Infrared Near-field Imaging and Spectroscopy of Sunset Yellow MADQUAT Polymer Liquid Crystals

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(Dated: August 12, 2016)

Previous studies have demonstrated storing digital information in DNA, however a simpler synthetic analogue of DNA may be better suited. A liquid crystal mixture mimicking DNAs structure would allow for information storage as well as a better understanding of its counterparts properties. Scattering scanning near-field optical microscopy (*s*-SNOM) and spectroscopy are promising measurement techniques for studying this synthetic DNA. *s*-SNOMs ability to identify the individual components in the liquid crystal structure makes this measurement technique favorable. We report here on preliminary measurements which show unexpected resonance peaks between synthetic DNA components, and interesting crystal formation.

I. INTRODUCTION

Though DNA information storage has been demonstrated in the past[1], a functioning synthetic DNA analogue has yet to be demonstrated. Replacing both the nucleotides and the sugar-phosphate back bone of the DNA with two alternatives components could result in a functioning analogue. This analogue holds potential for information storage, better understand of its counterpart, and perspective in the natural evolution of DNA.

DNAs nucleotides are hydrophobic while its sugar-phosphate backbone is hydrophilic, similarly to form such a structure the involved liquid crystals must have the same properties. Commonly used as a food dye, Sunset Yellow FCF (disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate) is ideal for replacing the DNAs nucleotides. While Sunset Yellow alone does not produce any ordered structure, in combination with MADQUAT (poly(2-dimethylamino)ethyl methacrylate) methyl chloride quaternary salt) polymer an ordered structure does occur. Sunset Yellow and this polymer produce a liquid crystal that have similar structure to DNA during its discotic phase[2]; when LCs orient themselves in a cylindrical structure. The hydrophobic Sunset Yellow is encapsulated by the hydrophilic MADQUAT polymer. The polymer is hypothesized to wrap around the stacking Sunset yellow molecules (figure 1) similar to the double helix structure seen in DNA[3].

FIG. 1. Hydrophilic Sunset Yellow FCF surrounded by a MADQUAT polymer in a double helix structure similar to DNA.

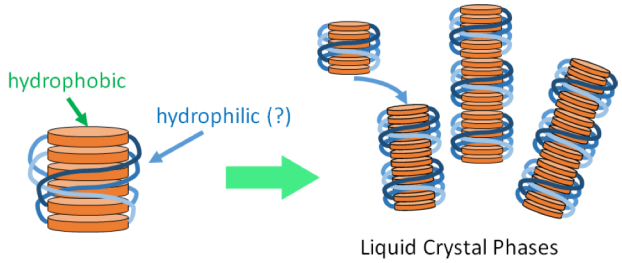
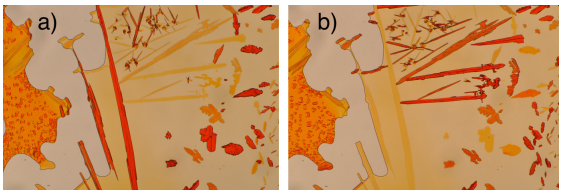


FIG. 2. Light polarization shows birefringent properties of crystals indicating stacking structure. a) Horizontal b) Vertical



Although it is clear that the MADQUAT polymer and Sunset Yellow molecules have distinct properties when combined (figure 2), it is unclear how the components co-crystallize. Studies on liquid crystallization of DNA[4] have suggested ideas on how this ordered stacking occurs, however it is unclear if these findings apply to its Sunset/MATQUAT synthetic counterpart. In order to further understand this interaction and structure use *s*-SNOM (Scattering Scanning Near-Field Optical Microscopy). This measurement technique allows for nanoscale resolution. While X-ray crystallography would be useful, the small crystal sizes of the samples make *s*-SNOM a favorable measuring technique. *s*-SNOM is also useful in identifying the individual components isolated or mixed which is ideal for studying synthetic liquid crystals co-crystallization.

II. EXPERIMENTAL

A. AFM Topography

Two measuring techniques are used in order to make observations on the sample. The first, AFM topography, was used to identify the crystals height and morphology (figure 3). The system can make these measurements

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through the position of the tip relative to the sample. As the sample moves in a raster pattern a beam reflects off the top of the cantilever and into a detector, relaying the height and morphology at each location. This method is often used to locate and characterizes the morphology of the liquid crystal mixture.

FIG. 3. AFM Topography: Tip located underneath cantilever. Samples platform moves horizontally, while cantilever tapping is done vertically.

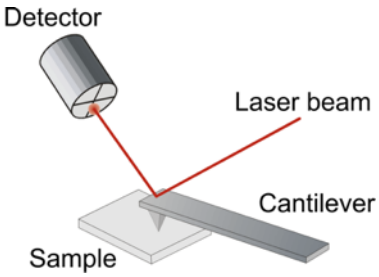
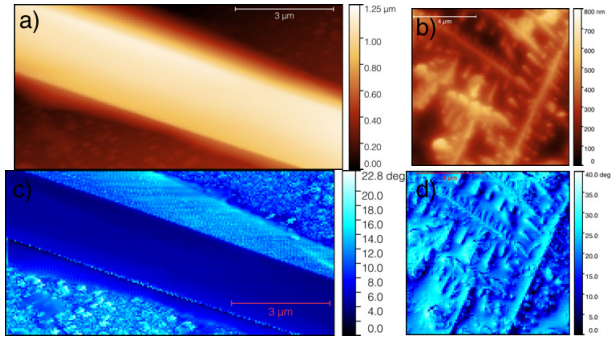


FIG. 4. AFM topography data shows two sample heights (a, b) as well as tip tapping phase (c, d). Different crystal formations can be seen, shown images from same sample. Details as to how specific crystal formations occur is unclear.



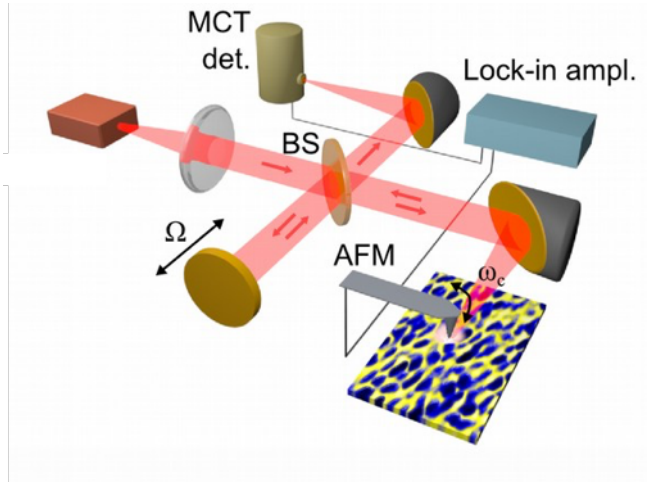
B. Nano-spectroscopy

The second measurement technique used was through Scattering Scanning Near-field Optical Microscopy (*s*-SNOM). *s*-SNOM uses the same metal tip in AFM topography to enhance scattered radiation in the near-field of the sample. The radiation carries information about the nano-scale optical properties of the sample such as the amplitude and phase.

This technique uses two non-linear process in order to convert our 1064nm pump laser into a mid-infrared wavelength specific to our sample. A mode-locked femtosecond Erbium oscillator laser pumps through an Optical Parametric Oscillator (OPO), producing tunable near infrared signal and idler beams by a periodically fanned polled lithium niobate (PPLN) crystal. The signal and idler then recombine in a $AgGaS_2$ crystal, producing tunable mid infrared pulses by difference frequency generation.

This beam is sent through a beam splitter in which half the light is directed to the sample while the other half is sent to a reference arm. Using the same tip and cantilever as used in the AFM topography, this time we position our beam to illuminate the region between the sample and the tip. The tip allows for the scattered radiation to be amplified and near-field information stored in the beams wavelength. After interacting with the sample the scattered radiation is sent back to the beam splitter where its path meets with the other initial half. The reference arm moves back and forth for interferometric detection of the near-field signal.

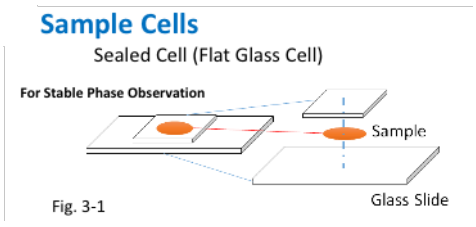
FIG. 5. Schematic of *s*-SNOM. Beam path split between reference arm and sample, later recombines into MCT detector.



III. SAMPLE PREPARATION

We drop-cast the Sunset Yellow and polymer on glass, BaF_2, and Au substrates. Au drop casting was eventually adopted as it produced clearer results during nano-spectroscopy. This was due to Aus strong, broadband, non-resonant optical response. Samples were placed between two slides, then heated until all the water evaporated. During the evaporation process it was observed that the crystallization of the Sunset Yellow and the MADQUAT polymer appeared when there was 10% or less water present. Samples were completely dried before measurement.

FIG. 6.



IV. RESULTS

FIG. 7. Sunset Yellow FCF and MADQUAT polymer FTIR spectrum.

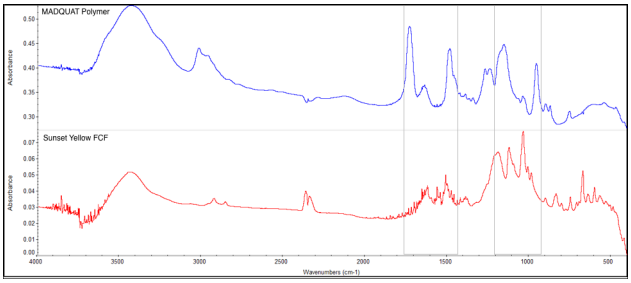
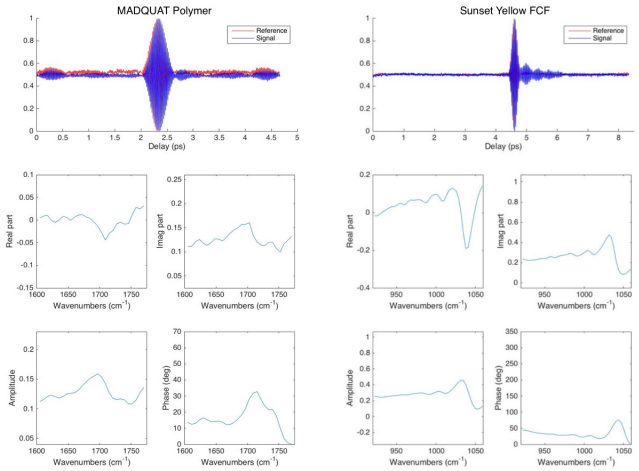


FIG. 8. Blue in interferogram graphs are result of sample resonances, red are Au substrate reference resonances. (Right) Interferogram data from Sunset Yellow sample, Fourier transform results in graphs below. Same peaks visible in sample and FTIR data. (Left) Interferogram data from MADQUAT polymer, same peaks visible in FTIR data. Polymer resonance weaker than Sunset Yellow. Symmetrical ends in interferogram due to water lines.

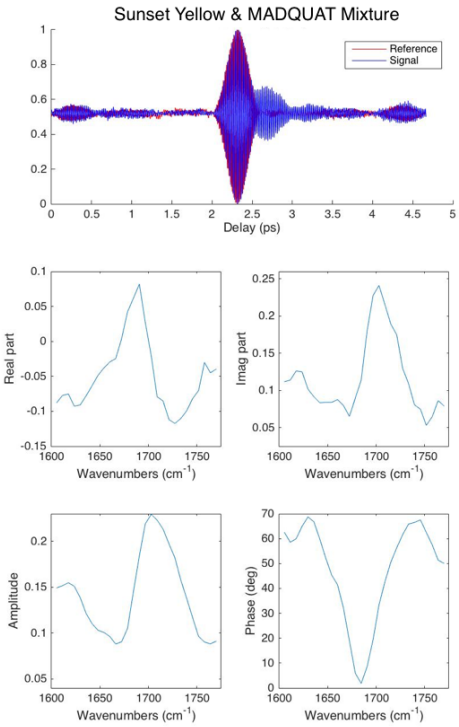


The resulting information from the *s*-SNOM measuring technique is in the form of an interferogram. An interferogram is the resulting interference between the reference beam and the beam which interacted with our sample. When combined properly a scan revealing the interaction between the sample and the beam is shown, as is visible at the top of figure 8 9. The interferogram data can be Fourier transformed to create a spectrum and comprehend the data more easily, as shown at the bottom of figure 8 9. To be able to further investigate how the Sunset Yellow and MADQUAT polymer interact with one another, we begin by measuring them individually. The results were then compared to far-field measurements collected using Fourier Transform infrared spectroscopy (FTIR) (figure 7) of the samples prepared using a powdered version of the sample in a KBr pellet.

s-SNOM spectra (figure 7) reveal a peak around 1030 cm-1, the same peak is visible in the FTIR spectrum for Sunset Yellow. In Fig. 10 a peak around 1700 cm-1 is shown, the FTIR spectrum for the MADQUAT polymer reveals an identical one. As expected we were able to clearly identify both the Sunset Yellow and the MADQUAT polymer on their own. It is important to mention here that the Sunset Yellow had a far stronger signal when compared to the MADQUAT polymer by itself. This implies that these same peaks and signal strengths should be seen in the crystal mixture.

The following step was an identical measurement except on the crystal mixture itself. While one would expect that the Fourier transform would reveal the same data as seen when the two components were measured by themselves, this was not the case. The result was that we saw very little Sunset Yellow signal if at all, and instead a MADQUAT signal far stronger than when it had been measured alone.

FIG. 9. Sunset Yellow and MADQUAT Polymer mixture interferogram. Reveals strong carbonyl resonance, signal is stronger than when polymer is alone. It is difficult to tell if any of the Sunset Yellow FCF spectra is visible in the data.



V. CONCLUSIONS

A study of this synthetic DNA could help understand some of its original counterparts properties. Addition-

ally, similar to how DNA stores information, this liquid crystal has the potential to do so as well. AFM topography revealed new and previously unknown crystal structures and morphology. Followed by the *s*-SNOM measurements we find that clearly an interaction between the Sunset Yellow and the MADQUAT polymer is occurring. In the future more trials will be performed to insure the above data is accurate. We will also extend this work to explore additional DNA mimetic materials and liquid crystal forming molecule-polymer mixtures.

VI. ACKNOWLEDGEMENTS

I would like to thank Prof. Markus Raschke, Prof. Noel Clark and the REU program as a whole for allowing me to do this research. I thank and appreciate all the help from the graduate students in the Raschke group. Special thanks to Eric Muller, Ben Pollard, and Akihiro Yamaguchi for putting time and effort into this project.

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