

Graphene Oxide Liquid Crystals as a Versatile and Tunable Alignment Medium for the Measurement of Residual Dipolar Couplings in Organic Solvents

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Table S8. One bond ^1H - ^{13}C residual dipolar couplings for menthol in 2 mg/mL GO LCs compatible with acetone ($\Delta\nu\text{Q} = 4.26$ Hz)

Figure S34. RDC sason flamsteed projection (left), interia and alignment of axis frame of camphor molecule (right).

Experimental Section

Preparation of GO

We prepared GO sheets from natural graphite flakes with average lateral size of 3.5 μm , including two steps: pre-oxidized graphite, and oxidation for GO sheets. In the pre-oxidation step, 5 g graphite powder, 300 mL sulfuric acid, 4.2 g $\text{K}_2\text{S}_2\text{O}_8$ and 6.2 g P_2O_5 were added successively into a 500 mL flask and the mixture was kept at 80 $^\circ\text{C}$ for 5 h. After cooling to room temperature, the mixture was diluted with 2 L water and vacuum-filtered and washed with water using a 0.22 μm pore polycarbonate membrane. The solid was dried in air at room temperature for 2 days. In the second step, the preoxidized graphite was added into 200 mL concentrated H_2SO_4 (0 $^\circ\text{C}$), and then 15 g KMnO_4 was added slowly under continuous stirring. After the introduction of KMnO_4 , the mixture was heated to 35 $^\circ\text{C}$ and stirred for 2 h. The mixture was then diluted with 2L water, followed by dropwise addition of 10 mL 30% H_2O_2 . The mixture was left undisturbed for 2 days and the nearly clear supernatant was decanted. Using centrifugation washing method, the precipitate was repeatedly washed with water, 1M HCl solution and water successively. After gentle stirring, we obtained GO aqueous dispersions finally.

Characterization

POM observations were performed with a Nikon E600POL on GO LC samples in planar cells. SEM images were taken on a Hitachi S4800 field-emission SEM system, and GO was dip-coated on the silica substrate. AFM images of GO sheets were taken in the tapping mode by carrying out on a NSK SPI3800, with samples prepared by spin-coating from GO diluted aqueous solutions (about 0.05 mg/mL) onto freshly exfoliated mica.

DFT computation

All the calculations were performed with the B3LYP3 method implemented in Gaussian 09 program.¹ The basis set of 6-311G (d,p) was used.

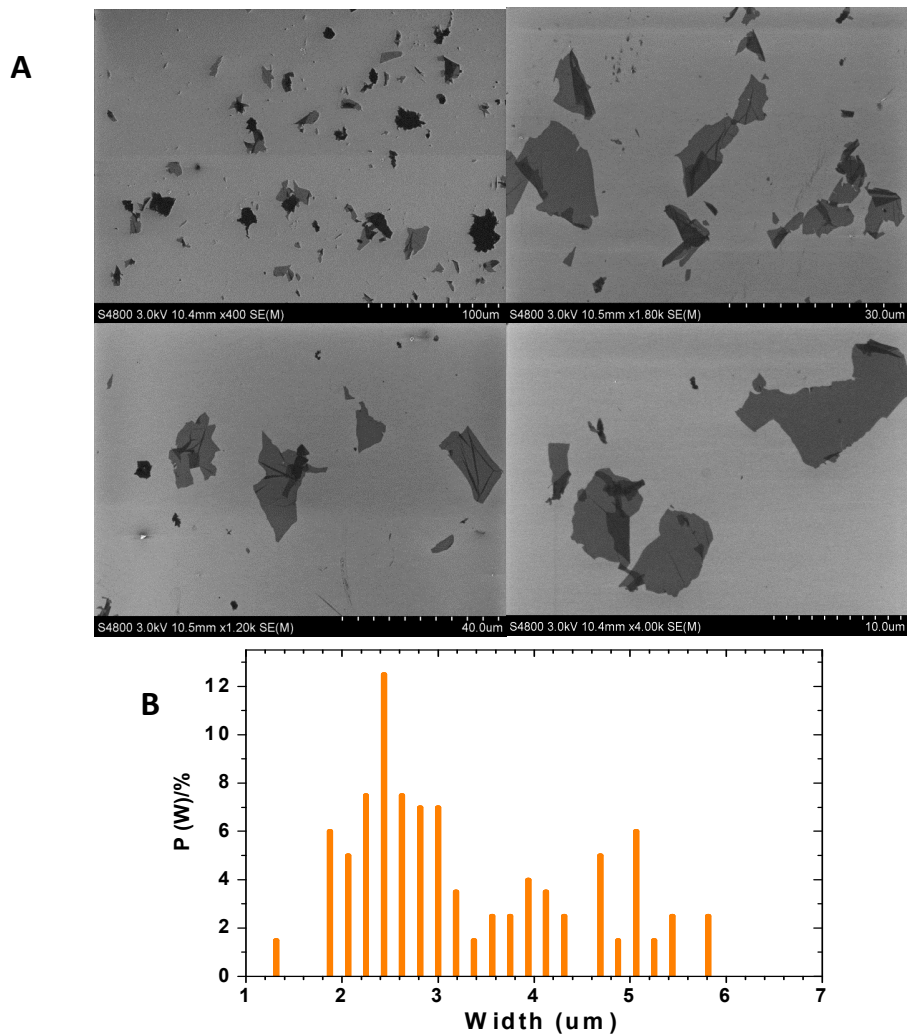


Figure S1. (A) SEM images of GO sheets on silica and the corresponding distribution $P(w)$ (B) of GO sheets counted from their SEM images in (A)

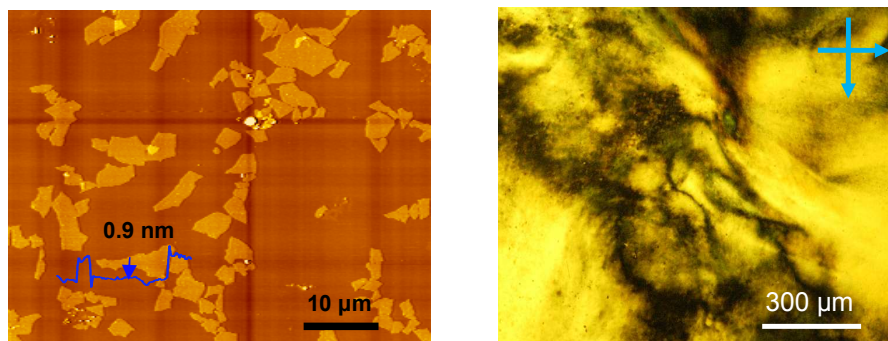


Figure S2. AFM image of GO sheets on mica (left). POM image of GO aqueous liquid crystals at the concentration of 1 mg/mL, exhibiting typical Schlieren texture of nematic mesophases (right).



Figure S3. GO LCs produced by large scale for the measurement of RDCs.

NMR experiment and RDCs analysis

NMR protocols

The NMR spectra were recorded at room temperature (298K) on a Bruker AVANCE-III 500 NMR spectrometer (500.13MHz for ^1H NMR; 76.77MHz for ^2H NMR; 125.76MHz for ^{13}C NMR, respectively) equipped with a 5-mm BBFO probe (Bruker Instruments Inc., Germany). The pulse conditions were as follows: for the ^1H NMR spectra, spectrometer frequency 500.063 MHz, spectral width (SW) 10 ppm, pulse 90° , acquisition time (AQ) 5.4 s, relaxation delay (RD) 2.000 s, and Fourier Transform (FT) size 32-K data point; An exponential window function with a line-broadening factor of 1Hz was applied to the FID before Fourier transformation. For NOESYPR1D ^1H NMR, the mixing time D8 was 0.01s. The ^2H NMR acquisition was recorded using the lock channel. For the CLIP-HSQC spectra, the conditions are as follows: AQ 0.103 s, RD 1.000 s, and SW 10 ppm (^1H) and 80 ppm (^{13}C). A one-bond coupling constant was 145.0 Hz. LB 1Hz for F2 and 0.3 Hz for F1 were applied before Fourier transformation. All data were analyzed and processed using Bruker Topspin 2.1 (2008) software.

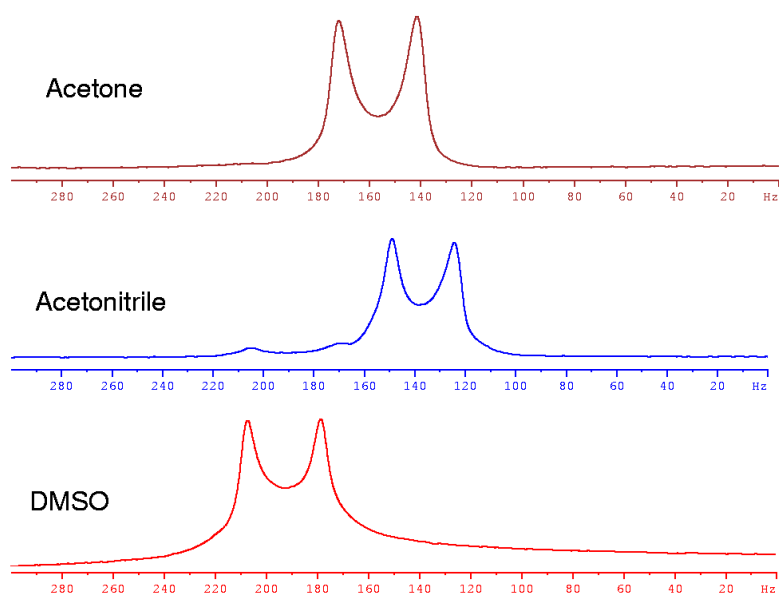


Figure S4. Quadrupolar splitting observed in the ^2H NMR spectra of the solvent in different dilute liquid crystalline systems. 3.8 mg/mL GO compatible with different organic solvents, acetone (brown), acetonitrile (blue), DMSO (red). The quadrupolar ^2H splitting is 30.71, 23.89 and 27.00 Hz, respectively.

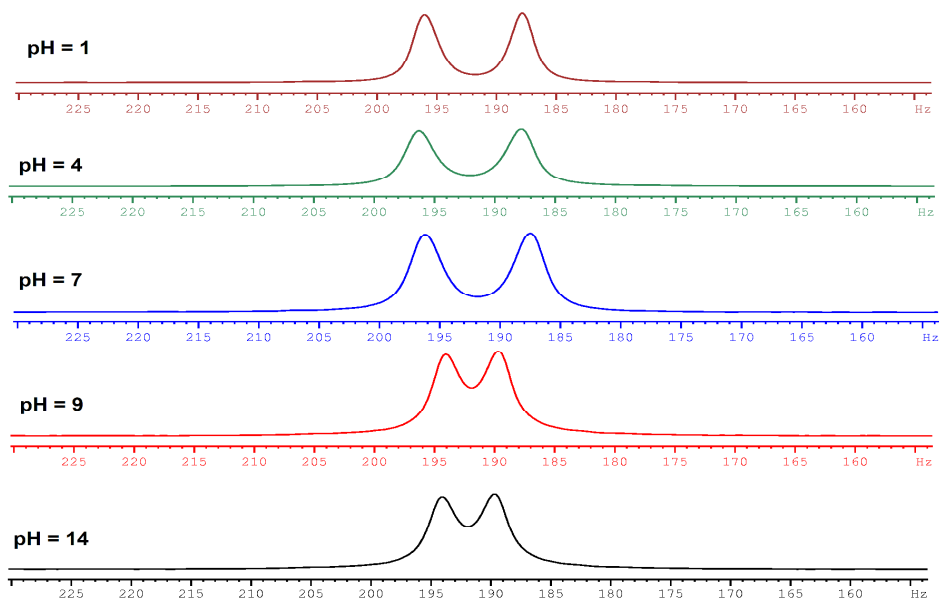


Figure S5 1D ^2H spectra of the LCs sample at various pH level. These spectra were collected at 25 °C with eight scans.

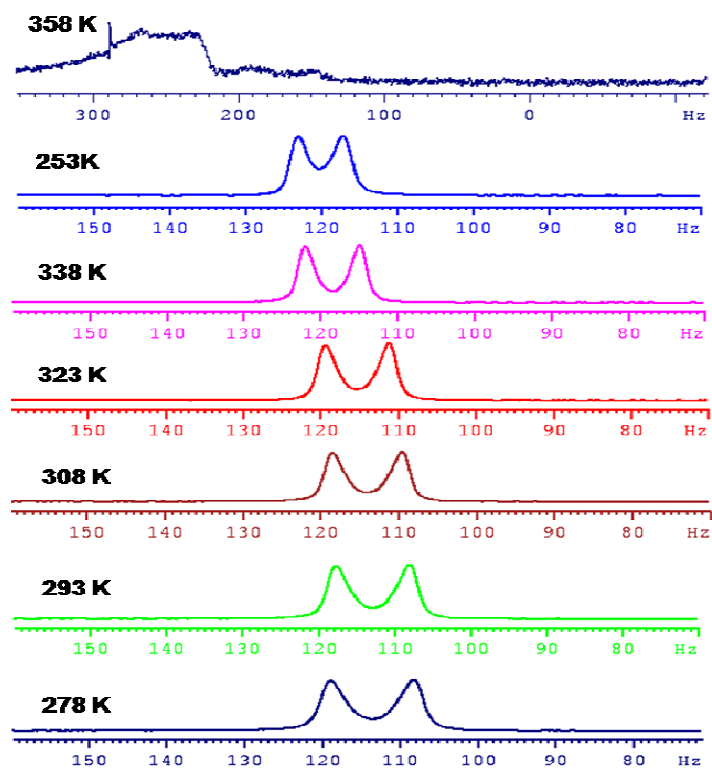


Figure S6 1D ^2H spectra of the LCs sample were recorded at various temperatures.

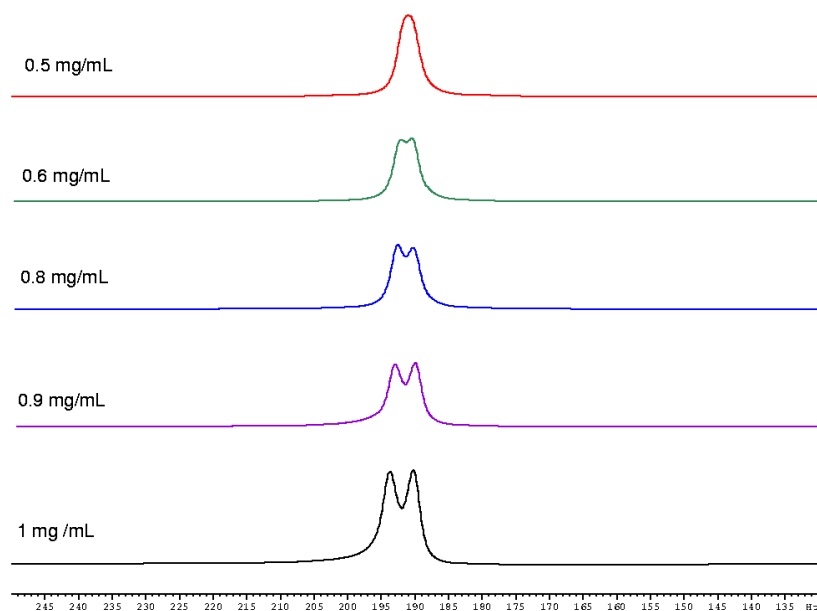


Figure S7 1D ^2H spectra of the sample containing 0.5, 0.6, 0.8, 0.9 and 1 mg/mL GO in DMSO/water system (top to bottom). These spectra were collected at 25 °C with eight scans.

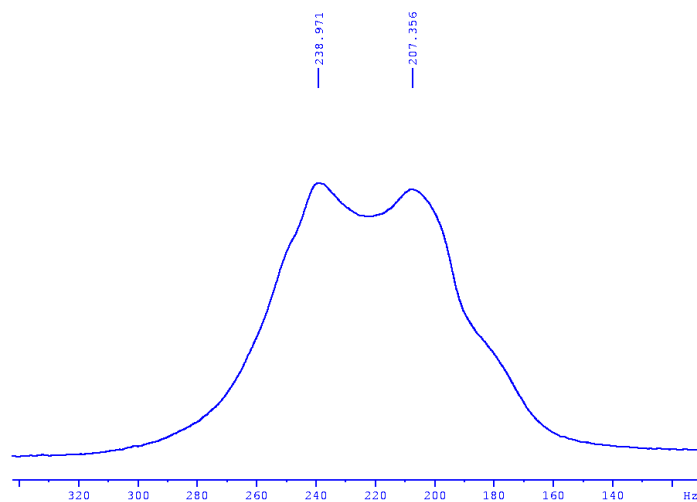


Figure S8 1D ^2H spectra of the sample containing 5 mg/mL GO in DMSO/water system. These spectra were collected at 25 °C with eight scans.

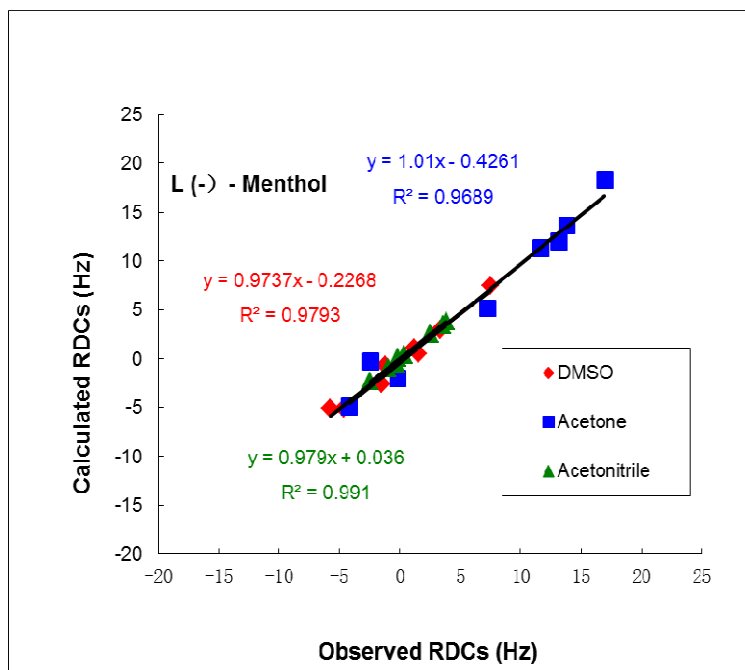


Figure S9. Correlation between observed $^1\text{D}_{\text{C,H}}$ RDCs and calculated RDCs for the known structure of L(-)-menthol in different LC systems (compatible with DMSO, acetone, acetonitrile) by using an alignment tensor obtained from the SVD fit.

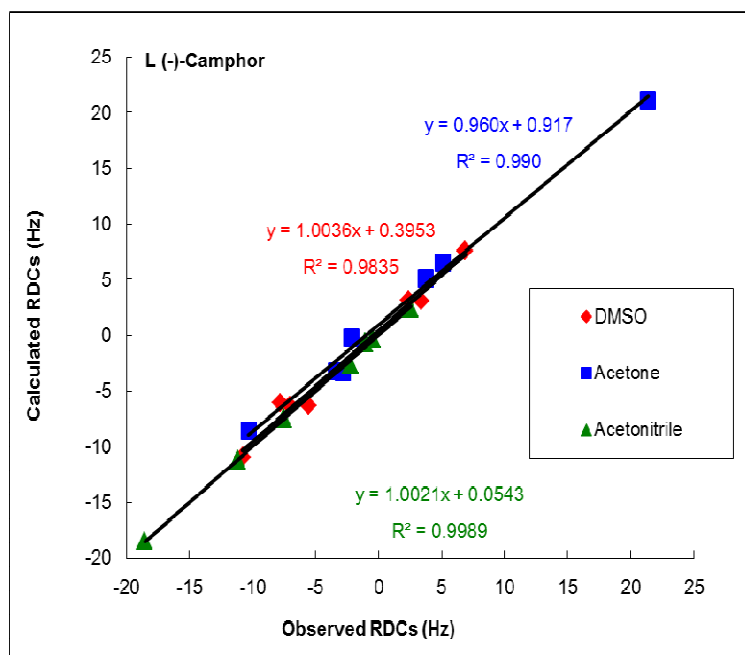


Figure S10. Correlation between observed $^1D_{C,H}$ RDCs and calculated RDCs for the known structure of L(-)-camphor in different LC systems (compatible with DMSO, acetone, acetonitrile) by using an alignment tensor obtained from the SVD fit.

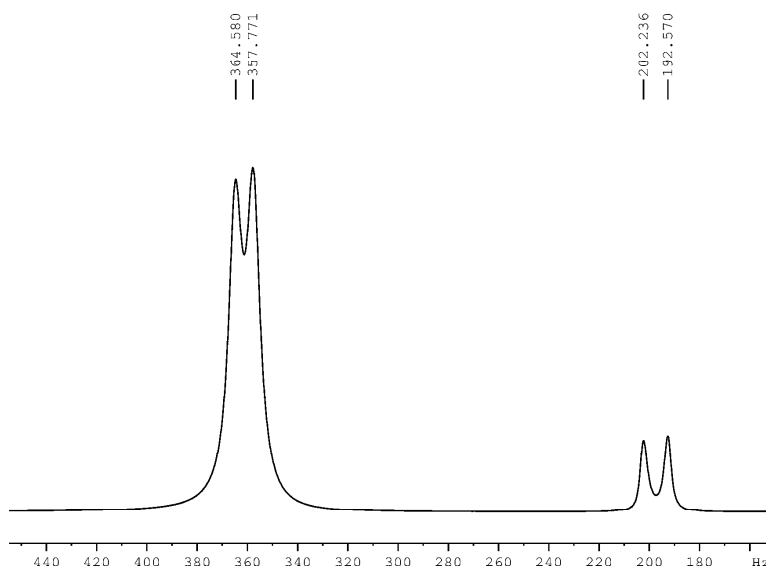
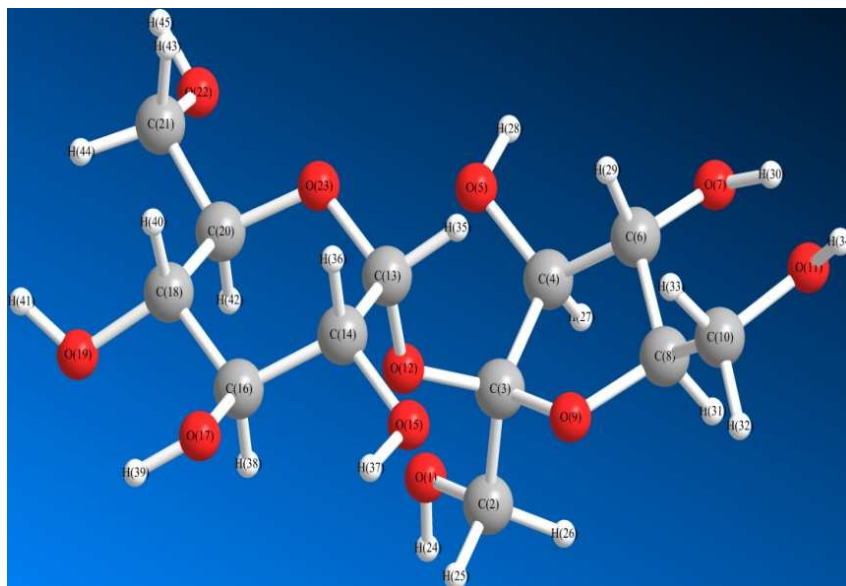


Figure S11. 2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing D-sucrose (2 mg/mL GO LC phase) in D_2O and trace DMSO, pH 7 with resulting $\Delta\nu_Q = 6.81$ Hz (D_2O), 9.67 Hz (DMSO).



Scheme S1. The structure of sucrose and the atomic labeling.

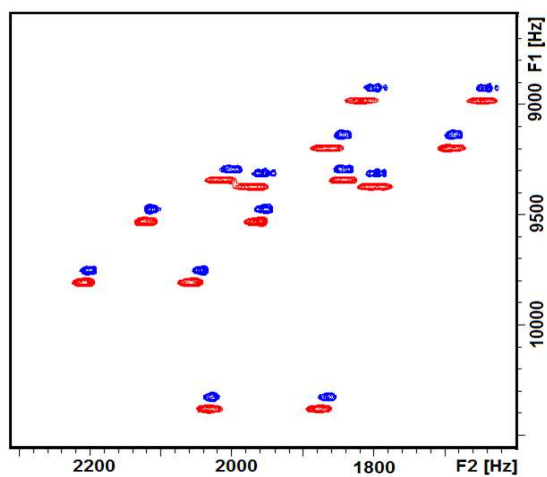


Figure S12. Parts of 500 MHz ^1H , ^{13}C -Clip-HSQC spectra of sucrose in isotropic phase (D_2O , blue contours) and in 2 mg/mL GO LCs (anisotropic, red contours).

Table S1. One bond ^1H - ^{13}C residual dipolar couplings for sucrose in GO LCs ($\Delta\nu\text{Q} = 6.81$ Hz)

	$D_{\text{CH}} \text{ Hz}^*2$
$\text{C}_4, \text{H}_{27}$	17.22[3.89]
$\text{C}_6, \text{H}_{29}$	3.75[0.81]
$\text{C}_8, \text{H}_{31}$	0.8[0.29]
$\text{C}_{13}, \text{H}_{35}$	12.98[0.63]
$\text{C}_{14}, \text{H}_{36}$	15.68[3.93]
$\text{C}_{16}, \text{H}_{38}$	13.48[1.20]
$\text{C}_{18}, \text{H}_{40}$	-4.89[0.52]
$\text{C}_{20}, \text{H}_{42}$	15.36[0.86]

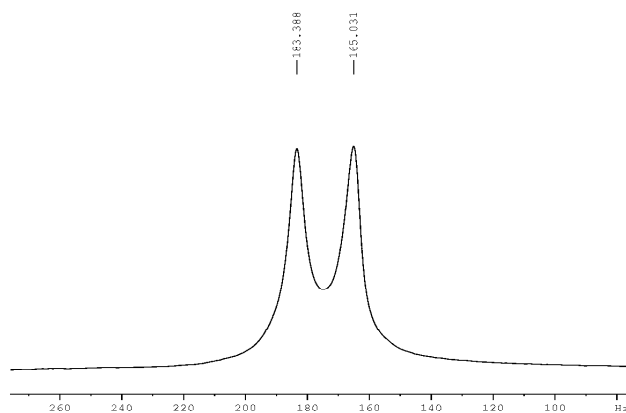


Figure S13. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-proline (3.5 mg/mL GO LC phase) in H_2O and trace DMSO with resulting $\Delta\nu\text{Q} = 18.35\text{Hz}$.

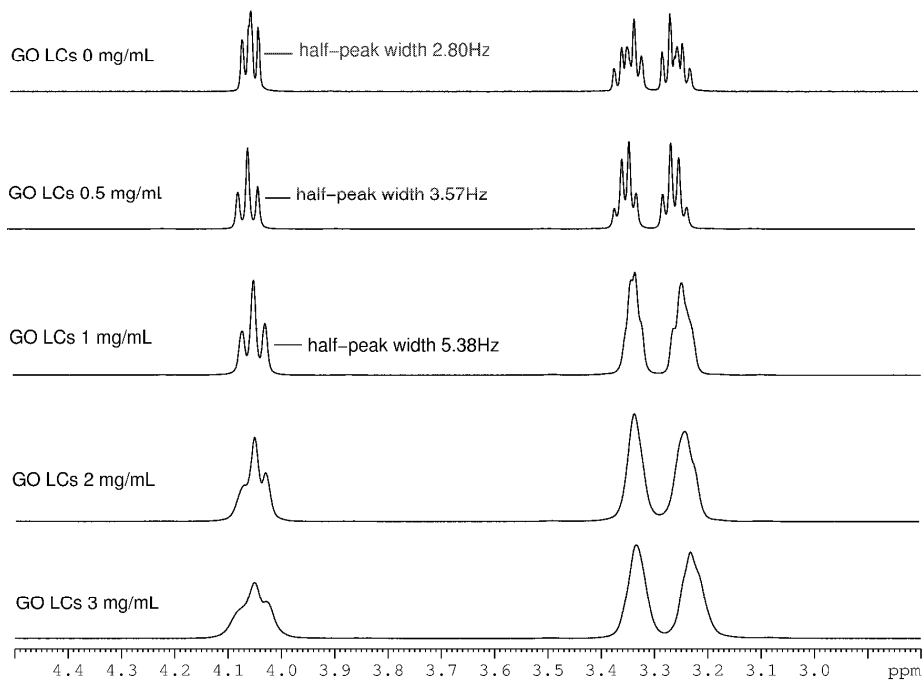


Figure S14. A portion stacking ^1H NMR spectra of the anisotropic sample containing 10 mg L-proline in various concentrations of GO LCs.

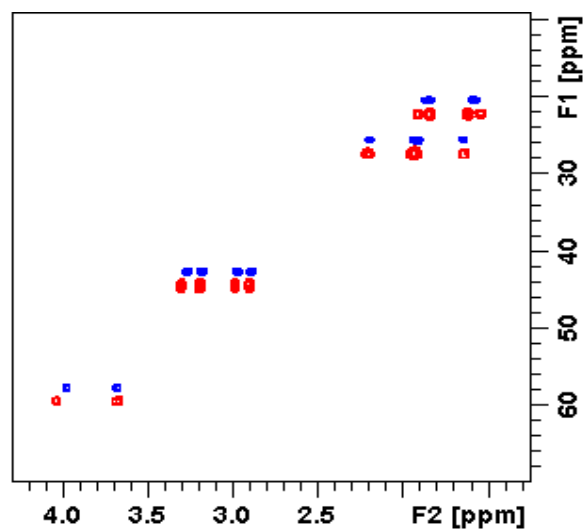
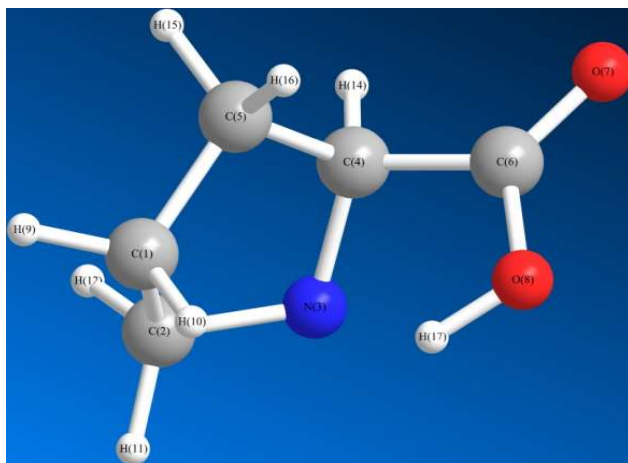


Figure S15. A portion of the 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-proline in the isotropic phase (D_2O , blue contours) and in 2 mg/mL GO LCs (anisotropic, red contours).



Scheme S2. The structure of proline, with the atomic labelling used in the calculations.

Calculated RDCs –Tensor properties

Table S2. One bond ^1H - ^{13}C residual dipolar couplings for proline in GO LCs ($\Delta\nu\text{Q} = 18.35$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C_1, H_9	-15.70[2.46]	-15.51[0.39]
$\text{C}_2, \text{H}_{11}$	6.10[0.96]	6.29[0.46]
$\text{C}_2, \text{H}_{12}$	-1.60[0.83]	-1.78[0.49]
$\text{C}_5, \text{H}_{15}$	10.40[1.20]	10.43[0.53]
$\text{C}_5, \text{H}_{16}$	-3.90[0.65]	-3.58[0.36]
$\text{C}_4, \text{H}_{14}$	16.10[3.82]	16.25[0.52]

a. An experimental standard error of 0.5Hz is used for the calculations in MSpin .

Calculated Corresponding alignment tensor for proline in GO LC aqueous.

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = -2.426e-04$ Std. Dev = $7.339e-06$

$\langle A_y \rangle = -3.716e-04$ Std. Dev = $2.593e-05$

$\langle A_z \rangle = 6.142e-04$ Std. Dev = $2.612e-05$

Quality factors statistic

$\langle Q \rangle = 0.046$

StdDev(Q) = 0.013

Highest Q = 0.093

Lowest Q = 0.019

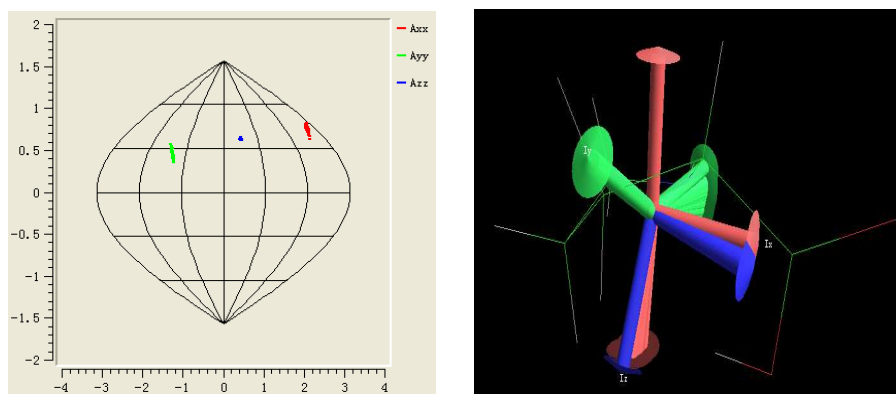
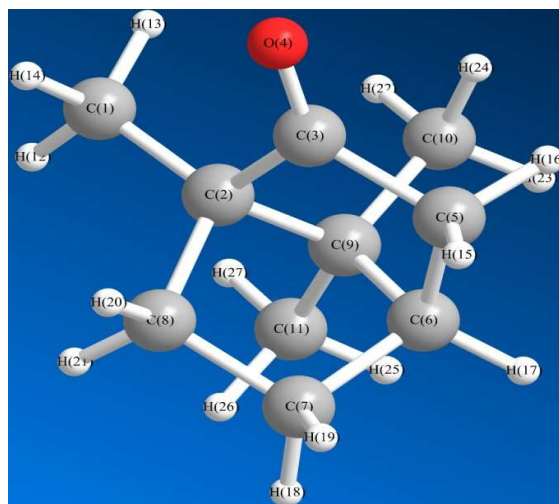


Figure S16. RDC sason flamsteed projection (left), inertia and alignment of axis frame of proline molecule (right).



Scheme S3. The structure of camphor, with the atomic labelling used in the calculations.

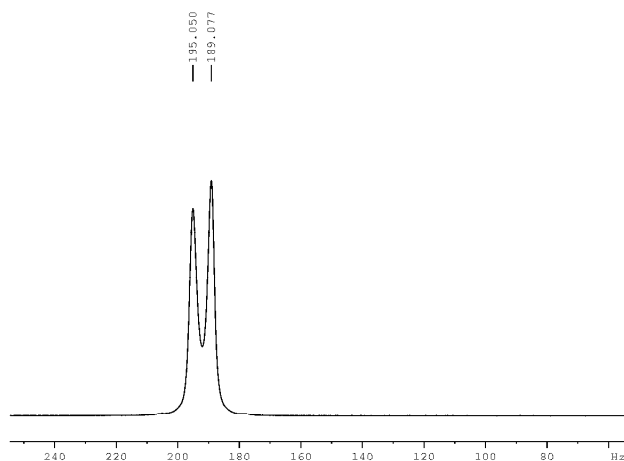


Figure S17. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-camphor (2.0 mg/mL GO LCs phase) in H_2O and 50% DMSO with resulting $\Delta\nu\text{Q} = 5.98$ Hz.

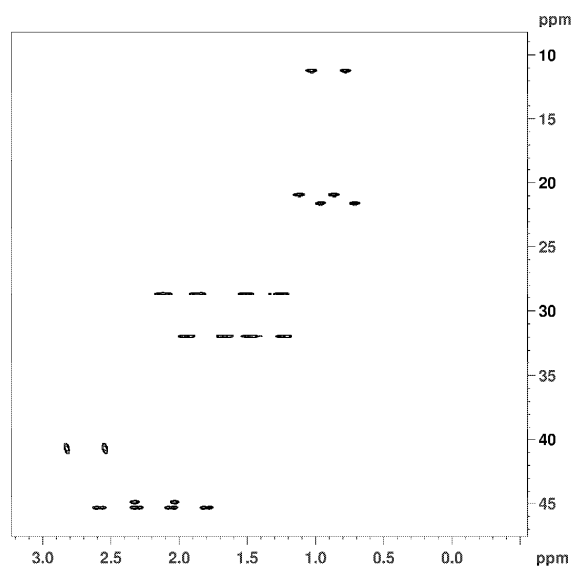


Figure S18. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-camphor in 2 mg/mL GO LCs with the DMSO/water system.

Calculated RDCs –Tensor properties

Table S3. One bond ^1H - ^{13}C residual dipolar couplings for camphor in 2 mg/mL GO LCs compatible with DMSO ($\Delta\nu_Q = 5.98$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C₈,H₂₁	3.42[±0.43]	3.07[0.49]
C₈,H₂₀	-10.76[±1.22]	-10.95[0.50]
C₇,H₁₈	-7.00[±0.31]	-6.34[0.46]
C₇,H₁₉	-7.81[±0.27]	-6.02[0.32]
C₆,H₁₇	2.35[±0.26]	3.13[0.43]
C₅,H₁₆	6.86[±1.07]	7.65[0.50]
C₅,H₁₅	-5.57[±0.12]	-6.35[0.31]

Calculated Corresponding alignment tensor for camphor in GO LCs with DMSO.

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = -2.557\text{e-}05$ Std. Dev = $1.119\text{e-}05$

$\langle A_y \rangle = -1.595\text{e-}04$ Std. Dev = $4.391\text{e-}05$

$\langle A_z \rangle = 1.851\text{e-}04$ Std. Dev = $4.720\text{e-}05$

Quality factors statistic

$\langle Q \rangle = 0.147$

Std Dev(Q) = 0.009

Highest Q = 0.195

Lowest Q = 0.133

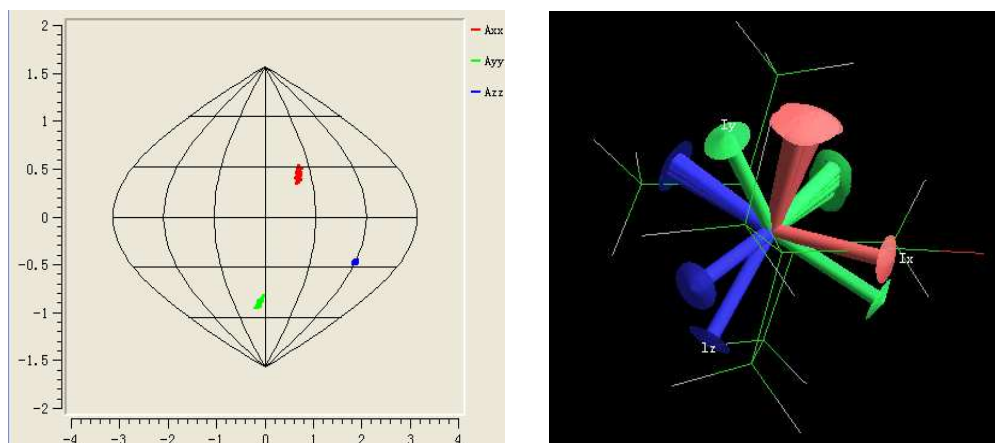


Figure S19. RDC sason flamsteed projection (left), inertia and alignment of axis frame of camphor molecule (right).

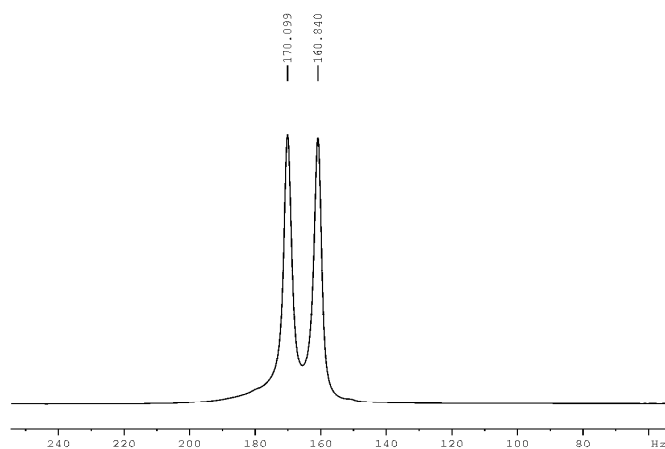


Figure S20. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-camphor (2.0 mg/mL GO LCs phase) in H₂O and 50% acetone with resulting $\Delta\nu\text{Q} = 9.25$ Hz.

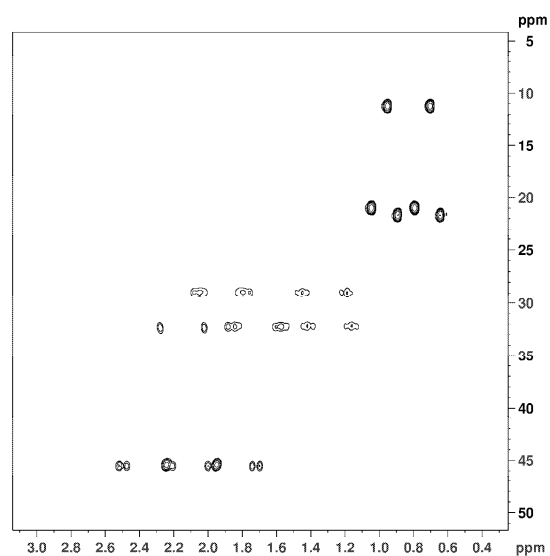


Figure S21. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-camphor in 2 mg/mL GO LCs with the acetone/water system.

Calculated RDCs –Tensor properties

Table S4. One bond ^1H - ^{13}C residual dipolar couplings for camphor in 2 mg/mL GO LCs compatible with acetone ($\Delta\nu_Q = 9.25$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C ₈ ,H ₂₁	21.38[1.26]	21.12[0.49]
C ₈ ,H ₂₀	-2.80[0.14]	-3.33[0.50]
C ₇ ,H ₁₈	3.72[1.06]	5.13[0.46]
C ₇ ,H ₁₉	-2.15[0.42]	-0.17[0.32]
C ₆ ,H ₁₇	-10.30[0.48]	-8.58[0.43]
C ₅ ,H ₁₆	5.10[0.30]	6.56[0.50]
C ₅ ,H ₁₅	-3.37[0.65]	-3.18[0.31]

Calculated Corresponding alignment tensor for camphor in GO LCs aqueous with acetone.

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = 8.037\text{e-}05$ Std. Dev = $7.313\text{e-}06$

$\langle A_y \rangle = 2.253\text{e-}04$ Std. Dev = $9.533\text{e-}06$

$\langle A_z \rangle = -3.057\text{e-}04$ Std. Dev = $7.135\text{e-}06$

Quality factors statistic

$\langle Q \rangle = 0.142$

Std Dev(Q) = 0.005

Highest Q = 0.169

Lowest Q = 0.135

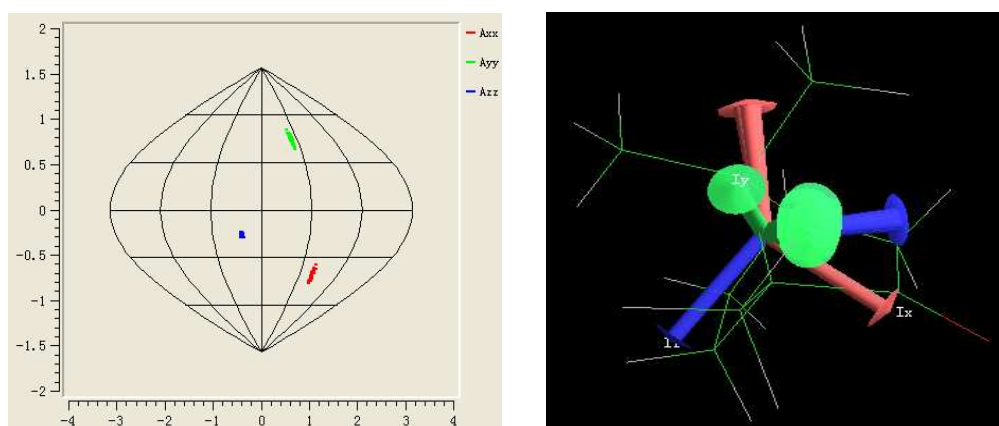


Figure S22. RDC sason flamsteed projection (left), inertia and alignment of axis frame of camphor molecule (right).

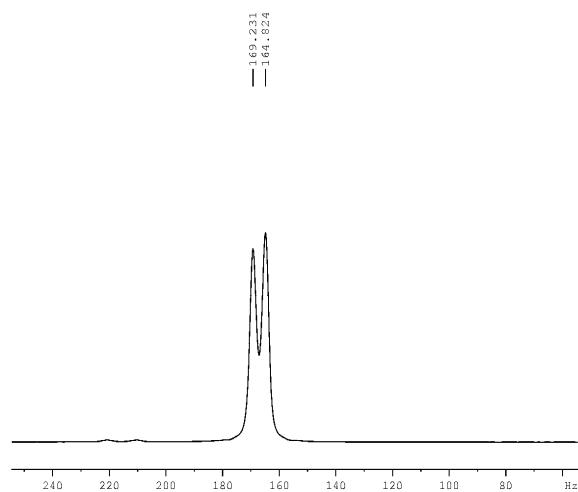


Figure S23. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-camphor (2.0 mg/mL GO LCs phase) in 40% H_2O , 10% D_2O and 50% CH_3CN with resulting $\Delta\nu_Q = 4.41$ Hz.

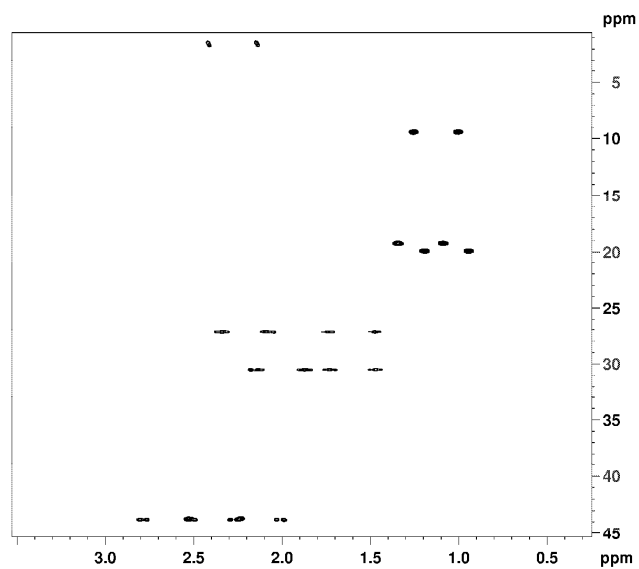


Figure S24. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-camphor in 2 mg/mL GO LCs with the CH_3CN /water system.

Calculated RDCs –Tensor properties

Table S5. One bond ^1H - ^{13}C residual dipolar couplings for camphor in 2 mg/mL GO LC compatible with CH_3CN ($\Delta\nu\text{Q} = 4.41$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C₈,H₂₁	-11.19[1.62]	-11.17[0.49]
C₈,H₂₀	-18.54[0.64]	-18.52[0.50]
C₇,H₁₈	-7.45[0.78]	-7.46[0.46]
C₇,H₁₉	-2.20[1.44]	-2.59[0.32]
C₆,H₁₇	-0.48[0.18]	-0.33[0.43]
C₅,H₁₆	2.52[0.86]	2.49[0.50]
C₅,H₁₅	-1.07[0.74]	-0.62[0.31]

Calculated Corresponding alignment tensor for camphor in GO LCs with CH_3CN .

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A'x \rangle = 3.756\text{e-}05$ Std. Dev = $7.796\text{e-}06$

$\langle A'y \rangle = 3.227\text{e-}04$ Std. Dev = $7.633\text{e-}06$

$\langle A'z \rangle = -3.603\text{e-}04$ Std. Dev = $1.027\text{e-}05$

Quality factors statistic

$\langle Q \rangle = 0.055$

Std Dev(Q) = 0.013

Highest Q = 0.113

Lowest Q = 0.028

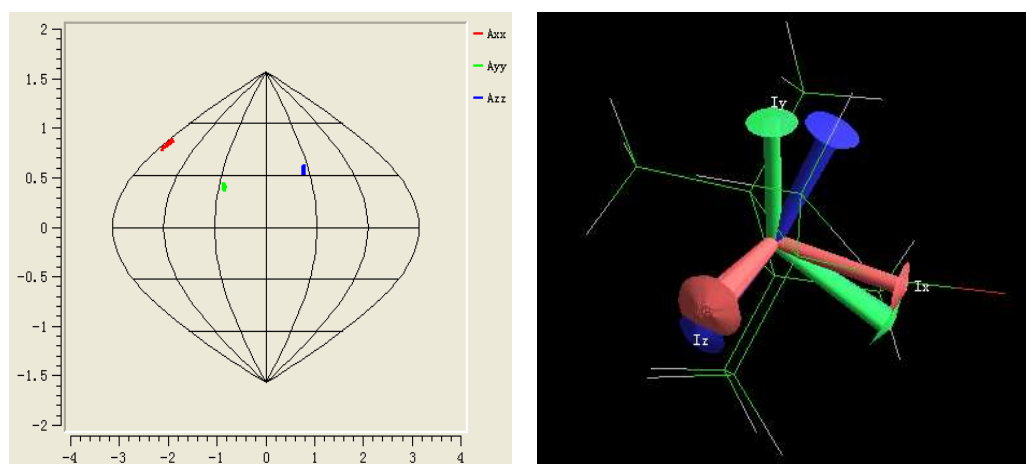
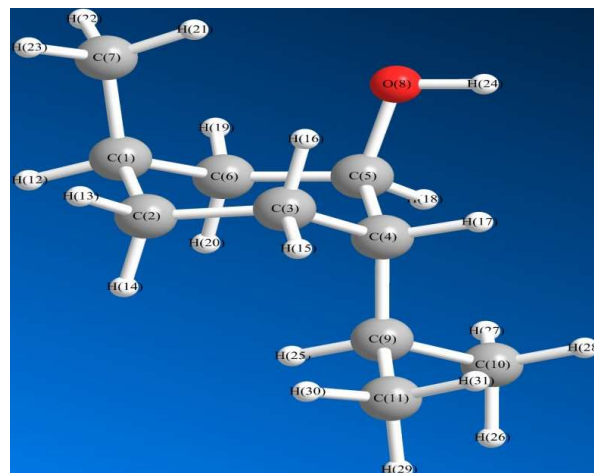


Figure S25. RDC sason flamsteed projection (left), inertia and alignment of axis frame of camphor molecule (right).



Scheme S4. The structure of menthol, with the atomic labelling used in the calculations.

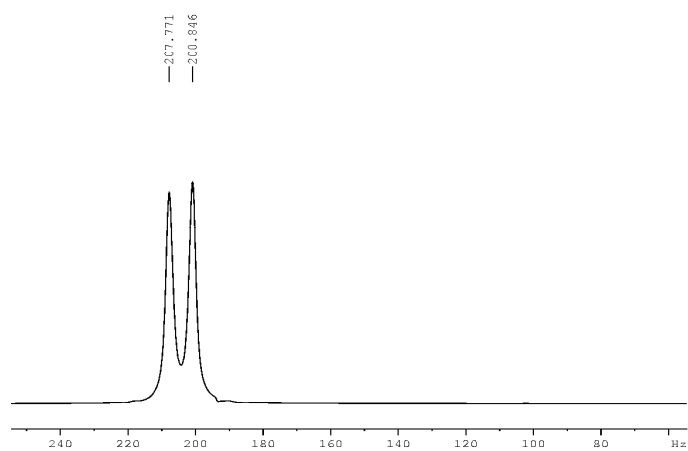


Figure S26. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-menthol (2.0 mg/mL GO LCs phase) in 40% H₂O, 10% D₂O and 50% DMSO with resulting $\Delta\nu_Q = 6.93$ Hz.

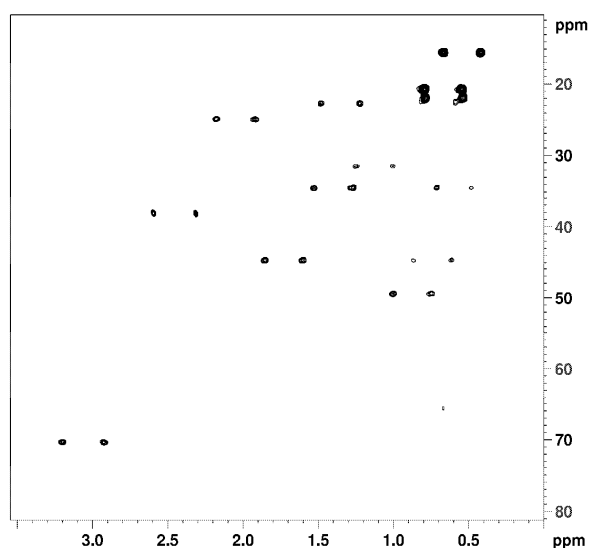


Figure S27. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-menthol in 2 mg/mL GO LCs with the DMSO/water system.

Calculated RDCs –Tensor properties

Table S6. One bond ^1H - ^{13}C residual dipolar couplings for menthol in 2 mg/mL GO LCs compatible with DMSO ($\Delta\nu\text{Q} = 6.93$ Hz)

Atom number	Exp. DCH [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C ₁ ,H ₁₂	-1.20[0.63]	-0.66[0.46]
C ₂ ,H ₁₃	-5.72[1.65]	-5.12[0.38]
C ₂ ,H ₁₄	1.19[1.51]	1.08[0.43]
C ₃ ,H ₁₆	3.33[0.78]	2.97[0.33]
C ₅ ,H ₁₈	1.57[1.08]	0.55[0.34]
C ₆ ,H ₁₉	-1.50[1.12]	-2.54[0.35]
C ₆ ,H ₂₀	-4.63[0.26]	-5.06[0.46]
C ₄ ,H ₁₇	7.54[2.05]	7.53[0.45]

Calculated Corresponding alignment tensor for menthol in GO LCs with DMSO.

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = -1.718e-04$ Std. Dev = $3.008e-05$

$\langle A_y \rangle = -3.493e-04$ Std. Dev = $3.957e-05$

$\langle A_z \rangle = 5.212e-04$ Std. Dev = $4.135e-05$

Quality factors statistic

$\langle Q \rangle = 0.184$

Std Dev(Q) = 0.016

Highest Q = 0.232

Lowest Q = 0.158

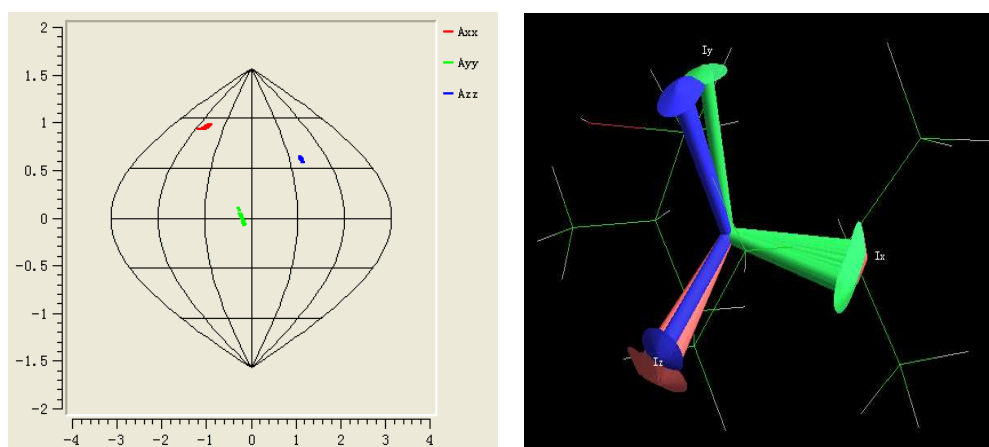


Figure S28. RDC sason flamsteed projection (left), interia and alignment of axis frame of menthol molecule (right).

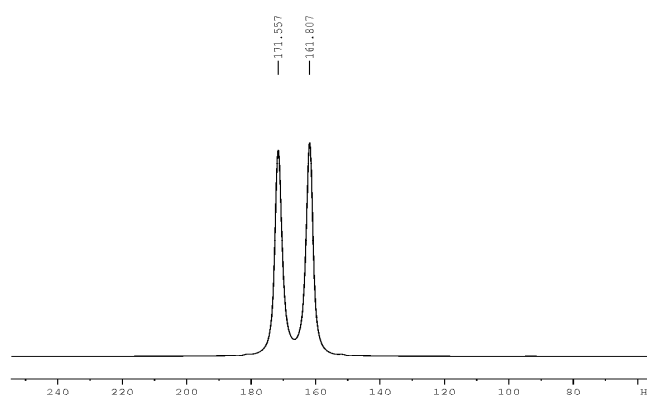


Figure S29. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-menthol (2.0 mg/mL GO LCs phase) in H₂O and 50% acetone with resulting $\Delta v_Q = 9.75$ Hz.

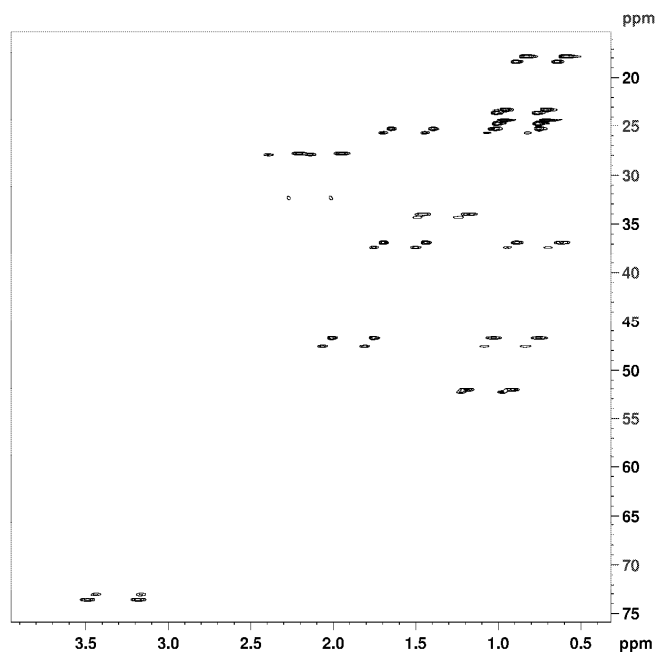


Figure S30. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-menthol in 2 mg/mL GO LCs with the acetone/water system.

Calculated RDCs –Tensor properties

Table S7. One bond ^1H - ^{13}C residual dipolar couplings for menthol in 2 mg/mL GO LCs compatible with acetone ($\Delta\nu_Q = 9.75$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C ₁ ,H ₁₂	16.95[0.54]	18.32[0.42]
C ₂ ,H ₁₃	11.66[3.00]	11.32[0.39]
C ₂ ,H ₁₄	-0.20[0.31]	-2.03[0.42]
C ₃ ,H ₁₆	-2.41[1.60]	-0.23[0.34]
C ₅ ,H ₁₈	13.82[1.14]	13.63[0.36]
C ₆ ,H ₁₉	-4.15[0.77]	-4.95[0.52]
C ₆ ,H ₂₀	13.18[0.36]	12.02[0.45]
C ₄ ,H ₁₇	7.25[0.32]	5.17[0.31]

Calculated Corresponding alignment tensor for menthol in GO LCs with acetone.

Distribution size=128

Distribution type=Gaussian

RDC general Std. Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = -3.355e-04$ Std. Dev = $3.604e-05$

$\langle A_y \rangle = -1.094e-03$ Std. Dev = $3.233e-05$

$\langle A_z \rangle = 1.430e-03$ Std. Dev = $4.157e-05$

Quality factors statistic

$\langle Q \rangle = 0.143$

Std Dev(Q) = 0.003

Highest Q = 0.152

Lowest Q = 0.138

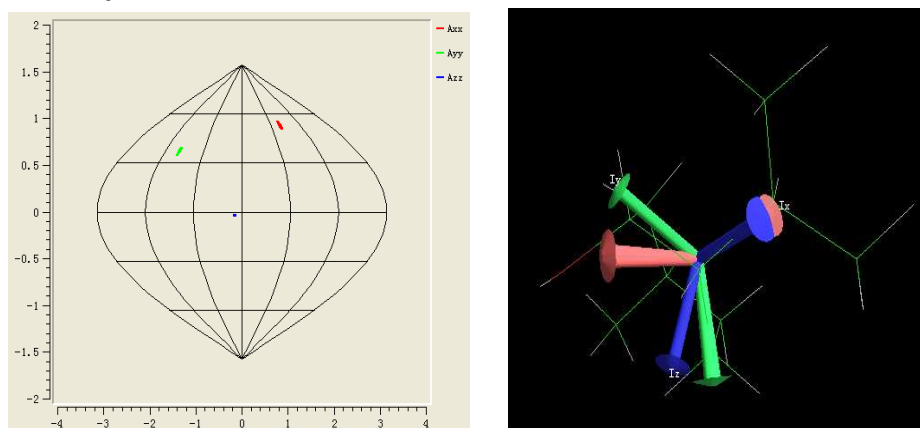


Figure S31. RDC sason flamsteed projection (left), interia and alignment of axis frame of proline molecule (right).

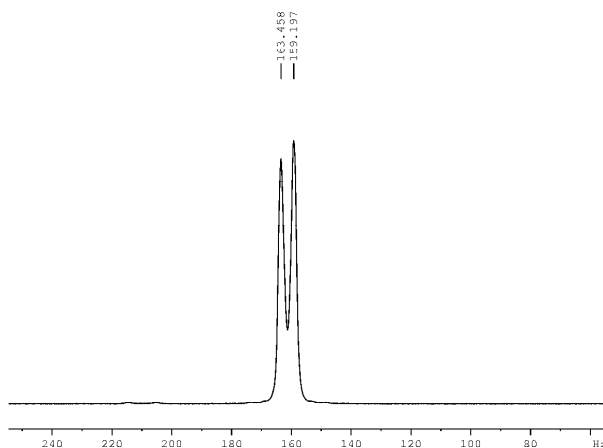


Figure S32. ^2H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of the anisotropic sample containing 10 mg L-camphor (2.0 mg/mL GO LCs phase) in 40% H_2O , 10% D_2O and 50% CH_3CN with resulting $\Delta\nu\text{Q} = 4.26$ Hz.

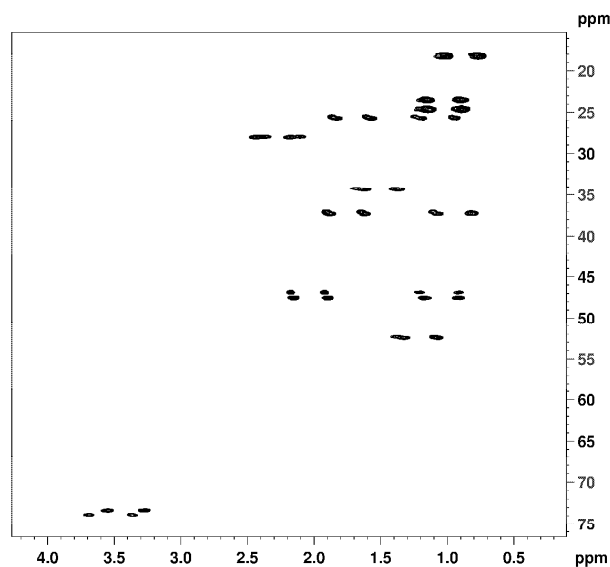


Figure S33. The 500 MHz ^1H , ^{13}C -CLIP-HSQC spectra of L-menthol in 2 mg/mL GO LCs with the CH_3CN /water system.

Calculated RDCs –Tensor properties

Table S8. One bond ^1H - ^{13}C residual dipolar couplings for menthol in 2 mg/mL GO LCs compatible with acetone ($\Delta\nu_Q = 4.26$ Hz)

Atom number	Exp. D_{CH} [Std.Dev] Hz*	Comp.RDC [Std.Dev] Hz ^a
C₁,H₁₂	3.57[0.72]	3.47[0.42]
C₂,H₁₃	-2.46[1.76]	-2.31[0.39]
C₂,H₁₄	-0.21[0.68]	-0.58[0.42]
C₃,H₁₆	-0.18[0.24]	0.17[0.34]
C₅,H₁₈	-0.98[0.54]	-0.97[0.36]
C₆,H₁₉	2.51[0.51]	2.54[0.52]
C₆,H₂₀	3.83[0.46]	3.83[0.45]
C₄,H₁₇	0.38[1.10]	0.47[0.31]

Calculated Corresponding alignment tensor for menthol in GO LCs with CH₃CN.

Distribution size=128

Distribution type=Gaussian

RDC general Std.Dev=0.5 Hz

Alignment tensor

$\langle A_x \rangle = 4.783e-05$ Std.Dev = $3.333e-05$

$\langle A_y \rangle = 2.179e-04$ Std.Dev = $1.704e-04$

$\langle A_z \rangle = -2.657e-04$ Std.Dev = $1.901e-04$

Quality factors statistic

$\langle Q \rangle = 0.194$

Std Dev(Q) = 0.045

Highest Q = 0.308

Lowest Q = 0.094

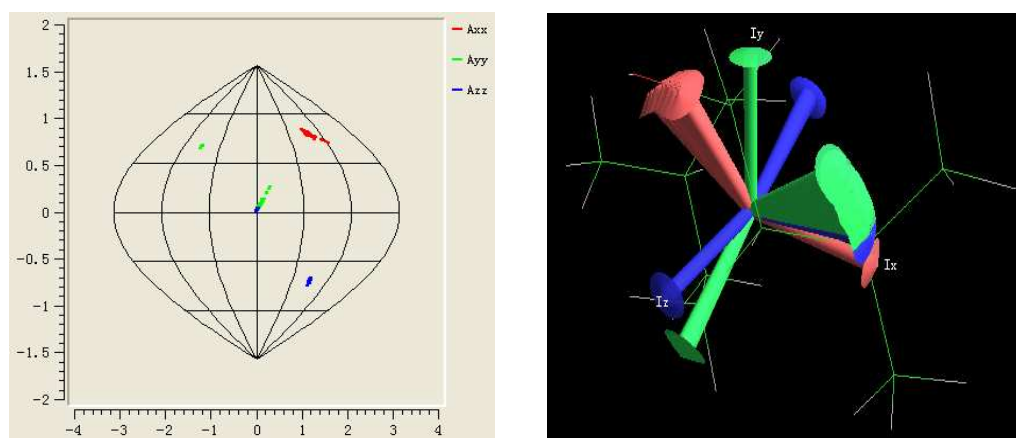


Figure S34. RDC sason flamsteed projection (left), interia and alignment of axis frame of menthol molecule (right).

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