REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
20-05-2014	Final Report	1-May-2008 - 14-Mar-2014

4. TITLE AND SUBTITLE
Final Report: Integrated Sensing Using DNA Nanoarchitectures, Norton, Marshall U

5a. CONTRACT NUMBER
W911NF-08-1-0109

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
622622

6. AUTHORS
Michael L. Norton

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Marshall University
Marshall University Research Corporation
401 11th Street
Huntington, WV 25701 -2225

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
54521-EL.12

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The objective of the NanoArchitectures initiative is the generation of well defined arrays of DNA capable of supporting molecular systems demonstrating switching phenomena. Parallel efforts have been in place to forward the objective of large scale structures and installation of molecular components. In particular the research has transitioned from 0D (stand alone origami) to 1D (chains of origami). Although forays into 2D (both limited structures and unlimited structures) has been performed, the emphasis is on 1D growth since defects and the source of defects may be more readily "traced" in 1D systems than in 2D systems. We have observed that the lengths of

15. SUBJECT TERMS
DNA, Nanostructures, Origami, Arrays, nanoparticle, Organization, nanoparticle arrays, THz spectroscopy

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Michael Norton
UU	UU	UU	UU		19b. TELEPHONE NUMBER 304-696-6627

Report Title

Final Report: Integrated Sensing Using DNA Nanoarchitectures, Norton, Marshall U

ABSTRACT

The objective of the NanoArchitectures initiative is the generation of well defined arrays of DNA capable of supporting molecular systems demonstrating switching phenomena. Parallel efforts have been in place to forward the objective of large scale structures and installation of molecular components. In particular the research has transitioned from 0D (stand alone origami) to 1D (chains of origami). Although forays into 2D (both limited structures and unlimited structures) has been performed, the emphasis is on 1D growth since defects and the source of defects may be more readily “traced” in 1D systems than in 2D systems. We have observed that the lengths of 1D systems far exceeds the length scale of extant 2D systems. Because there are approaches which can expand 1D systems in a second dimension, creating 2D systems (which are a pre-requisite to controlled 3D systems), our emphasis has been placed on control of 1D system growth. Yield information is much more rigorously obtained when the system is organized into arrays. Similarly, quantitative evaluation of the performance of individual nanosystems will be much improved by the organized, rather than the current, disorganized placement of such systems.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/09/2014	7.00	Masudur Rahman, Boris Gelmont, Michael L. Norton, Tatiana Globus, Igor Sizov. Sub-THz spectroscopic characterization of vibrational modes in artificially designed DNA monocrystal, Chemical Physics, (11 2013): 121. doi: 10.1016/j.chemphys.2013.08.015
05/09/2014	9.00	Xiaoning Zhang, Masudur Rahman, David Neff, Michael Louis Norton. DNA origami deposition on native and passivated molybdenum disulfide substrates, Beilstein J. Nanotechnol. , (04 2014): 501. doi: 10.3762/bjnano.5.58
05/13/2014	8.00	Tsai Chin Wu, Masudur Rahman, Michael L. Norton. From Nonfinite to Finite 1D Arrays of Origami Tiles, Accounts of Chemical Research, (05 2014): 0. doi: 10.1021/ar400330y
05/13/2014	10.00	Masudur Rahman, David Neff, Michael L. Norton. Rapid, high yield, directed addition of quantum dots onto surface bound linear DNA origami arrays, Chemical Communications, (02 2014): 3413. doi: 10.1039/c3cc49637f
07/30/2011	1.00	Michael L. Norton, Masudur Rahman. Two-Dimensional Materials as Substrates for the Development of Origami-Based Bionanosensors, IEEE Transactions on Nanotechnology, (09 2010): 0. doi: 10.1109/TNANO.2010.2060494
08/11/2012	2.00	B. Scott Day, Larry R. Fiegland, Erik S. Vint, Wanqiu Shen, John R. Morris, Michael L. Norton. Thiolated Dendrimers as Multi-Point Binding Headgroups for DNA Immobilization on Gold, Langmuir, (10 2011): 0. doi: 10.1021/la202444s
08/11/2012	3.00	Michael L. Norton, Reza M. Zadegan. Structural DNA Nanotechnology: From Design to Applications, International Journal of Molecular Sciences, (06 2012): 0. doi: 10.3390/ijms13067149
08/17/2013	4.00	Anshuman Mangalum, Masudur Rahman, Michael L. Norton. Site-Specific Immobilization of Single-Walled Carbon Nanotubes onto Single and One-Dimensional DNA Origami, Journal of the American Chemical Society, (02 2013): 2451. doi: 10.1021/ja312191a
08/17/2013	5.00	W. Zhang, E. R. Brown, M. Rahman, M. L. Norton. Observation of terahertz absorption signatures in microliter DNA solutions, Applied Physics Letters, (01 2013): 23701. doi: 10.1063/1.4775696
TOTAL:		**9**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Poster

Rahman, M. (Presenter & Author), Warner, C. N. (Author Only), Day, B. S. (Presenter & Author), Wang, B., Norton, M. L. (Author Only), National ACS Meeting and Expo, "Surface Plasmon Resonance Detection of Mn2+ Binding to Iron Responsive Element-mRNA," ACS, Indianapolis, IN. (September 2013).

Poster
Design of Length Specific 1D Arrays Using Origami Tiles
Tsai Chin Wu, Masudur Rahman and Michael L. Norton FNANO 2014, Snowbird, Utah. Apr 14, 2014

Poster
Contrast Switching in Plasma Patterning of Graphite using DNA Origami as a Lithography Mask Masudur Rahman, David Neff, and Michael L. Norton FNANO 2014, Snowbird, Utah. Apr 14, 2014

Oral Presentations

Rahman, M. (Presenter & Author), Neff, D. (Author Only), Norton, M. L. (Author Only), National ACS Meeting and Expo, "2013 Modification of surface bound DNA nanoarchitectures with biomolecules and conjugates," ACS, Indianapolis, IN. (September 8, 2013).

Rahman, M. (Author Only), Schrieber, T. (Author Only), McIlvain, M. (Author Only), Johnson, M., Bakhshi, T. (Author Only), Neff, D. (Author Only), Norton, M. L. (Presenter & Author), National ACS Meeting and Expo, "Probing large DNA nanostructure self-assembly," ACS, Indianapolis, IN. (September 8, 2013).

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received		Paper
08/17/2013	6.00	E. R. Brown, W. Zhang, E. A. Mendoza, Y. Kuznetsova, S. R. J. Brueck, M. Rahman, M. L. Norton, E. Duco Jansen, Robert J. Thomas. Concentration methods for high-resolution THz spectroscopy of nucleic-acid biomolecules and crystals, SPIE BiOS. 21-JAN-12, San Francisco, California. : ,
TOTAL:	**1**	

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper
TOTAL:	

Number of Manuscripts:

Books

Received	Paper
TOTAL:	

Patents Submitted

Patents Awarded

Awards

none for this period

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Ariful Haque	0.50	
Joshua Botkin	0.20	
FTE Equivalent:	**0.70**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Manjira Kumar	0.20
FTE Equivalent:	**0.20**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Kevin Vang	0.20	Biology
FTE Equivalent:	**0.20**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
David Neff	0.40
FTE Equivalent:	**0.40**
Total Number:	**1**

Sub Contractors (DD882)

1 a. Texas A&M University

1 b. Department of Chemical Engineerin

College Station TX 77842

Sub Contractor Numbers (c): E1406238
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 12/12/13 12:00AM
Work Description (e): The Texas A &M group led by Jorge Seminario, will figure out how to set the origami f
Sub Contract Award Date (f-1): 12/12/13 12:00AM
Sub Contract Est Completion Date(f-2): 3/14/14 12:00AM

---

1 a. Wright State University

1 b. Wright State University
3640 Colonel Glenn Highway
Dayton OH 454350001

Sub Contractor Numbers (c): R1200956
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 4/11/12 12:00AM
Work Description (e): Equipment only subcontract to Dr. Brown at Wright State University for Thz Characteriz
Sub Contract Award Date (f-1): 4/11/12 12:00AM
Sub Contract Est Completion Date(f-2): 7/16/12 12:00AM

---

1 a. Wright State University

1 b. 3640 Colonel Glenn Highway

Dayton OH 454350001

Sub Contractor Numbers (c): R1200956
Patent Clause Number (d-1): 52.227-11
Patent Date (d-2): 4/11/12 12:00AM
Work Description (e): Equipment only subcontract to Dr. Brown at Wright State University for Thz Characteriz
Sub Contract Award Date (f-1): 4/11/12 12:00AM
Sub Contract Est Completion Date(f-2): 7/16/12 12:00AM

Inventions (DD882)

Scientific Progress

Please see attachment

Technology Transfer

Final Scientific Progress Report: Integrated Sensing Using DNA Nanoarchitectures, Norton, Marshall U

1. Foreword

This award has spanned an appreciable fraction of the entire "lifetime" of DNA structural chemistry. With the broad objective of the generation of well-defined arrays of DNA capable of supporting molecular systems demonstrating switching phenomena, we have used this grant as a mechanism to enable us to perform the fundamental research which is necessary to support the development of applications of this new technology. Parallel efforts have been made to forward these objectives, which are, I believe, critical for moving forward: The assembly of large scale structures with uniquely addressable locations and the precise installation of molecular components on these species. Rather than catalog each of our small steps, which are well enumerated in the monthly and annual reports, an effort is made here to overview the state of the art as moved forward by this fundamental effort in the chemical sciences. Lasting contributions have been made in 5 supporting areas: One dimensional arrays, Surface Immobilization strategies, Modeling of DNA based Nanostructures, Large Scale Assembly Dynamics and THz characterization.

2. Table of Contents:

3. List of Illustrations and Tables

Figure 2 (Left) One dimensional arrays generated using the building blocks shown in Figure 1. (Right) Two single walled carbon nanotubes arranged into parallel configuration through binding with one dimensional origami array.

Figure 3 AFM images demonstrating the use of 1D origami to organize (left) Quantum Dots and (right) gold nanoparticles into a linear array format.

Figure 4 (Left) Three frames from a high speed AFM video in which growing number of bound molecules can be observed in frames 1-3 (white points are bound streptavidin molecules). (Rigtht) The plot of fractional surface coverage vs time can be fit using the equation presented below the AFM images to yield an adsorption rate constant of 5×10^5 .

Figure 5 2X2 (left) and 3X3 (right) arrays of cross shaped origami (yellow spots denote streptavidin).

Figure 6 Process for immobilizing single stranded DNA on a gold surface.

Figure 7 Simulation of origami structure using Chimera for visualization

Figure 8 Closeup of bases in model for Cross Shaped Origami.

Figure 9 A stick model showing all atoms in a small region of the Cross Shaped Origami construct.

Figure 10 (Left) Fluorescence vs temperature curve and (Right) first derivative of fluorescence vs temperature curve obtained for slow annealing of cross structures in 0D, 1D and 2D formats.

Figure 11 (Left) Transmission spectrum derived for sample containing 13mer solution. (Right) Lorentz oscillator fit to the attenuation coefficient around the 720 GHz resonance

4. **Statement of the problem studied**

In order for a technology to be useful, it must be timely. A key driver for molecular scale assembly of optoelectronic components is that either optical or high frequency (eg THz) signals will at some point be readily launched and processed at significantly subwavelength length scales. While such launching, in a highly multiplexed format is near technical feasibility, the manipulation of these signals at the individual molecular size scale is even further from common practice. Parallel development in several areas must be made before systems for molecular scale signal processing in the optical and THz regimes will be realized. Molecular sensing was perceived as a particularly useful mechanism for the demonstration of switching, which is one form of signal manipulation. In this research we have sought to progress from the “bottom up” the engineering requirements for very high yield which will be necessary for actual applications while simultaneously collaborating with others (specifically Dr. Elliott Brown, Wayne State U and Tatiana Globus, U of Virginia) to both determine the DNA background THz signatures, since detection and signaling will require discrimination against these signatures and to determine the instrumental configurations necessary to interrogate a minimal number of DNA structures, with the terminal objective, not met yet principally for economic reasons, of observing THz signatures from single molecular structures.

5. Summary of the most important results

1. One dimensional arrays and target capture

Although we have certainly worked with a number of constructs, which have evolved through the course of this program of research, our focus is currently in the development of a ca 100 nm X 100 nm X 2 nm building block first conceived by Seeman's group (Liu et al., 2011[1]. Figure 1 displays the design and observed structure of that construct, which Liu used to generate 2D structures with a broad range of length scales and containing the building blocks in rotationally randomized orientations.

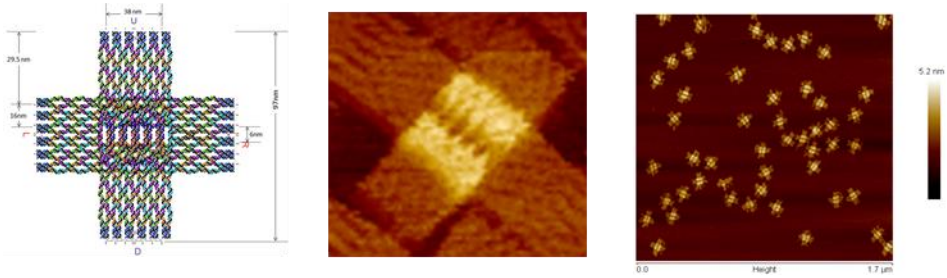

Figure 1 Cross shaped tile building block, design, high resolution AFM image of single cross species and low resolution image demonstrating reproducibility of these block structures.

We have demonstrated that these block structures can be used to generate long 1 dimensional arrays (Figure 2 left), which can be used to align carbon nanotubes (CNT's) (Figure 2 right). The alignment of CNT's was a natural outgrowth of the Architectures program, with significant overlap and feedforward into the MURI program. Although these CNT's were selected for study because 6,5 CNT's are among the most fluorescent ones identified to date, there is reason to anticipate that in addition to these semiconducting CNT's, metallic CNT's can similarly be placed. The "automatic" placement of CNT's has been very difficult to accomplish using standard lithographic methods, making DNA a potentially competitive strategy for organization of these 1D particles.

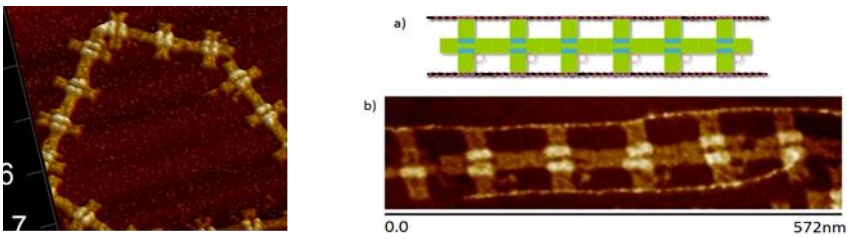

Figure 2 (Left) One dimensional arrays generated using the building blocks shown in Figure 1. (Right) Two single walled carbon nanotubes arranged into parallel configuration through binding with one dimensional origami array.

The regular spacing of the origami species into an array configuration enables a level of quality evaluation not readily practicable with individual origami species. We have recently published[2] (Rahman, 2014), that 1D origami can be used as a template for the high yield organization of semiconductor Qdots into an arrayed configuration (Figure 3, left). Similarly, gold nanoparticles can be arranged, as is readily seen in Figure 3, right.

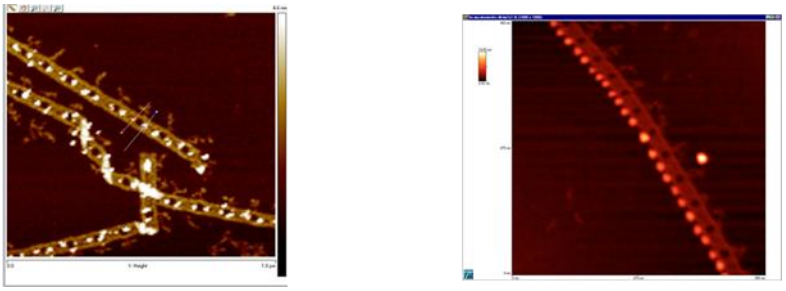

Figure 3 AFM images demonstrating the use of 1D origami to organize (left) Quantum Dots and (right) gold nanoparticles into a linear array format.

While arranging particles with high yield in configurations potentially amenable to integration into laboratory experimental use if not use in commercial products is important, each of these particle assembly processes is also an example of stochastic switching of the composition of the DNA based architectures. Using very high resolution imaging methods, such as AFM, we can observe the time scale of this assembly process. We have used streptavidin as an example molecule to be captured into a sensing platform, with results shown in Figure 4. While it may well be argued that streptavidin is not a species of interest in terms of bioweapons, there are two major motivations for our use of this material. First it is not hazardous, and can be handled safely, second, it is a very well parameterized species and third, its residence time is very long and therefore it can be imaged in its bound state on a substrate. These properties make it ideal for troubleshooting systems at the nanoscale.

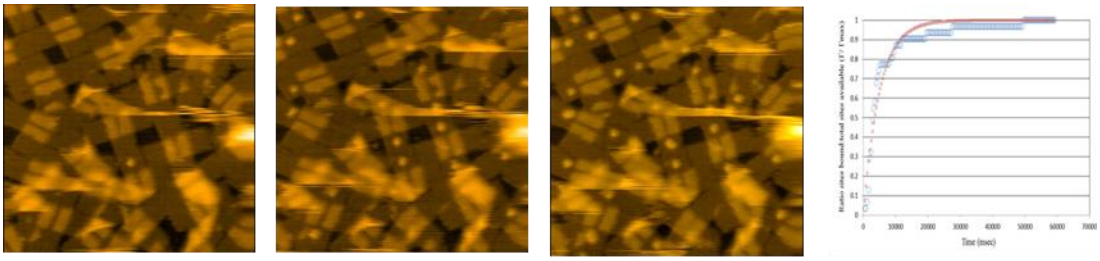

Image Size = 400nm X 400nm

$$\Gamma = \Gamma_{max}(1 - \exp(-k_{ads} c_b t))$$

$$k_{ads} = 5 \text{ X } 10^5 \text{ L mol}^{-1}\text{s}^{-1}$$

Figure 4 (Left) Three frames from a high speed AFM video in which growing number of bound molecules can be observed in frames 1-3 (white points are bound streptavidin molecules). (Rigtht) The plot of fractional surface coverage vs time can be fit using the equation presented below the AFM images to yield an adsorption rate constant of 5 X 10^5 .

The ability to directly observe adsorption at the nanoscale and to observe the dynamics of the reaction, using a sample size only 400 nm X 400 nm cannot be performed, to our understanding, without the use of DNA Origami platforms. Although entirely regular platforms were not available at the time of this experiment, 200 nm X 200 nm (2X2 arrays) and 300 nm X 300 nm arrays (3X3 origami arrays) can now routinely be generated in this laboratory (Figure 5). The ability to sense and organize biomolecules on this size scale is only, at this time, possible using DNA nanotechnology.

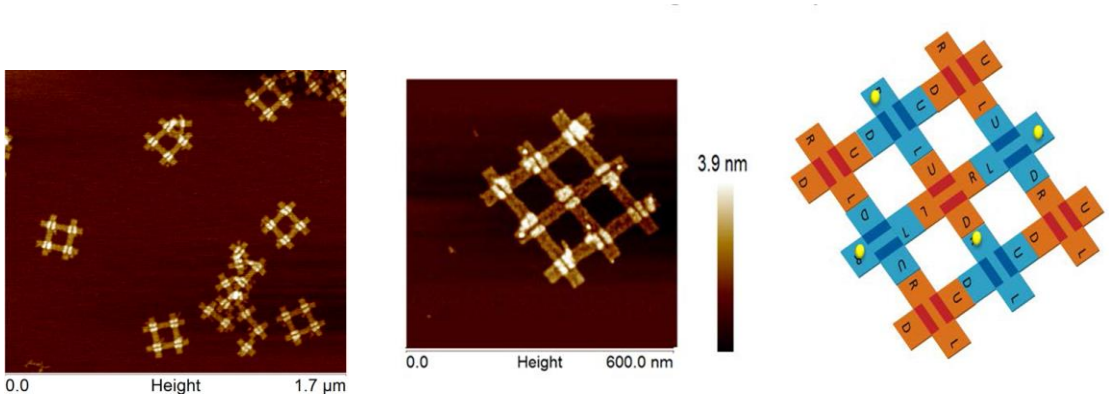

Figure 5 2X2 (left) and 3X3 (right) arrays of cross shaped origami (yellow spots denote streptavidin).

2. Surface Immobilization strategies

One of the most important unmet challenges in DNA nanostructure field is site specific immobilization of nanostructures on surfaces. We have developed (and reported 3) one of the most robust methods for associating DNA with surfaces. This method, described in cartoon form in Figure 6, uses dendrimers to provide multipoint adhesion of a single stranded DNA component on a surface.

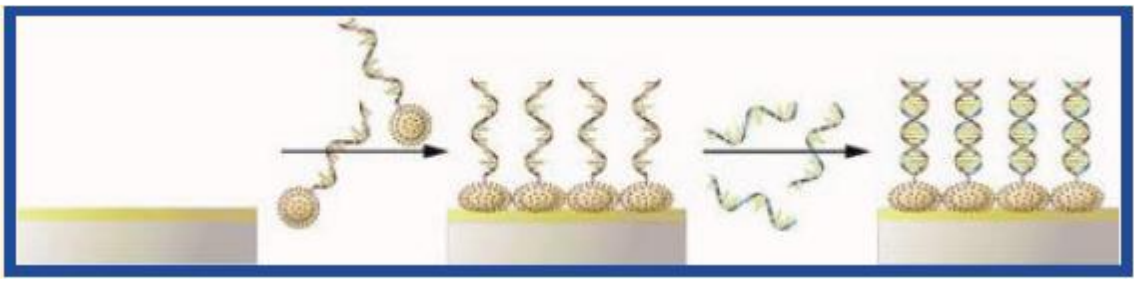

Figure 6 Process for immobilizing single stranded DNA on a gold surface.

The gold surface is first exposed to a single stranded DNA sequence which is covalently bound to a dendrimer (shown as a round species). These dendrimer species are Generation 3 PAMAM dendrimers with ~ 30 thiol groups to bind the dendrimer/DNA construct to the surface. This binding approach demonstrates strong resistance to strand loss from the surface, even with prolonged exposure to buffer solutions at high temperature (95°C). We are applying this chemistry for SPR (surface plasmon resonance) studies almost daily, and we anticipate that the approach will be applied by other laboratories. In order to fully utilize this attachment chemistry, we need to fabricate “gold dot” attachment sites on the SiOX surface, in order to immobilize DNA based nanostructures. We are working with a group at PSU (Chad Eichfeld of PSU’s Nanofabrication Facility) to use ebeam lithography to generate such arrayed attachment sites. Large scale organization of large scale origami arrays will be necessary in order for the analytical efforts we are developing to become fieldable.

3. Modeling of DNA based Nanostructures

We have recently been collaborating with Jorge Seminario of Texas A&M University. The objective is to realistically simulate the dynamics of an entire origami structure, first without surface modification, then with selected modifications. At this time, there is only one published report (in 2013 [4]) for atomistic simulations of origami structures, and the simulated structures were "basic" rather than functional. Ground truth for these reported structures has been attempted using cryo-TEM, however the best microscopy seems to be only achievable using modelling. We anticipate that these simulation studies will continue, and that departures between designed structures and actual structures will become increasingly important as functional materials are developed for actual applications. The cross shaped structure shown in Figure 1 above is the one simulated. In design, the structure is planar, on the flat mica surface, the structure is planar (it is conformal, lacking rigidity as a 2 nm thick polymer sheet. The simulated structure is shown in Figure 7 below.

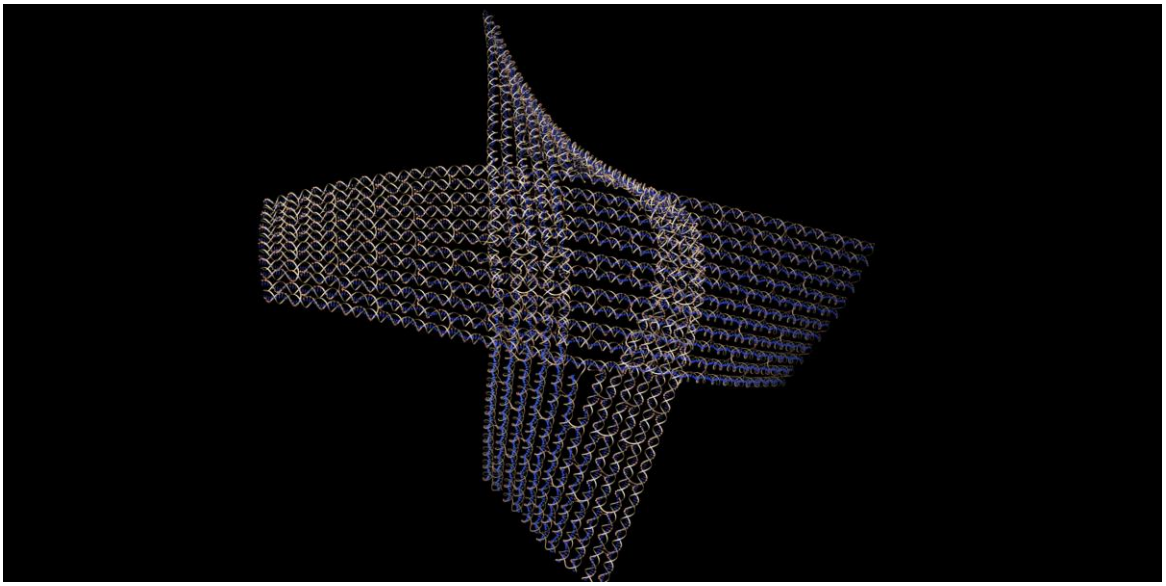

Figure 7 Simulation of origami structure using Chimera for visualization

Although this simulation will be refined in the future, already in this rough form it is obvious that the solution structure is non planar and, when catenated (chained together) will result in a twisted ribbon structure. This is quite consistent with the observed folding found when long 1D structures are formed in solution then deposited on mica.

Higher magnification views are readily obtained once a model has been created. Figure 8 displays half of the DNA bases, to improve clarity.

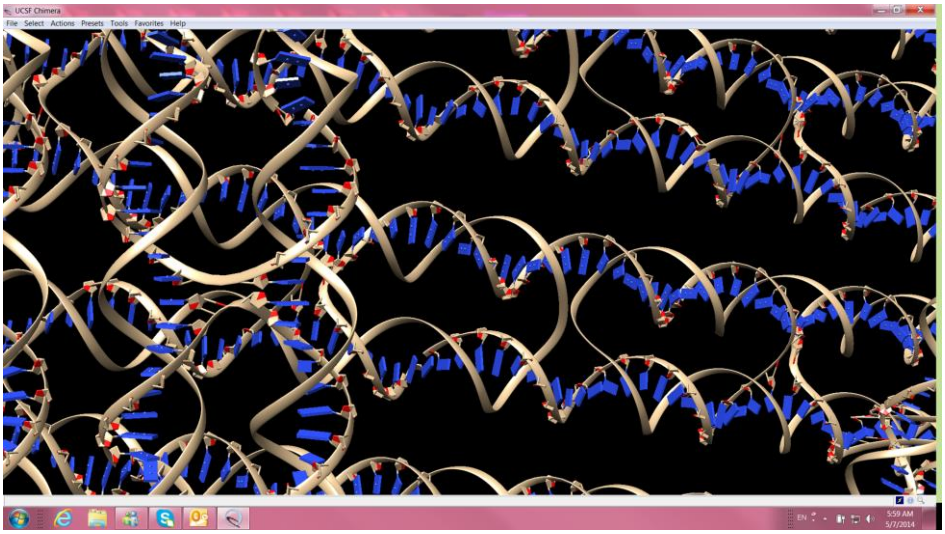

Figure 8 Closeup of bases in model for Cross Shaped Origami.

Although the view is a bit complex, the view shown in Figure 9 will become important as functional species are added to the top of the structure, to interact with solution species, particularly protein species of interest.

The consortium Dr. Seminario belongs to affords to him use of the second largest computing system available for non-government use. Although such computing power is unlikely to become available to commercial users at a rate sufficiently low to enable common use, these computations can be used to provide parameters which can be used in less complex simulations. At this moment, the applications of interest for this research would benefit from knowledge of the locations of molecules associated with the surface with sub-nm resolution, because optical interactions, including FRET (fluorescence resonant energy transfer) is sensitive to distances at the d^6 power. Certainly the dynamics of these systems, particularly in the solution phase, will become of great importance. Through this collaboration, we have a window into the fluctuations and static structural aspects determining the optical responses of these systems.

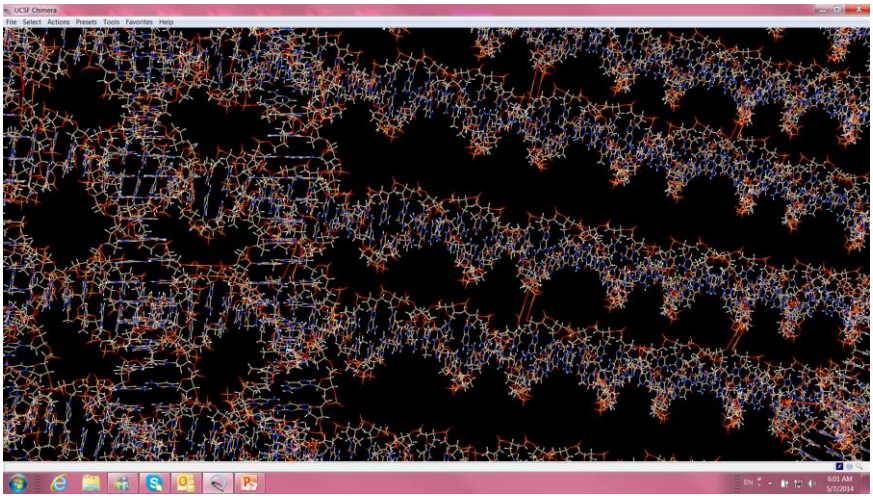

Figure 9 A stick model showing all atoms in a small region of the Cross Shaped Origami construct.

4. Large Scale Assembly Dynamics determined using annealing curves for 1D origami constructs.

We have used a Real Time PCR system (RT PCR) to study the temperatures at which self assembly processes occur in the block structure, in the 1D, catenated origami structures and in 2D. The real time data, and the resulting derivatives of the fluorescence intensity of an intercalating dye (Sybr Green) in solution with the Origami components are plotted below as a function of temperature during a very slow cooling process, are shown in Figure 10. It is our interpretation of these diagrams that all three systems assemble as blocks at the same temperature interval, between 60 and 70 ^{o}C. In the block (0D) system, there is no more evolution of the system at lower temperatures. The one dimensional systems first form a core or block structure at this higher temperature, then at a much lower temperature, the catenation (daisy chaining) of the component "blocks" occurs. Although we have seen evidence for this in the case of the cross origami structure, we have extended these studies to two similar "windowed" origami constructs with different sequences.

The derivative for the 2D case shown in Figure 10 right, shows a relatively indistinct peak, near the 0D assembly peak, corresponding, we believe, to these two processes, block formation and block binding. In the case of the 2D structures we are not certain why there is a size limitation for observed arrays. Our best hypotheses are either: 1) that the twist (see simulations above) contribute to a loss of planarity for the large assemblies or that 2) the imperfectly formed structures are not capable of joining in an error free manner, causing sufficient defects in the nascent 2D structure to terminate growth. A third hypothesis is that grain boundary defects occur, perhaps due to a large nucleation density. In other projects, we are seeking to control nucleation in these systems. AFM images (not shown) indicate well formed 0, 1 and 2D structures resulting from these experiments.

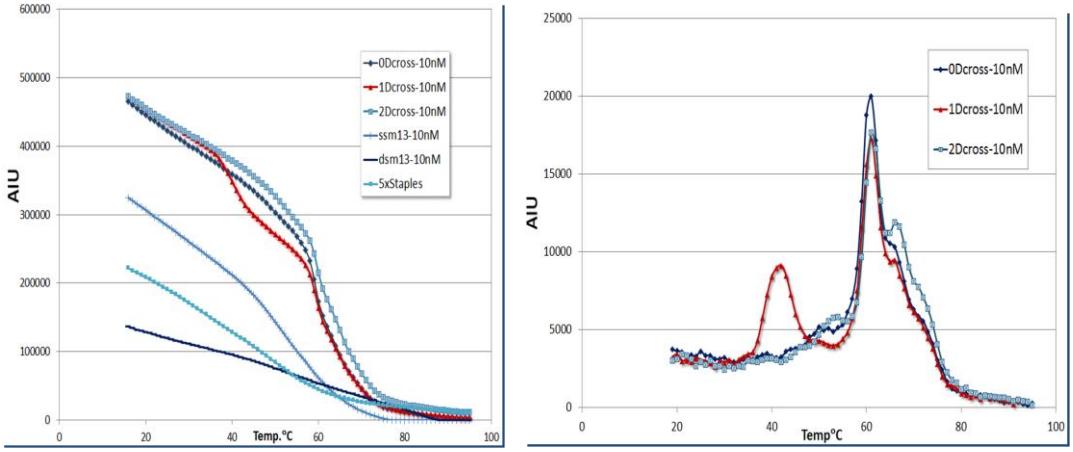

Figure 10 (Left) Fluorescence vs temperature curve and (Right) first derivative of fluorescence vs temperature curve obtained for slow annealing of cross structures in 0D, 1D and 2D formats.

5. THz characterization

Despite the significance of DNA as a molecule central to biology, its complexity has limited the amount of information available concerning its dynamics. It has long been postulated that DNA would have

vibrations in the THz range, and that these vibrations would interact with THz frequency photons. Although simulations of molecules of sufficient length to have utility are still limited, experiments of increasingly high quality are being performed. In an attempt to determine the absorption properties of solution phase DNA, 13mer oligonucleotides were studied using a microliter solution cell. These experiments, performed in the laboratory of E. R. Brown, resulted in the spectroscopic signature observed in Figure 11 (left) and the absorption detailed in Figure 11(right). [5] The analysis of this spectroscopic feature yields an absorption strength of 2.6X1016 cm-1/mol, a linewidth of 0f 48 GHz and a damping time of 6.6 ps for the resonance centered at ~717 GHz. Instrumental broadening in prior studies had distorted and perhaps hidden the observed features.

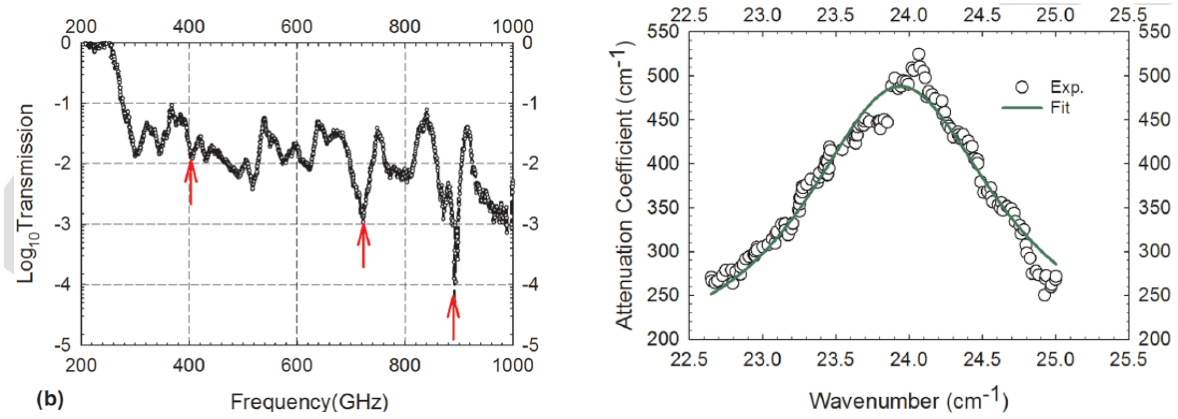

Figure 11 (Left) Transmission spectrum derived for sample containing 13mer solution. (Right) Lorentz oscillator fit to the attenuation coefficient around the 720 GHz resonance

Because future spectroscopic characterization of oriented biomolecules may require the use of a DNA nanostructure substrate, it is important to determine the background attributable to DNA.

6. Bibliography

1. Liu, W.; Zhong, H.; Wang, R.; Seeman, N. C.: Crystalline two-dimensional DNA-origami arrays. *Angew Chem Int Ed Engl* **2011**, *50*, 264-7.

2. Rahman, M., Neff, D. and Norton, M.L; Rapid, high yield, directed addition of quantum dots onto surface bound linear DNA origami arrays, Chem. Commun., v. 50, 3413-3416, 2014.

3. Day, B. Scott, Fiegland, Larry R., Vint, Erik S., Shen, Wanqiu, Morris, John R., and Norton, Michael L.; Thiolated Dendrimers as Multi-Point Binding Headgroups for DNA Immobilization on Gold, Langmuir, 27(20), 12434-12442, 2011.

4. Yoo, Jejoong and Aksimentiev, Aleksei; In situ structure and dynamics of DNA origami determined through molecular dynamics simulations, PNAS, V 110, no 50, 20099-20104, 2013.

5. Zhang, W., Brown, E.R., Rahman, M. and Norton, M.L.; Observation of terahertz absorption signatures in microliter DNA solution, Applied Physics Letters, 102, 23701- 23704, 2013.