Supporting information

Photopatterned azo poly(amide imide) layers as aligning substrates of holographic liquid crystal diffraction gratings for beam steering applications

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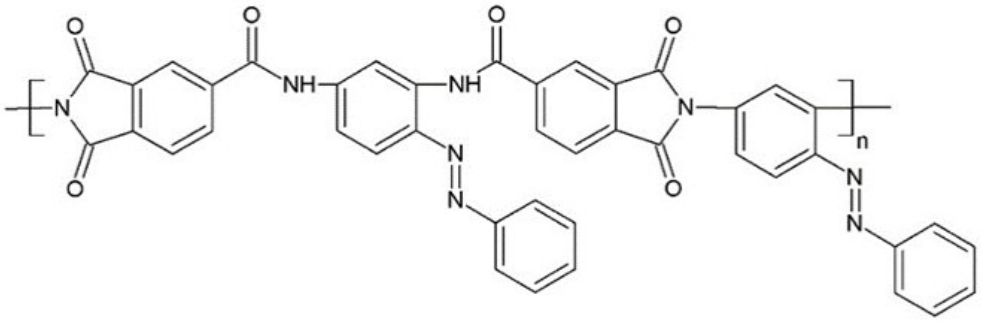
Figure S1. Chemical structure of the PAI azo poly(amide imide) aligning material.



Theoretical model regarding molecular orientation within LC layer

In this work, we refer to a planar LC cell of the thickness *d* along the *z*-axis (Fig. S2 a) and molecular director specified as $\hat{n} = [\sin\varphi\cos\phi,\ \sin\varphi\sin\phi,\ \cos\varphi]$, where φ and ϕ are orientation angles defining director orientation in space (Figs. S2 b). Without external voltage applied, orientation angle φ takes values of π/2 in the whole volume of LC layer and ϕ has a uniform

distribution along cell thickness with the boundary conditions defined as $\phi_0=\pi y/\Lambda$ (Fig. S2 c), where Λ is the grating period along the y-axis, shown as an inset in Fig. 7b.

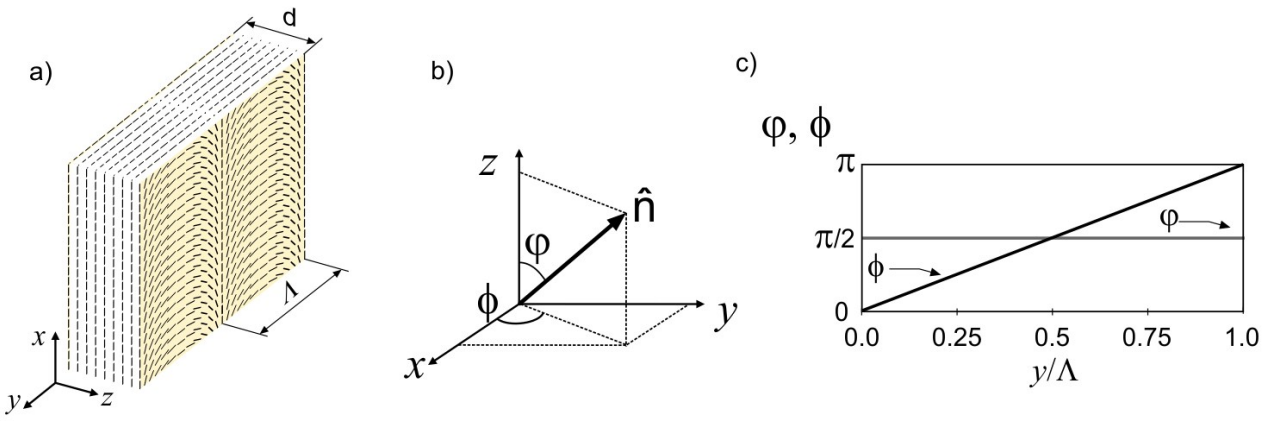


Figure S2. a) Schematic draw of the analyzed LC cell with the thickness of d. Black sectors indicate molecular alignment within LC layer as forced by the boundary conditions. b) Spatial orientation of the director specified by the orientation angles ϕ and φ. c) Orientation angles along y-direction (in the section limited to the single spatial interval of the periodic structure) when no voltage is applied to the LC cell.

While the effective angular orientation of the molecular director in the nematic phase is related to the optical axis of the corresponding uniaxial crystal, it means that an external electric field, which can modify spatial distribution of the director via reorientation, can change thus effective refractive index distribution within LC layer. Exemplarily, for the y-polarized light beam, which has been used as the probe in the experimental part of this work, the effective refractive index is changing with the orientation angles φ and ϕ and it is expressed as:

$$n_{eff,y}(\varphi,\phi)=\frac{n_o n_e}{\sqrt{n_o^2\sin^2\varphi\sin^2\phi+n_e^2\cos^2\varphi+n_e^2\sin^2\varphi\cos^2\phi}}, \quad \text{(S1)}$$

where n_o and n_e are ordinary and extraordinary refractive indices, respectively.

When analyzing LC cell with the electric voltage applied, the free energy of the liquid crystal consists of the terms related to the elastic free energy arising from the spatial nonuniformity in the director orientation and the electric free energy related to the influence of the external electric field. Any change of mentioned energy terms results in reorientation of LC molecules in order to minimize free energy in the new arrangement. Ultimate equilibrium in the system, established when its free energy is minimized, can be modeled by a relevant set of the Euler-Lagrange (E-L) equations. The latter, called here as reorientation equations, are obtained for a specific definition of molecular director and after calculating partial derivatives of free energy density with respect to orientation angles and their spatial derivatives, respectively. In particular, the case considered here,

it has been assumed that no change in the molecular director orientation takes place along the *x*-direction and that no other direction of the electric field except this along the z-axis (which is dominant) should be considered in the reorientation equations. Moreover, while assuming data characteristic for 5CB LC, it has been not relevant to apply typical one elastic constant approximation to describe the elastic forces when minimizing free energy. Following assumptions for elastic constants corresponding to splay, twist and bend deformations, i.e. $K_{11}=2\cdot K_{22}$ and $2\cdot K_{33}=3\cdot K_{11}$ [1] have been made instead, representing thus the intermolecular restoring forces that balance the torque externally induced by an electric field. Eventually, a set of Euler-Lagrange equations for $\partial\varphi/\partial x=0$ and $\partial\phi/\partial x=0$, as well as for external electric field assumed to be acting only along *z*-direction is stated as follows:

$$\begin{aligned}
&\frac{\partial^2\varphi}{\partial y^2}\left[1+\sin^2\phi\left(1+\sin^2\varphi\right)\right]+\left(\frac{\partial\varphi}{\partial y}\right)^2\left[\frac{1}{2}\sin^2\phi\sin 2\varphi\right]+\frac{\partial^2\varphi}{\partial y\partial z}\left[\sin 2\varphi\sin\phi\right]+\\
&+\frac{\partial\varphi}{\partial y}\frac{\partial\varphi}{\partial z}\left[\cos 2\varphi\sin\phi\right]+\frac{\partial^2\varphi}{\partial z^2}\left[2+\cos^2\varphi\right]+\left(\frac{\partial\varphi}{\partial z}\right)^2\left[-\frac{1}{2}\sin 2\varphi\right]+\\
&+\frac{\partial\varphi}{\partial y}\frac{\partial\phi}{\partial y}\left[\sin 2\phi\left(1+\sin^2\varphi\right)\right]+\frac{\partial\varphi}{\partial y}\frac{\partial\phi}{\partial z}\left[-\frac{1}{2}\sin 2\varphi\cos\phi\right]+\frac{\partial\varphi}{\partial z}\frac{\partial\phi}{\partial y}\left[\frac{1}{2}\sin 2\varphi\cos\phi\right]+\\
&+\frac{\partial^2\phi}{\partial y^2}\left[\frac{1}{4}\sin 2\varphi\sin 2\phi\right]+\left(\frac{\partial\phi}{\partial y}\right)^2\left[-\frac{1}{2}\sin 2\varphi\left(1+\sin^2\phi+4\sin^2\varphi\sin^2\phi\right)\right]+\\
&+\frac{\partial^2\phi}{\partial y\partial z}\left[-\sin^2\varphi\cos\phi\right]+\frac{\partial\phi}{\partial y}\frac{\partial\phi}{\partial z}\left[\sin^2\varphi\sin\phi\left(1-4\cos^2\varphi-2\cos 2\varphi\right)\right]+\\
&+\left(\frac{\partial\phi}{\partial z}\right)^2\left[-\frac{1}{2}\sin 2\varphi\left(3-4\sin^2\varphi\right)\right]-\frac{\varepsilon_0\Delta\varepsilon}{2K_{22}}\sin 2\varphi\left|E_z\right|^2=0
\end{aligned}\tag{S2}$$

$$\begin{aligned}
&\frac{\partial^2\varphi}{\partial y^2}\left[\frac{1}{8}\sin 2\varphi\sin 2\phi\right]+\left(\frac{\partial\varphi}{\partial y}\right)^2\left[-\frac{3}{4}\sin^2\varphi\sin 2\phi\right]+\frac{\partial^2\varphi}{\partial y\partial z}\left[-\frac{1}{2}\sin^2\varphi\cos\phi\right]+\\
&+\frac{\partial\varphi}{\partial y}\frac{\partial\varphi}{\partial z}\left[-\frac{3}{4}\sin 2\varphi\cos\phi\right]+\frac{\partial\varphi}{\partial y}\frac{\partial\phi}{\partial y}\left[\sin 2\varphi\left(1+\sin^2\phi\left(2\sin^2\varphi-\frac{1}{2}\right)\right)\right]+\\
&\frac{\partial\varphi}{\partial y}\frac{\partial\phi}{\partial z}\left[\sin^2\varphi\cos\phi\left(3\cos^2\varphi-\sin^2\varphi\right)\right]+\frac{\partial\varphi}{\partial z}\frac{\partial\phi}{\partial y}\left[\sin^2\varphi\sin\phi\left(3\cos^2\varphi-\sin^2\varphi\right)\right]+\\
&+\frac{\partial\varphi}{\partial z}\frac{\partial\phi}{\partial z}\left[\frac{1}{2}\sin 2\varphi\left(3-4\sin^2\varphi\right)\right]+\frac{\partial^2\phi}{\partial y^2}\left[\sin^2\varphi\left(1-\frac{1}{2}\cos 2\varphi\sin^2\phi\right)\right]+\\
&+\left(\frac{\partial\phi}{\partial y}\right)^2\left[-\frac{1}{4}\sin^2\varphi\sin 2\phi\cos 2\varphi\right]+\frac{\partial^2\phi}{\partial y\partial z}\left[\sin^2\varphi\sin 2\varphi\sin\phi\right]+\\
&+\frac{\partial\phi}{\partial y}\frac{\partial\phi}{\partial z}\left[\frac{1}{2}\sin 2\varphi\sin^2\varphi\cos\phi\right]+\frac{\partial^2\phi}{\partial z^2}\left[\frac{1}{2}\sin^2\varphi\left(3\cos^2\varphi+\sin^2\varphi\right)\right]=0
\end{aligned}\tag{S3}$$

with $\Delta\varepsilon$ being the low-frequency electric anisotropy and K_{22} the elastic constant for twist deformation.

The system of Equations (S2) and (S3) can be solved using typical relaxation schemes, with the ADSOR scheme applied in this situation. Precisely, reorientation equations have been discretized and solved self-consistently with use of a numerical relaxation algorithm with the square mesh filling the region of the LC cell between the glass plates and reduced to the region of one grating period in the *y*-direction. Fixed boundary conditions have been applied for both orientation angles at the glass plates planes (i.e. $\phi(y, z=0)= \phi(y, z=d)= \phi_0(y)$; $\varphi(z=0)= \varphi(z=d)=\pi/2$) and periodic boundary conditions at the boundaries of the calculation window in the *y*-direction. Such reorientation equations describe the LC elastic response to electrical excitation. It should be noted that deformation can be divided into two stages: first, molecules are tilted toward the electric field direction and then, bending of the sinusoidal splay structure related to the boundaries conditions occurs. It is worth noting that in the analyzed case, initial orthogonality between the direction of the electric field and the orientation of the molecular long axis corresponds to a threshold effect known as Fredericks transition.

References

1 A.V. Zakharov, M.N. Tsvetkova, V.G. Korsakov, *Polym. Liq. Cryst.* **44(9)**, (2002), 1715.