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To whom it may concern,

Enclosed is the final technical report with SF298 prepared for the project titled "Scanning Tunneling Microscopy and Spectroscopy of Liquid Crystal Thin Films". This work was supported under the award number N00173-19-1-G021.

I hope you will find our findings exciting. Let me know if you need additional information from me.

Thank you for your consideration!

Sincerely,

Pavithra Pathirathna

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This project aims to obtain topographical images of a liquid crystal material, 4'-pentyl-4-cyanobiphenyl (5CB), on a single layer of graphene on silicon carbide (SiC) using a scanning tunneling microscope (STM). Based on the high-resolution STM images, it is apparent that anchored 5CBs on the graphene layer is arranged in a single-row arrangement. The length of alkyl chains was also calculated (~7 Å) using the STM images. It is in good agreement with what is reported in the literature, thus confirming our predicted molecular arrangement.

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Liquid crystal, 4'-pentyl-4-cyanobiphenyl (5CB), Scanning tunneling microscope, Single-row arrangement

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Scanning Tunneling Microscopy and Spectroscopy of Liquid Crystal Thin Films

FINAL TECHNICAL REPORT

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Prepared For:

Defense Technical Information Center

December 2021

CONTENTS

EXECUTIVE SUMMARY

This project aims to obtain topographical images of a liquid crystal material, 4'-pentyl-4-cyanobiphenyl (5CB), on a single layer of graphene on silicon carbide (SiC) using a scanning tunneling microscope.

BACKGROUND

Understanding how liquid crystals (LC) align differently on various surfaces is an exciting research question in liquid crystal display industry. Surface imaging techniques such as scanning tunnelling microscopy (STM) have been a powerful tool to find answers to this question[1]. In STM, a sharp metal wire tip is brought very close to the imaging surface using a piezoelectric controller by applying a voltage to the sample or to the tip. When the tip is close enough, a bias voltage is applied that allows electrons to tunnel through the barrier (air, vacuum, etc.), resulting in tunnelling current. This current is dependent on the distance between the tip and the substrate, applied voltage, and the local density of states of the sample[2]. Moreover, when the tip is scanned over the surface, surface images can be drawn using the intensities of tunnelling current, thus making a powerful surface analysis technique.

Several STM-based studies have been performed to image LC on sample bases such as molybdenum disulfide (MoS_2) and highly oriented pyrolytic graphite (HOPG)[3–5]. MoS_2 has low conductivity; thus, obtaining a clear image of LC without interferences from the sample base is relatively easy. Conversely, HOPG is more conductive; hence, acquiring images of LC without having artifacts from the HOPG layer is challenging. In this study, we used a single layer of graphene on SiC, which has slightly different properties than HOPG.

Based on the arrangement of the LC molecules, they can be either found as a smectic or nematic phase[6]. While LC has a layered molecular structure in the smectic phase, no ordered structure is in the nematic phase. Furthermore, single-row(monolayer) structures are formed when cyanobiphenyl head groups and alkyl tails alternate in each row[3]. A double-row(bilayer) structure is formed when cyano groups are formed facing one another[3]. Consequently, based on the studies conducted with LC on MoS_2 and HOPG, it was proposed that these single-row and double-row arrangements are formed by anchoring structures from nematic and smectic phases, respectively[3,4]. It was also found that the phase sequence in the anchoring regions on MoS_2 can occur in both nematic and smectic phases depending on what occurs first (from high to low temperature). In contrast, the phase sequence in the anchoring region on HOPG occurs only in the smectic phase[3]. Furthermore, MoS_2 can form both single and double row structures, while HOPG only forms double row structures. However, it must be noted that SiC has single-layer graphene on top of silicon carbide; therefore, it is possible to result in a different arrangement of LC than what was observed with HOPG.

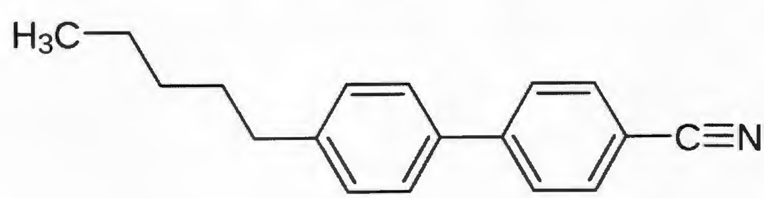

Figure 1: Chemical Structure of 4'-pentyl-4-cyanobiphenyl

The LC of interest in this experiment is 5CB. While there are STM studies conducted with higher cyanobiphenyls (CBs) such as 8CB, 10CB, etc[7]., to study the molecular arrangement on different sample bases, to the best of our knowledge, no STM study has been performed on 5CB on graphene/SiC surfaces. 5CB is nematic in bulk at room temperature. Cyanobiphenyl group is common in other CBs, and as seen in **Figure 1**, 5CB has a relatively short alkyl chain of only five carbon atoms. The length of the CB group is reported to be 11 Å, and the size of the alkyl chain is calculated to be 6.75 Å[4]. Because all CBs have the same cyanobiphenyl group, the differences of structures in the anchoring phase can be attributed to the influence of the alkyl tail. However, Frommer[5] reported that nCB with $n \leq 6$ is below a threshold limit of the alkyl group's influence on the ordering of molecules. The author also found that 7CB has an alternate packing for CBs in graphite, which has an odd number of carbon atoms in its alkyl moiety. Thus, it is possible that 7CB can have both single and double row arrangements on graphite surfaces. *Based on these findings, we hypothesize that different phenomena may govern the arrangement of molecules in 5CB, and the alkyl moiety of 5CB may behave similarly to that of 7CB. Because 5CB is nematic at room temperature, we hypothesize it forms a single-layer structure.*

EXPERIMENTS AND DATA ANALYSIS

We conducted a series of experiments as outlined below to obtain STM images of bare HOPG, 5CB on HOPG, bare graphene - SiC, and 5CB on graphene - SiC. All these imaging experiments were repeated at multiple locations, with several times.

STM imaging of HOPG

All our STM images were collected using the RHK SPM1000 control module and associated software. Before we moved into complicated samples, we wanted to ensure whether we could establish the experimental conditions to obtain high-resolution STM images of simple, bare HOPG. As seen in **Figure 2**, we collected ultra-high molecular resolution of bare HOPG, thus showcasing our instrument's power to perform more sophisticated measurements.

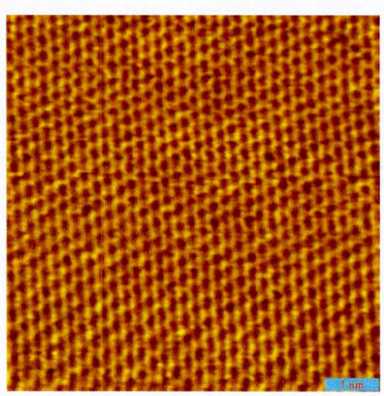

Figure 2: A representative STM image of bare HOPG (70 x70 Å). The famous honeycomb structures of C atoms on HOPG are clearly visible in the image. Experimental conditions were set point of 500 pA and a sample bias of -1.1 V.

STM imaging of 5CB on HOPG

Previous studies[3] have reported that in the absence of the smectic phase, the energetically favorable anchoring phase does not form on HOPG; thus, no periodic patterns can be found for a nematic LC on HOPG. Interestingly, our STM images of 5CB on HOPG agree with this phenomenon. As seen in **Figure 3**, there are no patterns of periodicity observed in the STM image for 5CB on HOPG. We attribute this to the absence of an energetically favorable anchoring phase of 5CB on HOPG.

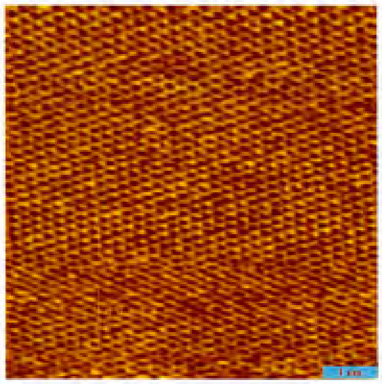

Figure 3: A representative STM image of 5CB on HOPG (70 x70 Å). Experimental conditions were set point of 500 pA and a sample bias of -1.0 V.

STM imaging of bare SiC

After performing imaging on HOPG, we moved to collect STM images on graphene-SiC. As with bare HOPG, we first imaged a plain graphene-SiC sample. As seen in **Figure 4,** clear rings of graphene are visible on the image and are different from what was seen with HOPG owing to the difference in the conductive properties and the arrangement of single layer vs. monolayer as mentioned above.

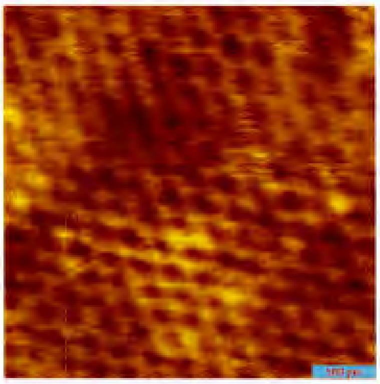

Figure 4: A representative STM image of bare graphene-SiC (30 x 30 Å). Experimental conditions were set point of 700 pA and a sample bias of -1.0 V.

STM imaging of 5CB on graphene-SiC

Having confirmed that we can obtain clear images of bare graphene-SiC, we imaged 5CB on the garaphene-SiC layer. As seen in **Figures 5**, there are two apparent, distinct regions with different light intensities. The bright areas represent the cyanobiphelyl groups with a higher electron density, and the darker valley regions represent the alkyl groups with a relatively lower electron density. A well-defined, repeating pattern can be observed in the images below, indicating that 5CB is following an ordered arrangement on the surface of the graphene-SiC. However, it must also be noted that because graphene is highly conductive, it also appears in the background of this image.

Additionally, it is essential to confirm that we are imaging the anchored 5CB on the graphene-SiC layer, not the 5CB in bulk. This is mainly because the anchoring phase is strongly affected by molecule-molecule and molecule-substrate interactions and is vastly different from the behavior of LC in bulk. The presence of faint interfering signals from graphene confirms that these images were originated from the anchored 5CB.

Although removing the appearance of graphene layer from these images is challenging, we tried to image only the top 5CB layer by moving the tip away from the sample. We varied the sample bias from -1.2 V to -2.2 V; however, as we retracted the tip away, the images of the 5CB layer became a blur (**Figure 6**). Interestingly, the resolution of the graphene layer remained persistent regardless of the sample bias, confirming it is incredibly challenging to remove it.

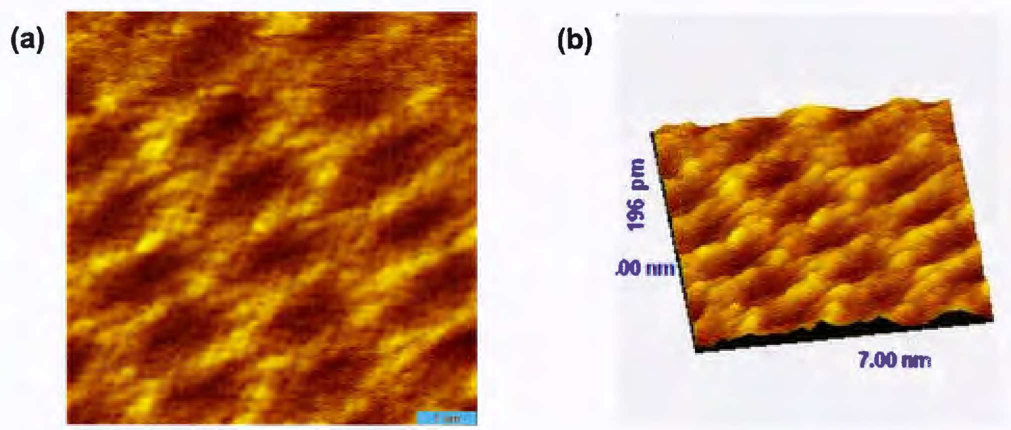

Figure 5: (a) A representative STM image of 5CB on graphene-SiC (70 x70 Å). Experimental conditions were set point of 700 pA and a sample bias of -1.2 V. (b) 3D image of (a). The bright areas represent the cyanobiphelyl groups and the darker valley regions represent the alkyl groups. Graphene layer still appears on the background.

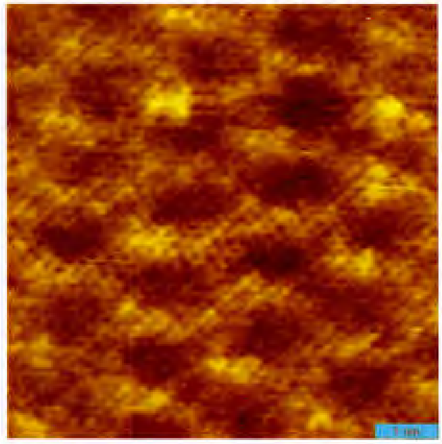

Figure 6: A representative STM image of 5CB on graphene-SiC (70 x70 Å). Experimental conditions were set point of 700 pA and a sample bias of -1.8 V. No clear bright areas and dark areas. Graphene layer still appears on the background.

Based on the STM images we obtained, we conclude that 5CBs are arranged in a single-row arrangement on the graphene-SiC substrate (**Figure 7**). This finding is in good agreement with previous studies[3,5]. As seen in **Figure 7**, the blue-colored oval represents the cyanobyphenyl groups, and the distance between these ovals represents the length of alkyl chains. We also calculated the length of alkyl chains using our model, and it is ~7 Å and is in good agreement with what was reported previously[4]. However, it must be noted that the alkyl tails from the opposite molecules can overlap slightly, thus, reducing the distance between adjacent cyanobiphenyl head groups.

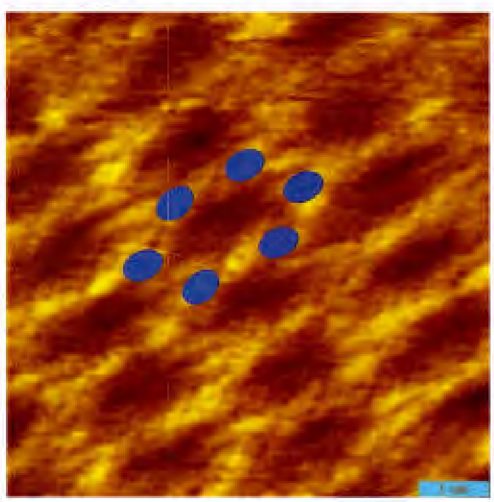

Figure 7: Assignment of molecular arrangement of 5CB on SiC-graphene. Cyanobyphenyl groups are represented in blue-colored ovals.

CONCLUSION

In summary, we imaged bare HOPG, 5CB on HOPG, bare graphene-SiC, and 5CB on graphene-SiC using STM. We did not observe any periodicity patterns or anchoring of 5CB on

HOPG. In contrast, we observed a single-row molecular arrangement of 5CB on graphene-SiC, and our calculation of alkyl chains' lengths is in good agreement with previous studies.

TIMELINE

The following table summarizes the approximate schedule at which the tasks were completed over the course of the project. There were periods where the instrument wasn't working correctly, and we had to troubleshoot the device.

Table 1: Summary of tasks

Task #	Task	Start date	End date
1	Imaging- HOPG	Oct-2020	Feb-2021
2	Imaging- 5CB on HOPG	Feb-2021	March-2021
3	Imaging- graphene-SiC	March-2021	April-2021
4	Imaging- 5CB on graphene-SiC	May-2021	August-2021
5	Data Analysis	August-2021	September-2021

SUPPLEMENTARY DATA

We optimized STM imaging parameters (setpoint, bias potential, etc.) to obtain high-resolution images on HOPG and graphene-SiC via a series of experiments as shown below.

Optimization of imaging of bare HOPG

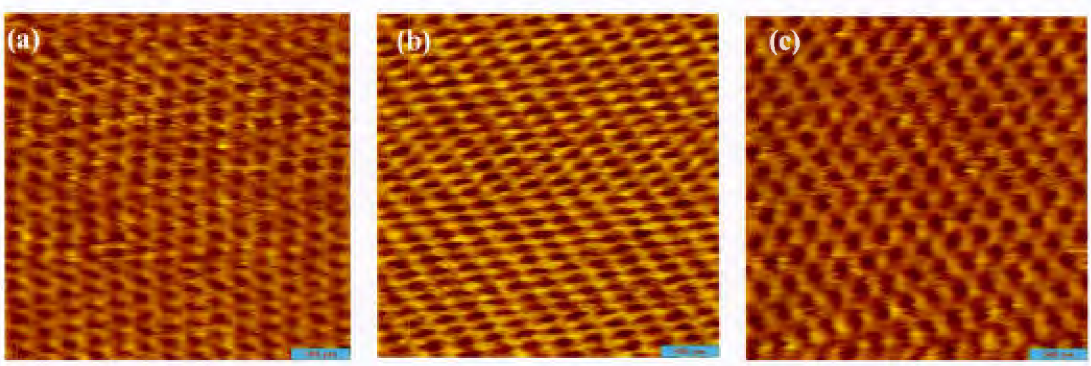

Figure S1: Representative images (30 x30 Å) of bare HOPG taken with setpoint: 200 pA, sample bias: 0.2 V.

Optimization of imaging of 5CB on HOPG

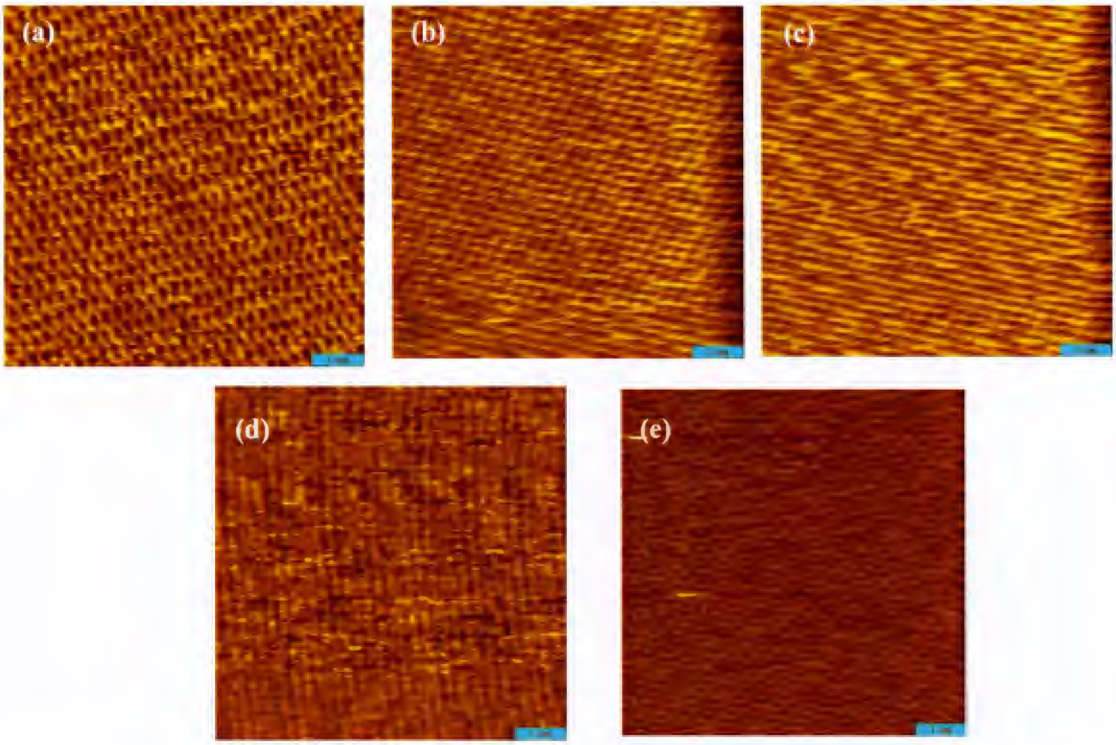

Figure S2: Representative images (70 x 70 Å) of 5CB on HOPG taken with setpoint: 300 pA and sample bias: (a) -0.7 V. (b) -0.8 V (c) -0.9 V (d) -1.0 V and (e) -1.1 V. There are no periodicity patterns of 5CB was observed under any of the experimental conditions tested.

Optimization of imaging of bare graphene-SiC

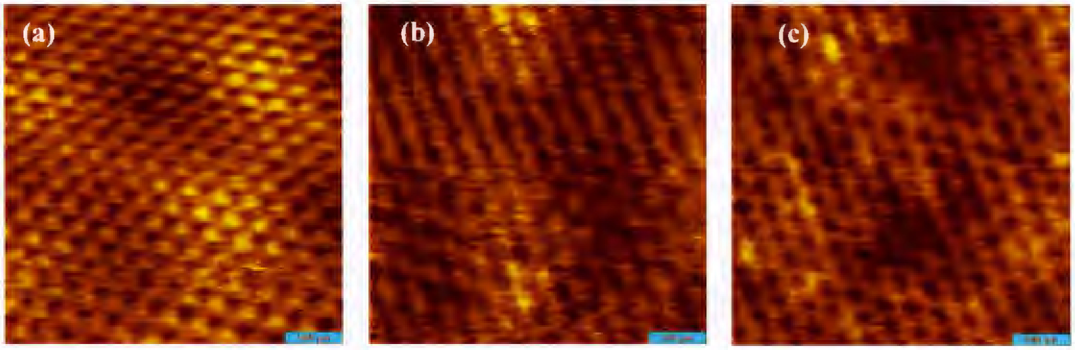

Figure S3: Representative images (30 x 30 Å) of bare graphene-SiC taken with (a) setpoint: 300 pA and sample bias: -1.0 V (b) setpoint: 500 pA and sample bias: -0.8 V (c) setpoint: 700 pA and sample bias: -1.0 V

Optimization of imaging of 5CB on graphene-SiC

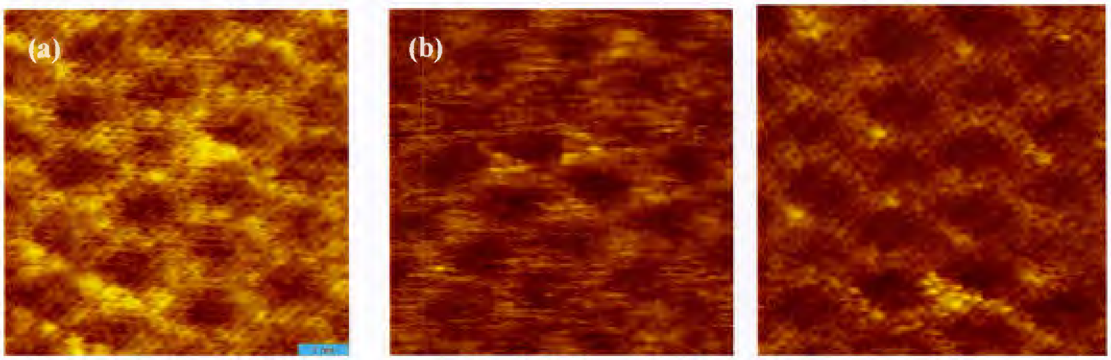

Figure S4: Representative images (70 x 70 Å) of 5CB on graphene-SiC taken with setpoint: 700 pA and sample bias: (a) -1.8 V (b) -2.0 V and (c) -2.2 V. As seen, when the tip was moved away from the substrate by applying a high sample bias, the resolution of 5CB lost while the underneath graphene layer still appears on the image.

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