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DNA thermotropic liquid crystals controlled by positively charged catanionic bilayer vesicles†

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I. Experimental section

I.1. Chemicals and materials. Anionic surfactant, sodium laurate (NaL), was purchased from Fluka Chemika AG, and used without further purification. Cationic surfactants, dodecyltrimethyl-ammonium bromide (DTABr) and 1-dodecylpyridinium bromide (DPBr), were purchased from J&K Chemical Co. Ltd and used without further purification. Cationic surfactant, (11-ferrocenylundecyl)-trimethylammonium bromide (FTABr) was synthesized as previously reported.[1] Salmon testes double-strand DNA (dsDNA) sodium salt with 125 base pair (125 bp) was obtained from Acros (Fairlawn, NJ. The single-stranded DNA stock solution (125 bp) was prepared by thermal degradation of dsDNA solution at 95 °C for 45 min and then being immediately dipped into ice bath for fast cooling to prevent renaturation. The secondary structure of ssDNA has no significant changes compared with dsDNA (Fig. S1).

Ultrapure water was used with a resistivity of 18.2 MΩ·cm from a UPH-IV water purifier.

I.2 Sample preparation. The final concentration of positively charged catanionic vesicles (DTABr + NaL → DTAL + NaBr) was 5.0 mM DTABr and 2.0 mM NaL and equilibrated for about 1 month at 25 ^{o}C before mixing with ssDNA. A stock ssDNA solution of 10.0 mM was prepared. 5 mL DTAL vesicle solution was added into several tubes and different volumes of stock ssDNA solution were dropped in these tubes. The total volume of the solution was 10 mL. The concentration of ssDNA was from 0.5 to 5.0 mM. When positively charged cationic DTAL vesicles were mixed with

ssDNA solution, the insoluble complexes, DNA-DTAL precipitates form. The obtained DNA-DTAL precipitates were centrifuged at 12000 rpm for 30 min to remove the water and the DNA-DTAL complex solution can be obtained. Finally, the DNA-DTAL complexes were lyophilized at -65 °C for 24 h before further characterization.

DNA-DPL and DNA-FTAL complexes were prepared essentially in the same manner as described for DNA-DTAL complexes.

I.3 Cryo transmission electron microscopy (cryo-TEM) observations of positively charged catanionic vesicles. A drop of sample solution (~4 μL) was dropped on a grid in a high humidity environment (> 90%). The excess sample was blotted up by using two pieces of blotting paper, leaving a thin film sprawling on the grid. Then the grid was quickly plunged into liquid ethane which was liquefied with liquid nitrogen. The vitrified sample was transferred into a sample holder (Gatan 626) and observed on a JEOL JEM-1400 TEM which was operated at 120 kV. The images were recorded on a Gatan multiscan CCD.

I.4 Freeze-fracture transmission electron microscopy (FF-TEM) observations of DNA-DTAL liquid crystals. FF-TEM measurements were carried out to obtain microstructures of DNA-DTAL liquid crystals at c_{DNA} = 1.8 and 5.0 mM, respectively. For the solid sample (~0.1 g) of DNA-DTAL complexes after dehydration and freeze drying were placed in specimen carries and closed to be heated at 70 °C for storage 1 week to reach equilibrium. The specimen carrier was inserted rapidly into the liquid ethane at -175 °C which was cooled with liquid nitrogen. After that, under a condition of -175 °C and 10^{-7} Pa, the DNA-DTAL samples were fractured and replicated by using the Leica EM BAF 060 equipment. Pt/C at 45° and C at 90° were

sprayed onto the fracture surface forming a 2.5 nm thick film. The replicas were observed with a JEOL JEM-1400 electron microscope operating at an accelerating voltage of 120 kV.

I.5 Small-angle X-ray scattering (SAXS). SAXS measurements were performed using a SAXSess MC2 high flux SAXS instrument (Anton Paar, Austria, Cu Kα, λ = 0.154 nm), equipped with a Kratky block-collimation system and using an image plate (IP) as the detector.

I.6 Zeta potential measurements. The zeta potential of the vesicle/DNA complex supernatants was measured by using the Malvern zetasizer ZS with a DTS1070 folded capillary cell. Each sample was determined three times at 25 °C.

I.7 Polarization optical microscopy (POM) observations. The birefringent textures of samples were characterized on a Carl Zeiss Axioskop 40 light microscope (Jena, Germany).

I.8 Fourier transform infrared spectroscopy (FT-IR) measurements. The FT-IR spectra were measured on a VERTEX-70/70v FT-IR spectrometer (Bruker Optics, Germany). Spectra over 4000-400 cm^{-1} were obtained by taking 64 scans with a final resolution of 4 cm^{-1}. Spectral manipulation was performed by the OPUS 6.5 software package (Bruker Optics, Germany).

I.9 Rheological characterization. The rheological experiments were measured on a Haake RheoStress 6000 rheometer with a vertebral plate sensor system. In oscillatory measurements, an amplitude sweep at a fixed frequency of 1 Hz was carried on to ensure that the selected stress was in the linear viscoelastic region. The viscoelastic properties of the vesicle/DNA complexes were acquired by oscillatory

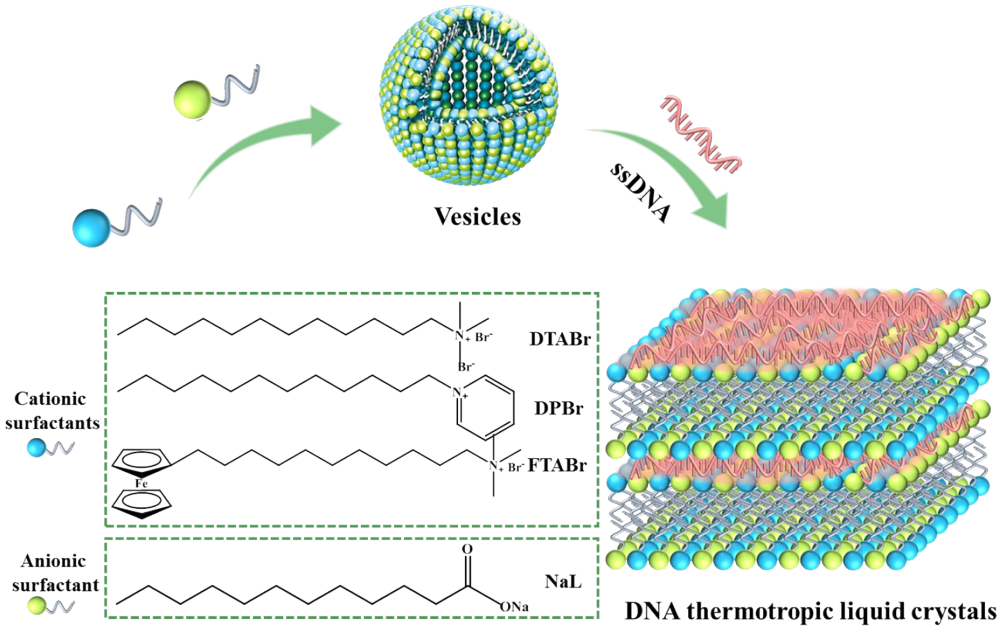
measurements in the frequency range of 0.1-10 Hz.

I.10 Thermal gravity analysis (TGA). TGA was measured by a Rheometric Scientific TGA1500 (Piscataway, NJ) to investigate the thermal properties of the vesicle/DNA complexes. Measurements were carried out under nitrogen using 8-10 mg samples with a heating rate of 10 °C/min from room temperature to 600 ^{o}C.

I.11 UV-visible absorbance spectra. A U-4100 UV-visible spectrometer was employed to examine the UV spectra of DNA. All solutions were filled in 10 mm path length cells, and the scanning wavelength ranged from 220 nm to 320 nm at a scan rate of 400 nm/min.

I.12 Circular dichroism measurements (CD). The CD spectroscopy was measured by a JASCO J-810 spectropolarimeter. Vesicle/DNA complex supernatants were located in 1 mm path length cells, and the scanning speed was controlled at 200 nm/min with the measuring range of 220-320 nm. Each sample was measured three times.

II. Supplementary Figures and Tables



Scheme S1. Formation process of the long range ordered DNA-catanionic surfacatnt complexes from positively charged catanionic bilayer vesicles and DNA. Single-tailed cationic surfactants, dodecyltrimethylammonium bromide (DTABr), 1-dodecylpyridinium bromide (DPBr), (11-Ferrocenylundecyl)-trimethylammonium bromide (FTABr), and anionic sodium laurate (NaL) were selected for constructing positively charged catanionic bilayer vesicles, respectively.

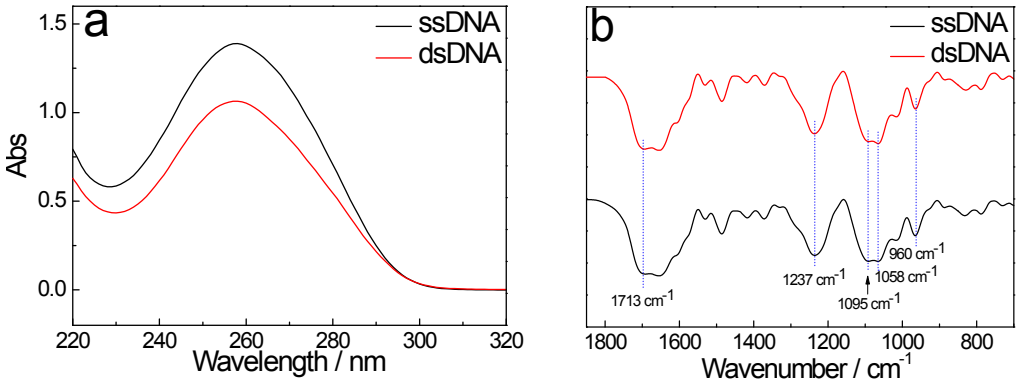


Fig. S1. UV-visible (a) and FT-IR (b) spectra of ssDNA and dsDNA.

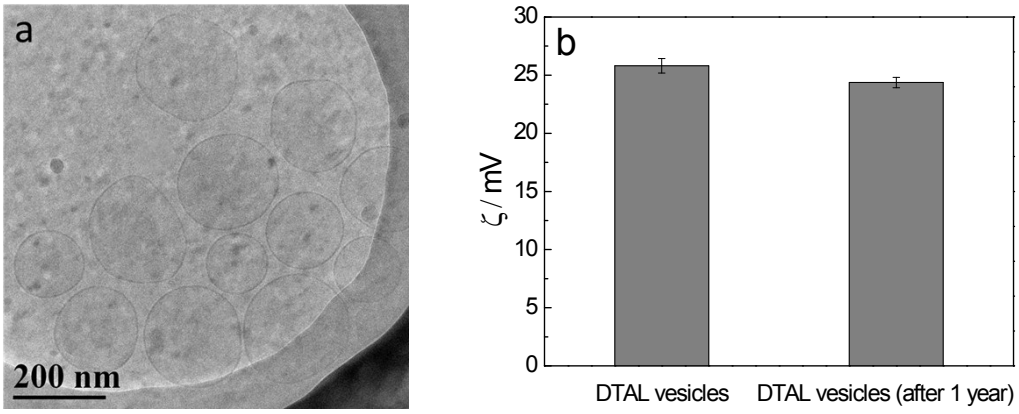


Fig. S2. The cryo-TEM image (a) and zeta potential (b) of DTAL vesicles stored at room temperature for one year. The size and spherical structures of the vesicles have not changed significantly, and the zeta potential is basically unchanged from 25.8 ± 0.6 mV to 24.4 ± 0.5 mV after one year, which strongly illustrated the stability of DTAL vesicles.

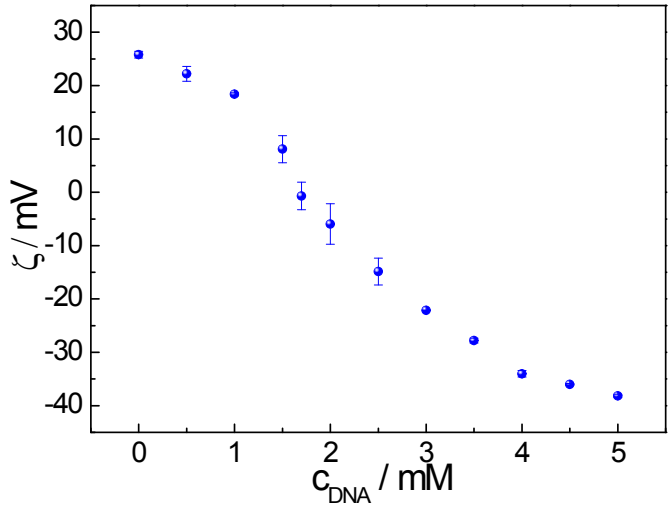


Fig. S3. Zeta potentials of DTAL complexes at different DNA concentrations.

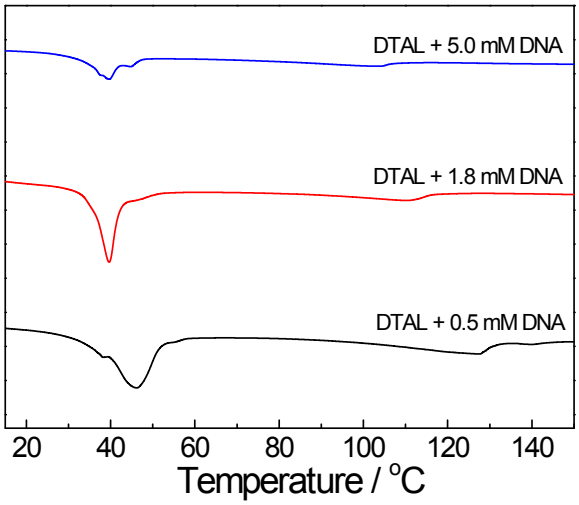


Fig. S4. DSC results of DNA-DTAL complexes with different DNA concentrations.

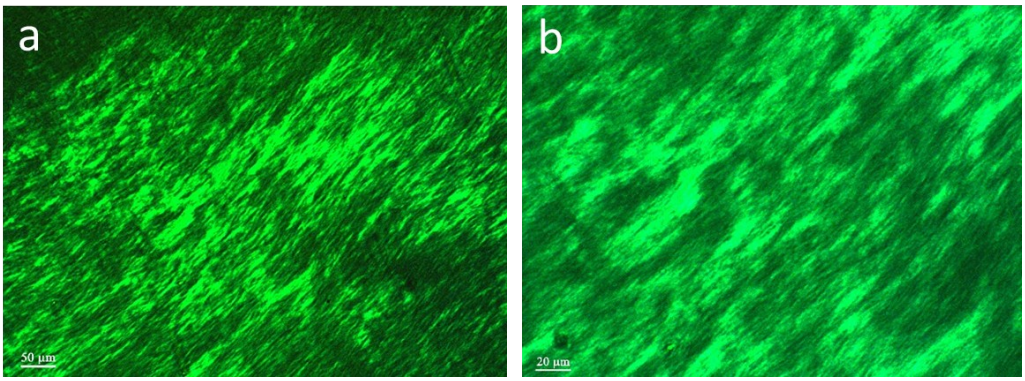


Fig. S5. Typical POM images of DNA-DTAL liquid crystals at c_{DNA} = 1.8 mM, T = 70 °C.

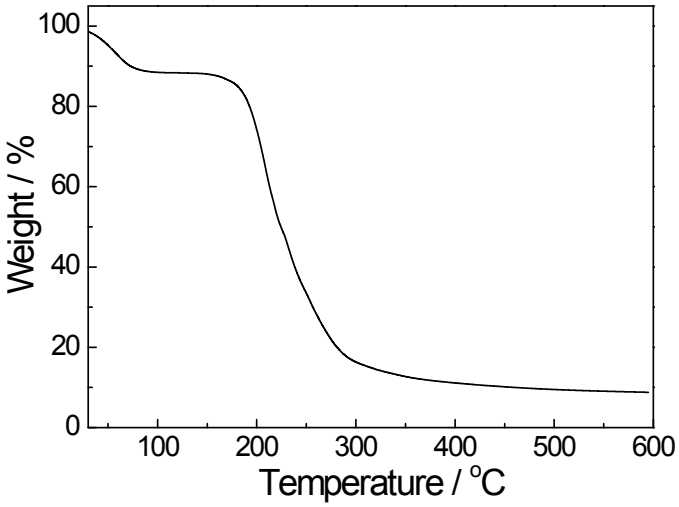


Fig. S6. TGA analysis of the DNA-DTAL complexes with c_{DNA} = 1.8 mM.

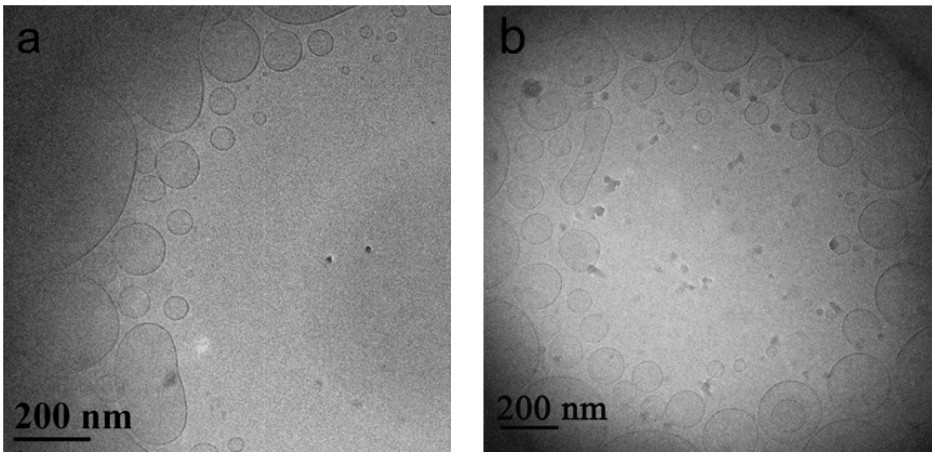


Fig. S7. Cryo-TEM images of positively catanionic bilayer vesicles of DPL (a) and FTAL (b), $c_{cationic}$ = 5.0 mM and $c_{anionic}$ = 2.0 mM.

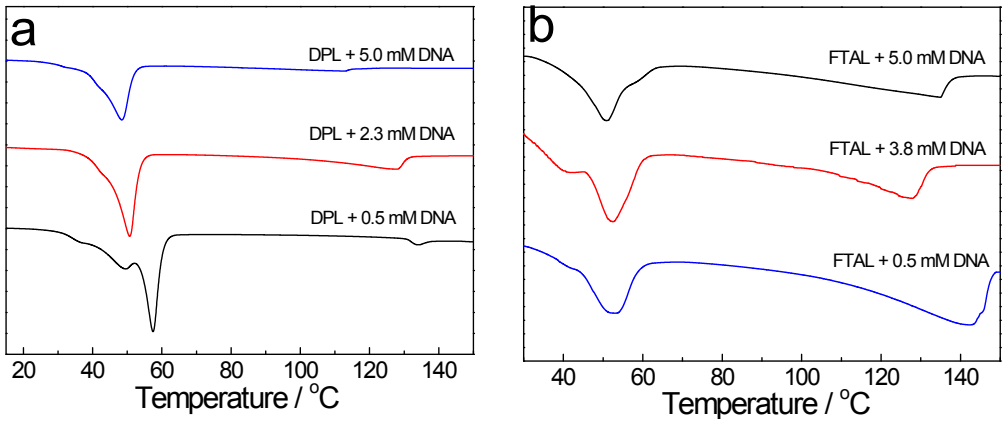


Fig. S8. DSC results of DNA-DPL (a) and DNA-FTAL (b) complexes with different DNA concentrations.

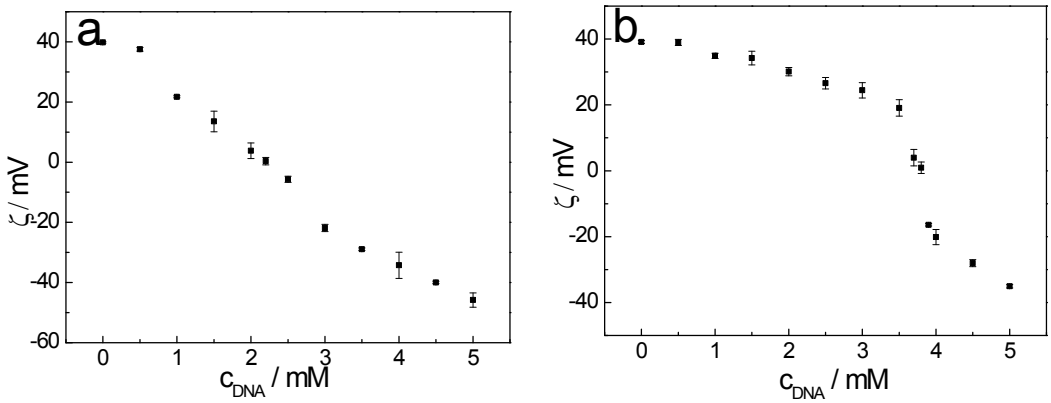


Fig. S9. Zeta potentials, ζ, of DNA-DPL (a) and DNA-FTAL (b) systems at different DNA concentrations.

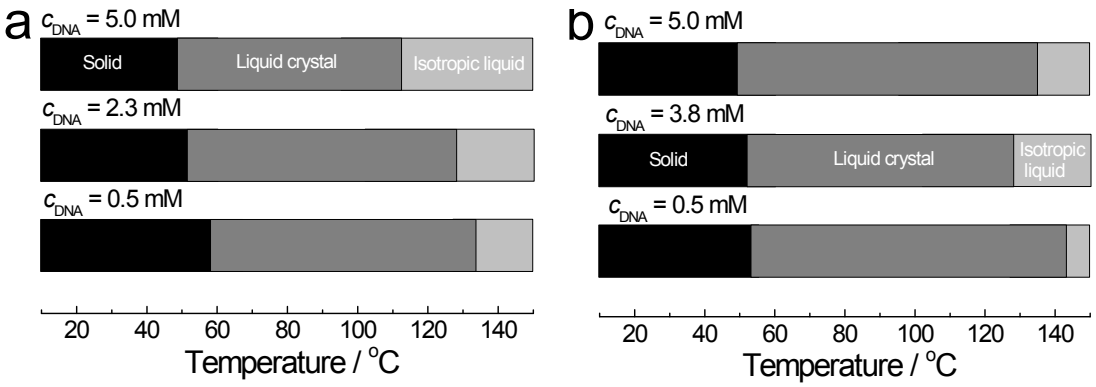


Fig. S10. Phase diagrams of DNA-DPL (a) and DNA-FTAL (b) complexes from the amorphous solid to thermogenic liquid crystal and then to isotropic liquid with the increase of temperature at three DNA concentrations.

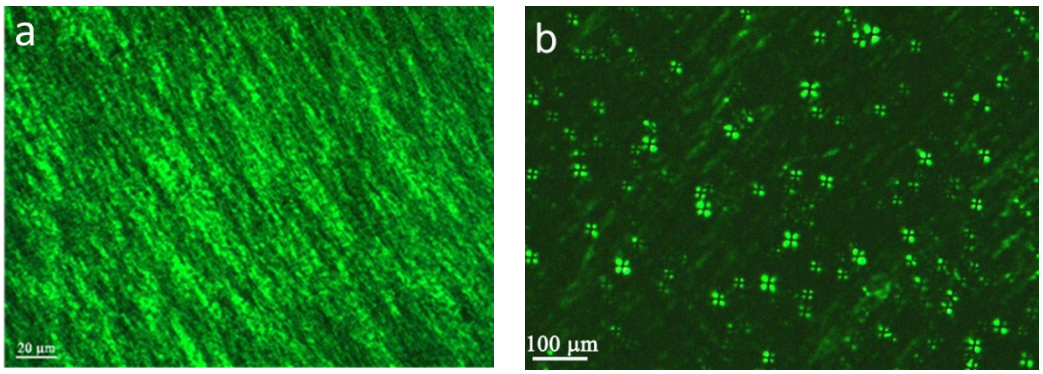


Fig. S11. Typical POM images of DNA-DPL (a) and DNA-FTAL (b) for thermogenic liquid crystals at c_{DNA} = 2.3 and 3.8 mM, T = 70 °C.

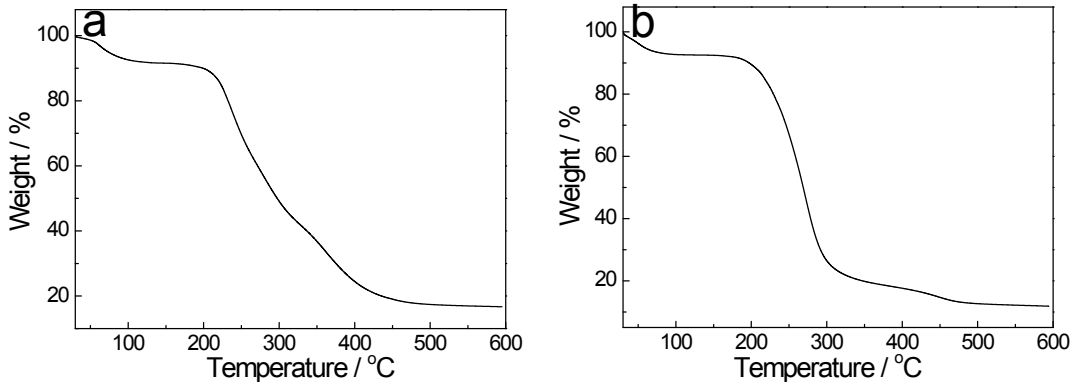


Fig. S12. TGA analyses of the DNA-DPL (a) and DNA-FTAL (b) complexes with c_{DNA} = 2.3 and 3.8 mM, respectively.

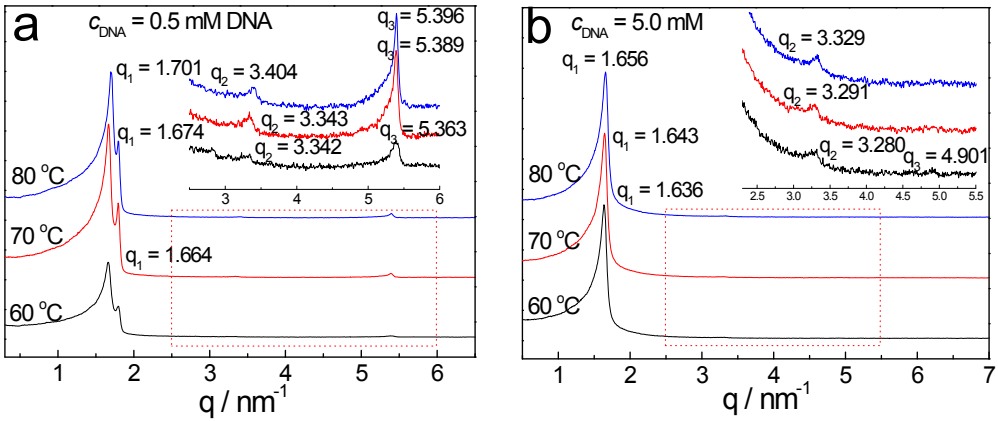


Fig. S13. Representative SAXS patterns of DNA-DTAL complexes with different DNA concentrations, c_{DNA} = 0.5 (a) and 5.0 mM (b) within liquid crystal region, T = 60, 70 and 80 °C.

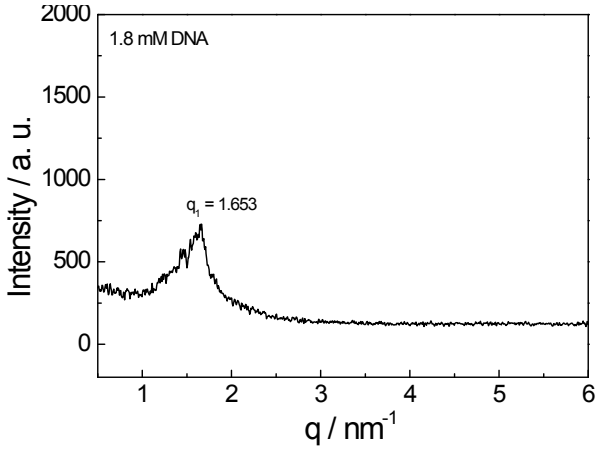


Fig. S14. SAXS pattern of DNA-DTAL complex at 25 °C, c_{DNA} = 1.8 mM.

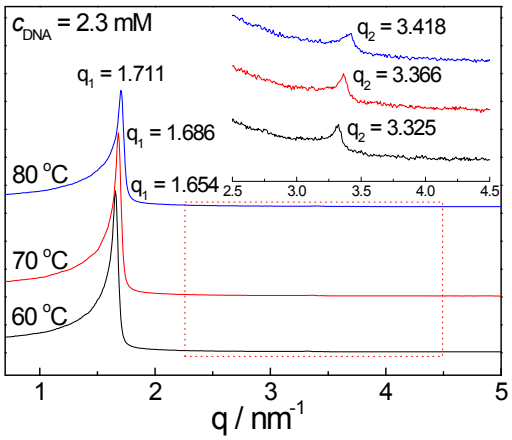


Fig. S15. Representative SAXS pattern of DNA-DPL complex with c_{DNA} = 2.3 mM at ζ = 0 mV.

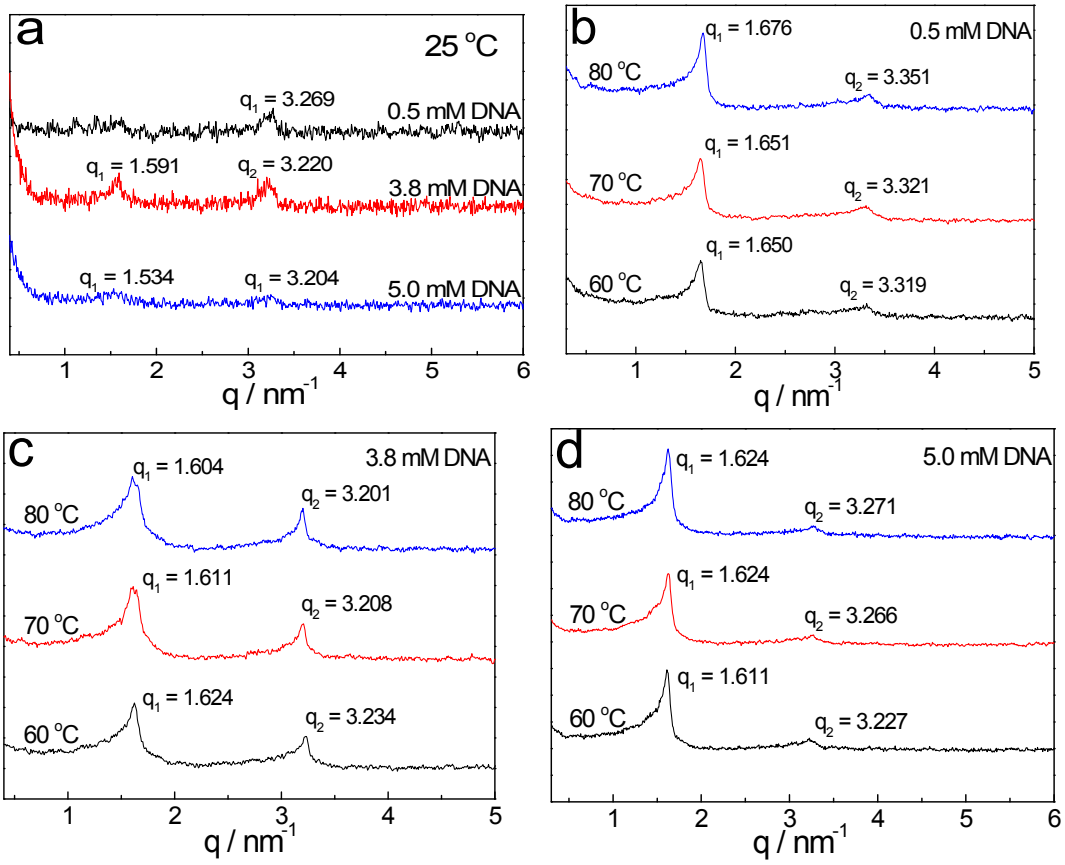


Fig. S16. Representative SAXS patterns of DNA-FTAL complexes with different DNA concentrations at T = 25 °C (a) outside the liquid crystal region, 60, 70 and 80 °C within the liquid crystal region.

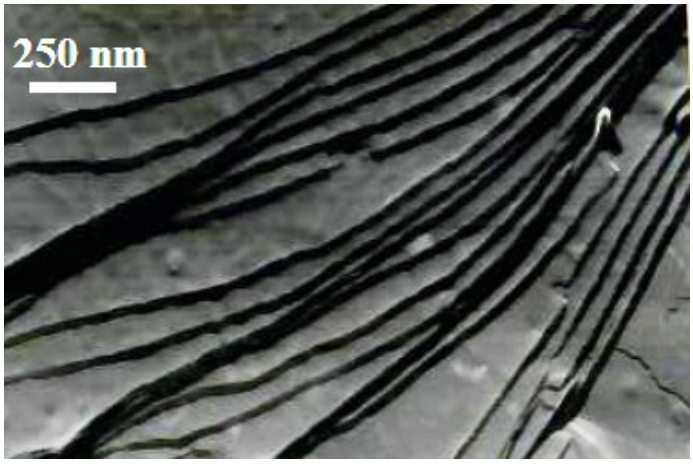


Fig. S17. A typical FF-TEM image of DNA-DTAL thermotropic liquid crystals with c_{DNA} = 5.0 mM, c_{DTABr} = 5.0 mM and c_{NaL} = 2.0 mM.

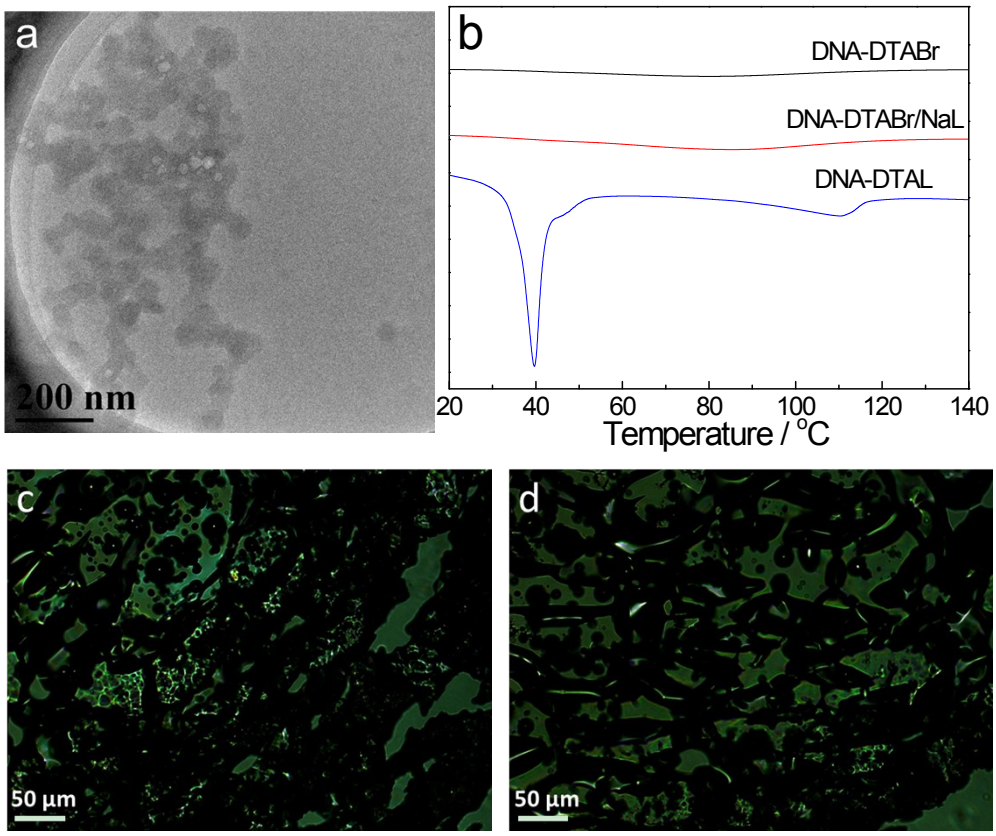


Fig. S18. A typical cryo-TEM image of DNA-DTABr solution (a), the DSC spectra of DNA-DTABr, DNA-DTABr/NaL and DNA-DTAL (b). Representative POM images for DNA-DTABr (c) and DNA-DTABr/SL (d) at 70 °C. The complexes were dehydrated.

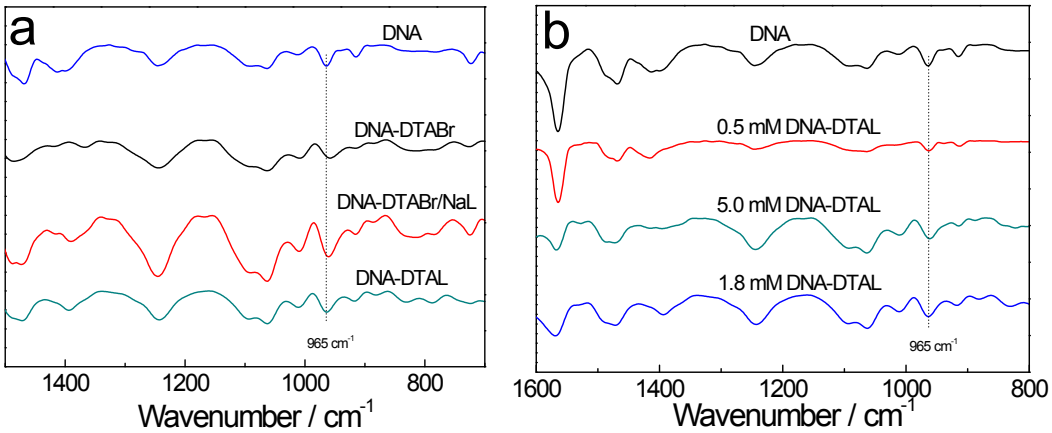


Fig. S19. (a) FT-IR spectra of DNA-DTABr, DNA-DTABr/NaL, and DNA-DTAL systems, c_{DNA} = 1.8 mM, c_{DTABr} = 5.0 mM and c_{NaL} = 2.0 mM. (b) FT-IR spectra of DNA-DTAL complexes with different DNA concentrations.

References

1 T. Saji, K. Hoshino, Y. Ishii and M. Goto, *J. Am. Chem. Soc.* 1991, **113**, 450-456.