

Materials and Methods

The mesogen-grafted SiO₂ nanoparticles were synthesized in a straightforward manner as shown in **Scheme 1**. All chemicals and solvents were purchased from commercial suppliers and used without further purification. LUDOX TM-40 was purchased from Aldrich. ¹H NMR spectra were recorded on a Bruker 400 MHz Nuclear Magnetic Resonance (NMR) spectrometer using deuterated chloroform (CDCl₃) as solvent at room temperature. The chemical shifts were reported using the standard 7.24 ppm for CDCl₃. UV-visible spectra were collected on a PerkinElmer Lambda 25 UV-Vis spectrometer with 1 nm resolution. Transmission electron microscopy (TEM) micrographs and energy dispersive X-ray spectrum (EDX) were obtained using a FEI Tecnai TF20 FEG TEM equipped with 4k UltraScan CCD camera. The diluted analyzed samples were placed in a TEM copper grids pre-coated with a thin carbon film (Cu-400 CN) purchased from Pacific Grid Tech. Thermogravimetric data were obtained using a TGA 2950 Thermogravimetric analyzer from TA instruments. Textures of liquid crystalline nanocomposites were observed by a Leitz Laborlux 12 Pol Polarizing Optical Microscope (POM) with a hot stage attached Mettler-Toledo with temperature controller (FP90). Electro-optical properties were measured using a voltage generator from Stanford Research Systems model DS345, an amplifier from LC Technologies, Inc., and a fiber optic spectrometer from Ocean Optics USB000+.

Synthesis of SiO₂-NH₂ Nanoparticles

For the synthesis of SiO₂-NH₂ nanoparticles, the commercially available SiO₂-OH nanoparticles (LUDOX TM-40, an aqueous colloidal suspension) were used. For the functionalization of SiO₂-OH nanoparticles to SiO₂-NH₂, 2.5 mL of LUDOX TM-40 solution was placed in a centrifuge tube, and then 5 mL of water was added and sonicated in order to well disperse the SiO₂-OH

nanoparticles in a larger amount of water. Then, a same amount of ethanol was placed in the tube and sonicated for 10 minutes in order to transfer the nanoparticles to ethanol. The mixture was sonicated, centrifuged 25 minutes at 7,500 rpm and the solvent layer was removed. The residue was dispersed in ethanol, and this step was repeated twice in order to remove excess of water and avoid gelation when (3-amino propyl)-triethoxy silane (APTES) is added. Then 10 mL of the dispersed solution of ~80 mg/mL of SiO₂-OH in ethanol was added dropwise to a solution containing APTES (170 μL, 0.70 mmol), in 10 mL of ethanol and heated to 70 °C for 48 hours under continuously stirring and nitrogen atmosphere.¹ When reaction was finished, the reaction mixture was centrifuged and dispersed in ethanol and precipitated in a large amount of hexanes, sonicated, centrifuged 25 minutes at 7,500 rpm; this step was repeated two times. Finally, the SiO₂-NH₂ nanoparticles were dispersed and sonicated in 20 mL of tetrahydrofuran and some portion was dried for ¹H NMR and TGA analysis.

Synthesis of M-SiO₂ Nanoparticles

The mesogen 4'-octyl-4-biphenylcarboxylic acid (8BCA, 50 mg, 0.16 mmol), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, 30 mg, 0.15mmol) and 20 mL of THF were placed in a one neck round bottom flask and stirred at 40 °C, and the solution of SiO₂-NH₂ nanoparticles in THF was added dropwise and reacted for 2 days under the same conditions.² When reaction was completed, the mixture was centrifuged at 7500 rpm for 20 minutes, the supernatant was removed. The precipitate was dissolved in THF and re-dispersed in a mixture of MeOH and THF (1:1) in order to remove the by-product urea and other unreacted materials and centrifuged at 7500 rpm for 25 minutes. Subsequently, the supernatant was removed and the residue dispersed in THF and centrifuged at 7500 rpm for 15 minutes. This procedure was repeated twice. Then, the remaining solid was dissolved in a large amount of CHCl₃ and washed with water and the organic layer was separated, the solvent was then removed by rotate evaporation and the product was dried, weighted and analyzed by ¹HNMR, TGA, Fluorescence, and TEM. Finally, a stock solution containing 0.5 mg/mL was prepared for further experiments in DFCLC host.

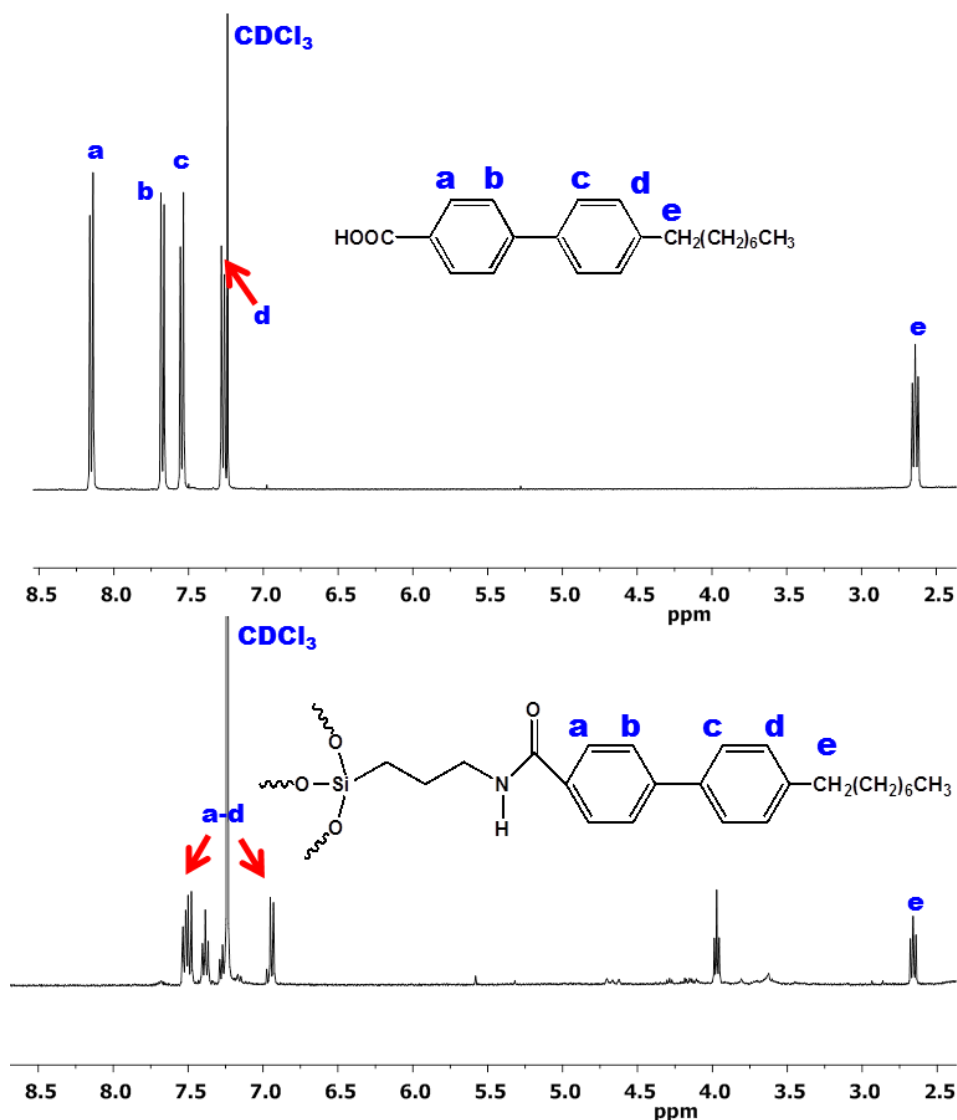


Figure S1. Partial ¹H NMR spectra of the mesogen (8BCA, top) and M-SiO₂ nanoparticles (bottom) in CDCl₃.

In both spectra as shown in Figure S1, the triplet at around 2.6 ppm could be assigned for the methylene group directed linked to the aromatic core (C₇H₁₅-CH₂-Ar). In the M-SiO₂ spectra, the signals from the aromatic groups were observed, however the aromatic signals (*e.g.* around 8.20 ppm) from the free mesogen (top) disappeared in ¹H NMR spectrum of M-SiO₂ (bottom); the triplet around 4 ppm could be assigned for the methylene group directly linked to the amide, which suggests the covalently coupling of the mesogen to the nanoparticle, *i.e.*, M-SiO₂. The change of the chemical environment of the aromatic groups results in the shift to lower fields when the mesogen is linked through an amide link to the SiO₂ core.

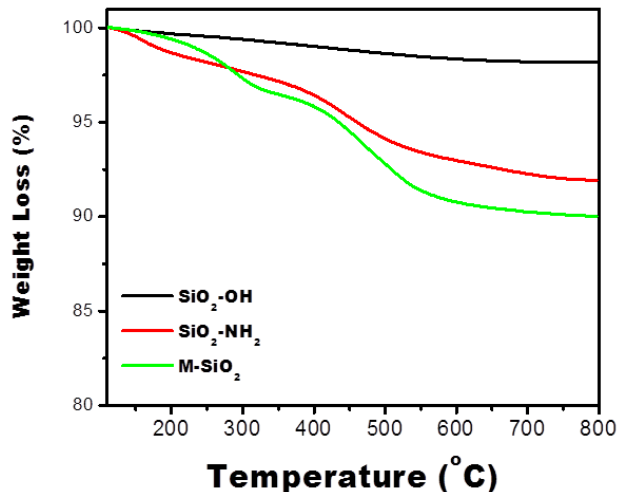


Figure S2. Thermogravimetric analysis (TGA) of silica and mesogen functionalized SiO₂ nanoparticles with a heating rate of 10 °C/min.

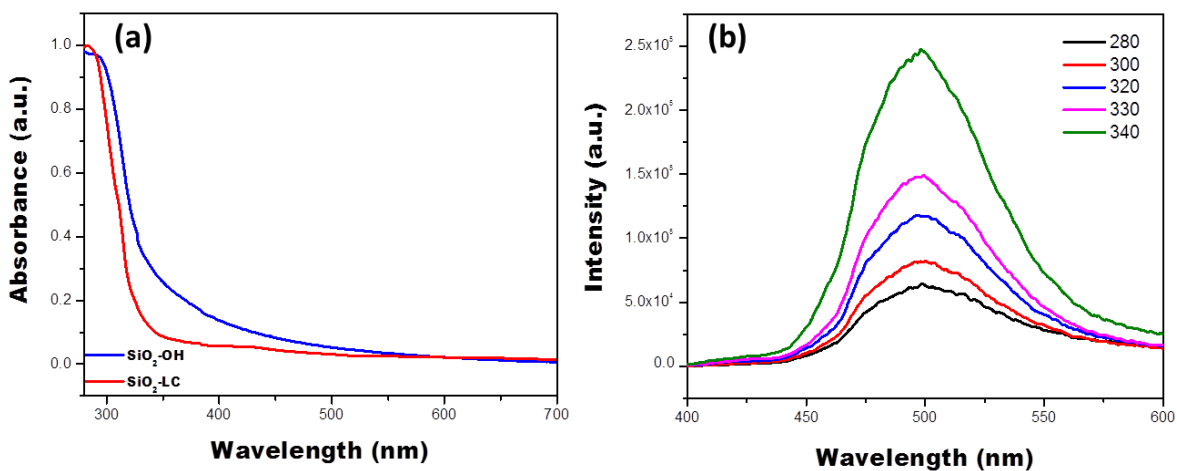


Figure S3. (a) UV-Visible spectra of SiO₂-OH nanoparticles in water (blue line) and hybrid M-SiO₂ nanoparticles in chloroform (red line), and (b) Photoluminescence spectra of M-SiO₂ nanoparticles under different excitation wavelength in CHCl₃.

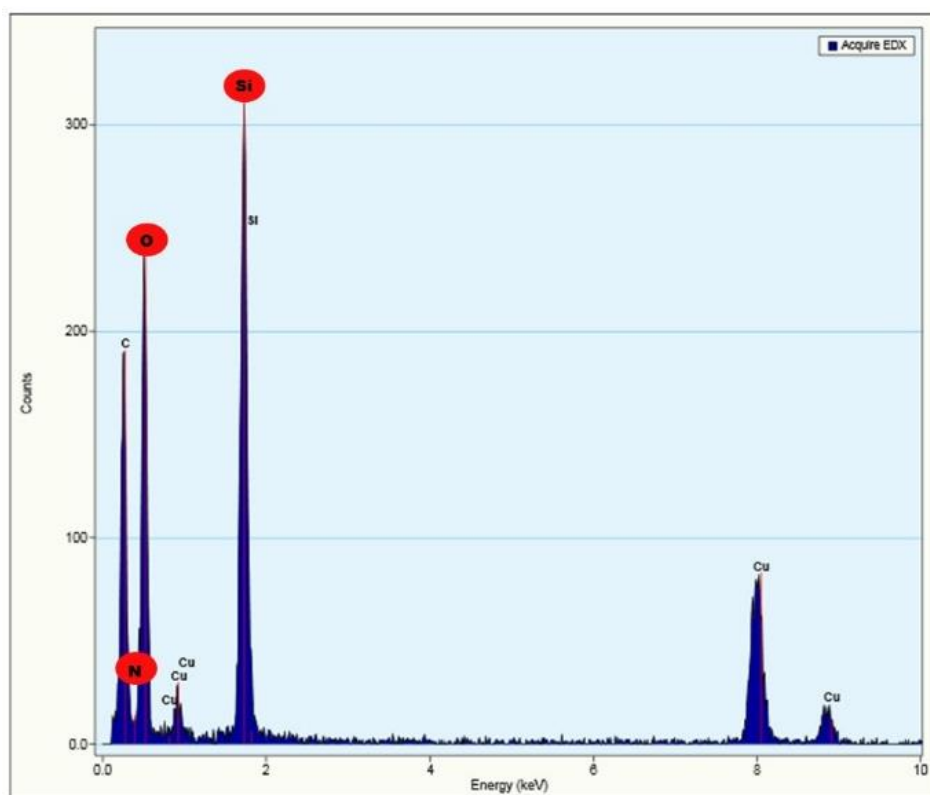
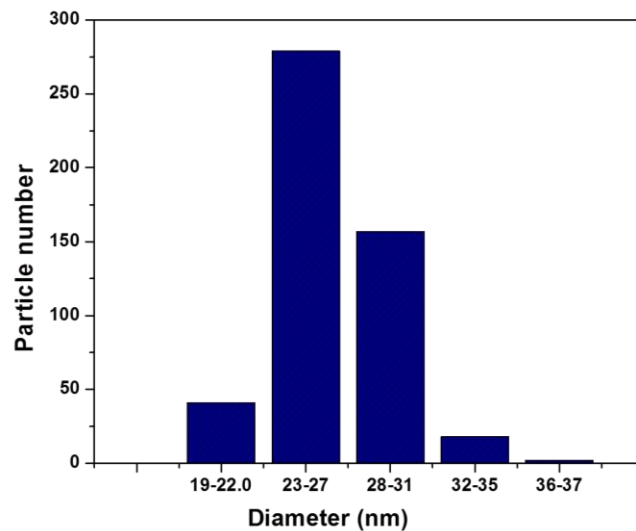


Figure S4. Top: Size distribution of the M-SiO₂ nanoparticles calculated from TEM images considering 500 nanoparticles. The mean diameter of M-SiO₂ nanoparticles is 26.97±2.92 nm. Bottom: Energy-dispersive X-ray (EDX) spectrum of M-SiO₂ nanoparticles featuring significant elements (Si, O and N) present in the mesogen-grafted nanoparticles.

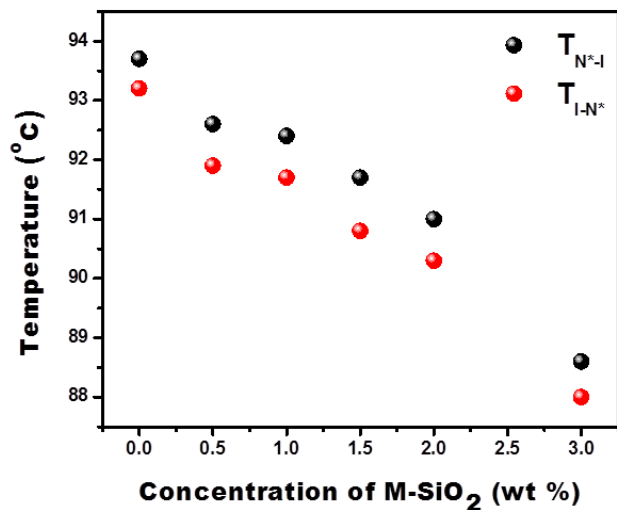


Figure S5. Cholesteric (N*)-Isotropic (I) and I-N* phase transition temperatures of M-SiO₂ doped DFCLC nanocomposites. Note: The phase transition temperatures were measured using a hot stage under a POM with a heating or cooling rate of 0.2°C/min. The measurements were repeated three times and averaged to report the final data.

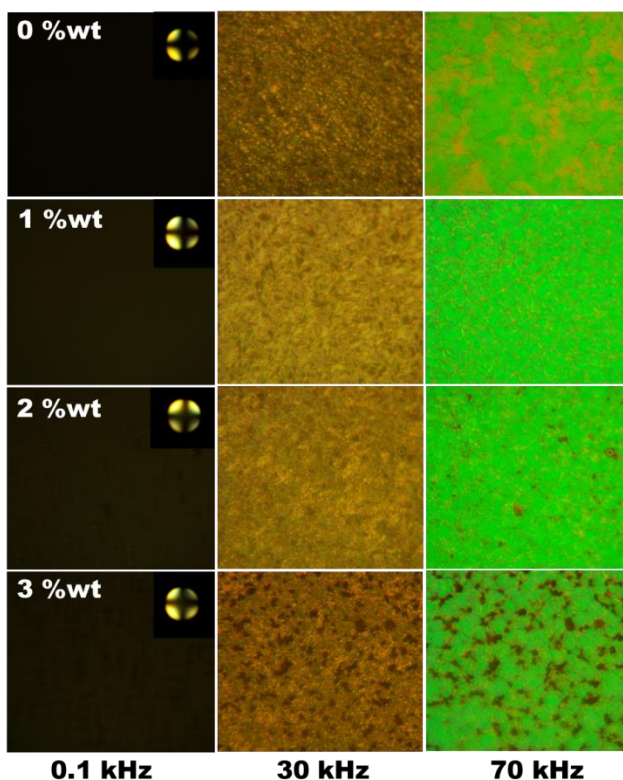


Figure S6. Polarized optical microscopy textures of M-SiO₂ /DFCLCs nanocomposites at different frequencies of the AC field developing the homeotropic (left), focal conic (middle) and planar (right) states. Inset: conoscopic observations of the homeotropic state.

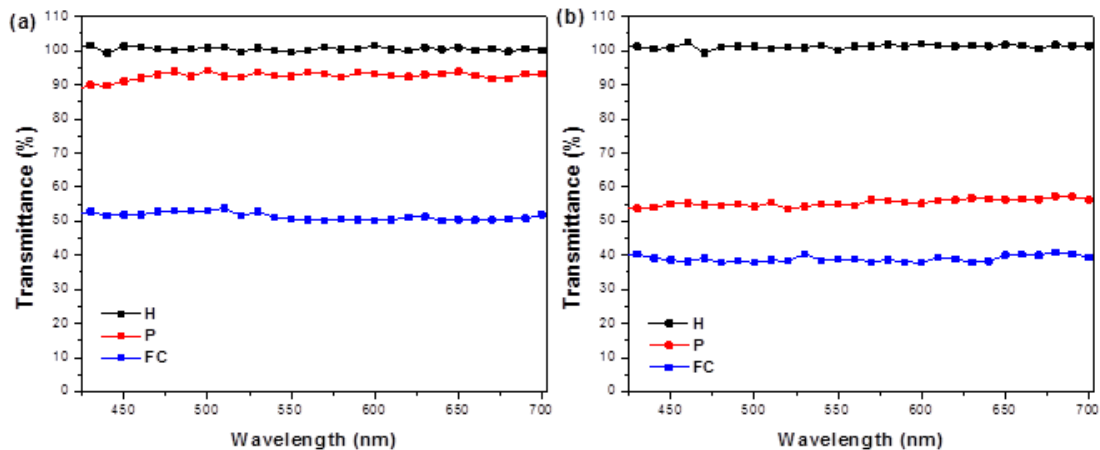


Figure S7. Transmission spectra of the three different states: Homeotropic (H, 0.1 kHz), Focal Conic (FC, 30 kHz) and Planar (P, 70 kHz) for (a) the pure DFCLC host and (b) DFCLC host doped with 2 wt% M-SiO₂ nanoparticles.

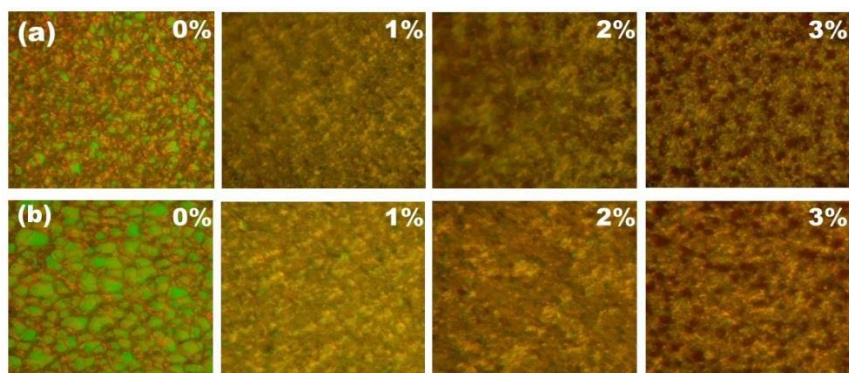


Figure S8. POM textures of M-SiO₂/DFCLC nanocomposites with different nanoparticle concentrations in the focal conic state after (a) 5 minutes and (b) 3 days of removing the electric field at 30 kHz.

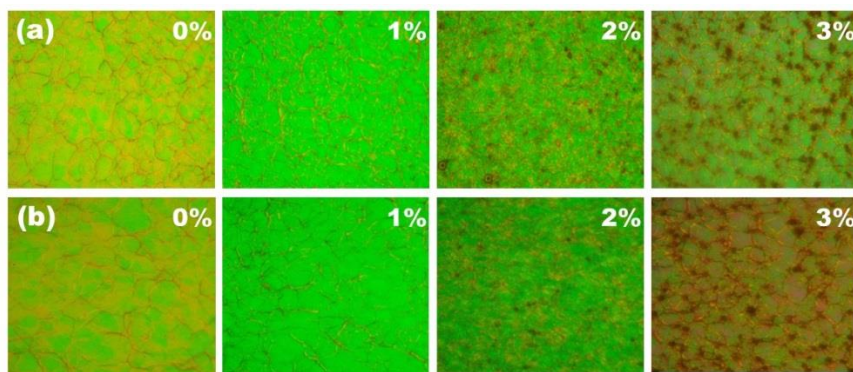


Figure S9. POM textures of M-SiO₂/DFCLC nanocomposites with different nanoparticle concentration in the planar state after (a) 5 minutes and (b) 3 days of removing the electric field at 70 kHz.

References

1. a) H. –S. Jung, D. –S. Moon, J. –K. Lee, *J. Nanomater.* **2012**, 593471; b) C. Li, J. Han, C. Y. Ryu, B. C. Benicewicz, *Macromol.* **2006**, 39, 3175.
2. Y. Deligiannakis, G, A. Sotiriou, S.E. Prastinis, *ACS Appl. Mat. Interfaces*, **2012**, 4, 6609.