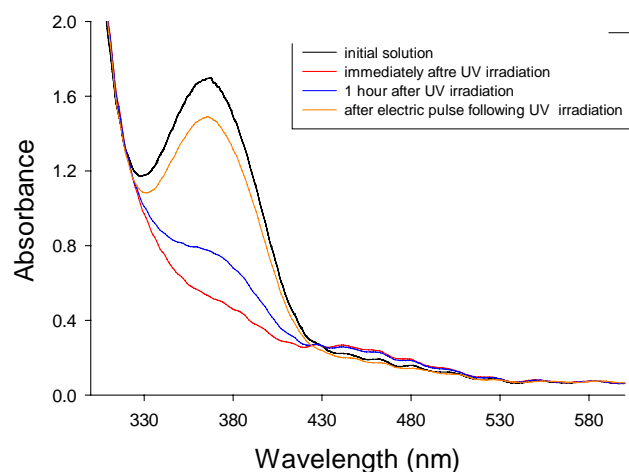


Figure S6

5) Effect of A Supporting Electrolyte Added in The Azobenzene Derivative Solution

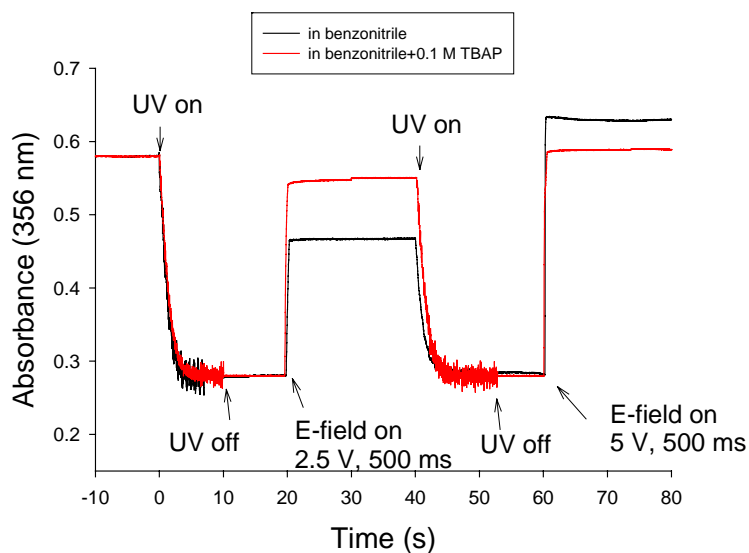


Figure S7

Figure S7 compares the cis-trans isomerization under an applied voltage for HHBazo dissolved in anhydrous benzonitrile and in the same solution with 0.1 M of tetrabutylammonium perchlorate (TBAP). Judging from the increase in absorbance of trans-azobenzene, it is clear that adding the supporting electrolyte to the solution facilitates electrode reactions by reducing the ohmic potential drop between electrodes and increasing the real electrode potential on electrode surface. At 2.5 V potential difference ($0.5 \text{ V } \mu\text{m}^{-1}$), the electrolysis is more important in the presence of the supporting electrolyte and the isomerization proceeds further. When the voltage was increased to 5 V, the two solutions showed similar efficiency of cis-trans isomerization as the voltage is much higher than the decomposition potential.

6) Effect of Absolute Potential Difference

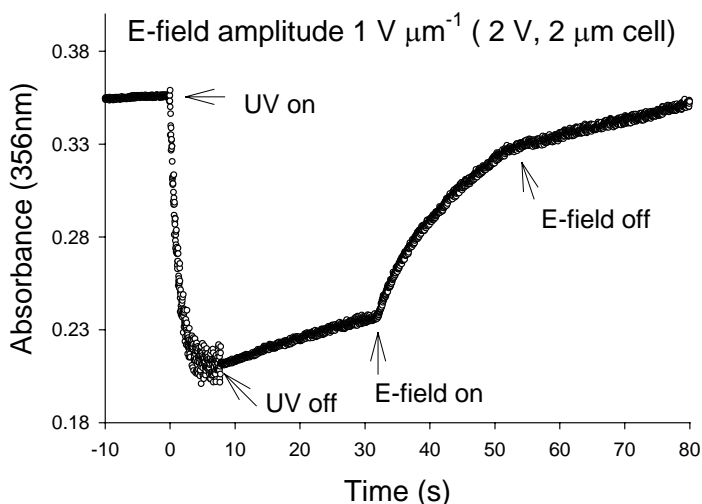


Figure S8

Figure S8 shows the kinetics of cis-trans isomerization under a potential difference of 2 V and 20 s duration. The same benzonitrile solution of HHBAzo as in Fig.1 was filled in an ITO-coated cell of 2 μm gap. With the same E field strength of 1 V μm^{-1} , the rate of isomerization is much slower (~ 70% isomerization after 20 s) as compared to Fig.1b (5 V applied to 5 μm gap cell) where the isomerization is completed within 250 ms. Application of the very low potential difference of 2 V apparently produces much smaller current and thus generates a very small amount of radical anions of cis-azobenzene; consequently, long electrolysis time is necessary to carry out the cis-trans isomerization, which is not completed even after 20 s of potential application while 0.5 s was sufficient to complete the reaction at 5 V. Note that in Figure S8 the apparent increase in absorbance after turning off the UV light was due to changes in baseline of the spectra in this test, rather than thermal relaxation of cis-azobenzene.