Supplementary materials for:

Characterization of the sub-micrometer hierarchy levels in the twist-bend nematic phase with nanometric helices via photopolymerization. Explanation for the sign reversal in the polar response.

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Control of polymerization process:

A brief heating of the sample to a higher temperature phase can be used to evaluate results of polymerization process as texture in the irradiated area is preserved and shows clear contrast to the surroundings. When the sample is heated to a temperature in its isotropic state, areas of the cell polymerized in LC phases, still exhibited birefringence when the cell is observed between the crossed polarizers. On the other hand, areas polymerized in the isotropic state remained isotropic (i.e. dark texture observed between the crossed-polarizers) on consequent cooling to LC phases.

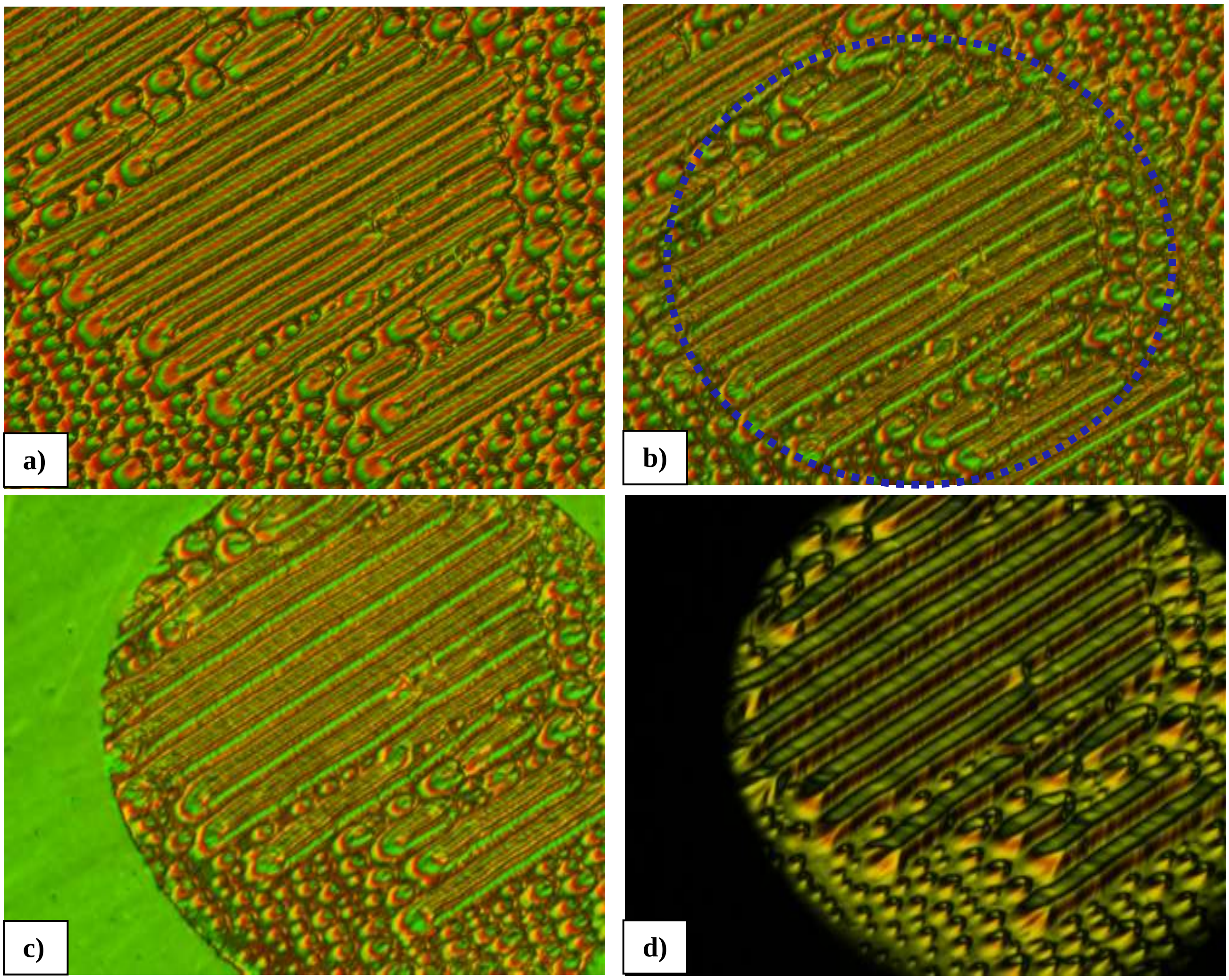

Figure S1. POM images of: a) original texture of the N_{TB} phase; b) immediately after UV irradiation of the area highlighted by the circle; c) Sample is heated to the N phase. d) Sample is heated to the Iso phase.

Additional SEM images:

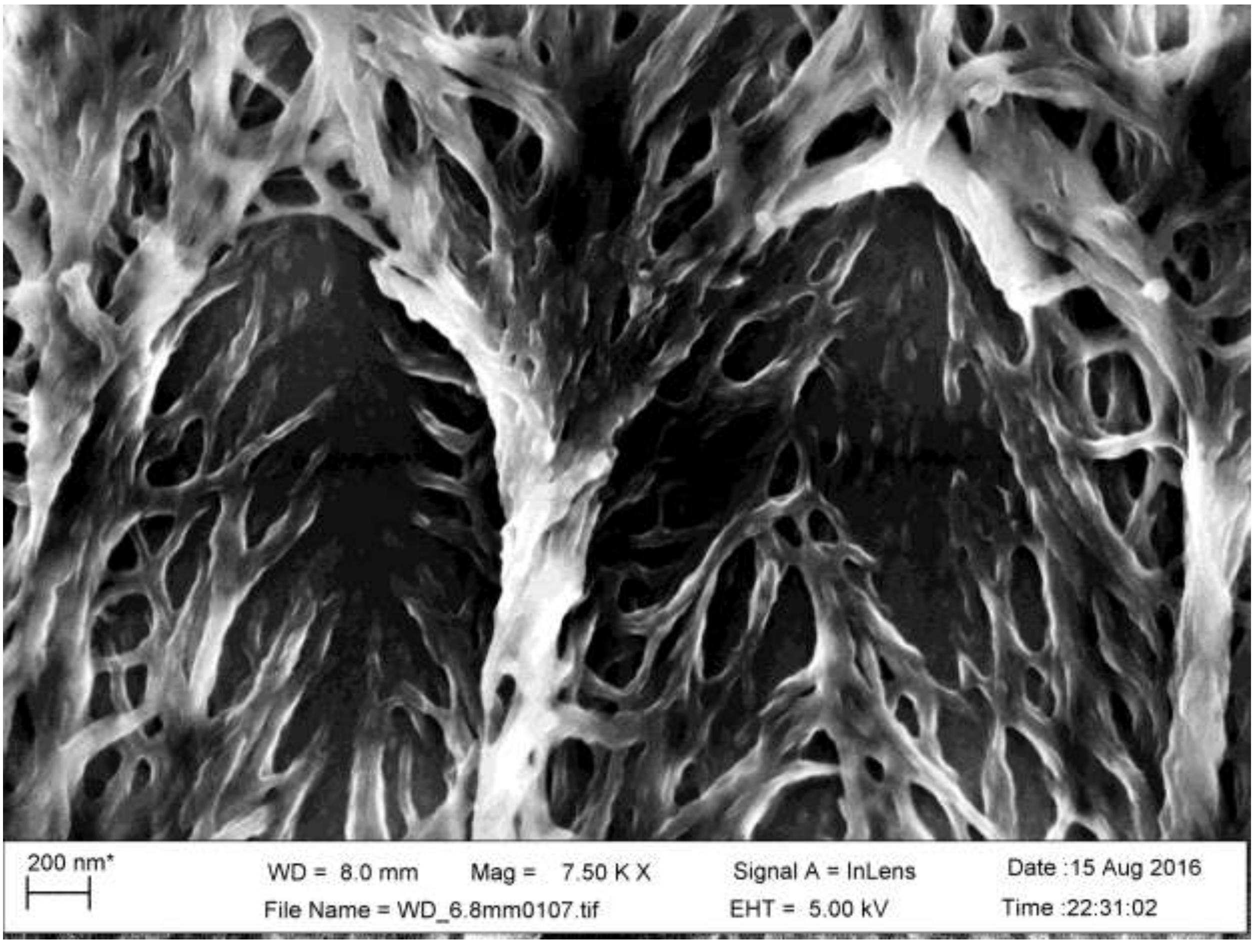

Figure S2. High-magnification image. Selected by white frame on the S3.

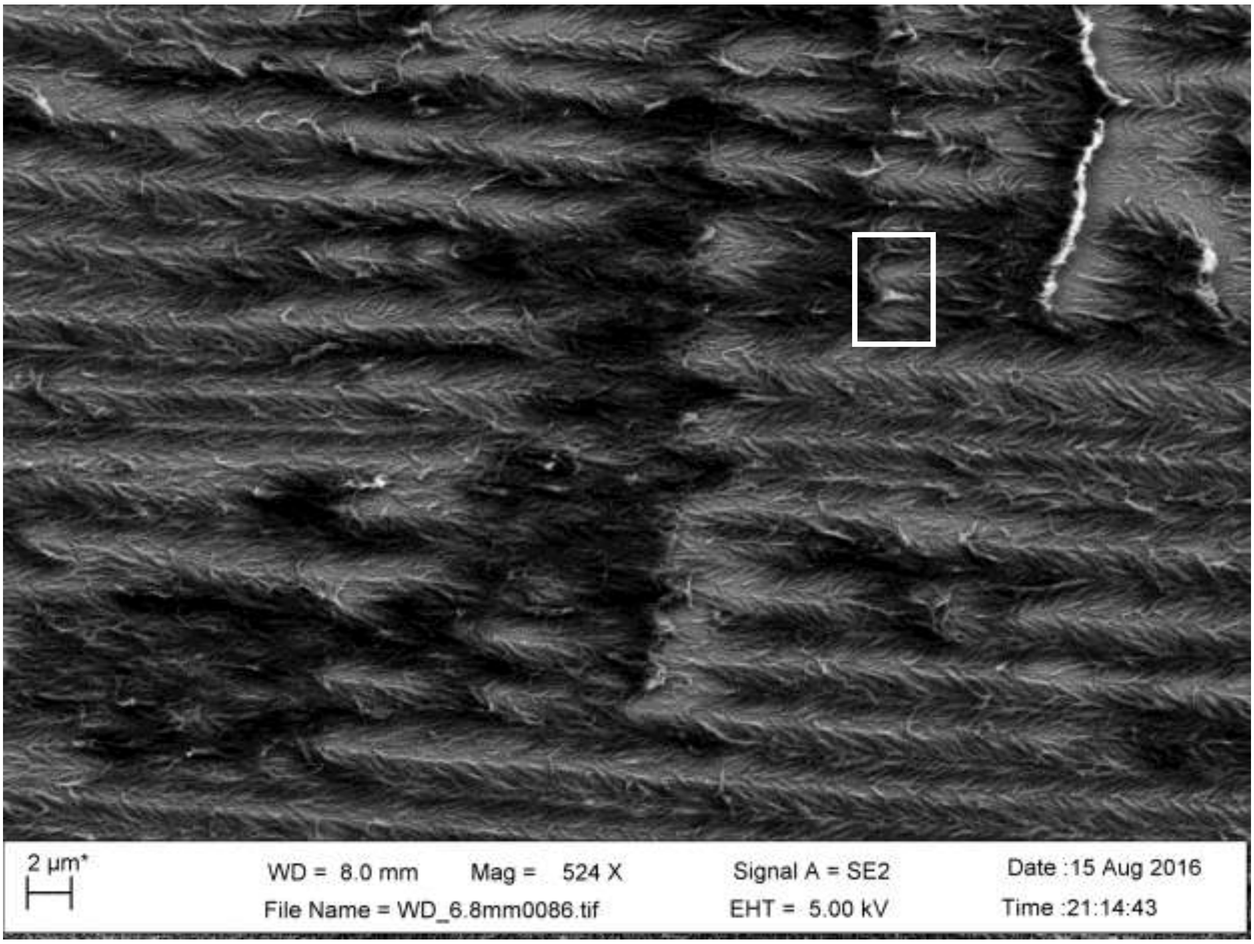

Figure S3. Wide area view of a 2 micrometre cell.

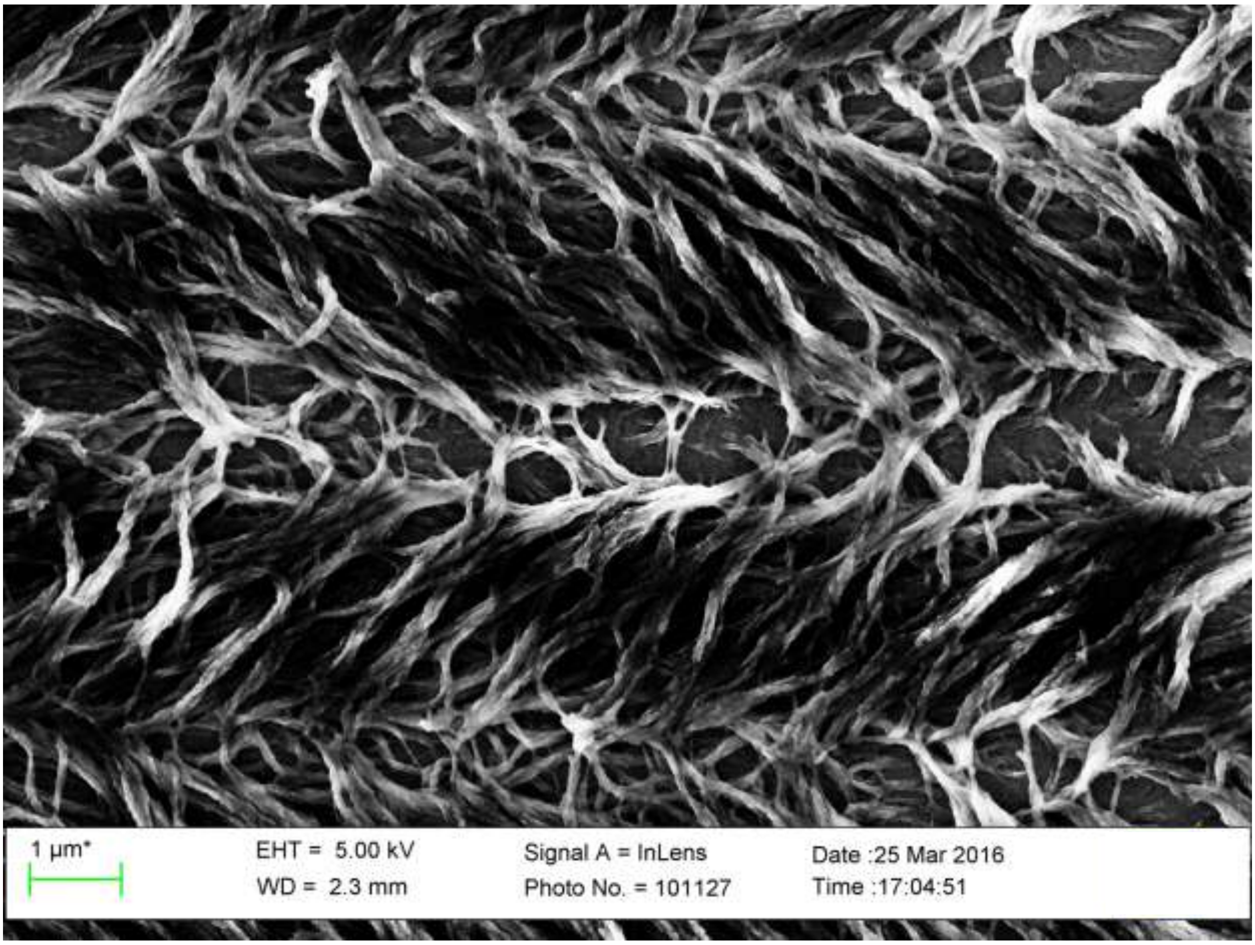

Figure S4. Detailed view of the “fishbone” pattern in 4 μm cell.

Sign reversal of the electro-optic response.

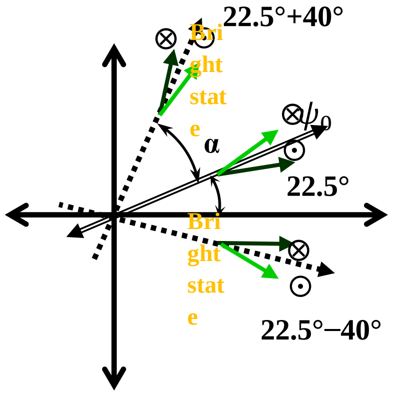

Figure S5. Schematic of the polar response. Solid arrows: analyser and polarizer, double line arrow: cell rubbing direction, dotted lines: average director in “fish-bone” structure for α≈ ±40°. Dark green arrows: director deviated under electric field towards dark positions by angle ψ_0. Bright green arrows: director deviated under electric field towards dark positions by angle ψ_0. The electric field directions in each case are normal to the cell plane and marked accordingly.

Transmittance between crossed polarizers:

$$I(t) = I_0 \sin^2(2\theta) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \qquad (*)$$

$\frac{\pi d \Delta n}{\lambda}$ – birefringence, cell gap, wavelength, assumed constant

Position of optical axis is given by: θ=22.5° ± $\alpha(T)$ + $\psi_0\sin(\omega t)$, where

22.5° - angle between polarizer and cell rubbing direction, fixed during the experiment,

α(T) – temperature-dependent angle between average axis of the helix and the rubbing direction $\psi_0\sin(\omega t)$ – response to electric field $E\sin(\omega t)$, ω – angular frequency of applied field, t – time.

Since $\sin^2(2\theta) = \frac{1-\cos(4\theta)}{2}$, one can present varying with time components of the transmittance as:

$$\cos(4\theta) = -\sin(4\psi_0 \sin(\omega t)) \sin\big(4(22.5° \pm \alpha)\big) + \cos(4\psi_0 \sin(\omega t)) \cos\big(4(22.5° \pm \alpha)\big) \qquad (**)$$

It is known that the amplitude of the optical response is a small angle (ψ_0<1°). i.e. $\sin(4\psi_0 \sin(\omega t)) \approx 4\psi_0 \sin(\omega t)$.

Therefore the first harmonic in ω given by the first term in (**) is:

$$4 \sin\big(4(22.5° \pm \alpha)\big) \psi_0 \sin(\omega t).$$

Note that when the absolute value of α exceeds 22.5° (α=±22.5°, sin (0) = sin(180°) = 0), the first harmonic coefficient is changing its sign as illustrated on the schematic. The deviation of director from its positions in the low-temperature “fish-bone” structure (dashed lines: α≈ ±40°) results in opposite change of the transmitted intensity (*) as compared to the same deviation from the rubbing direction (double line: α = 0°).

By expanding the second term in (**) and assuming small response amplitude we obtain:

$$\cos(4\psi_0 \sin(\omega t)) \approx 1 - \frac{(4\psi_0 \sin(\omega t))^2}{2} = 1 - 8\psi_0^2 (\frac{1-\cos(2\omega t)}{2})$$

$$\cos(4\psi_0 \sin(\omega t)) \cos\big(4(22.5° \pm \alpha)\big) \approx \cos\big(4(22.5° \pm \alpha)\big) (1 - 8\psi_0^2 (\frac{1-\cos(2\omega t)}{2}))$$

Therefore, the second harmonic of the response is given by

$$4\psi_0^2 \sin(\pm 4\alpha) \ \cos(2\omega t)$$

Note that the second harmonic coefficient is an odd function of α. Thus the second harmonics of the signals from the two bands of the “fishbone structure” (i.e. with opposite values of α) will cancel out. Therefore the second harmonic of the signal observed in the experiments with averaging over a wide N_{TB} sample area is produced mainly by the birefringence change caused by the out of plane deviation of the director.