

**Azobenzene-decorated cellulose nanocrystals as photo-switchable chiral solutes in
nematic liquid crystals**

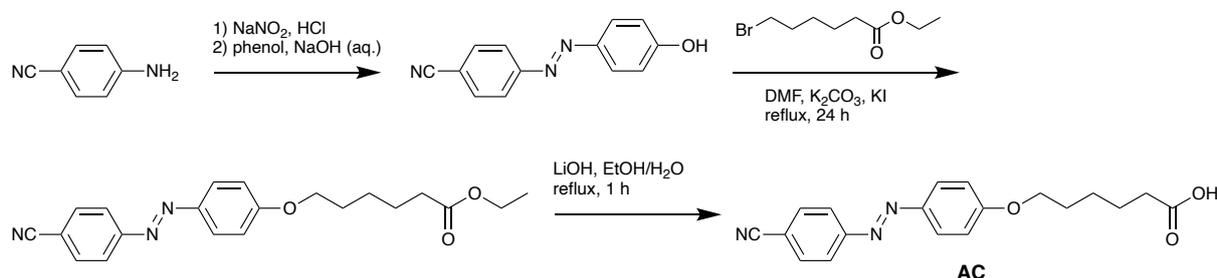
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Electronic Supporting Information (ESI)

S1. Synthesis

S1.1 Carboxylic ligands

S1.1.1 Synthesis of AC



Scheme S1 Synthesis pathway for AC carboxylic acid-terminated cyano-azobenzene ligand.

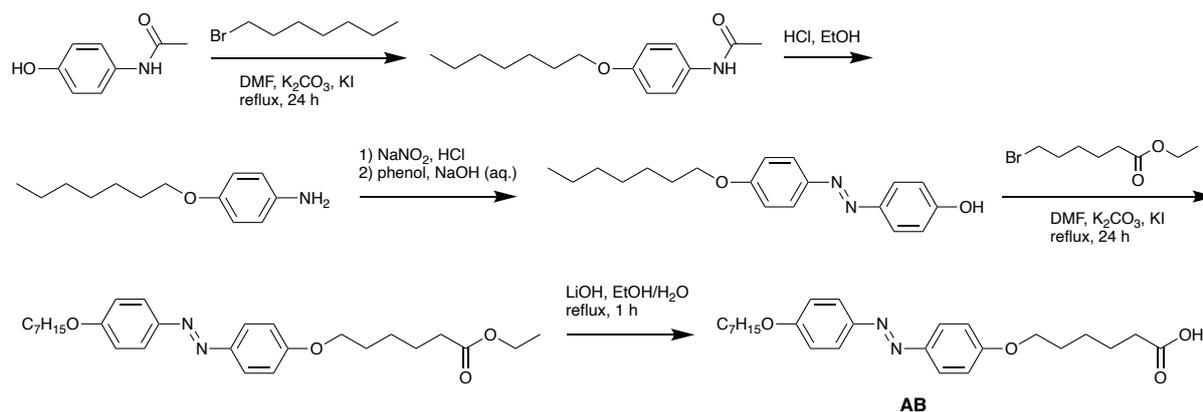
Reaction 1. 10 mmol 3-Aminobenzonitrile was dissolved in 5 mL of water, and 5 mL of HCl was added to it and cooled to 0 °C in an ice-salt bath. A freshly prepared sodium nitrite (10 mmol) solution in 3 ml of water was added to the mixture over a period of 15 minutes. The mixture was stirred for 1 hour below 0 °C to observe a clear diazonium salt solution. The resulting solution was slowly added to the solution of phenol and 20 mmol of sodium hydroxide prepared in the water at 0 °C. The reaction mixture was then stirred for 4 hours. Thereafter, the mixture was adjusted to pH = 7, filtered, and washed with water. The crude product was recrystallized with ethanol to yield 1.2 g (yield: 55%).^{S1}

Reaction 2. To a round bottom flask was added ethyl 6-bromohexanoate (3.5 mmol), 4-[4-(cyanophenyl)azo]phenol (2.5 mmol), anhydrous K₂SO₃ (4 mmol) followed by a catalytic amount of KI, followed by 20 mL dry DMF. The mixture was refluxed under a nitrogen atmosphere for 24 hours and monitored by TLC. Thereafter, the mixture was extracted with CH₂Cl₂. The organic phase was dried with anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. After drying, the crude product was recrystallized in absolute ethanol, to give an orange powder (0.7 g, yield: 80%).^{S1} ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.97 (dd, *J* = 8.6, 1.7 Hz, 4Ar-H), 7.81 (d, *J* = 8.9 Hz, 2Ar-H), 7.03 (d, *J* = 9.0 Hz, 2Ar-H), 4.17 (q, *J* = 7.1 Hz, OCH₂), 4.09 (t, *J* = 6.4 Hz, OCH₂), 2.38 (t, *J* = 7.4 Hz, 2H), 1.95 – 1.83 (m, 2H), 1.82 – 1.69 (m, 2H), 1.61 – 1.52 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

Reaction 3. The as synthesized ethyl 6-[4-(4-cyanophenylazo)phenoxy]-hexanoate from reaction 2 (1.2 mmol) was dissolved in 10 mL of absolute ethanol, then slowly added onto LiOH (1.5 mmol) dissolved in 1 mL of DI water. The mixture was refluxed for 1 hour. The mixture was poured into water and adjusted to pH = 2. It caused the solid to precipitate. The solid formed was filtered and washed with water, followed by washing with cold ethanol. The crude product was recrystallized in ethanol to give an orange solid (0.3 g, yield: 76%).^{S1, S2} ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 10.00 (s, COOH), 7.97 (dd, *J* = 9.0, 0.8 Hz, 4Ar-H), 7.82 (d, *J* = 8.8 Hz, 2Ar-H), 7.04 (d, *J* = 9.0 Hz, 2Ar-H), 4.10 (t, *J* = 6.4

Hz, OCH₂), 2.45 (t, *J* = 7.4 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.83 – 1.71 (m, 2H), 1.66 – 1.57 (m, 2H). ¹³C NMR (DMSO-d₆, 100 MHz, δ /ppm): *trans* 174.92 (C=O), 162.91, 154.64, 146.50, 112.98 (Ar-C) 134.25, 125.79, 123.37, 115.70 (Ar-CH), 119.01 (CN), 68.51 (OCH₂), 34.08, 28.76, 25.55, 24.71 (CH₂), *cis* 174.92 (C=O), 167.62, 162.35, 153.95, 146.55 (Ar-C), 136.22 (CN), 129.20, 125.36, 122.42, 115.59 (Ar-CH), 68.42 (OCH₂), 34.08, 28.79, 25.57, 24.71 (CH₂).

S1.1.2 Synthesis of AB



Scheme S2 Synthesis pathway for AB carboxylic acid aliphatic chain-terminated azobenzene ligand.

Reaction 1. To a round bottom flask was added 1-bromoheptane (45 mmol), acetaminophen (30 mmol), anhydrous K₂SO₃ (45 mmol) followed by a catalytic amount of KI, followed by 60 mL dry DMF. The mixture was refluxed under a nitrogen atmosphere for 24 hours and monitored by TLC. Thereafter, the mixture was extracted with CH₂Cl₂. The organic phase was dried with anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. After drying, the crude product was recrystallized with absolute ethanol, to give a white powder (5.2 g, yield: 70%).^{S2, S3}

Reaction 2. 4-Heptyloxyacetanilide (15 mmol) was dissolved in ethanol (100 mL), and 7.5 mL of concentrated HCl in ethanol (25 mL) was added dropwise. The reaction mixture was heated to reflux for 12 h, cooled, poured into ice-water mixture. The white solid thus obtained was extracted with ether, washed with water (3 × 100 mL), brine solution (3 × 100 mL), and dried over anhydrous Na₂SO₄. The solvent was removed with a rotary evaporator to give off-white crystals (5.2 g, yield: 75%).^{S2, S3}

Reaction 3. 15 mmol 4-heptyloxyaniline was dissolved in 7.5 mL of water, and 7.5 mL of HCl was added to it and cooled to 0 °C in an ice-salt bath. Freshly prepared sodium nitrite (1.2 g) solution in 5 mL of water was added to the mixture over a period of 15 minutes. The mixture is stirred for 1 hour below 0 °C to observe a clear diazonium salt solution. This solution was then slowly added to the solution of phenol and 1.5 g of sodium hydroxide prepared in the water at 0 °C. The reaction mixture is

stirred for 4 hours. After 4 hours, the mixture was adjusted to pH = 7, filtered, and washed with water. The crude product was recrystallized with ethanol (0.9 g, yield: 20%).^{S2}

Reaction 4 was performed according to the synthesis procedure described in **Reaction 1** above.

Reaction 5. The resulting ethyl 6-[4-(4-heptyloxyphenylazo)phenoxy]-hexanoate (2.55 mmol) was dissolved in 10 mL of absolute ethanol, then slowly added onto LiOH (3.18 mmol) dissolved in 1 mL of DI water. The mixture was refluxed for 1 hour. The mixture was poured into water and adjusted to pH = 2. The solid formed was filtered and washed with water, followed by cold ethanol. The crude product was recrystallized in ethanol to give an orange solid (*m.p.* = 172 °C, 1 g, yield: 93%).^{S2} ¹H NMR (DMSO-d₆, 400 MHz, δ /ppm): 12.03 (s, COOH), 7.83 (d, *J* = 9 Hz, 4Ar-H), 7.10 (d, d, *J* = 8.6 Hz, 4Ar-H), 4.07 (t, *J* = 6.5 Hz, 2-OCH₂), 2.28 – 2.22 (m, 2H), 1.81 – 1.70 (m, 4H), 1.58 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.48 – 1.25 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (DMSO-d₆, 100 MHz, δ /ppm): 174.93 (COOH), 161.35, 146.52, 122.61, 114.93 (Ar-C), 124.59, 115.41 (Ar-CH), 68.38, 55.40 (OCH₂), 34.08, 31.71, 29.08, 28.91, 28.83, 25.92, 25.58, 24.73, 22.53 (9CH₂), 14.44 (CH₃).

S1.1.3 NMR spectra

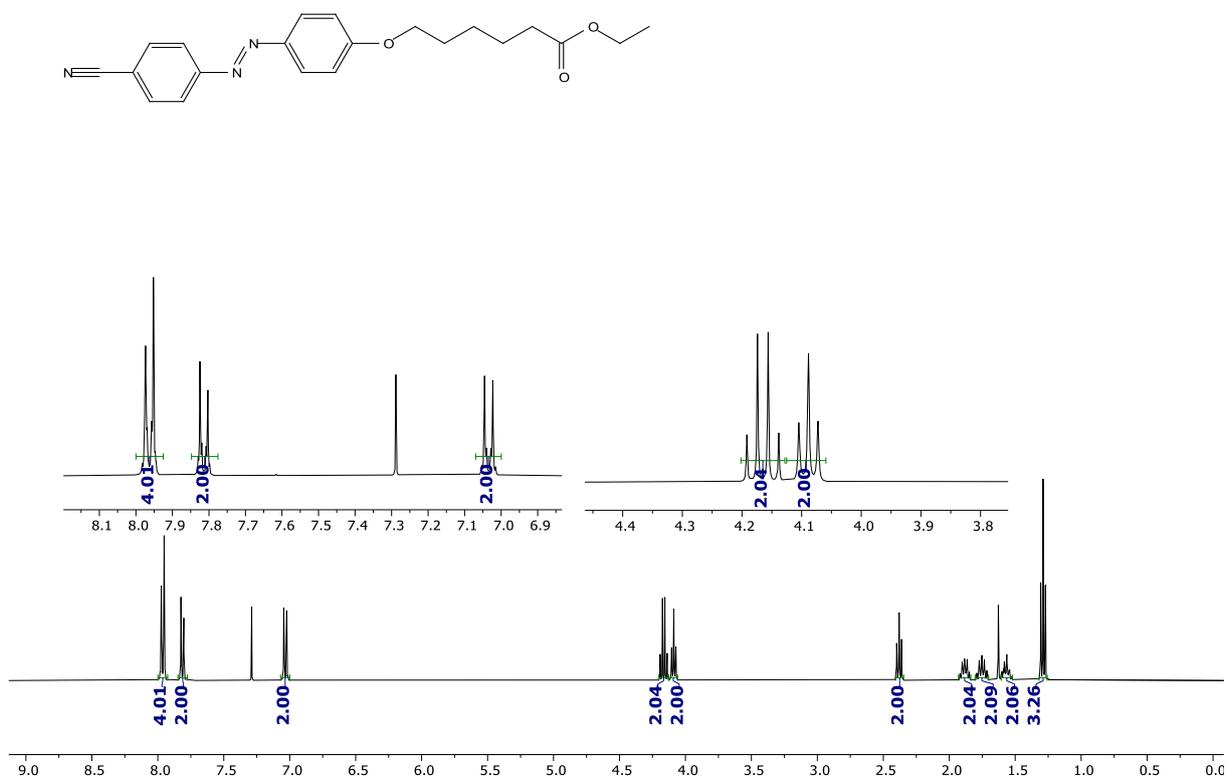


Fig. S1 ¹H NMR spectrum of ethyl 6-[4-(4-cyanophenylazo)phenoxy]-hexanoate in CDCl₃.

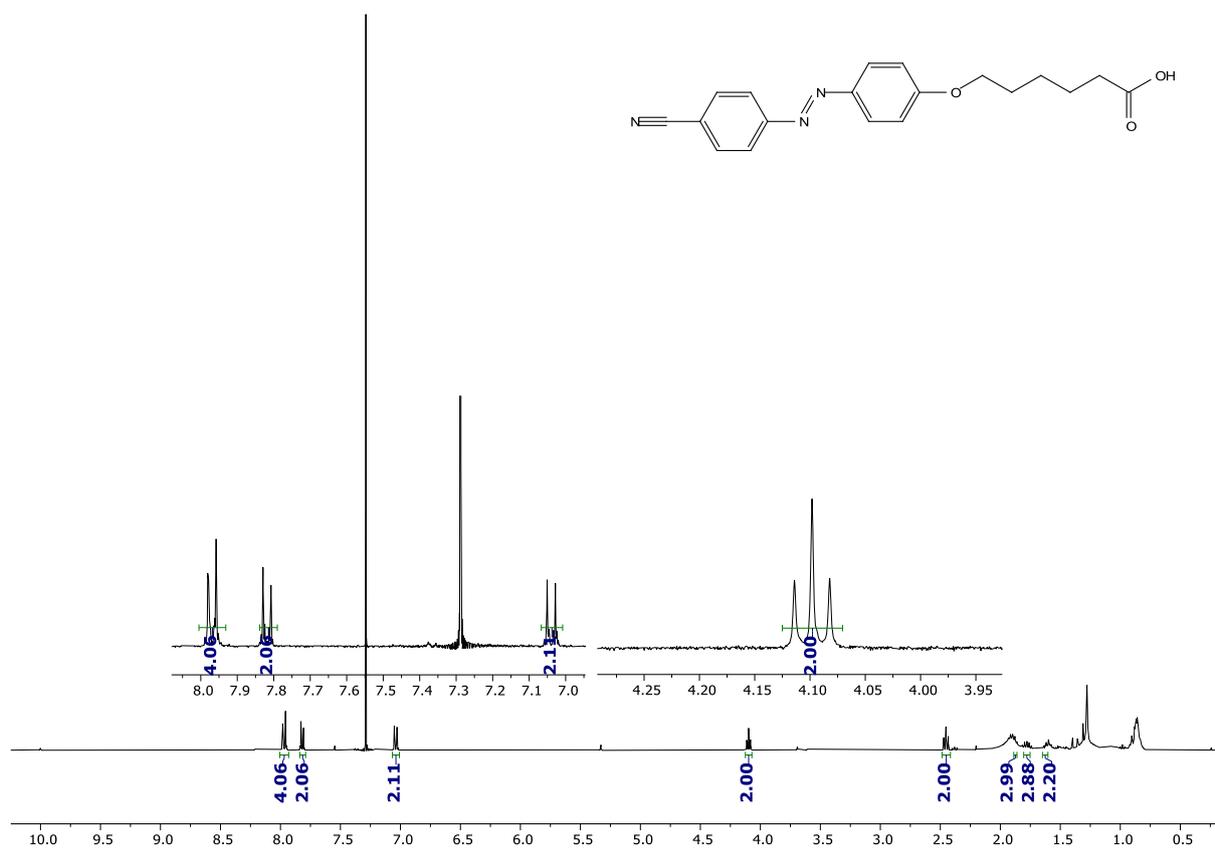


Fig. S2 ¹H NMR spectrum of AC in CDCl₃.

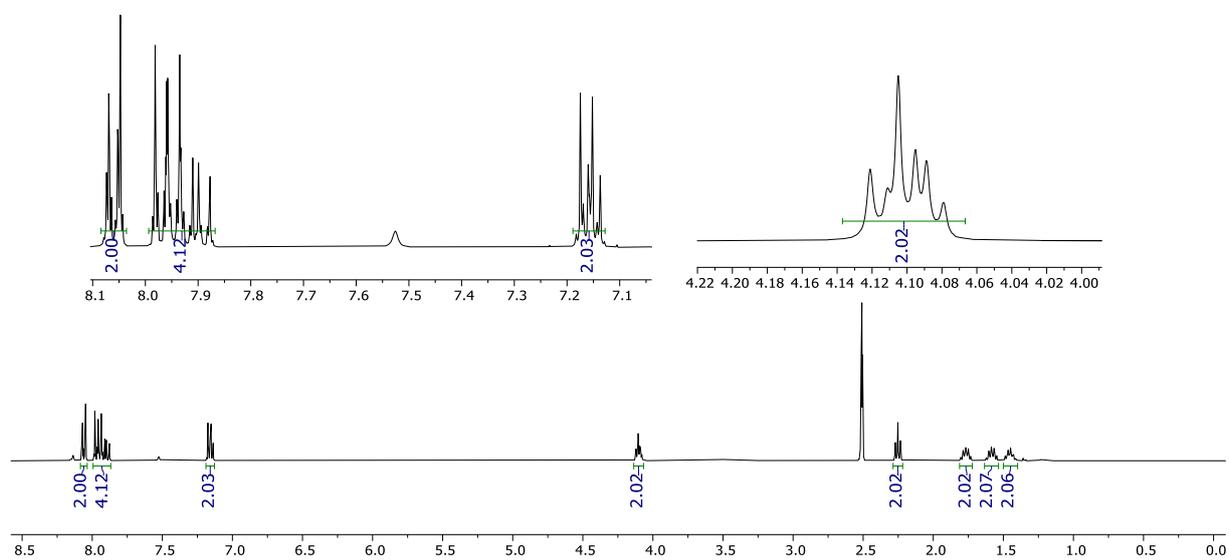


Fig. S3 ¹H NMR spectrum of AC in DMSO-d₆. Both *trans* and *cis* isomer are detected in this more polar solvent.

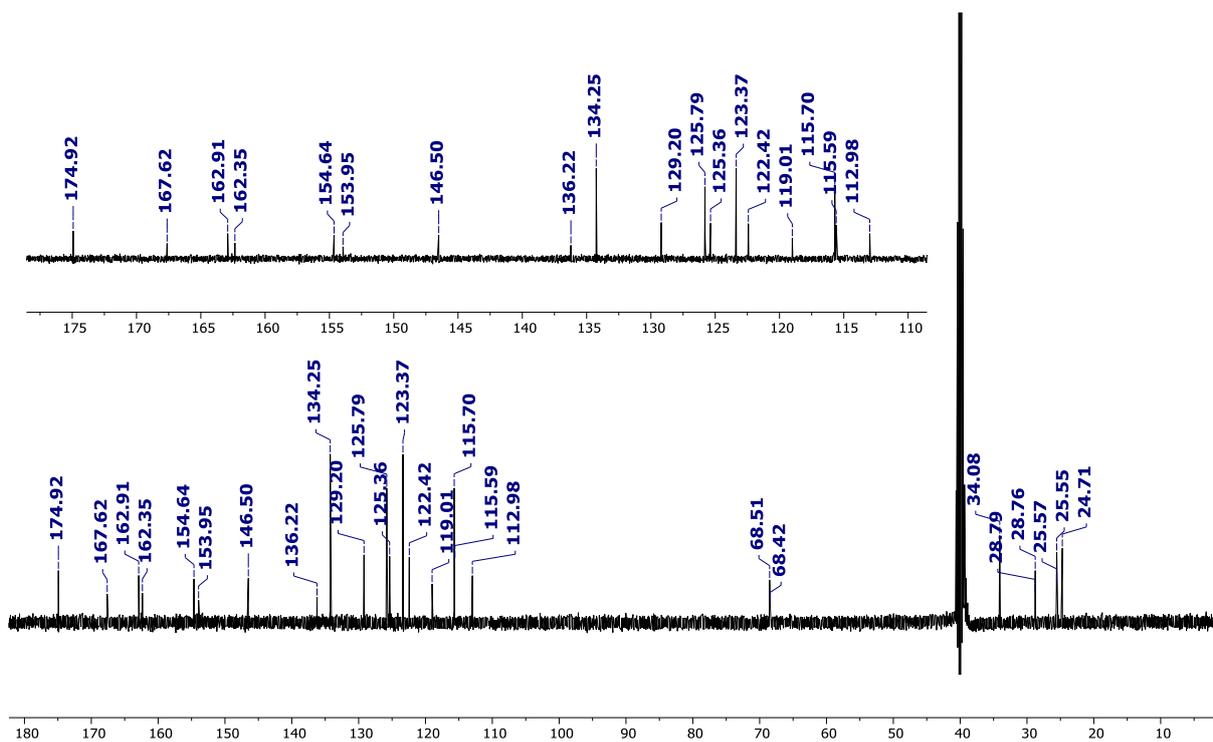


Fig. S4 ^{13}C NMR spectrum of AC in DMSO- d_6 .

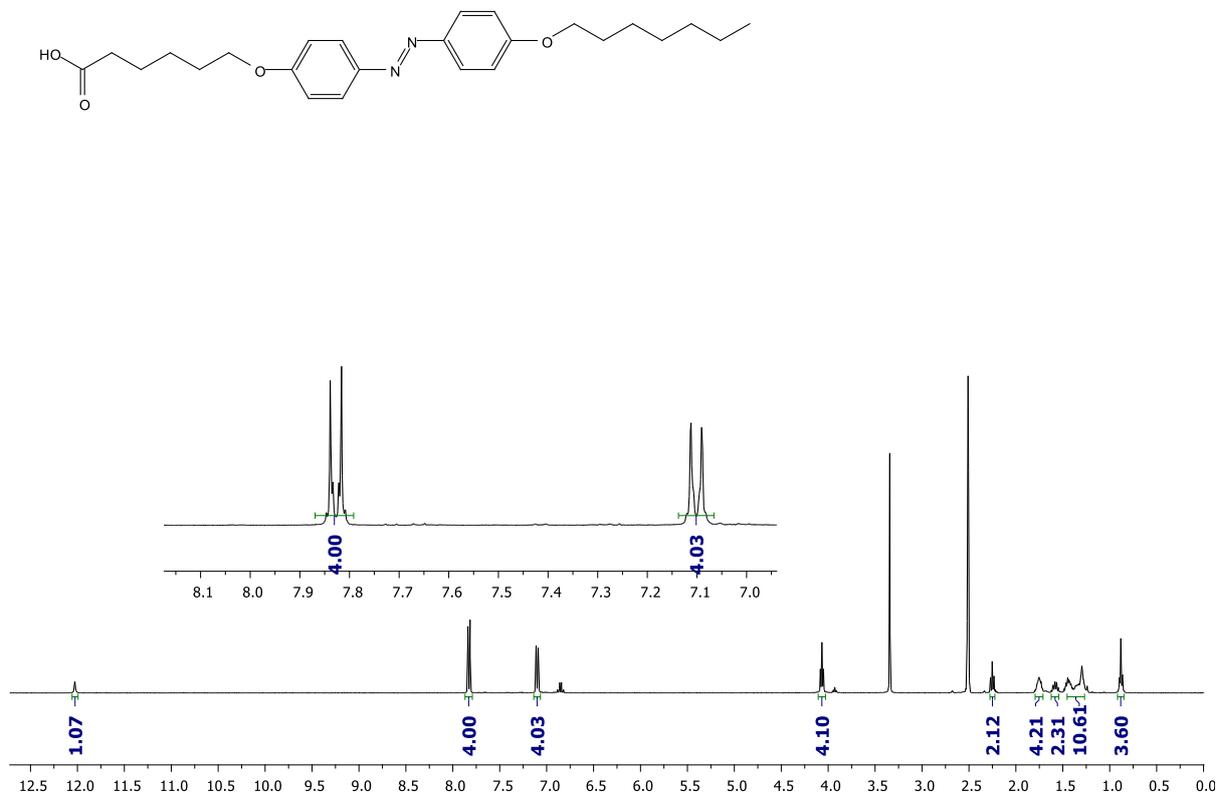


Fig. S5 ^1H NMR spectrum of AB in DMSO- d_6 .

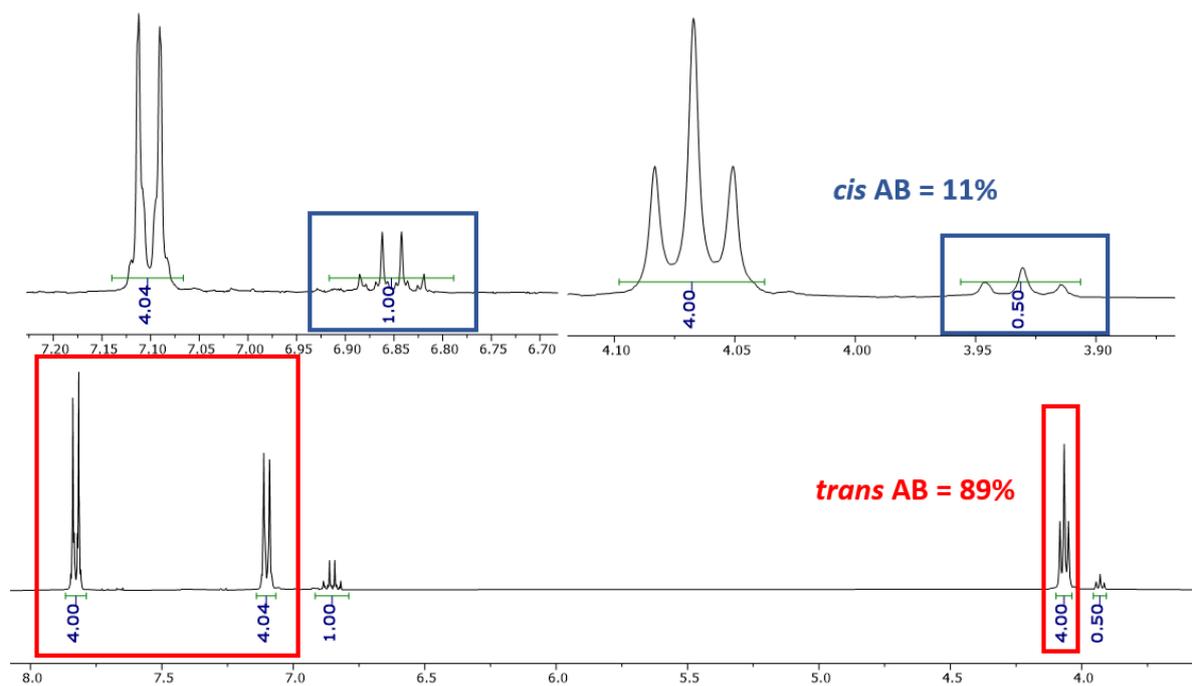


Fig. S6 Sections of the ^1H NMR spectrum of AB in DMSO- d_6 (shown in Fig. S5 above) analyzing the ratio between *trans* and *cis* isomers in this more polar solvent.

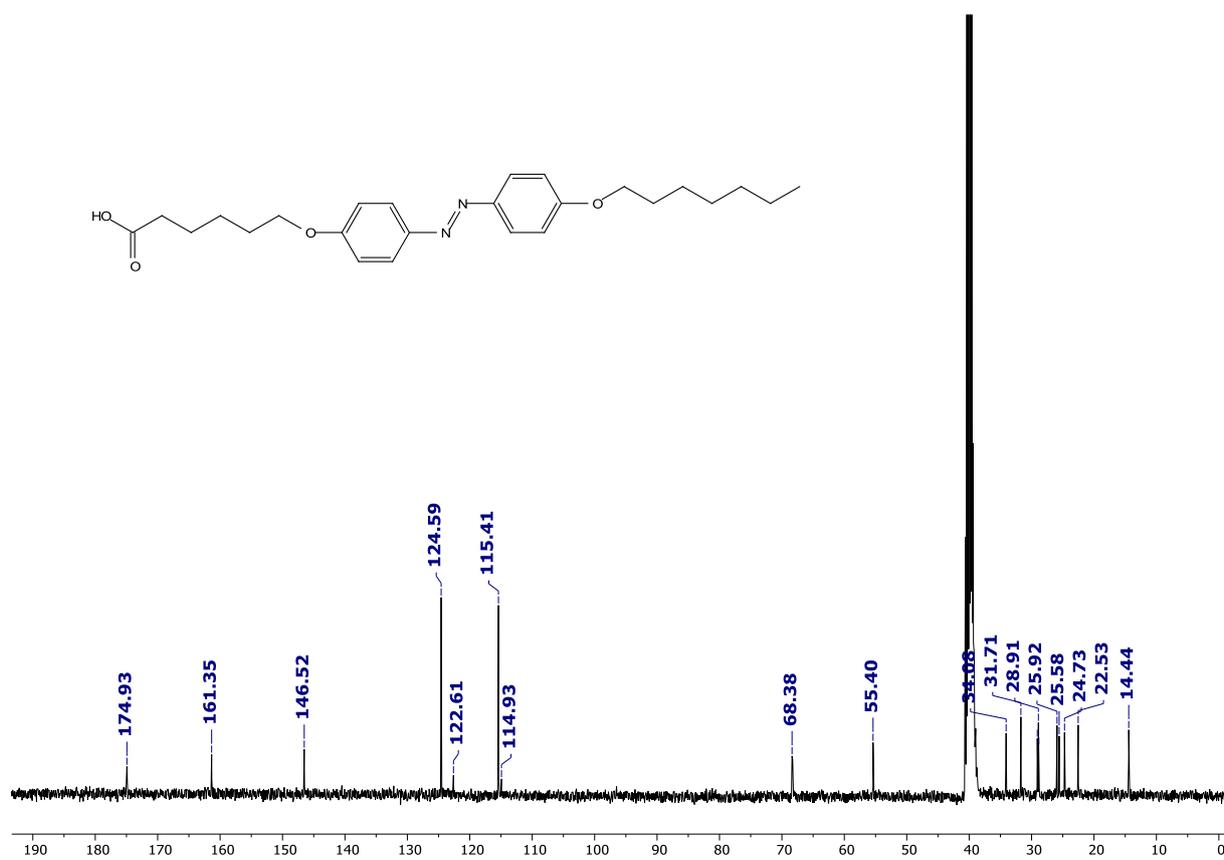
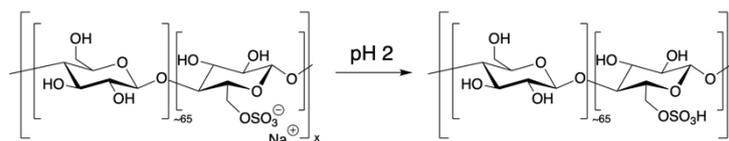


Fig. S7 ^{13}C NMR spectrum of AB in DMSO- d_6 .

S1.2 Functionalization of CNCs

1.2.1 Acidification of CNCs sodium salt

As described in previous work,¹⁶ CNCs were treated by acidification with a solution of 1N HCL to pH = 2 to render them more soluble in organic solvents, followed by dialysis (MWCO = 20,000) against Milli-Q water for 3 days or until the pH remained stable. Dialysis water was replaced with fresh Milli-Q Water twice daily. It was stored in a closed container at room temperature until next use.



1.2.2 Functionalization with azobenzene pendants

10 mL of an aqueous dispersion of CNCs (100 mg) was poured into a round bottom flask, and 10 mL of DMF was added under stirring. The water and a small amount of DMF in the mixture were then evaporated using a rotary evaporator and subjected to a solvent exchange. EDC-HCL (0.16 g, 1 mmol) in 2 mL of DMF was added to the CNCs in cooled DMF after addition of DMAP (0.09 g, 0.66 mmol). Then, 0.26 mmol of the corresponding carboxylic acid terminal functional ligand was added to the mixture under rapid stirring, and the reaction was allowed to stir for 24 hours at room temperature. Functionalized CNCs were purified by centrifugation at 6,000 rpm for 10 minutes and the supernatant was discarded and replaced with ethyl acetate and the purification steps were repeated six times.¹⁶

S2. Characterization of functionalized CNCs

S2.1 FT-IR spectroscopy

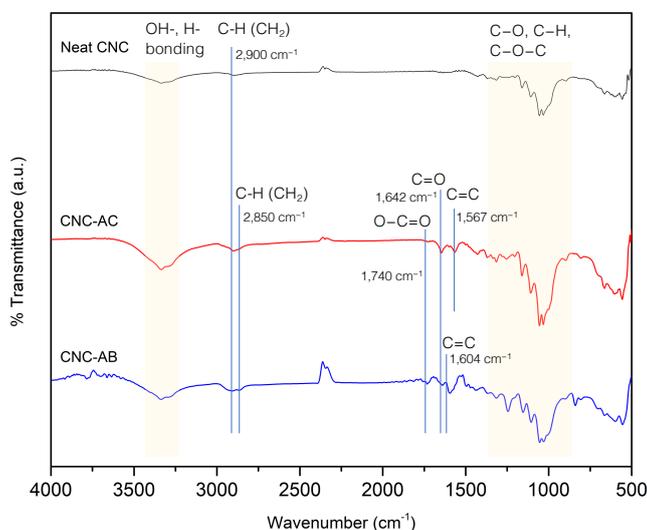


Fig. S8 FT-IR spectra of: (black line) unfunctionalized CNCs, (red line) CNC-AC, and (blue line) CNC-AB.

S2.2 CP-MAS ^{13}C NMR spectroscopy

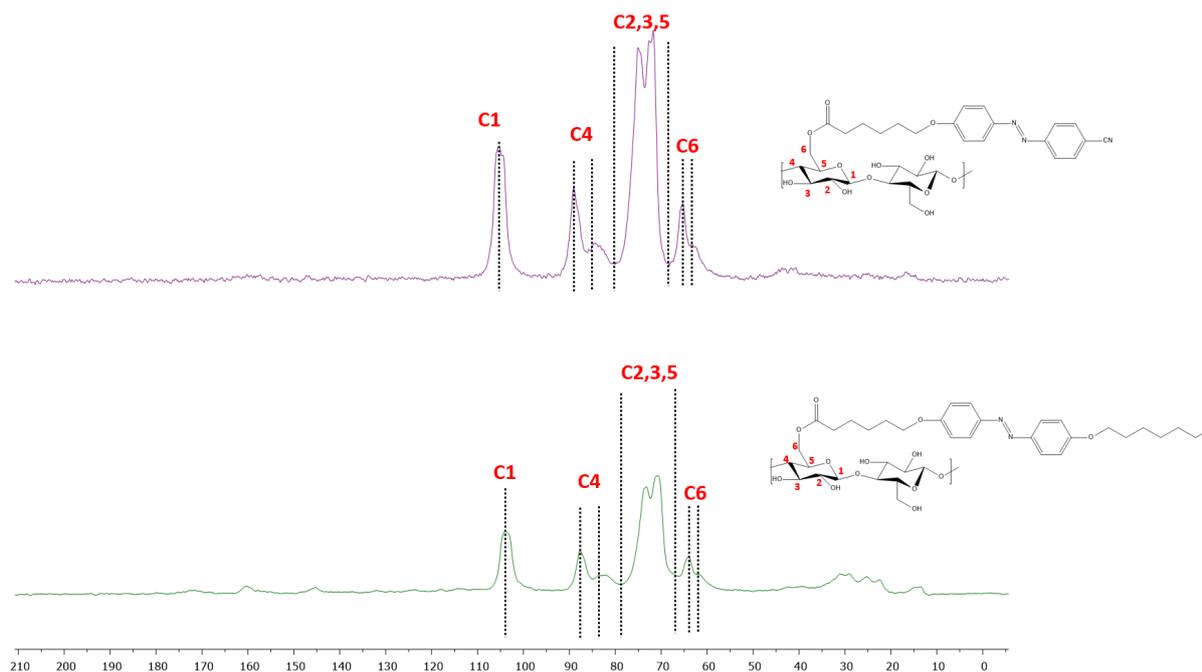


Fig. S9 Solid-state cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR spectra of functionalized CNCs: (top) CNC-AC and (bottom) CNC-AB.

S2.3 XPS analysis – calculation of the degree of surface functionalization (*DSF*)

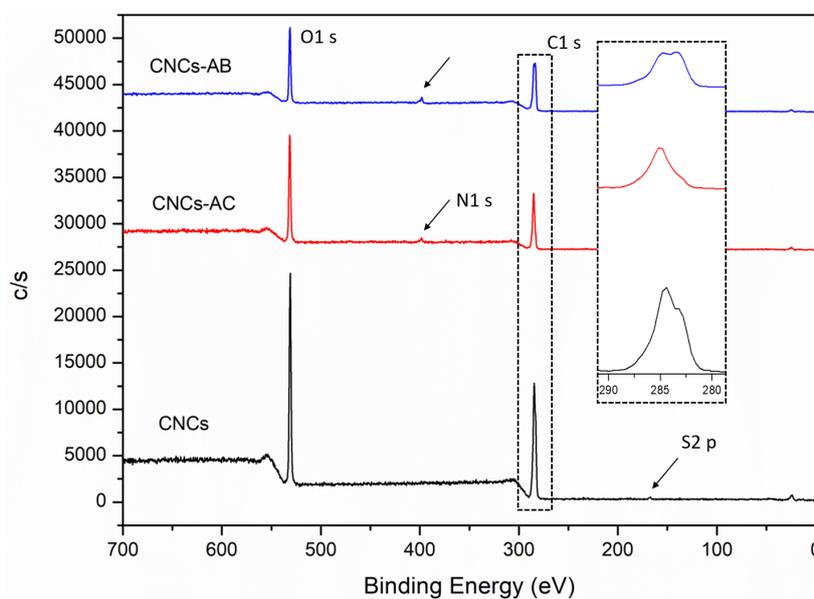
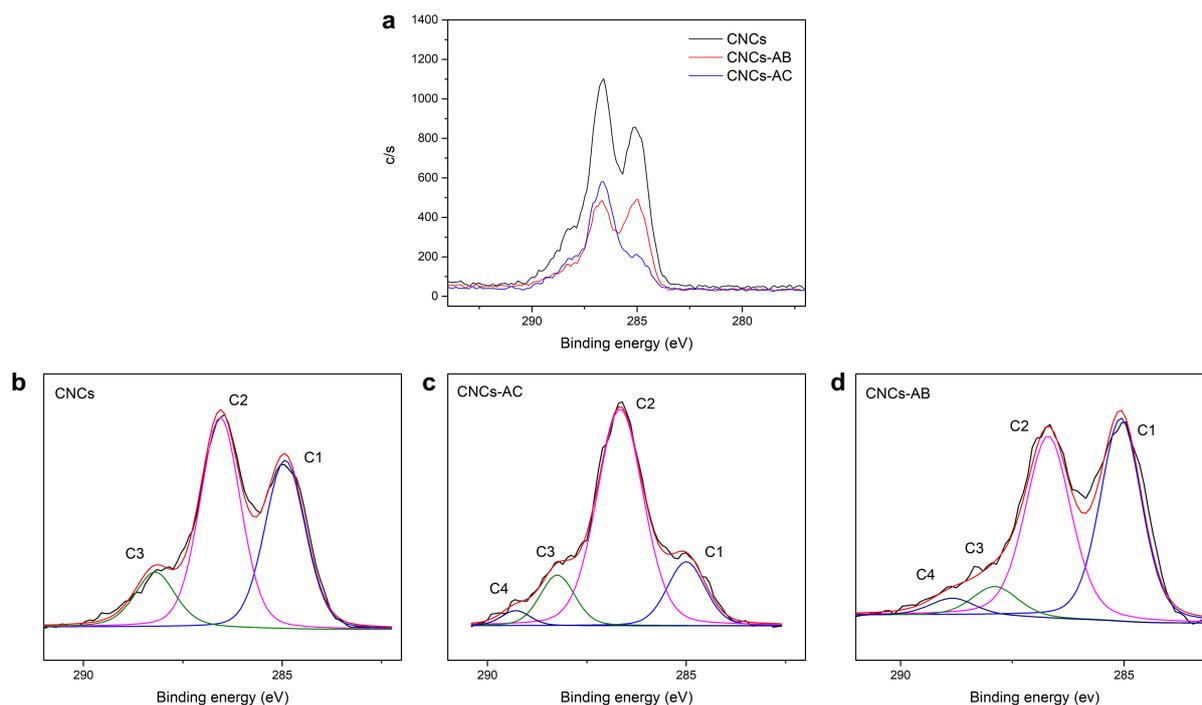


Fig. S10 XPS survey spectra of the CNC samples with signal assignments, O (oxygen), C (carbon), S (sulfur) and N (nitrogen); for values, see Table S1.

Table S1. Mass concentration of each element for unmodified and functionalized CNCs.

Sample	Experimental Values				
	C [%]	O [%]	N [%]	S [%]	O/C
neat CNCs	66.8	32.8	0	0.3	0.5
CNC-AC	59.4	38.4	2.0	0.1	0.64
CNC-AB	69.8	27.1	3.0	0.1	0.38

**Fig. S11** (a) Survey of all high-resolution spectra of the C1s peak of the CNCs samples. Deconvolution of the spectra: (b) neat CNCs, (c) CNCs-AC, and (d) CNC-AB; for type of C1s carbon (C1 to C4, see Table S2).**Table S2.** Deconvolution C1s extracted from XPS experimental data.

Sample	Decomposition of C1s				<i>DSF</i>
	C-H, C-C	C-O	O-C-O	O-C=O	
	C1 (%)	C2 (%)	C3 (%)	C4 (%)	
neat CNCs	37.1	47.1	15.8	0	0
CNC-AC	16.5	68.5	11.9	2.9	0.10
CNC-AB	44.7	43.9	7.1	4.1	0.17

For the calculation of the degree of surface functionalization (*DSF*; values given in Table S2), it was considered that for each cellulose subunit there are five carbons in the C2 (C-O) molecular environment. This analysis followed a protocol for acylated CNCs established by Rodionova *et al.* (see reference [57] in the main text; applied in references [16] and [17] in the main text) adjusted here for the azobenzene-modified CNCs. The AC substitution adds two and the AB substitutions adds four. Therefore, 3/7th of

the percentage peak contribution of C2 corresponds to the contribution of a single carbon unit in the C4 environment for AC and for AB 5/9th of the C2 environments is used due to the four additional C2 environments in the aliphatic side chain junctions. Since the CNCs are esterified predominantly at the hydroxy group at carbon-C6 and considering the low degree of sulphonation seen in the XPS survey spectra, this leads to one C4 from the resulting carboxylate for CNC-AC and CNC-AB (the percentage concentration in the C4 (O-C=O) (%) environment is proportional to the number of ester bonds; see Eq. S1 and Eq. S2).

$$DSF_{CNC-AC} = \frac{C4(\%)}{\frac{3}{7}C2(\%)} \quad \text{Eq. S1}$$

$$DSF_{CNC-AB} = \frac{C4(\%)}{\frac{5}{9}C2(\%)} \quad \text{Eq. S2}$$

S2.4 TGA analysis

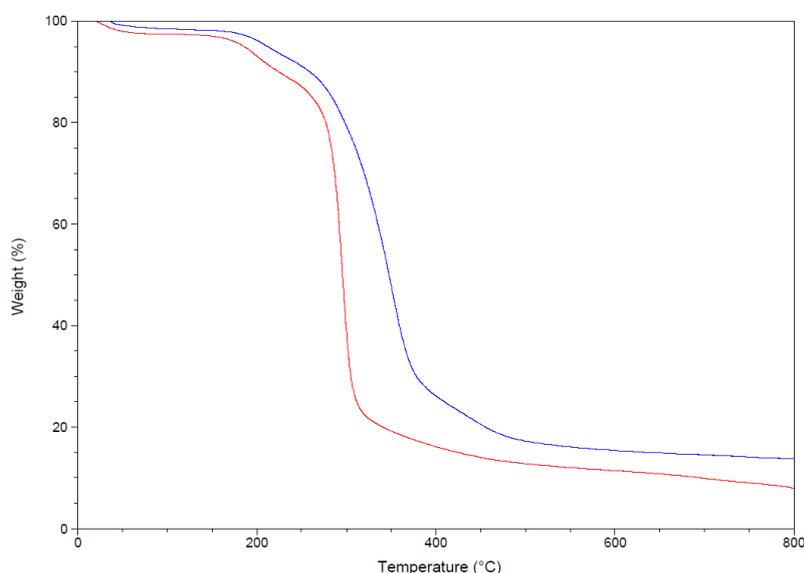


Fig. S12 TGA plots of the functionalized CNCs: (blue line) CNC-AB and (red line) CNC-AC. The TGA for the unmodified CNCs was recorded previously – see reference [16] in the main text.

S2.5 TEM analysis

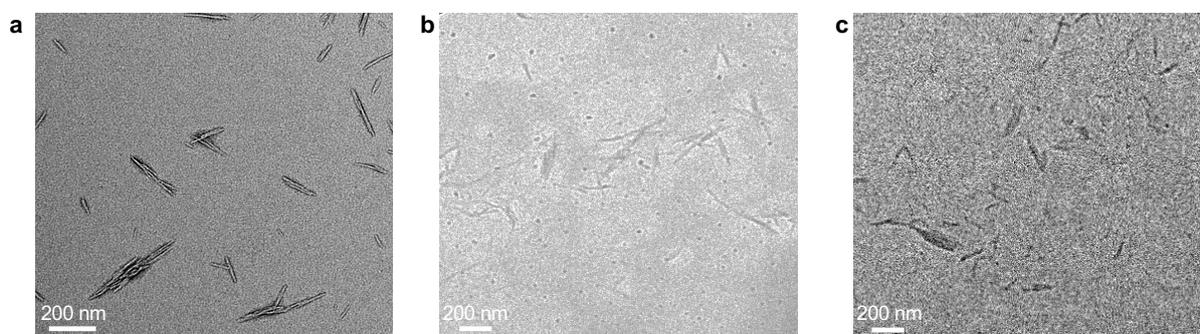


Fig. S13 TEM images of: (a) unmodified CNCs, (b) CNC-AC, and (c) CNC-AB.

S3. N-LC mixtures

S3.1 Helical pitch measurements and β_w calculations

To prepare the mixtures of the CNCs in the N-LC host, concentrations of CNCs ranging from 0.05 to 0.2 wt.% in Felix-2900-03 were stirred in DMF overnight at 60 °C. The solvent was removed under high vacuum. Homogeneous distribution was achieved by mild and pulsed sonication at 60 °C (when in the induced N*-LC phase). Two precleaned glass substrates were filled with the prepared mixtures by capillary force. Cells were placed on the heating/cooling stage at 60 °C, and the samples were then slowly cooled at a rate of 1 °C min⁻¹ until a fingerprint texture was observed (between 50 and 45 °C).

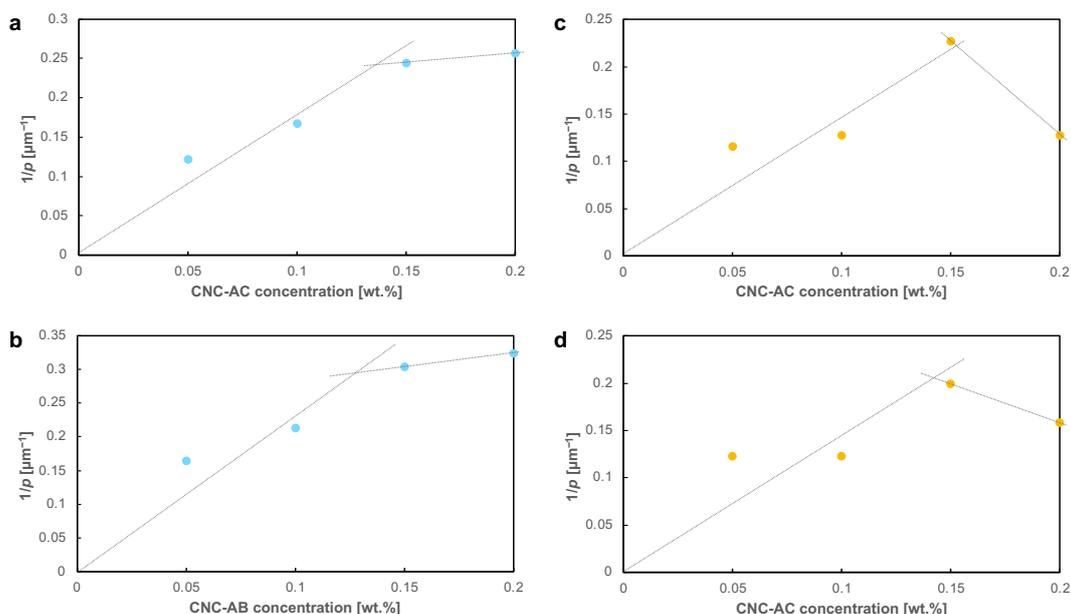


Fig. S14 Plots of the inverse helical pitch ($1/p$) vs. the concentration of CNCs: (a, b) CNC-AC and CNC-AB before UV illumination, and (c, d) CNC-AC and CNC-AB after UV illumination at $\lambda = 365$ nm. To calculate β_w , only the first three data points were used, since for all concentrations of 0.2 wt.% the pitch suddenly increases non-linearly, indicating either a saturation of the pitch or, and more likely, the beginning of CNC aggregation.

S3.2 Spectral (deconvoluted) UV-vis data in support of miscibility arguments for the two CNCs

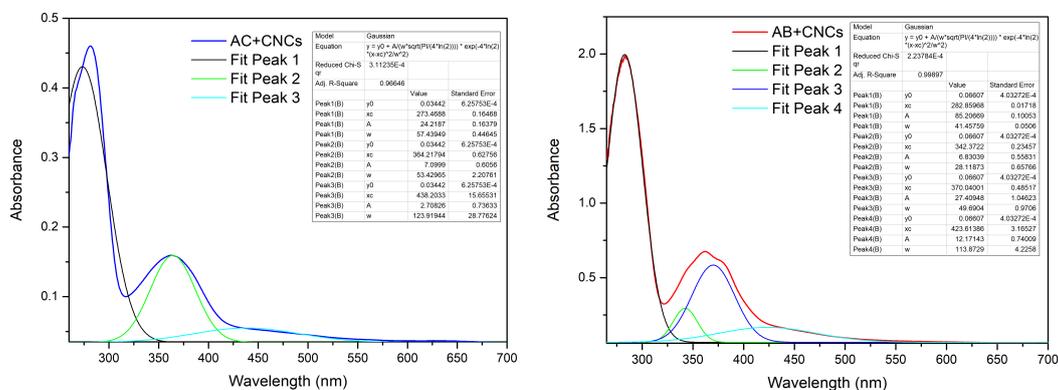


Fig. S15 Deconvolution of the UV-vis spectra to delineate the ratio between *trans* and *cis* isomers for: (left) CBNC-AC and (right) CNC-AB.

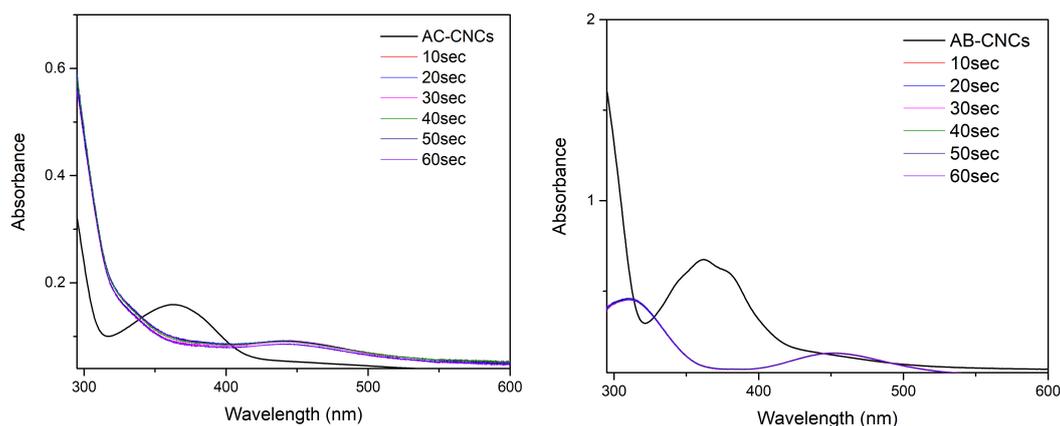


Fig. S16 UV-vis spectra before and after illumination with UV light at $\lambda = 365$ nm at time intervals of $t = 10$ s up to $t = 1$ min: (left) CNC-AC and (right) CNC-AB. The after-illumination spectra are in each case quasi-identical.

S3.3 Reversibility and photoswitch timescale

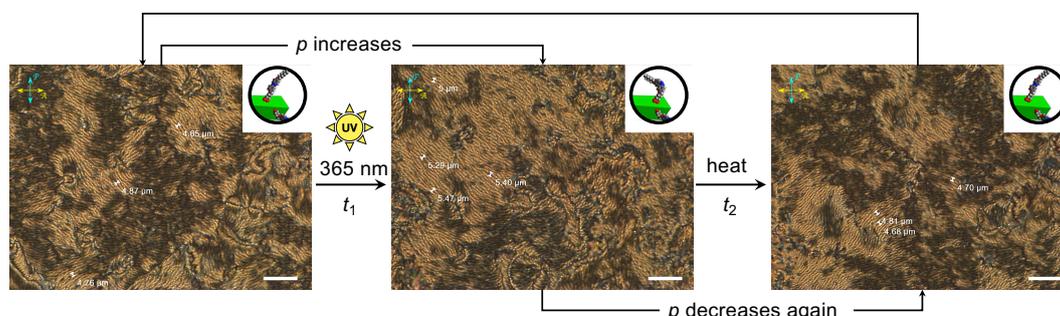


Fig. S17 POM photomicrographs (crossed polarizers) of Felix-2900-03 + 0.1 wt.% CNC-AB at $T = 45$ °C between untreated glass slides before (left) and during (middle) illumination with UV light at a wavelength of $\lambda = 365$ nm. A noticeable increase in p with UV illumination is initially fast (t_1 is in seconds) with p further increasing with continued exposure. The thermal *cis*-to-*trans* back relaxation, as previously reported, depends greatly on the chemical architecture of the system and is rather slow^{S4} (t_2 is tens of minutes or more); thus, heating above T_{ISO-N} is faster to regain the initial value of p (right). Scale bars = 50 μm .

S4. References

- S1 G. Mao, J. Wang, S. R. Clingman, C. K. Ober, J. T. Chen, E. L. Thomas, *Macromolecules* 1997, **30**, 2556-2567. <https://doi.org/10.1021/ma9617835>.
- S2 S. Balamurugan, P. Kannan, K. Yadupati, A. Roy, *J. Mol. Struct.* 2011, **1001**, 118-124. <https://doi.org/10.1016/j.molstruc.2011.06.027>.
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- S4 J. García-Amorós, D. Velasco, *Beilstein J. Org. Chem.* 2012, **8**, 1003-1017. <http://doi.org.10.3762/bjoc.8.113>.