ELECTRONIC SUPPLEMENTARY INFORMATION

Physical gels made of liquid crystalline B4 phase

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1. Experimental

The ^{1}H NMR spectra were recorded at 500 MHz NMR Varian Unity Plus spectrometer. Proton chemical shifts (δ) are reported in ppm 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 hermetic aluminum pans and kept in nitrogen atmosphere during measurement, both heating and cooling scans with rate 5-10 deg/min were applied.

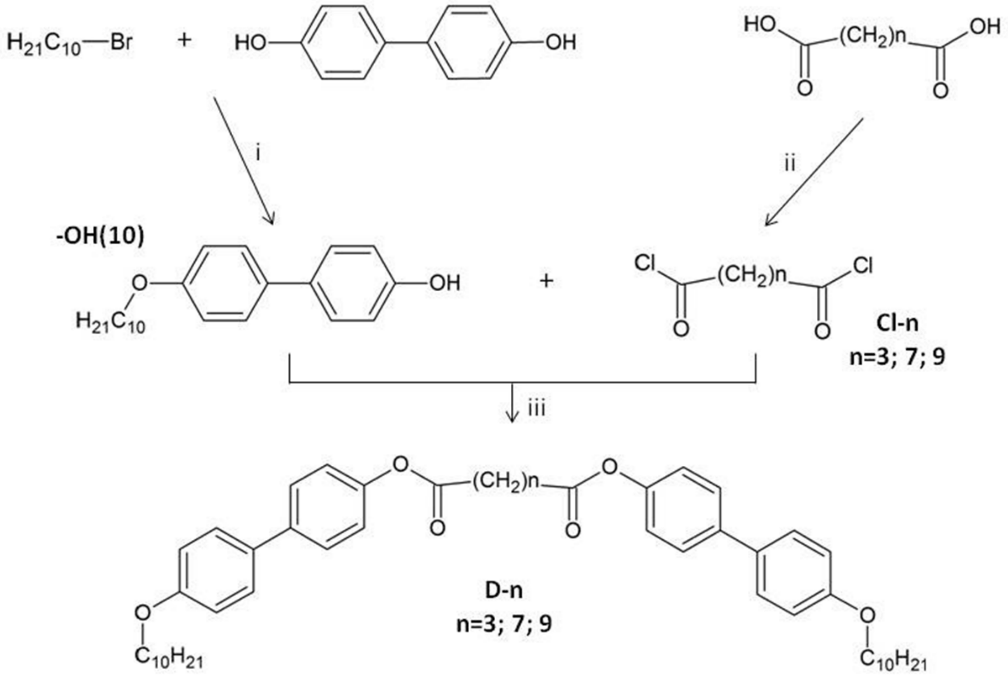
X-ray diffractograms in broad angle range were obtained with Bruker D8 GADDS system equipped with Vantec2000 area detector. Parallel CuK$_\alpha$ line was formed with Goebel mirror and point collimator. Samples were prepared either in thin-walled glass capillaries or as a droplet on a heated surface.

The optical studies were performed using Zeiss Imager A2m polarizing microscope equipped with Linkam heating stage. AFM images were taken with Veeco Nanoscope V microscope working in tapping mode. 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. The AFM picture was taken for the sample deposited on Au surface, and cooled to the room temperature from isotropic melt.

2. Organic synthesis

The general procedure for the synthesis of compounds *D=3; D=7; D=9* is presented in Scheme S1.



Scheme S1. General procedure for the synthesis of compounds D-3; D-7; D-9. Reagents and conditions: (i) KI, K_2CO_3, DMF, 90°C (ii) $SOCl_2$, room temperature; (iii) TEA, DMAP, DMF, 70°C

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Following abbreviations are used:

TEA – triethylamine

DMF – dimethylformamide

DMAP – 4-dimethylaminopyridine

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-7. Yield: 92%, 96%, respectively.

Preparation of 4-decyloxy-4'-hydroxybiphenyl (-OH(10))

To the 4,4'-dihydroxybiphenyl (7,44 g; 0,04 mol) dissolved in 300 mL of DMF in the ambient temperature was added K_2CO_3 (11,04 g; 0,08 mol) and KI (13,28 g; 0,08 mol). Obtained mixture was stirred at the 50˚C for 15 min and after this time the solution of 1-bromodecane (4.42 g; 0,02 mol) in 40 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 500 mL of distilled water to precipitate crude product, which was then collected by filtration. After washing with methanol the resultant product was dried and purified by silica gel column chromatography (eluent: chloroform/acetone = 10/1) to give 3.26g (50%) of 4-decyloxy-4'-hydroxybiphenyl (**-OH(10)**) as a white solid.

Preparation of (D-9)

To the solution of 4-decyloxy-4'-hydroxybiphenyl (-OH(10)) (1,30 g; 0,004 mol) in anhydrous DMF (120 mL) redistilled and dried triethylamine (0,4 g; 0,04 mol) and catalytic amount of DMAP was added and the mixture was vigorously stirred whilst undecanedioil chloride (Cl-9) (0,51g; 0,002 mol) was added dropwise at the 50°C. The resultant solution was stirred for a further 24 h at the 70°C. Next it was cooled down at the room temperature and added to 100 mL of distilled water to precipitate crude product, which was then collected by filtration. After washing with methanol the resultant product was dried and purified by silica gel column chromatography (eluent: chloroform) to give 1.5g (90%) of D-9 as a white solid. The same procedure was applied to obtain homologues D-3; D-7. Yield: 88%, 86%, respectively.

Compound D-9

^{1}H NMR ($CDCl_3$, 500MHz) δ=0.88 (t, 6H, J=7.08Hz, 2xCH_3); 1.23-1.89 (m, 46H, 2x$(CH_2)_8$ and $(CH_2)_7$); 2.58 (t, 4H, J=7.44Hz, -CH_2COO-); 3.99 (t, 4H, J=6.59Hz, -CH_2O-); 6.93-7.55 (m, 16H, C_{ar}-H)

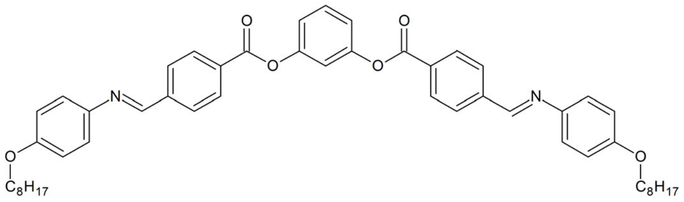
Compound D-7

^{1}H NMR ($CDCl_3$, 500MHz) δ=0.88 (t, 6H, J=7.08Hz, 2xCH_3); 1.23-1.89 (m, 42H, 2x$(CH_2)_8$ and $(CH_2)_5$); 2.58 (t, 4H, J=7.44Hz, -CH_2COO-); 3.99 (t, 4H, J=6.59Hz, -CH_2O-); 6.93-7.55 (m, 16H, C_{ar}-H)

Compound D-3

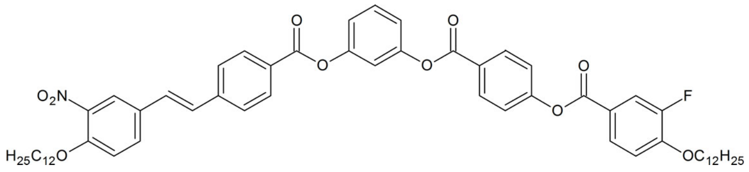
^{1}H NMR ($CDCl_3$, 500MHz) δ=0.88 (t, 6H, J=7.08Hz, 2xCH_3); 1.23-1.89 (m, 34H, 2x$(CH_2)_8$ and (CH_2)); 2.58 (t, 4H, J=7.44Hz, -CH_2COO-); 3.99 (t, 4H, J=6.59Hz, -CH_2O-); 6.93-7.55 (m, 16H, C_{ar}-H)

3. Other materials tested for gelation ability



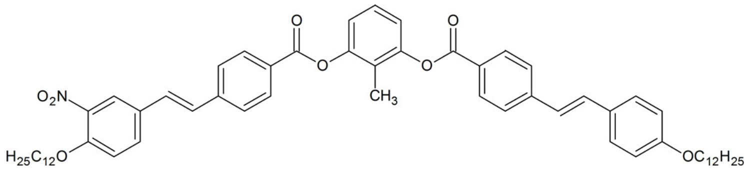
B_4 140 B_3 152 B_2 174 Iso

Forms gel in toluen



Cr 104.5 DC[a] 132.5 Iso

Does not form gel in toluen



Cr 143.3 DC[a] 148.9 Iso

Does not form gel in toluen

[a] DC stands for Dark Conglomerate phase

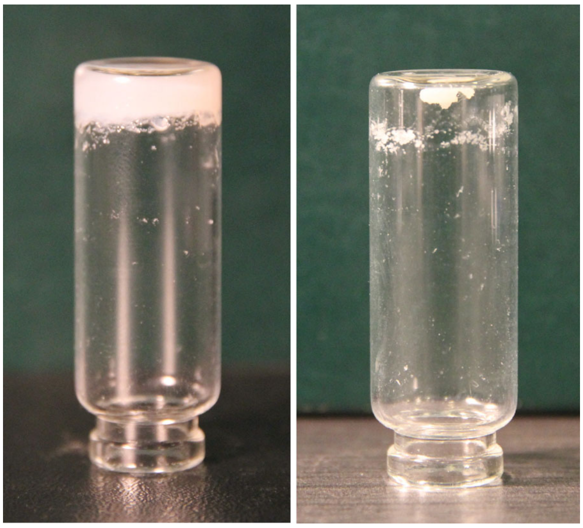


Figure S-1. Comparison of the volume of freshly prepared gel (dimer n = 7 in toluene) and the xerogel obtained after evaporation of the solvent over 7 days.