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Supporting Information

An Alignment Medium for Measuring Residual Dipolar Couplings in Pure DMSO: Liquid Crystals from Graphene Oxide Grafted with Polymer Brushes

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1. Experimental Procedures

Materials

Graphite powder (4μm) was purchased from Qingdao Henglide Graphite Co. Ltd.. Trifluoroethyl methacrylate was bought from Aladdin without purification.2,2'-azobis-(2-methyl-propionitrile). (AIBN) was bought from Aladdin and employed after twice recrystallization. All other regents such as DMF and DMSO were purchased from Aladdin and employed without purification. Estrone and dihydroartemisinin were purchased from J&K China Chemical Ltd. without purification.

Instrumentation

Scanning Electron Microscopy (SEM): Scanning electron microscopy (SEM) images were recorded on a Hitachi S4800 field emission SEM system to verify the morphology of GO and GO-g-TFEMA.

Fourier-Transform Infrared (FTIR): IR spectra were recorded on a Bruker EQUINOX55 instrument with 16 scans.

Thermal Gravimetric Analysis (TGA): TGA was measured on a Perkin-Elmer S II TGA instrument with a heating rate of 5 ^{o}C/min from 100°C to 550^{o}C under a 100.0 mL/min nitrogen flow.

Small-angle X-ray scattering (SAXS)： SAXS experiments were performed by the Shanghai Synchrotron Radiation Facility, using a fixed wavelength of 1.03 nm, a sample-to-detector distance of 5 m and an exposure time of 20 s.

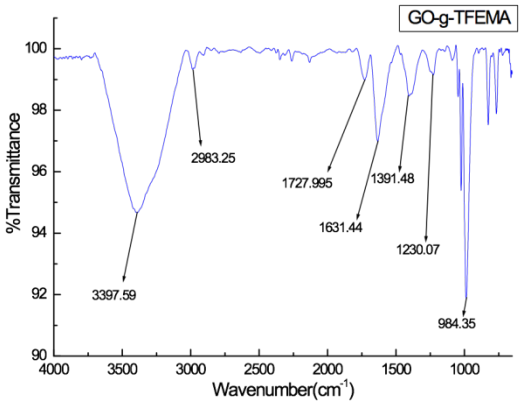
Synthesis of GO-g-TFEMA

Graphene oxide was prepared from natural graphite powder with an average lateral size of 4.00 μm using a modified Hummers method[1,2]. The detailed procedure is given as follows: 1.00 g natural flake graphite and 60.00mL concentrated sulfuric acid were placed in a round-flask. Next 1.20 g $K_2S_2O_3$ and 0.80 g P_2O_5 were added and then stirred at 80 ^{o}C for 5 h. The black reaction mixture was poured into 250 mL deionized ice-water. The resulting precipitate was filtrated off, washed with deionized water until the upper layer was neutral. The precipitate was added into 60.00 mL concentrated sulfuric acidcooled in an ice bath. Then, 3.00 g $KMnO_4$ was added into the reaction mixture slowly over 20 min under stirring. The mixture was stirred at 50 ^{o}C for 5 h and then poured into 200 mL deionized ice-water with vigorous stirring. To remove the residual KMnO4, 35% H2O2 was added into the mixture until the color turned bright yellow. The mixture was washed with deionized water several times until the pH reached ca.7, and followed by washing with diluted HCl for 3 times.

The resulting GO (100 mg) was dispersed in 40 mL deionized water and sonicated (20 KHz) for 48 h in an ice bath. Then anhydrous DMF was used to remove residual H_2O by centrifugation at a speed of 15 000 rpm for 0.5-1 h (at least four times). The precipitate was re-dispersed in 125 mL anhydrous DMF, and then the monomer trifluoroethyl methacrylate (200mg) together with the radical initiator AIBN (86.00mg) was added to the solution under nitrogen in a 65 ^{o}C oil bath. After 20 h, the solution was transferred into a centrifuge tubes (4 * 50 mL) and centrifuged at a speed of 15 000 rpm for 0.5-1 h. The black precipitate at the bottom was collected. This procedure was repeated at least four times until the upper layer was colorless. 35 mL DMSO was used to disperse the precipitate and the same centrifugation procedure as described above was carried out and repeated (at least three times) to remove the DMF. Finally, DMSO-d_6 was used to remove residual DMSO solvent by centrifugation for at least 4 times.

2. Characterization of GO-g-TFEMA

Fourier-Transform Infrared (FTIR)



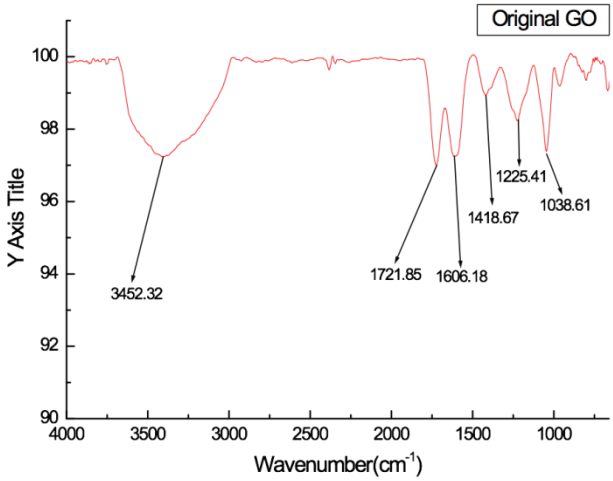


Figure S1: FT-IR spectra of GO-g-TFEMA (top) and unmodified GO (bottom).

Thermal Gravimetric Analysis (TGA)

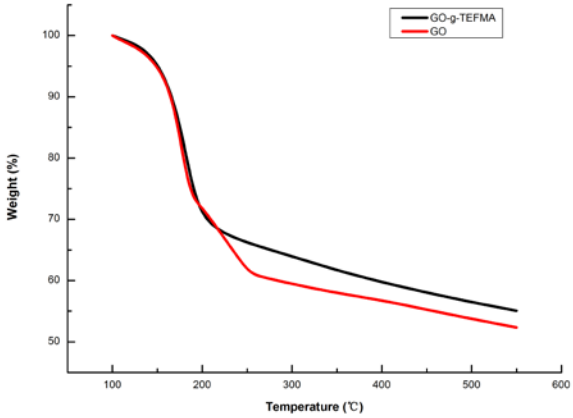
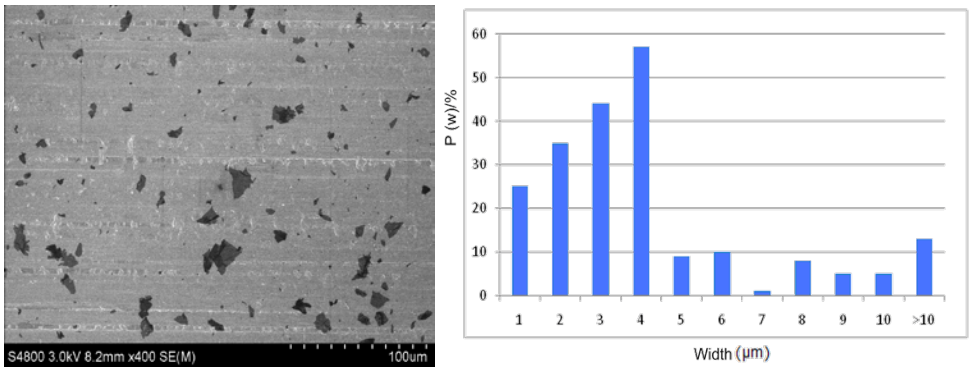


Figure S2: TGA spectrum of GO-g-TFEMA and unmodified GO.

SEM



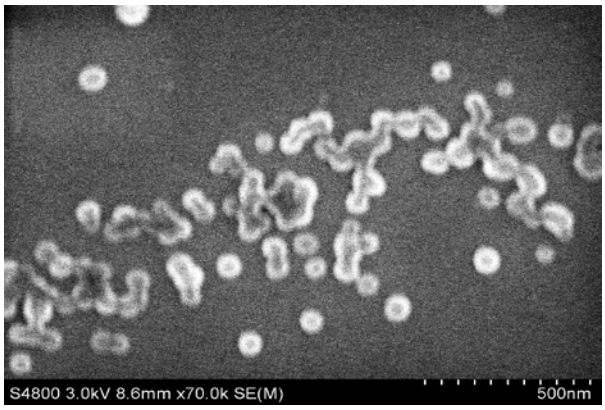


Figure S3: SEM images of 4.00 μm GO (top) and 80 nm GO-g-TFEMA (bottom).

SAXS

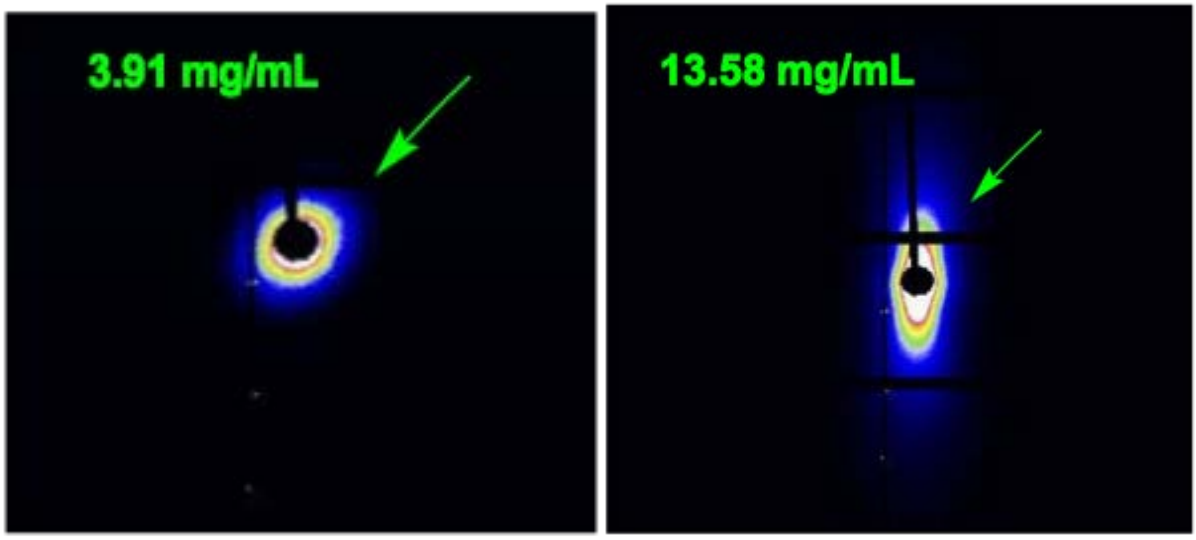


Figure S4: 2D scattering patterns of GO-g-TFEMA LCs under different concentrations.

3. NMR analysis

NMR experiments

All NMR experiments were performed on a Bruker Avance III NMR spectrometer at 500.13MHz for ^{1}H NMR, 76.77MHz for ^{2}H NMR, and 125.76MHz for ^{13}C NMR, equipped with a 5 mm room temperature probe (Bruker Instruments Inc., Germany). The experimental conditions were as follows: for the ^{1}H NMR spectra, spectrometer frequency 500.063 MHz, spectral width (SW) 10 ppm, pulse 90°, acquisition time (AQ) 5.40 s, relaxation delay (RD) 2.00 s, and Fourier Transform (FT) size 32K data point. An exponential window function with a line-broadening factor of 1 Hz was applied to the FID before Fourier transformation. The ^{2}H NMR acquisition was recorded using the lock channel. For the CLIP-HSQC spectra, the conditions were as follows: AQ 0.103 s, RD 1.000 s, and SW 10 ppm (^{1}H) and 80 ppm (^{13}C). One-bond coupling constant was set to 145.0 Hz. LB 1Hz for F2 and 0.3 Hz for F1 was applied before Fourier transformation. All data were analyzed and processed using Bruker Topspin 2.10(2008) software.

NMR spectra and RDC calculations

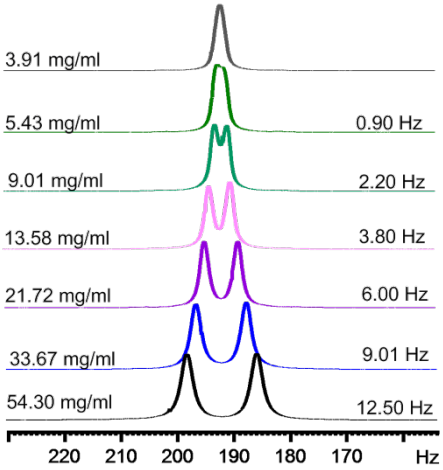


Figure S5: 1D ^{2}H spectra of GO-g-TFEMA LCs in dependence on concentration (3.91, 5.43, 9.01, 13.58, 21.72, 33.67 and 54.30 mg/mL) in DMSO-d_6 collected at 25 °C with eight scans.

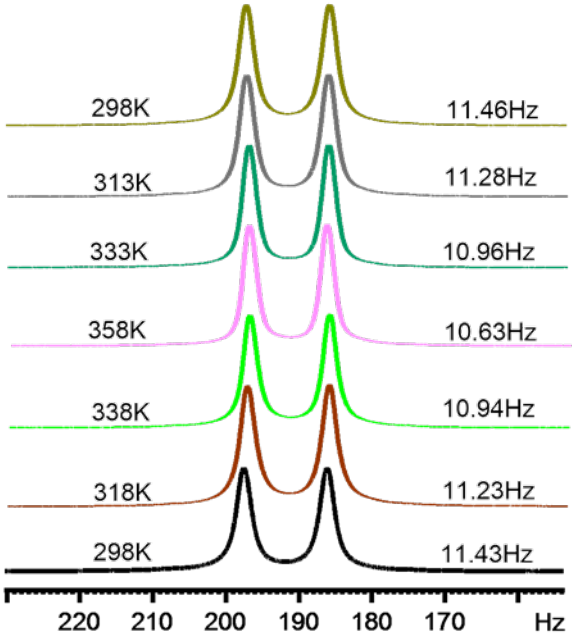


Figure S6: emperature dependent1D ^{2}H spectra of GO-g-TFEMA LCs in DMSO-d_6.

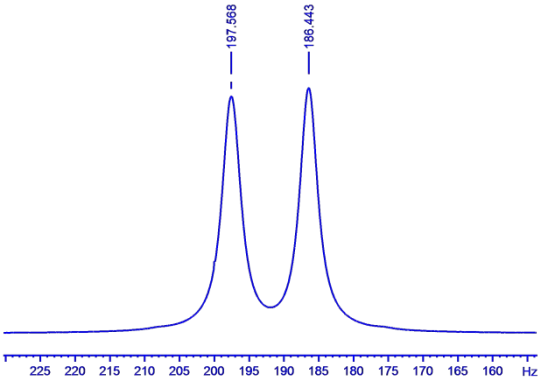


Figure S7: 1D^{2}H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of boc-L-tryptophan in GO-g-TFEMA LCs (47.80mg/mL GO-g-TFEMA) in DMSO-d_6(ΔνQ=11.1Hz).

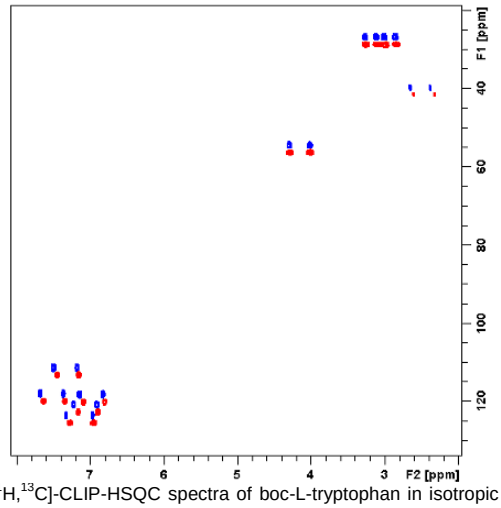
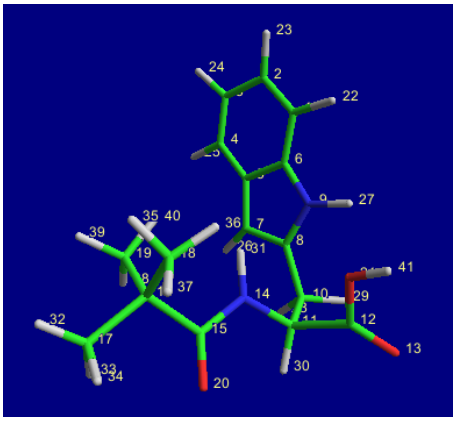


Figure S8: A spectral region of the 500 MHz [^{1}H,^{13}C]-CLIP-HSQC spectra of boc-L-tryptophan in isotropic phase (blue) and in 47.80 mg/mL anisotropic GO-g-TFEMA LC in DMSO-d_6 (red).



Scheme S1: Structure of boc-L-tryptophan with atom numbering.

Atom number	Exp. RDC (Hz)
C8,H26	-19.8
C1,H22	-12.0
C2,H23	-14.0
C3,H24	-25.4
C4,H25	-13.7
C10,H28	-3.4
C10,H29	2.2
C11,H30	-1.5

Table S1: $^{1}D_{CH}$ for boc-L-tryptophan in GO-g-TFEMA LC. ($\Delta\nu Q$ =11.1 Hz).

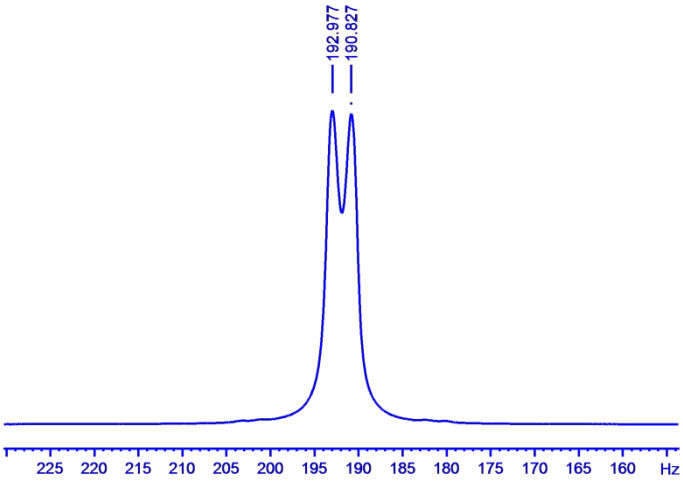


Figure S9: 1D ^{2}H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of estrone in GO-g-TFEMA LCs (9.0mg/mL GO-g-TFEMA) in DMSO-d_6 ($\Delta\nu Q$=2.2 Hz).

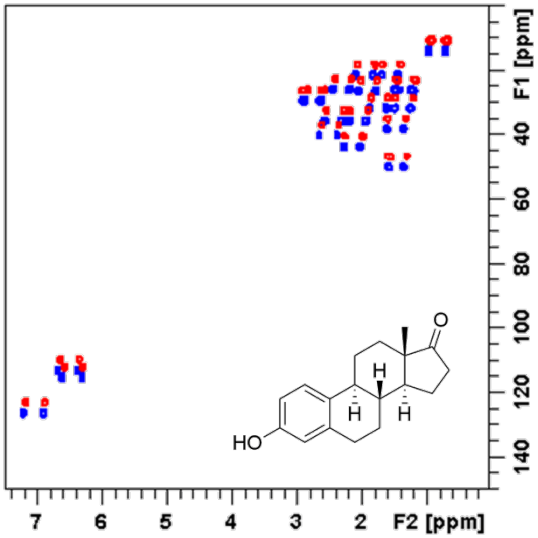
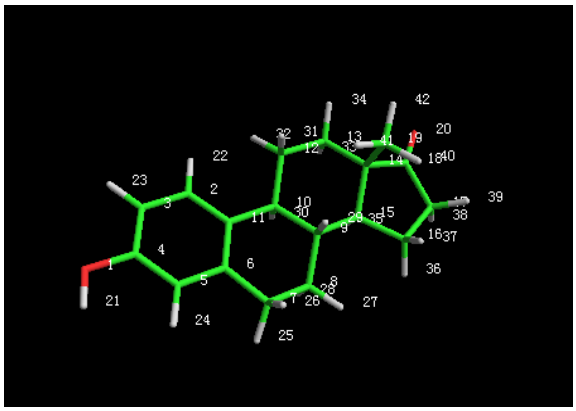


Figure S10: A spectral region of the 500 MHz [^{1}H,^{13}C]-CLIP-HSQC spectra of estrone in isotropic phase (blue) and in 9.0 mg/mL anisotropic GO-g-TFEMA LC in DMSO-d_6 (red).



Scheme S2: Structure of estrone and atom numbering.

Atom number	Exp. $^{1}D_{CH}$(Hz)	Comp. $^{1}D_{CH}$(Hz)
C2,H22	-16.6	-16.1
C5,H24	-14.9	-15.8
C3,H23	-15.0	-18.6
C15,H35	28.9	27.9
C10,H30	26.5	24.5

C9,H29	26.3	26.7
C17,H38	4.3	11.9
C17,H39	18.2	19.3
C13,H33	28.5	23.2
C13,H34	-6.8	-1.2
C7,H25	10.9	5.8
C7,H26	21.5	27.8
C12,H32	-3.0	-1.5
C16,H36	23.6	21.3
C16,H37	3.3	3.1
C7,H37	25.7	25.7
C19,H40	-12.3	-9.7
C19,H41	-12.3	-9.7
C19,H42	-12.3	-9.7

Table S2: $^{1}D_{CH}$ for estrone in GO-g-TFEMA LC (ΔνQ=2.2 Hz).

Following are the results of the RDC fitting for estrone:

Alignment tensor
Axx=0.000226769
Ayy=0.000317279
Azz=-0.000544047
Saupetensor
Sxx=0.000340153
Syy=0.000475918
Szz=-0.000816071
(0.473923,0.852648,0.219974,)
(-0.810684,0.520009,-0.269041,)
(-0.343786,-0.0508246,0.937672,)

SVD condition number is 2.38903
Axial component Aa=-0.000816071
rhombic component Ar=-9.05098e-05
rhombicity R=0.110909
Asimmetry parameter etha=0.166364
GDO=0.000948815
Euler Angles
Set 1
(-3.10257,20.1077,-59.6896)
Set 2
(176.897,159.892,120.31)
Q=0.192

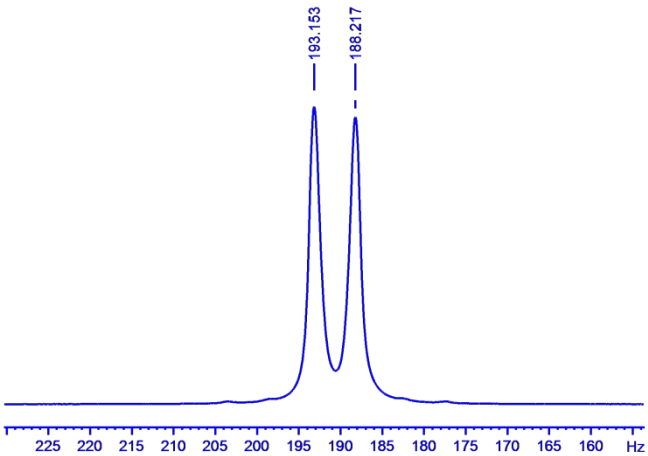


Figure S11: 1D ^{2}H NMR spectrum (76.8 MHz, proton NMR frequency: 500 MHz) of dihydroartemisinin in GO-g-TFEMA LCs (18.92 mg/mL GO-g-TFEMA) in DMSO-d_6 (ΔνQ=4.9 Hz).

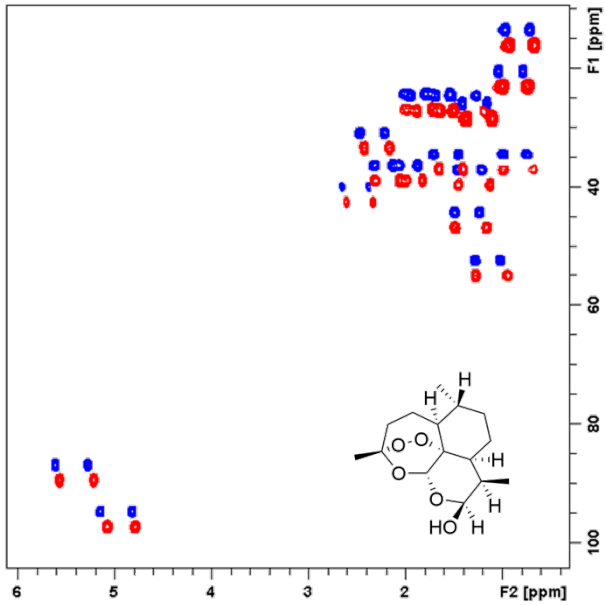
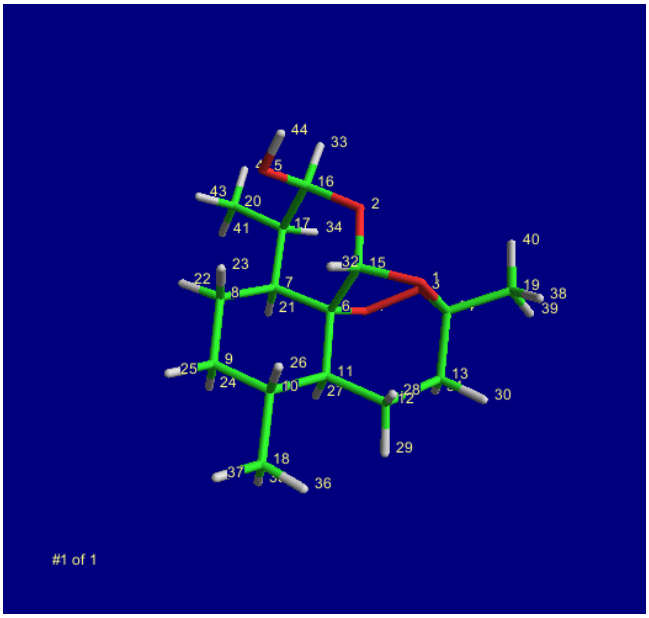


Figure S12: A spectral region of the 500 MHz [^{1}H,^{13}C]-CLIP-HSQC spectra of dihydroartemisinin in isotropic phase (blue) and in 18.92 mg/mL anisotropic GO-g-TFEMA LC in DMSO-d_6 (red)



Scheme S3. Structure of dihydroartemisinin and atom numbering.

Atom number	Exp. $^{1}D_{CH}$(Hz)	Comp. $^{1}D_{CH}$(Hz)
C11,H27	23.2	21.5
C12,H28	18.2	21.3
C12,H29	-7.4	-7.2
C13,H30	23.3	21.5
C13,H31	-3.7	-4.9
C15,H32	5.2	4.7
C7,H21	20.0	21.5
C9,H24	-4.8	-3.7
C9,H25	16.9	20.2

C10,H26	27.6	22.3
C17,H34	2.5	0.7
C16,H33	-11.7	-12.9
C20,H41	2.9	2.6
C20,H42	2.9	2.6
C20,H43	2.9	2.6
C18,H35	2.5	4.1
C18,H36	2.5	4.1
C18,H37	2.5	4.1
C19,H38	3.2	2.7
C19,H39	3.2	2.7
C19,H40	3.2	2.7

Table S3: $^{1}D_{CH}$ for dihydroartemisinin in GO-g-TFEMA LC(ΔνQ=4.9 Hz).

Following are the results of the RDC fitting for dihydroartemisin:

Alignment vector
Axx=0.000133261
Ayy=0.000204248
Azz=-0.000337509
(0.380693,-0.449927,-0.807861,)
(-0.368302,0.727581,-0.578774,)
(0.84819,0.517872,0.111276,)
SVD condition number is 6.92747
Axial component Aa=-0.000506264
rhombic component Ar=-7.09867e-05
rhombicity R=0.140217
Asimmetry parameter etha=0.210325
GDO=0.000591013
Euler Angles
Set 1
(77.8732,-58.0154,-44.0523)
Set 2
(-102.127,238.015,135.948)
Q = 0.146

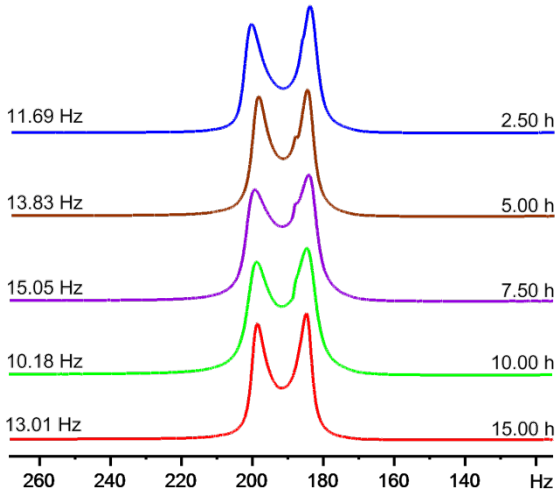


Figure S13: 1D ^{2}H spectra of 46.05 mg/mL GO-g-TFEMA LC in DMSO-d_6 in dependence on the reaction time(2.50 h,5.00 h,7.50 h,10.00 h,15.00 h) (top to bottom) collected at 25 °C with eight scans.

The extent of grafting,which can beexpressed by the average grafting density(d) and the average height (h),exerts a strong influence on the solubility as well as the aspect ratio (intrinsic aligning ability). A previous study showed that the extent of grafting can be tuned by the reaction time.[1] Therefore in this study we evaluated the aligning property of grafted GO LCs in dependence on the reaction time.Slight difference inthe absolute size of the quadrupolar splitting as shown in Figure S13 indicates that varying extent of grafting was insufficient to significantly modulate the aligning degree of grafted GO LCs.

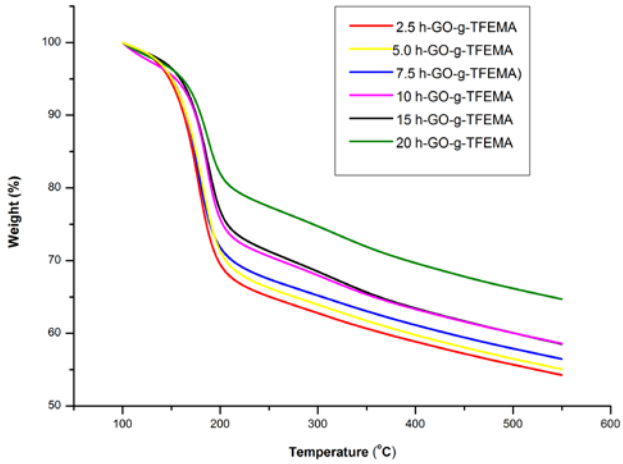


***Figure S14*:** TGA spectrum of GO-g-TFEMA in dependence on the reaction time.

***Figure S15*:** ^{1}H NMR of boc-L-tryptophan in the anisotropic GO-g-TFEMA LCs (blue) and in unmodified GO LC (50%DMSO-d_6 with 50% H_2O).

4. References:

(1) Xu, Z.; Gao, C. *Macromolecules* **2010**, *43*, 6716–6723.
(2) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339.