Electronic Supplementary Information to:

Optimization of photo-orientation rate of azobenzene-containing polymer

based on a kinetic model of photoinduced ordering

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Appendix A. The kinetics of photoisomerization in an aligned domain of liquid-crystalline material

The kinetic equation for photoisomerization reaction is as follows:

$$\frac{dx_c}{dt} = \left(1 - x_c(t)\right) I_\lambda \ln 10 \cdot \varepsilon_{t,\lambda}(\theta) l \varphi_{tc,\lambda} -$$
$$- x_c(t) I_\lambda \ln 10 \cdot \varepsilon_{c,\lambda}(\theta) l \varphi_{ct,\lambda} - k_{ct} x_c(t), \tag{A.1}$$

where $x_c(t)$ is molar fraction of cis-azobenzene fragments, I_λ is irradiating light intensity on wavelength λ, $\varphi_{tc,\lambda}$ and $\varphi_{ct,\lambda}$ are trans-to-cis and cis-to-trans isomerization quantum yields, k_{ct} is the rate constant of thermal cis-to-trans isomerization and $\varepsilon_{t,\lambda}(\theta)$ and $\varepsilon_{c,\lambda}(\theta)$ are molar absorbance of trans- and cis-azobenzene fragments, that depend on the angle θ between the domain director and the electric field vector of irradiating light. The orientation dependence of absorbance for *i*-th isomer is expressed by

$$\varepsilon_{i,\lambda}(\theta) = \overline{\varepsilon}_{i,\lambda}\left[1 + \delta_i \cdot \left(3\cos^2\theta - 1\right)\right], \tag{A.2}$$

where $\overline{\varepsilon}_i$ is the average molar extinction coefficient, δ_i is the product of anisotropy of extinction coefficient tensor and orientation order parameter of rank two for isomer *i*,

$$\delta = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\parallel} + 2\varepsilon_{\perp}} \cdot \left\langle \mathscr{D}_{0,0}^{2\,*} \right\rangle.$$

Experimentally it has been found that the characteristic time of thermal cis-trans isomerization is 4100 s, whereas the characteristic times of photochemical isomerization under used light intensities is in the order of tens of seconds. Therefore, the term $k_{ct}x_c(t)$ in the equation (A.1) can be neglected. The solution of eq. (A.1) can be written in the explicit form:

$$x_c(t) = \left(1 - \exp\left[-\left\{I_\lambda \ln 10 \varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta) + I_\lambda \ln 10 \varphi_{ct,\lambda}\varepsilon_{c,\lambda}(\theta)\right\} \cdot t\right]\right) \times$$
$$\times \frac{\varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta)}{\varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta) + \varphi_{ct,\lambda}\varepsilon_{c,\lambda}(\theta)} \tag{A.3}$$

Accordingly, the molar fraction of cis-azobenzene fragments in the stationary state is:

$$x_{c,\,\lambda}^{ps} = \frac{\varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta)}{\varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta) + \varphi_{ct,\lambda}\varepsilon_{c,\lambda}(\theta)} \tag{A.4}$$

and the inverse time of reaching photostationary state is:

$$\tau_\lambda^{-1} = \left(I_\lambda \ln 10 \varphi_{tc,\lambda}\varepsilon_{t,\lambda}(\theta) + I_\lambda \ln 10 \varphi_{ct,\lambda}\varepsilon_{c,\lambda}(\theta)\right) \tag{A.5}$$

According to expression (A.2), for irradiation with light polarized parallel to material director the effective extinction coefficient for i-th isomer is

$$\varepsilon_{i,\lambda}{}^\| = \bar{\varepsilon}_{i,\lambda}\left[1 + 2\delta_i\right]$$

and for irradiation with light of perpendicular polarization:

$$\varepsilon_{i,\lambda}{}^\perp = \bar{\varepsilon}_{i,\lambda}\left[1 - \delta_i\right]$$

By introducing denotation $\xi = \dfrac{\varphi_{tc}\bar{\varepsilon}_t}{\varphi_{tc}\bar{\varepsilon}_t + \varphi_{ct}\bar{\varepsilon}_c}$, the eqs. (A.4)–(A.5) can be rewritten as:

$$x_c^\| = \frac{\xi(1+2\delta_t)}{\xi(1+2\delta_t) + (1-\xi)(1+2\delta_c)}$$

$$x_c^\perp = \frac{\xi(1-\delta_t)}{\xi(1-\delta_t) + (1-\xi)(1-\delta_c)} \tag{A.6}$$

$$\tau_\|^{-1} = I \ln 10\left(\varphi_{tc}\bar{\varepsilon}_t(1+2\delta_t) + \varphi_{ct}\bar{\varepsilon}_c(1+2\delta_c)\right)$$

$$\tau_\perp^{-1} = I \ln 10\left(\varphi_{tc}\bar{\varepsilon}_t(1-\delta_t) + \varphi_{ct}\bar{\varepsilon}_c(1-\delta_c)\right),$$

where denotations $\parallel$ and $\perp$ correspond to irradiation with light polarized parallel and perpendicular to the material director, correspondingly. These expressions are identical to those given in the eqs. (1)–(3) of the main text.

Appendix B. The kinetics of photoisomerization of azobenzene-containing material upon bichromatic irradiation.

Upon the simultaneous irradiation with two light beams different wavelengths, first with wavelength $\lambda_1 = 390$ nm and intensity $\iota \cdot I_1$, second with wavelength $\lambda_2 = 457$ nm and intensity $(1-\iota)\cdot I_2$, photoisomerization takes place according to the following kinetic equation:

$$\frac{dx_c}{dt} = (1 - x_c(t))\cdot \iota I_1 \ln 10 \varepsilon_{t,1}(\theta)\varphi_{tc,1} - x_c(t)\cdot \iota I_1 \ln 10 \varepsilon_{c,1}(\theta)\varphi_{ct,1}$$
$$+ (1 - x_c(t))\cdot(1-\iota) I_2 \ln 10 \varepsilon_{t,2}(\theta)\varphi_{tc,2} - x_c(t)\cdot(1-\iota) I_2 \ln 10 \varepsilon_{c,2}(\theta)\varphi_{ct,2}$$

(B.1)

where subscripts 1,2 correspond to parameters at wavelengths λ_1 and λ_2. The photostationary state cis-concentration is:

$$x_c{}^{ps} = \frac{\iota I_1 \varepsilon_{t,1}(\theta)\varphi_{tc,1} + (1-\iota) I_2 \varepsilon_{t,2}(\theta)\varphi_{tc,2}}{\iota I_1 \left(\varepsilon_{t,1}(\theta)\varphi_{tc,1} + \varepsilon_{c,1}(\theta)\varphi_{ct,1}\right) + (1-\iota) I_2 \left(\varepsilon_{t,2}(\theta)\varphi_{tc,2} + \varepsilon_{c,2}(\theta)\varphi_{ct,2}\right)}$$

(B.2)

and the characteristic time of reaching photostationary state is

$$\tau^{-1} = \iota I_1 \left(\varepsilon_{t,1}(\theta)\varphi_{tc,1} + \varepsilon_{c,1}(\theta)\varphi_{ct,1}\right)\ln 10 +$$
$$+ (1-\iota) I_2 \left(\varepsilon_{t,2}(\theta)\varphi_{tc,2} + \varepsilon_{c,2}(\theta)\varphi_{ct,2}\right)\ln 10$$

(B.3)

By using expressions (A.4) and (A.5), one can notice that

$$I_j \varepsilon_{t,j}(\theta)\varphi_{tc,j}\ln 10 = x_{c,j}^{ps} \cdot \tau_j^{-1},$$

where characteristic times τ_1 and τ_2 correspond to monochromatic irradiation with unattenuated beams of light j=1,2. Then the equation (B.2) can be rewritten as:

$$x_c{}^{ps} = \frac{\iota x_{c,1}^{ps}\cdot\tau_1^{-1} + (1-\iota)x_{c,2}^{ps}\cdot\tau_2^{-1}}{\iota\tau_1^{-1} + (1-\iota)\tau_2^{-1}}$$

(B.4)

and the inverse time of reaching photostationary state is given by:

$$\tau^{-1} = \iota\tau_1^{-1} + (1-\iota)\tau_2^{-1}$$

(B.5)

By using the explicit forms of extinction coefficients in the cases of parallel and perpendicular orientation of irradiating light electric vector relative to the domain director:

$$\varepsilon_{c,t}{}^{\parallel} = \bar{\varepsilon}_{c,t}\left[1 + 2\delta_{c,t}\right]$$

$$\varepsilon_{c,t}{}^{\perp} = \bar{\varepsilon}_{c,t}\left[1 - \delta_{c,t}\right]$$

equations (B.4)–(B.5) can be written in the explicit form:

$$x_c^{\parallel} = \frac{\iota \cdot I_1 \bar{\varepsilon}_{t,1}\left(1 + 2\delta_{t,1}\right)\varphi_{tc,1} + (1-\iota)\cdot I_2 \bar{\varepsilon}_{t,2}\left(1 + 2\delta_{t,2}\right)\varphi_{tc,2}}{\iota \cdot I_1\left(\bar{\varepsilon}_{t,1}\left(1 + 2\delta_{t,1}\right)\varphi_{tc,1} + \bar{\varepsilon}_{c,1}\left(1 + 2\delta_{c,1}\right)\varphi_{ct,1}\right) + (1-\iota)\cdot I_2\left(\bar{\varepsilon}_{t,2}\left(1 + 2\delta_{t,2}\right)\varphi_{tc,2} + \bar{\varepsilon}_{c,2}\left(1 + 2\delta_{c,2}\right)\varphi_{ct,2}\right)}$$

$$x_c^{\perp} = \frac{\iota \cdot I_1 \bar{\varepsilon}_{t,1}\left(1 - \delta_{t,1}\right)\varphi_{tc,1} + (1-\iota)\cdot I_2 \bar{\varepsilon}_{t,2}\left(1 - \delta_{t,2}\right)\varphi_{tc,2}}{\iota \cdot I_1\left(\bar{\varepsilon}_{t,1}\left(1 - \delta_{t,1}\right)\varphi_{tc,1} + \bar{\varepsilon}_{c,1}\left(1 - \delta_{c,1}\right)\varphi_{ct,1}\right) + (1-\iota)\cdot I_2\left(\bar{\varepsilon}_{t,2}\left(1 - \delta_{t,2}\right)\varphi_{tc,2} + \bar{\varepsilon}_{c,2}\left(1 - \delta_{c,2}\right)\varphi_{ct,2}\right)}$$

or, in shorter terms:

$$x_c^{\parallel} = \frac{\iota\tau_{1,\parallel}^{-1}\cdot x_{c,1}^{\parallel} + (1-\iota)\tau_{2,\parallel}^{-1}\cdot x_{c,2}^{\parallel}}{\iota\tau_{1,\parallel}^{-1} + (1-\iota)\tau_{2,\parallel}^{-1}} \tag{B.6}$$

$$x_c^{\perp} = \frac{\iota\tau_{1,\perp}^{-1}\cdot x_{c,1}^{\perp} + (1-\iota)\tau_{2,\perp}^{-1}\cdot x_{c,2}^{\perp}}{\iota\tau_{1,\perp}^{-1} + (1-\iota)\tau_{2,\perp}^{-1}} \tag{B.7}$$

and the inverse times of reaching photostationary state are:

$$\tau_{\parallel}^{-1} = \iota \cdot \tau_{1,\parallel}^{-1} + (1-\iota)\cdot \tau_{2,\parallel}^{-1} \tag{B.8}$$

$$\tau_{\perp}^{-1} = \iota \cdot \tau_{1,\perp}^{-1} + (1-\iota)\cdot \tau_{2,\perp}^{-1} \tag{B.9}$$

which is identical to eqs. (4)–(7) of the main text.

Appendix C.

The unattenuated light intensities I_1 and I_2 were chosen such that the times of reaching photostationary state in the isotropic, unaligned sample would be equal for irradiation with each beam.

In this case, upon simultaneous irradiation with two beams of light with corresponding intensities ιI_1 and $(1-\iota)I_2$, the time of reaching photostationary state in isotropic sample τ_0 does not depend on intensity fraction ι, and the amplitude of absorbance change $\Delta A_0 = \left(\overline{\varepsilon_t} - \overline{\varepsilon_c}\right)lc_0 \cdot x_{c,0}$ linearly depends on ι (subscript "0" corresponds to the irradiation of the isotropic sample). Fig. C.1 shows the experimental dependence of ΔA_0 (left axis) and τ_0 (right axis) on ι.
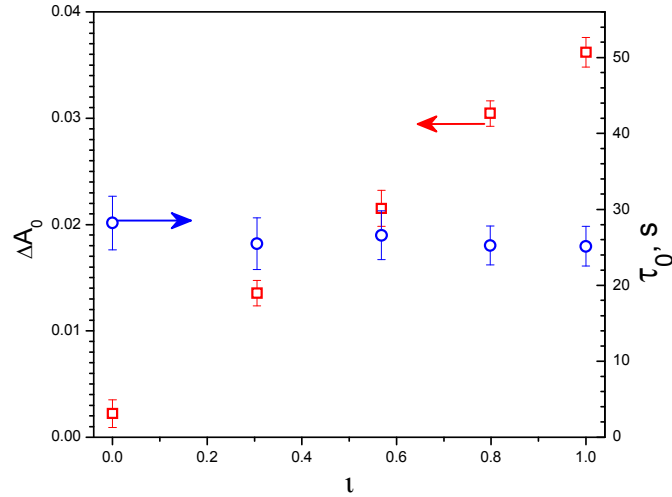

Fig. C.1. Characteristic time of reaching photostationary state in isotropic spin-coated sample of PAAzo6 (right axis) and initial change in absorbance due to trans-cis photoisomerization (left axis) as a function of intensity ratio of UV and visible light beams ι.

Appendix D. Modeling the kinetic curves of photoisomerization of PAAzo6 and determination of photochemical and optical parameters of the isomers.

Theoretical description of experimentally obtained $\Delta A = \left(\varepsilon_t - \varepsilon_c \right) l c_0 \cdot x_c{}^{ps}$, change in polarized absorbance of uniformly aligned sample of PAAzo6 during photoisomerization, and τ^{-1}, characteristic time of photoisomerization, was accomplished with the use of equations (B.6)–(B.9) (eqs. (4)–(7) in the main text).

Lines in Figure D.1 shows theoretical description of the experimentally obtained values. For the results shown in Fig. D.1a,b the model parameters were independently obtained from experiments on monochromatic irradiation of aligned sample of PAAzo6 with light of each wavelength. These experiments correspond to the points with $\imath = 0$ (visible light irradiation) and $\imath = 1$ (UV light irradiation). The number of fitted values was 14: $\Delta A_{\parallel}^{\parallel}$, $\Delta A_{\perp}^{\parallel}$, $\Delta A_{\parallel}^{\perp}$, $\Delta A_{\perp}^{\perp}$, $\tau_{\parallel}^{-1}$ and $\tau_{\perp}^{-1}$ for each irradiation wavelength, where super- and subscripts correspond to polarizations of the probe and the irradiating light beams, respectively, and the polarized absorbance of unirradiated sample in the pure trans-form, $A_{0,\parallel}$, $A_{0,\perp}$. The number of fitted parameters was 8 (their values are listed in Table D.1, second column). The fitting was performed by least-squares method, using eqs. (B.6)–(B.9) (eqs. (4)–(7) of the main text) with $\imath = 0$ and $\imath = 1$.

The obtained fit can be further refined, by using all experimental points shown in Fig. D.1 for determining the model parameters. In this case, the number of varied parameters remains 8, but the number of experimentally available values becomes as high as 32 (values $\Delta A_{\parallel}^{\parallel}$, $\Delta A_{\perp}^{\parallel}$, $\Delta A_{\parallel}^{\perp}$, $\Delta A_{\perp}^{\perp}$, $\tau_{\parallel}^{-1}$ and $\tau_{\perp}^{-1}$ for each $\imath$, and , and the polarized absorbance of unirradiated sample in the pure trans-form, $A_{0,\parallel}$, $A_{0,\perp}$). The achieved fitting results are shown in Fig. D.1c,d, and refined parameters are listed in Table D.1, column 3).

One can see that both the values of the obtained parameters and the quality of fit are similar for the two described approaches. That indicates that the applied model is appropriate to describe the conducted experiments. The difference of values listed in columns two and three of Table D.1 may serve as an estimate of errors of the determined model parameters.
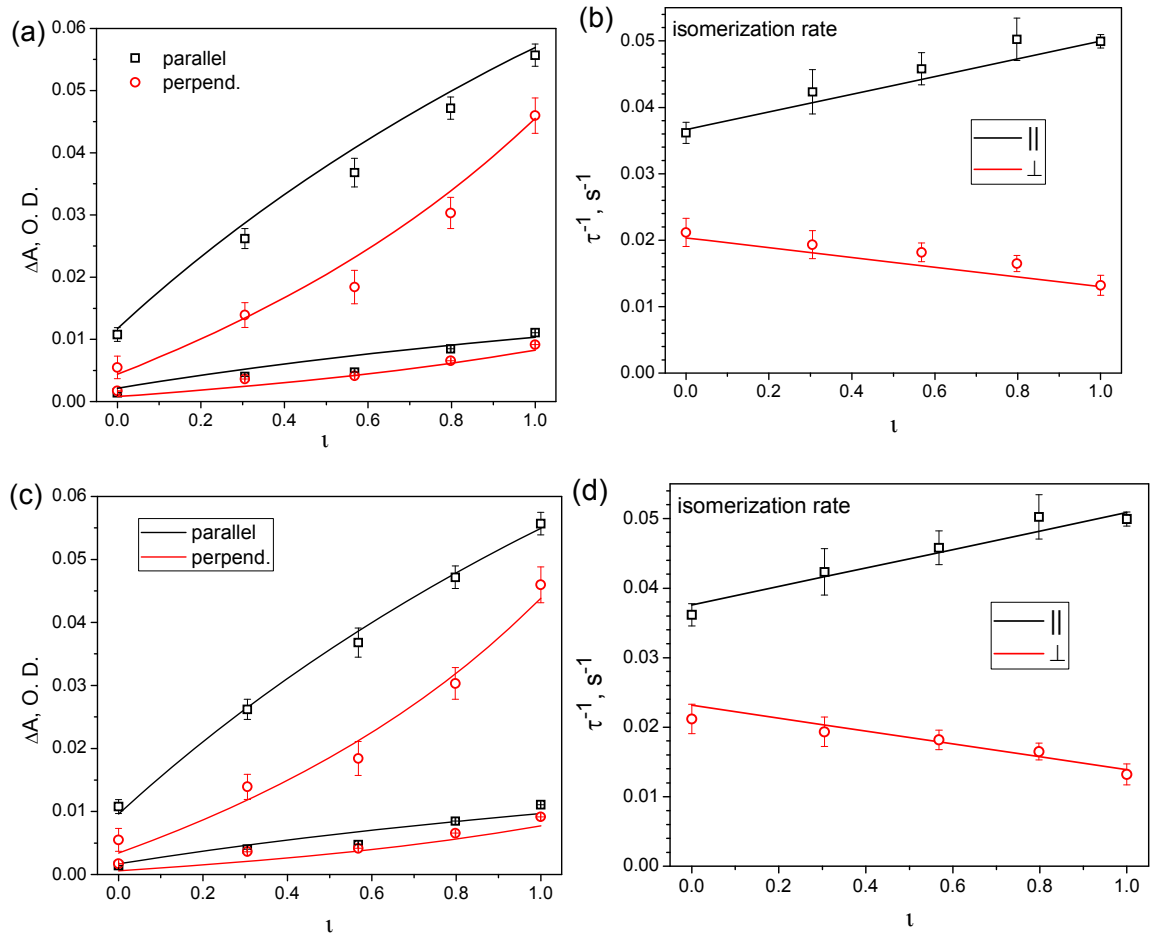
Fig. D.1. Values of absorbance change ΔA (a,c) and inverse time of reaching photostationary state τ^{-1} (b,d) depending on relative intensities of UV and visible light ι. Points show the experimentally obtained values, lines are results of modeling according to eqs. (4)–(7) of the main text. Results shown in (a,b) correspond to model parameters obtained independently from results on monochromatic irradiation (corresponding to $\iota = 0$ and $\iota = 1$); and results shown in (c,d) correspond to refinement of the parameters, by fitting of all experimental points in Fig. D.1.

Table D1. Values of photochemical and optical characteristics of azobenzene fragments in PAAzo6, corresponding to wavelengths of the two irradiating beams.

$\left(\dfrac{\varepsilon_c\varphi_c}{\varepsilon_t\varphi_t}\right)_{390\text{nm}}$	0.225	0.220
$\left(\dfrac{\varepsilon_c\varphi_c}{\varepsilon_t\varphi_t}\right)_{457\text{nm}}$	7.2	9.1
$\left(\dfrac{\varepsilon_c}{\varepsilon_t}\right)_{390\text{nm}}$	0.094	0.136
δ_t	0.559	0.545
δ_c	0.16	0.13
$\left(I\ln10\varepsilon_t\varphi_t\right)_{390}$	0.0208 s^{-1}	0.0215 s^{-1}
$\left(I\ln10\varepsilon_t\varphi_t\right)_{457}$	0.0031 s^{-1}	0.0028 s^{-1}
$A_0{}^{*}$	0.0326	0.0324

$^{*}A_0 = \overline{\varepsilon_t}lc_0$ is the average absorbance of the film in the pure trans-form.