Supporting Information

Near Infrared Light-Driven Liquid Crystal Phase Transition Enabled by Hydrophobic Mesogen Grafted Plasmonic Gold Nanorods

Karla G. Gutiérrez-Cuevas[a], Ling Wang[a], Chenming Xue[a], Gautam Singh[b], Satyendra Kumar[b], Augustine Urbas[c], and Quan Li[*, a]

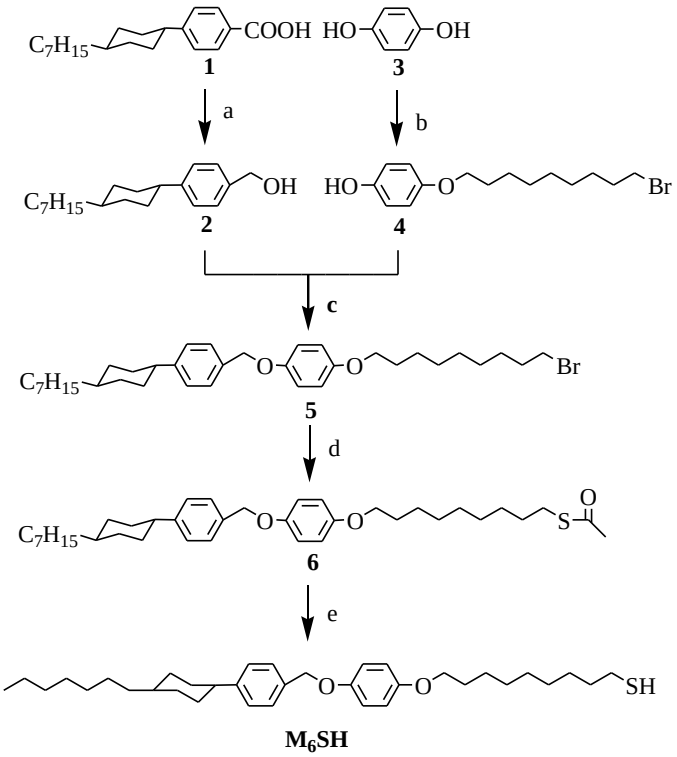
[a]Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, United States; [b]Department of Physics, Kent State University, Kent, Ohio 44242, United States; and [c] Materials and Manufacturing Directorate, Air Force Research laboratory WPAFB, Ohio 45433, United States

1. Experimental section

All chemicals and solvents were purchased from commercial supplies and used without further purification. ^{1}H NMR spectra were analyzed on a Bruker 400 MHz NMR spectrometer using deuterated chloroform ($CDCl_3$) as solvent at 25 ^{o}C. The chemical shifts were reported using the standard 7.24 ppm chemical shift for deuterated chloroform. ^{13}C NMR spectra were analyzed using the Bruker 400 MHz or Varian 200 MHz NMR spectrometer. Deuterated chloroform was used as solvent having a chemical shift standard of 77.0 ppm. All NMR data was processed using MestReNova 9.0.1 software. High resolution mass spectrometry (HRMS) was analyzed by Mass Spectrometry & Proteomics Facility of The Ohio State University. X-Ray measurements were analyzed by using the Rigaku Screen Machine with microfocus sealed X-Ray tube with Copper anode (λ=1.541870Å). The diffraction patterns were recorded using a high resolution Mercury 3CCD detector positioned 76.47 mm away from the capillary sample. The diffraction patterns were analyzed by using FIT2D software after subtracting the background measured with an empty capillary in the sample position or isotropic scattering. The data was calibrated against silver behenate or silicon standards traceable to the National Institute of Standards and Technology. UV-visible spectra were collected on a PerkinElmer Lambda 25 UV-Vis spectrometer at the resolution of 1 nm. Transmission electron microscopy (TEM) micrographs were obtained using a FEI Tecnai TF20 FEG TEM equipped with 4k UltraScan CCD camera. The diluted analyzed samples were placed in a TEM cupper grids

precoated with a thin carbon film (Cu-400 CN) purchased from Pacific Grid Tech. Planar cells used to characterize the thermotropic mesogen thiol was purchased from Instec, USA with a 9 μm thickness containing a polymer-coated and indium tin oxide (ITO) coated glass plates. Liquid crystal textures were observed using a Leitz polarized optical microscope (POM) with a temperature controller hot stage. M_6S-GNRs were weighted in a Mettler Toledo XP26 DeltaRange Microbalance. NIR light irradiations of samples were performed using an 808 NIR laser (Ningbo Lasever Inc.) with 2W power. Homemade cells of 25 μm thick without alignment layer were elaborated in our clean room facility for testing POM of nanocomposites and the NIR experiments.

2. Synthesis of liquid crystal thiol M_6SH



Scheme 1. Synthesis of liquid crystal thiol **M_6SH**. a) $LiAlH_4$, THF, reflux; b) $Br(CH_2)_9Br$, K_2CO_3, KI, CH_2Cl_2, reflux, c) PPh_3, DIAD, THF, 60 ^oC, d) KSAc, DMF/$CHCl_3$, room temperature; and e) TBACN, $CH_3OH/CHCl_3$, 50^oC.

2.1. Synthesis of 4-(*trans*-4-*n*-heptylcyclohexyl) benzyl alcohol (2).

In a 100 mL round bottom flask, 1.000 g (3.32 mmol) of acid **1** was placed and 60 mL of anhydrous THF were added.[1] The mixture was cooled with an ice bath for 15 minutes and

0.260 g (6.85 mmol) of $LiAlH_4$ where slowly added in small portions, then the reaction mixture was stirred and heated to reflux for 5 hours in N_2 atmosphere. After reaction was completed the mixture was quenched to 0 ^oC with an ice bath. Methanol was added slowly to decompose the excess of hydride, the resulting mixture was acidified to pH<5 with diluted hydrochloric acid and the organic phase was extracted with diethyl ether for 3 times. The solution was dried with $MgSO_4$ and solvent removed by rotate evaporation. The residue obtained was purified through column using dichloromethane as eluent to obtain the colorless gel **2**, Yield= 82.5%, ^1H NMR ($CDCl_3$, 400 MHz) δ: 0.92 (t, *J* = 7.29 Hz, 3H, C**H**$_3$-CH_2-), 1.08 (m, 2H, Cyclo-**H**), 1.20-1.35 (m, 13H –C**H**$_2$-, Cyclo-**H**), 1.49 (m, 2H, Cyclo-**H**), 1.92 (m , 4H, Cyclo-**H**), 2.15 (s, 1H, -O**H**), 2.50 (m, 1H, Cyclo-**H**), 4.65 (s, 2H, C**H**$_2$-OH), 7.23 (d, *J* = 8.44, 2H, Ar-**H**), 7.32 (d, *J* = 8.43 Hz, 2H, Ar-**H**); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.31, 22.90, 27.20, 29.59, 30.17, 32.14, 33.79, 34.55, 37.51, 37.63, 44.56, 65.33, 127.19, 127.32, 138.49, 147.61.

2.2. Synthesis of 4-(9-bromononyloxy) phenol (4).

In a 100 mL round bottom flask, 2.010 g (0.018 mol) of hydroquinone was mixed with 5.22 g (0.018 mol) of 1,9-dibromononane, 2.017 g (0.015 mol) of potassium carbonate and 10 mg (0.06 mmol) of potassium iodide in 60 mL of acetone. The reaction mixture was stirred and refluxed for 24 hours in N_2 atmosphere. After reaction, the mixture was filtrated and acetone was removed by rotate evaporation. The solid obtained was dissolved in dichloromethane and filtrated to remove the unreacted hydroquinone, the filtrate was concentrated using a rotate evaporator and purified by silica gel column and dichloromethane as eluent to afford **4**. ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.18 (m, 10H), 1.62 (tt, *J* = 6.72, *J* = 6.91 Hz, 2H, -C**H**$_2$-CH_2-Br), 1.87 (tt, *J* = 6.72, *J* =7.86, 2H, -C**H**$_2$-CH_2-O-), 3.43 (t, *J* = 6.83 Hz, 2H, -CH_2-C**H**$_2$-Br), 3.91 (t, *J* = 6.50 Hz, 2H, CH_2-C**H**$_2$-**O**), 4.23 (s, 1H, -O**H**), 6.6 (m, 4H,Ar-**H**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.14, 27.29, 27.83, 28.40, 28.49, 31.95, 33.21, 67.93, 114.82, 115.17, 148.53, 152.41.

2.3. Synthesis of intermediate bromide 5.

In a 100 mL round bottom flask, 0.509 g (2 mmol) of **2**, 0.62 g (1.97 mmol) of intermediate **4** and 0.511 g (1.95 mmol) of triphenylphosphine were placed.[1] Then 25 mL of anhydrous

THF were added. The solution was cooled to 0 ^{o}C with an ice bath and 0.41 g (2 mmol) of diisopropyl azodicarboxylate (DIAD) were added directly to the mixture, after 10 min in the ice bath the reaction mixture was stirred and refluxed overnight in N_2 atmosphere. After reaction was completed THF was removed by rotate evaporation and the concentrated mixture was suspended in 100 mL of hexane/diethyl ether (1:1), filtered over a silica gel bed and eluted with diethyl ether in order to remove triphenylphosphine oxide, this procedure was repeated for three times and after that the solvent was removed by rotate evaporation. The product was purified using silica gel column and dichloromethane as eluent obtaining a white solid. Yield= 32.8%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.9 (t, *J* = 6.74Hz, 3H, C**H$_3$**-CH_2-), 1.21-2.10 (m, 35H, Br-CH_2-(C**H$_2$**)$_7$-CH_2-O-, CH_3-(C**H$_2$**)$_5$-CH_2-, Cyclo-**H**), 2.60 (m, 1H, Cyclo-**H**), 3.41 (t, J=6.71, 2H, CH_2-C**H$_2$**-Br), 3.90 (t, *J* = 6.71 Hz, 2H, -CH_2-C**H$_2$**-O-), 5.00 (s, 2H, Ar-**CH_2**-O-Ar), 6.90 (m, 4H, Ar-**H**), 7.25 (m, 2H, Ar-**H**), -7.40 (m, 2H, Ar-**H**); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.11, 22.68, 25.99, 26.97, 28.12, 28.66, 29.24, 29.32, 29.37, 29.94, 31.91, 32.78, 33.59, 33.95, 34.33, 37.30, 37.42, 44.38, 68.54, 70.63, 115.36, 115.72, 127.00, 127.63, 134.61, 147.67, 152.99, 153.41. HRMS calcd for [$C_{35}H_{53}BrO_2Na^+$] 609.3107; found 609.3114

2.4. Synthesis of intermediate thioacetate 6.

Compound **5 (**0.570 g, 1 mmol) and potassium thioacetate (0.237 g, 2 mmol) were placed into a round bottom 100 mL flask. A mixture of 65 mL of $CHCl_3$: DMF 1:1 was added and stirred at room temperature in inert atmosphere for two days. After reaction, the mixture was dissolved in dichloromethane and washed with water to remove the excess of KSAc. The organic phase was dried with Na_2SO_4 and filtered. Dichloromethane was removed using rotate evaporation and the product was purified using silica column with a mixture of CH_2Cl_2: hexane as eluent. Product was obtained as white solid. Yield= 49.1%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.93 (t, *J* = 7.22 Hz, 3H, C**H$_3$**-CH_2-), 1.09 (m, 2H, Cyclo-**H**), 1.09-2.0 (m, 35H, -S-CH_2-(C**H$_2$**)$_7$-CH_2-O-, CH_3-(C**H$_2$**)$_5$-CH_2-, Cyclo-**H**), 2.35 (s, 3H, C**H$_3$**-CO-S), 2.50 (m, 1H, Cyclo-**H**), 2.90 (t, *J* = 7.69 Hz, 2H, -C**H$_2$**-S-CO-), 3.93 (t, ***J*** = 6.82 Hz, 2H, -CH_2-C**H$_2$**-O-), 4.99 (s, 2H, -Ar-C**H$_2$**-O-Ar-), 6.87 (m, 2H, Ar-**H**), 6.92 (m, 2H, Ar-**H**), 7.26 (m, 2H, Ar-**H**), 7.38 (m, 2H, Ar-**H**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.38, 22.49, 22.99, 27.20, 29.37, 29.53, 29.60, 29.62, 30.20, 30.25, 30.90, 32.21, 33.87, 34.58, 37.55,

37.67, 44.69, 68.89, 70.93, 115.59, 116.01, 127.29, 127.96, 134.89, 147.97, 153.25, 153.67, 196.44. HRMS calcd for [$C_{37}H_{56}O_3SNa^+$] 603.3842, found 603.3858

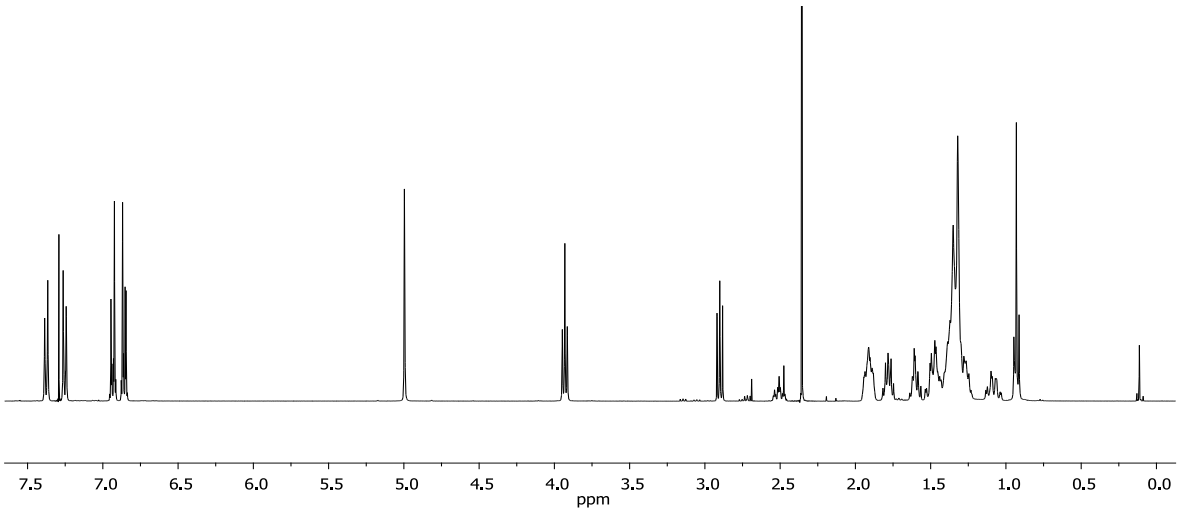


Fig. S1. ^{1}H NMR of thioacetate **6** in $CDCl_3$

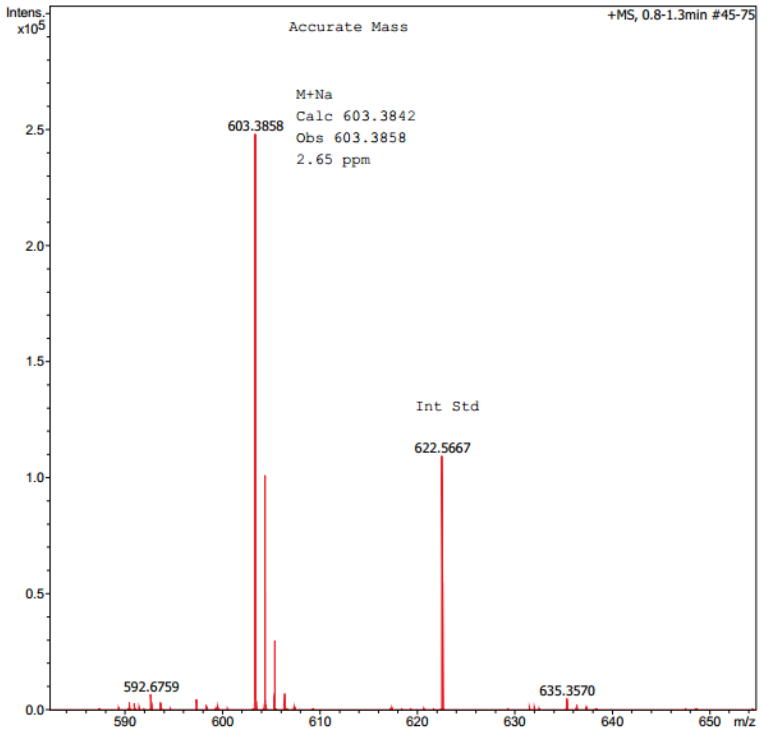


Fig. S2. High-resolution MS of thioacetate **6**.

2.5. Synthesis of mesogenic thiol M_6SH.

In a 50 mL round bottom flask, 0.2392 g (0.44 mmol) of **6** , 0.2350 g (0.87 mmol) of tetrabutylammonium cyanide and a mixture of 40 mL of $CHCl_3$:MeOH (3:1) were added. The reaction mixture was stirred and heated at 50 ^oC for 24 hours. After reaction was completed the mixture was extracted with $CHCl_3$ 3 times. The organic phase was washed with an ammonium chloride diluted solution and the organic layer was separated. The organic phase was then dried with $MgSO_4$, filtrated and solvent was removed by rotate evaporation. The product was purified using silica gel column using $CHCl_3$ as eluent to obtain a white solid. Yield= 64%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.91 (t, *J* = 6.73 Hz, 3H, C**H$_3$**-CH_2-), 1.07 (m, 2H, Cyclo-**H**), 1.25-2.0 (m, 35H, -S-CH_2-(C**H$_2$**)$_7$-CH_2-O-, CH_3-(C**H$_2$**)$_5$-CH_2-, Cyclo-**H**), 2.50 (m, 1H, Cyclo-**H**), 2.71 (t, *J* = 7.25 Hz, 2H, -C**H$_2$**-SH), 3.91 (t, *J* = 6.59 Hz, 2H, -CH_2-C**H$_2$**-O-), 4.98 (s, 2H, -Ar-C**H$_2$**-O-Ar-), 6.84 (m, 2H, Ar-**H**), 6.2 (m, 2H, Ar-**H**), 7.24 (m, 2H, Ar-**H**), 7.38 (m, 2H, Ar-**H**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.30, 22.89, 24.85, 26.30, 27.21, 28.55, 28.69, 29.19, 29.36, 29.40, 29.51, 29.53, 29.57, 29.59, 29.62, 30.14, 32.13, 33.80, 34.22, 37.52, 37.64, 39.37, 44.61, 68.78, 70.85, 115.58, 115.93, 127.23, 127.86, 134.83, 147.89, 153.20, 153.63. HRMS calcd for [$C_{35}H_{54}O_2SNa^+$] 561.3737, found 561.3743.

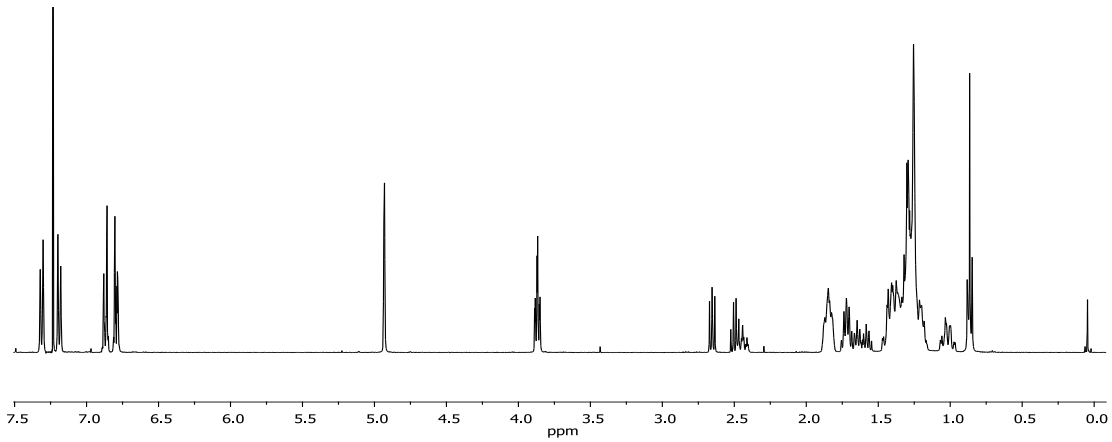


Fig. S3. ^{1}H NMR of mesogenic thiol **M$_6$SH** in $CDCl_3$

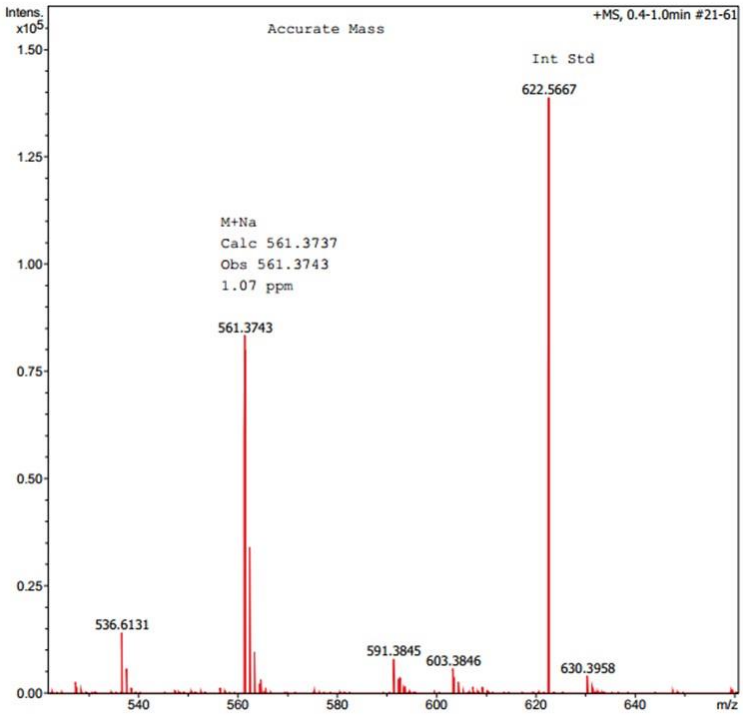


Fig. S4. High-resolution MS of mesogenic thiol **M_6SH**.

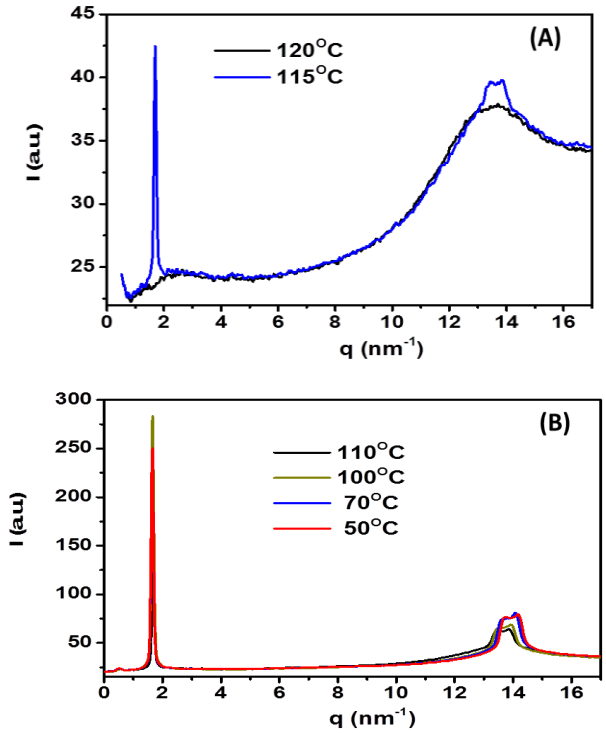


Fig. S5. Scattering intensity (I) versus scattering vector (q) scans of mesogenic thiol M_6SH at different temperatures (A and B). In the isotropic phase (120°C), both small angle and wide angle reflections are

diffuse. These diffuse peaks obeserved in isotropic phase change to sharp reflections at ~115°C, suggesting the mesophase to be very highly ordered smectic B (Sm B)

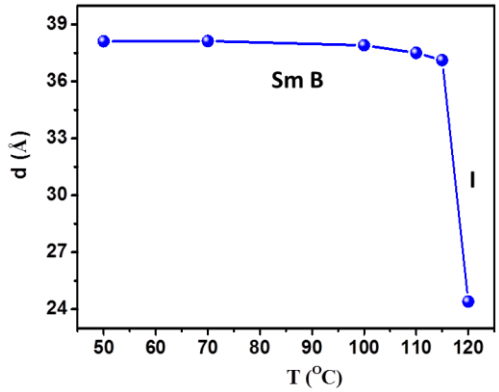


Fig. S6. Temperature-dependent d spacing of liquid crystal **M_6SH**.

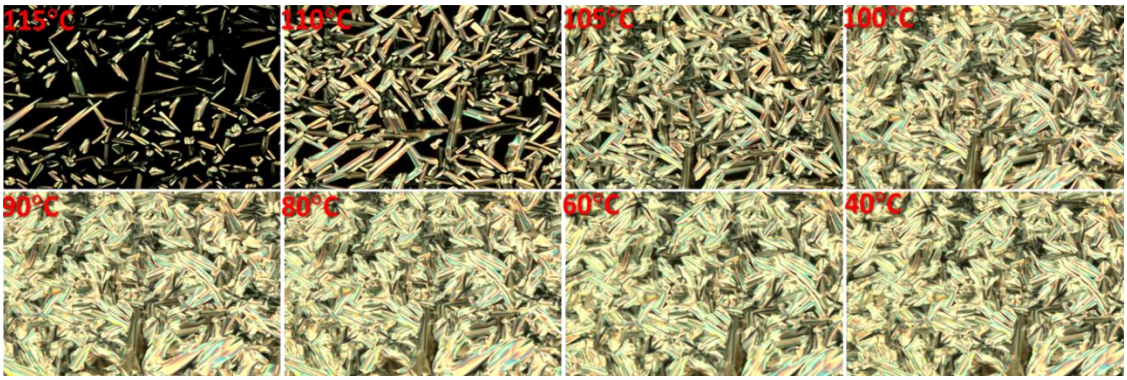


Fig. S7. POM textures of **M_6SH** at different temperatures between two untreated glass substrates.

3. Synthesis of CTAB-GNR.

For the synthesis of CTAB-GNR we followed the reference.[2]

4. Synthesis of M_6S-GNR

The solution of CTAB-GNRs was centrifuged 20 min at 7500 rpm three times to remove the excess free CTAB and other solution components and redispersed in 1.5 mL of water. Then, this aqueous solution of GNRs was added dropwise to a solution of 50 mg of **M_6SH** in 40 mL of THF, the reaction mixture was stirred at room temperature under nitrogen atmosphere for 3 days and centrifuged. After this time the GNRs were centrifuged 20 min at 7500 rpm, then the precipitate was dispersed in 10 mL of $CHCl_3$ and sonicated. After 10 mg of **M_6SH** was added into the solution and stirred for 24 hours, this process was repeated

twice in order to ensure well exchange. The resultant hybrid GNRs were centrifuged and washed with chloroform several times until there was no UV signal in the top layer solution, indicating absence free thiol molecules. Finally the hybrid **M_6S-GNR** was dried, weighted in a microbalance and a stock solution containing 0.2 mg/mL was prepared in $CHCl_3$. As illustrated in Fig. S8, **CTAB-GNRs** are only soluble in the top layer of the water phase. After the functionalization with mesogenic surfactant **M_6SH**, **M_6S-GNRs** were found to be soluble in the bottom layer of the organic phase.

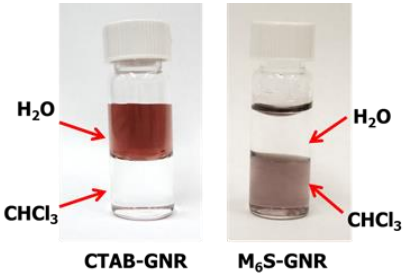


Fig. S8. Image of solutions of **CTAB-GNRs** (left) and **M_6S-GNRs** (right) in water and chloroform.

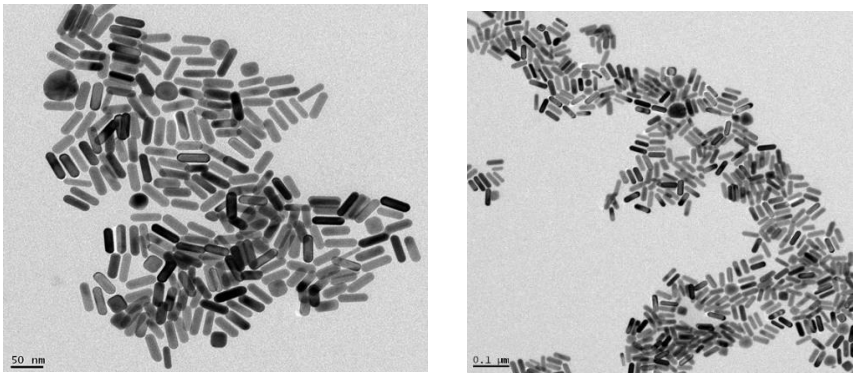


Fig. S9. TEM images of the mesogenic functionalized organosoluble **M_6S-GNRs**.

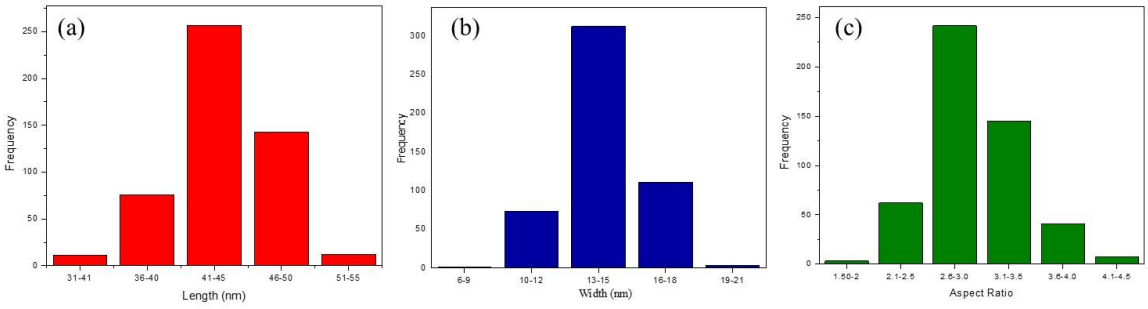


Fig. S10. Size distribution of **M_6S-GNRs**. (a) Length, (b) width and (c) aspect ratio considering 500 GNRs.

5. M_6S-GNRs/E7 liquid crystal nanocomposites

The commercially available nematic E7 is a eutectic mixture of liquid crystal components designed for display applications, consisting of a mixture of biphenyls: 25 wt% 4-cyano-4´-*n*-pentyl-1,1´-biphenyl (5CB), 51 wt% 4-cyano-4´-*n*-heptyl-1,1´-biphenyl (7CB), 16 wt% 4-cyano-4´-*n*-octyloxy-1,1´-biphenyl (8OCB) and 8 wt% 4-Cyano-4´´-*n*-pentyl-1,1´,1´´-terphenyl (5CT).

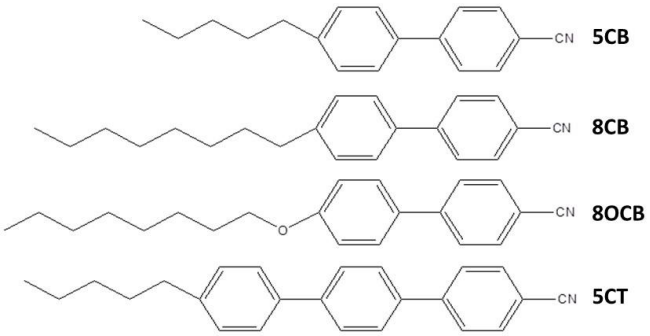


Fig. S11. Chemical structures of the components of E7.

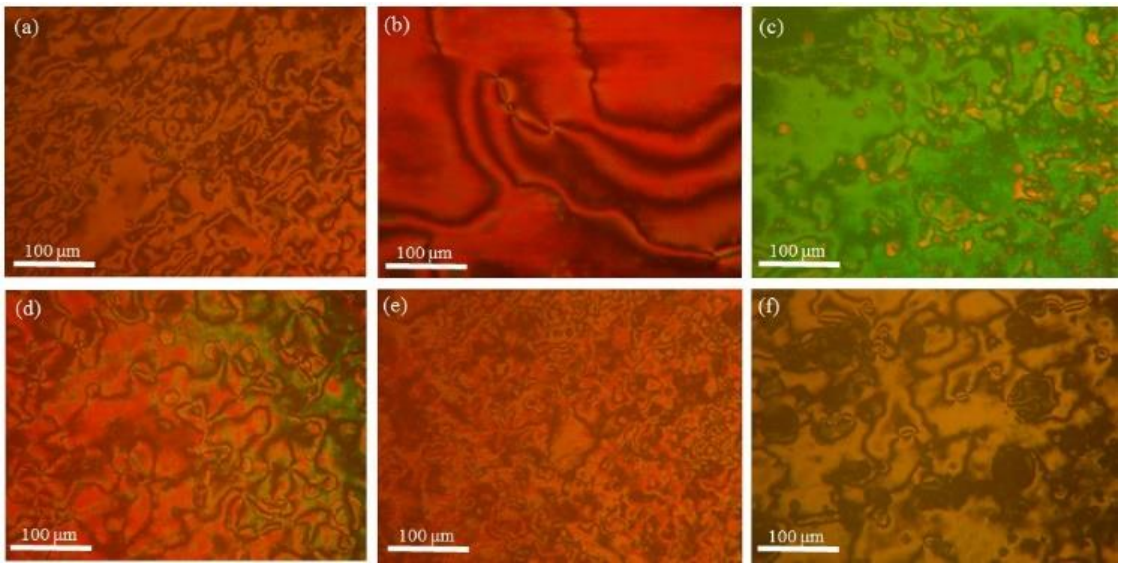


Fig. S12. Textures of composites **M_6S-GNRs**/E7 under cross polarized microscope with a) 0.01% b) 0.08%, c) 0.15%, d) 0.20%, e) 0.35% and f) 0.50% at 55 ^{o}C upon cooling from the isotropic state.

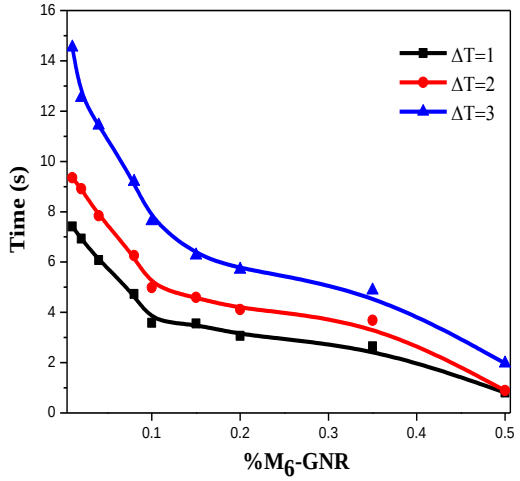


Fig. S13. Time dependence response curve of N-I transition at different concentrations of **M_6S-GNRs** in E7.

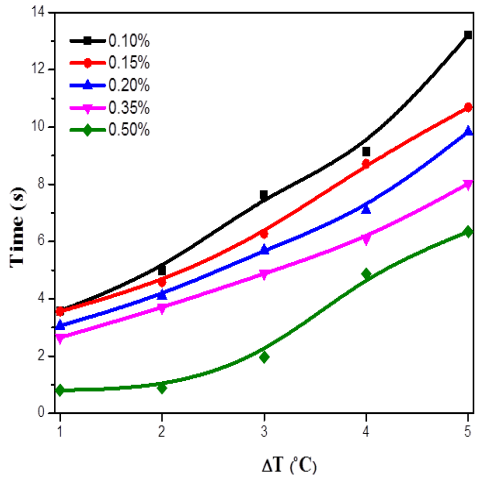


Fig. S14. Time dependence response curve of N-I transition at different **Δ**T values upon NIR irradiation.

Table S1. Clearing temperatures of **M_6-GNRs**/E7 composites at different concentrations

%M_6-GNR	**T_{N-I} (°C)**	**%M6-GNR**	**T_{N-I} (°C)**
0.00	60.1	0.10	60.3
0.01	60.2	0.15	59.9
0.02	60.2	0.20	59.6
0.04	60.3	0.35	59.6
0.08	60.9	0.50	59.2

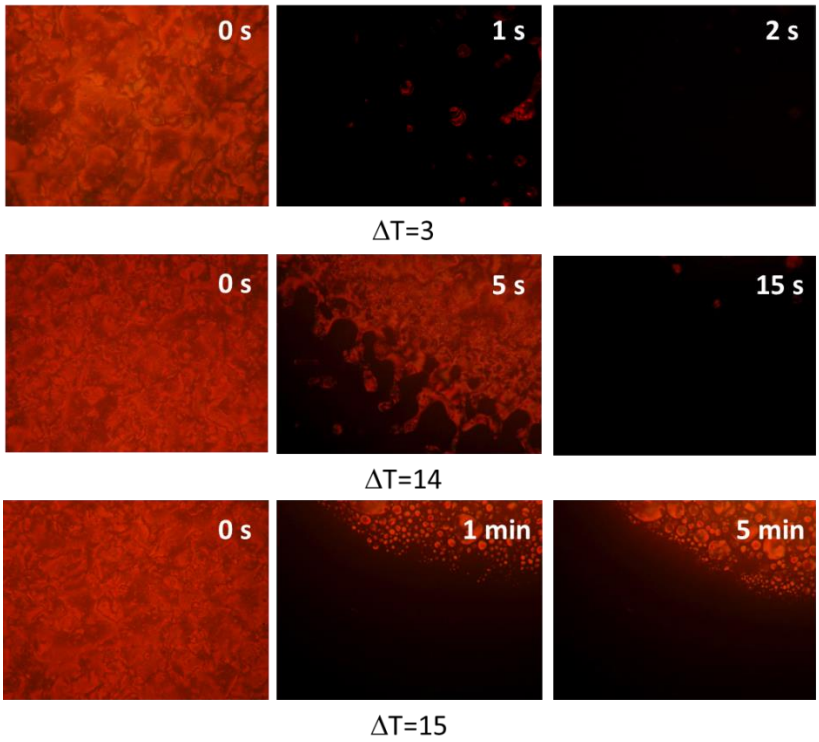


Fig. S15. POM texture change of composite 0.5% **M_6-GNRs** in E7 at ΔT = 3, 14 and 15 upon NIR irradiation.

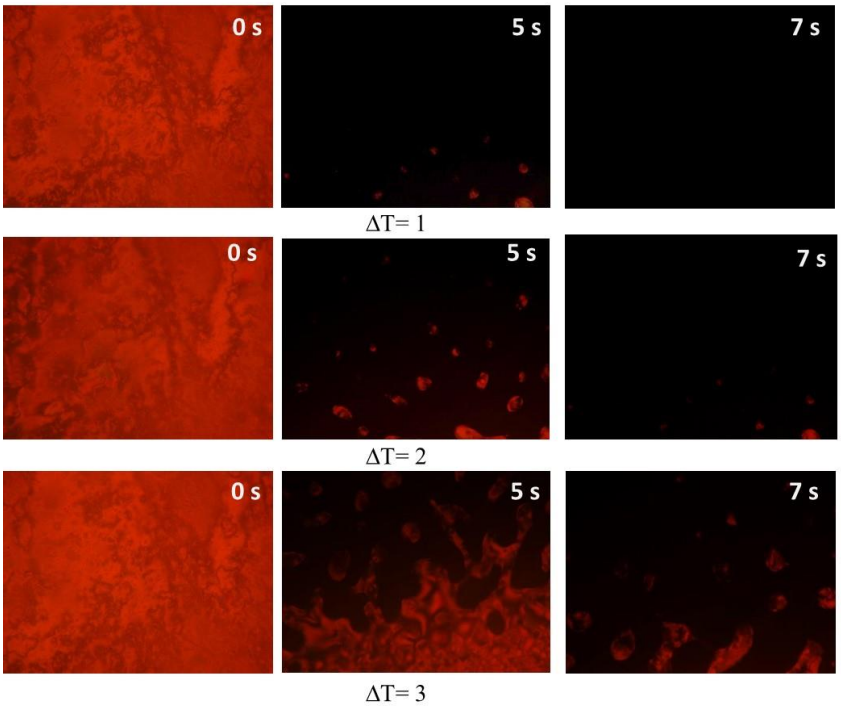


Fig. S16. POM texture change of composite 0.01% **M_6-GNRs** in E7 with different NIR irradiation times at ΔT=1, 2 and 3.

References

1. Q. Li, Y. Li, Ji Ma, D. Yang, T. J. White, T. J. Bunning, *Adv. Materials* **2011**, 23, 43, 5069-5073.
2. C. Xue, K. Gutierrez-Cuevas, M. Gao, A. Urbas, Q. Li, *J. Phys. Chem. C* **2013**, *117*, 21603−21608.