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Supporting Information

Photoresponsive helical nanofilaments of B4 phase

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1. Experimental

The ¹H NMR spectra were recorded at 500 MHz NMR Varian Unity Plus spectrometer. Proton chemical shifts are reported in ppm (δ) relative to the internal standard – tetramethylsilane (TMS δ =0.00 ppm). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constant (Hz).

Calorimetric studies were performed with TA DSC Q200 machine, samples of mass 1-3 mg were sealed in aluminum pans and kept in nitrogen atmosphere during measurement, both heating and cooling scans with rate 5-10 deg/min were applied.

The small angle X-ray diffraction (SAXRD) patterns for the powder as well as partially aligned samples were obtained with the Bruker Nanostar system. The CuK α radiation was used, patterns were registered with an area detector VANTEC2000. The temperature of the sample was controlled with precision of 0.1 K. Samples were prepared either in thin-walled glass capillaries or as droplets on heated surface. Broad angle diffractograms were obtained with Bruker D8 GADDS system (CuK α line, Goebel mirror, point beam collimator, Vantec2000 area detector) and/or with a Bruker D8 Discover system equipped with Anton Paar DCS-350 heating stage.

The optical studies were performed using Zeiss Imager A2m polarizing microscope equipped with Linkam heating stage. For optical studies glass cells, having ITO electrodes and polymer aligning layer were used with various thickness 1.5 to 10 microns. The same cells were also used for dielectric spectroscopy studies. Dispersion of dielectric constant was measured with Solartron SI 1260 Impedance Analyzer.

For the sample irradiation the light source Hamamatsu LC8 was used, equipped with interchangeable filters allowing for choosing UV or Vis illumination.

UV-Vis spectra were recorded with Shimadzu Shimadzu UV-3101PC spectrometer.

SEM images were recorded on Zeiss Merlin field emission microscope. The samples for SEM imaging were deposited on glass with Au layer in gel state and left for 24 hours. After slow evaporation of solvent and formation of the xerogel the sample was covered with a thin layer of Pd/Au.

2. Organic synthesis

Following abbreviations are used: TEA – triethylamine DMF – dimethylformamide DMAP – 4-dimethylaminopyridine EtOH – ethyl alcohol

The general procedure for the synthesis of compounds **D-n** is presented in Scheme S1.





Preparation of 4-decyloxyacetanilide

To the p-hydroxyacetanilide (15,12 g; 0,1 mol) dissolved in 500 mL of DMF in the ambient temperature was added K₂CO₃ (55,2 g; 0,4 mol) and KI (66,4 g; 0,4 mol). Obtained mixture was stirred at the 50°C for 15 min and after this time the solution of 1-bromodecane (22.12 g; 0,1 mol) in 100 mL of DMF was added dropwise. The mixture was stirred at 90°C for 24 h. Next it was cooled down at the room temperature and added to 700 mL of distilled water to precipitate crude product, which was then collected by filtration. After washing with methanol the resultant product was dried and analyzed for purity by TLC. No further purification was needed. (Yield: 26.81 g, 92%)

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Preparation of 4-decyloxyaniline

4-decyloxyacetanilide (21,0 g, 0,072 mol), KOH (20 g, 0,36 mol, 5 eq) and 300 mL of $H_2O/EtOH$ (1/5) solution were mixed in a 500 mL round bottomed flask and refluxed for 12h. After evaporating the solvents, cold water was added, the formed precipitate was filtered off and recrystallized from hexane to give the product as brown crystals (Yield: 16.16 g, 90%)

Preparation of 4-(4-decyloxy-phenylazo)-phenol

In a 500 mL two necked round bottomed flask 4-decyloxyaniline (10 g, 0,04 mol, 1 eq), HCl (5,85 g, 1,60 mol, 4 eq) and 200 mL of water were heated until the amine dissolved. The mixture was then cooled down with an ice bath and a cold solution of NaNO₂ (2,75 g, 0,04 mol, 1 eq) in 150 mL of H₂O was added. Solution of diazonium salt were added subsequently in 0°C to a solution of phenol (3,75 g, 0,04 mol, 1 eq), NaOH (7,20 g, 0,180 mol, 4,5 eq) in 250 mL of H₂O.

The reaction was then left for 45 min in RT and acidified with aqueous HCl. The formed precipitate was then filtered off and recrystallized from hexane to give the product as orange crystals (Yield: 9,66g, 68%)

Preparation of undecanedioil chloride (Cl-9)

To the round bottom flask undecanedioic acid (2,16 g; 0,01 mol) and thionyl chloride (2,9 mL; 0,04 mol) were added. This solution was stirred overnight at the room temperature. The thionyl chloride was removed from the mixture by the vacuum distillation to achieve 2,4 g (95% yield) of a transparent oil. The same procedure was applied to obtain homologues Cl-3; Cl-4; Cl-5; Cl-6; Cl-7; Cl-8; Cl-10; Cl-11. Yield: 92%, 96%, 93%, 92%, 94%, 96%, 95%, 96% respectively.

Preparation of (D-9)

To the solution of 4-(4-decyloxy-phenylazo)-phenol (0,709 g; 0,002 mol) in anhydrous THF (120 mL) redistilled and dried triethylamine (0,202 g; 0,020 mol) and catalytic amount of DMAP was added and the mixture was vigorously stirred whilst undecanedioil chloride (Cl-9) (0,253 g; 0,001 mol) was added dropwise. The resultant solution was stirred for a further 24 h at the room temperature. Next 100 mL of distilled water was added to the reaction mixture to precipitate crude product, which was then collected by filtration. After washing with methanol the resultant product was dried and analyzed for purity by TLC. No further purification was needed. (Yield: 0,729 g, 82%). The same procedure was applied to obtain homologues D-3; D-4; D-5; D-6; D-7; D-8; D-10; D-11. Yield: 88%, 86%, 83%, 88%, 84%, 86%, 83%, 86% respectively.

Spectral characterization of final compounds

COMPOUND D-3

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 34H, 2x(CH₂)₈ and (CH₂)); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, C_{ar}-H)

COMPOUND D-4

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 36H, 2x(CH₂)₈ and (CH₂)₂); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, Car-H)

COMPOUND D-5

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 38H, 2x(CH₂)₈ and (CH₂)₃); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, Car-H)

COMPOUND D-6

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 40H, 2x(CH₂)₈ and (CH₂)₄); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, Car-H)

COMPOUND D-7

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 42H, 2x(CH₂)₈ and (CH₂)₅); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, Car-H)

COMPOUND D-8

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 44H, 2x(CH₂)₈ and (CH₂)₆); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, Car-H)

COMPOUND D-9

¹H NMR (CDCl₃, 500MHz) δ=0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 46H, 2x(CH₂)₈ and (CH₂)₇); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, C_{ar}-H)

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COMPOUND D-10

¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 48H, 2x(CH₂)₈ and (CH₂)₈); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, C_{ar}-H) **COMPOUND D-11** ¹H NMR (CDCl₃, 500MHz) δ =0.89 (t, 6H, J=7.0Hz, 2xCH₃); 1.22-1.86 (m, 50H, 2x(CH₂)₈ and (CH₂)₉); 2.60 (t, 4H, J=7.4Hz, 2x(-CH₂COO-)); 4.03 (t, 4H, J=6.6Hz, 2x(-CH₂O-)); 6.93-7.95 (m, 16H, C_{ar}-H)

3. Results

Results of calorimetric studies performed for studied compounds D-n are collected in Table S1. Sol-gel transition temperature for the gels of dimer D-7 with various organic solvents are presented in Table S2.

Table S1. The transition temperatures and enthalpies for dimers as a function of number of methylene units, n, in the spacer

n	Phase transition temperatures/°C, enthalpies (in parentheses)/kJ mol ⁻¹
3	B4' 121.8(7.4) B4 177.3 SmC 178.6(2.0) Iso
4	Cr 145.6(45.8) SmJ 156.9(8.3) SmC 208.2(26.5) Iso
5	B4' 109.4(3.4) B4 156.0 SmC 164.7(18.3) Iso
6	Cr 129.5(45.8) SmJ 147.8(7.6) SmC 186.0(26.6) Iso
7	B4' 107.3(3.2) B4 148.9 SmC 154.1(5.6) N 157.2(3.9) Iso
8	Cr 130.9(49.2) SmJ 154.6(9.8) SmC 173.7(26.6) Iso
9	B4' 112.7(2.1) B4 146.9 N 151.0(2.8) Iso
10	Cr 134.1(49.5) SmJ 155.7(12.3) SmC 159.9(4.6) N 161.4 Iso
11	B ₄ ' 114.7(1.8) B ₄ 145.9(91.8) N [145.5(2.8)] Iso

Table 2. Sol-gel phase transitions temperatures detected from DSC studies for mixtures of dimer **D-7** (\sim 2% wt.) with different organic solvents. Transition enthalpies are not given as they are measured with large error due to some solvent evaporation at elevated temperatures, dissipate careful sealing of the samples.

Solvent	sol-gel phase transition temperature (°C)
Nitrobenzene	88.0
(R)-(+)-3-methylcyclohexanone	82.0
(+)-menthone	83.0
(-)-menthone	83.0

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Figure S1. Weakly birefringent, optically active texture of the B4 phase of dimer D-9 grown from nematic phase. Typically observed blue colour of B4 phase is hardly seen due to native yellow colour of azo derivatives. Alternating optical activity of neighbouring domains is clearly seen by slight de-crossing of polarizers (arrows) in opposite direction.

X-ray diffraction studies showed clearly a difference between molecular organization within the smectic layers in smectic C phase and both B4 phases. While in the former diffused high angle signal reflects liquid-like short range correlations between neighbouring molecules, in the later Bragg-type reflections evidence long range ordering present in layers of B_4 and B_4 phases (Fig. S2).



Figure S2. 2D xrd patterns obtained for dimer D-5 at (a) 155 °C, SmC phase, (b) 135 °C, B₄ phase and (c) 85 °C, B₄ 'phase. In (d) 2q dependence of diffracted intensity is given, obtained by integration of above patterns over azimuthal angle. The curves are vertically shifted for clarity.

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The unique phase sequence observed for dimers **D-3**, **D-5** and **D-7**, in which B_4 phase is formed below smectic phase allow for direct comparison of the width of xrd signals related to layer thickness in both phases. Much broader signal observed in B_4 phase does not reflect lowering of the smectic order parameter in this phase, instead it results from the finite size of the membranes from which helical filaments building the phase are formed (Figure S3).



Figure S3. Low angle xrd signals related to the layer thickness for dimer D-7 in SmC (black) and in the B4 phase (red).

Dimers **D**-**n** with odd number of carbon atoms in the linkage, show no miscibility for each other in B_4 phase, despite very small difference in their molecular structure. Xrd pattern obtained for nearly equimolar mixture of **D**-**3** and **D**-**11**, is composed of two series of commensurate signals (Figure S4), each of them reflecting layer thickness characteristic for the B_4 phase formed by each mixture components. Thus it could be concluded that even in case of the mixture with very similar compound the filaments of B_4 phase are always formed by pure compound.





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The change of the molecular structure of studied compounds, i.e. trans-cis isomerization of azo units, under UV irradiation was monitored by visible light absorption spectroscopy. Sample before irradiation has intensive $\pi - \pi^*$ excitation band at 350 nm, the band shift to ~315 nm after UV irradiation (Figure S5). The observed shift of $\pi - \pi^*$ excitation band is typical for trans-cis isomerization of azo units. No detectable changes in absorption spectrum were observed after turning off the UV light, evidencing that cis molecular form is stable in low concentration solution. The trans molecular form can be recovered by irradiation of the sample with intense visible ($\lambda > 400$ nm) light.



Figure S5. UV-Vis spectra for a solution of dimer D-5 in chloroform (c = 10^{-6} M), black line – sample before irradiation, red line - sample irradiated with UV light (λ = 365 nm) for 30s and blue line - sample re-irradiated with visible light (λ > 400 nm) for 30 s.

Studied compounds **D-n** with odd number n were used for preparation of mixtures with rod-like compounds forming smectic phases.



Figure S6. Molecular structure of rod-like compounds (**1** and **2**) used for preparing mixtures with dimers **D-n**, their phase sequences, transition temperatures and transition enthalpy changes (in parentheses, in J g⁻¹). Synthesis and properties od compound **2** have been described earlier [E. Dzik, J. Mieczkowski, E. Gorecka and D. Pociecha, *J. Mater. Chem.*, **15**, 1255-1262, (2005)].

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It was also found that the helical filaments of B_4 phase growing in the SmC* phase influence dynamic of ferroelectric matrix. The formation of B_4 phase filaments in the mixtures of dimers **D**-**n** with rod-like compounds **1** or **2**, within smectic matrix cause the confinement effects for the system, in result the azimuthal fluctuations of polarization vector (Goldstone mode) are suppressed and shifted to higher frequency comparing to the homogenous mixture. Apparently the filaments trap the SmC* phase and due to the interactions with surface of filaments the smectic behaves like in confined geometry (Figure S7).



Figure S7. (a) Temperature/frequency dependence of imaginary part of dielectric constant for mixture of compound **1** with dimer **D-5** (20 % wt.). Arrow indicates temperature at which filaments of B_4 phase start to separate from the SmC* matrix. (b) Relaxation frequency, f_r , and dielectric strength of the mode, $\Delta \varepsilon$, obtained by fitting the Cole-Cole formula to the measured dielectric dispersion. Appearance the confinement of ferroelectric phase between B_4 filaments causes increase of relaxation frequency and decrease of the mode strength.