REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
24-01-2020	Final Report	1-Sep-2018 - 31-May-2019

4. TITLE AND SUBTITLE
Final Report: Understanding Quantum Effects in 2D polymeric Systems

5a. CONTRACT NUMBER
W911NF-18-1-0381

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Arizona State University
ORSPA
P.O. Box 876011
Tempe, AZ 85287 -6011

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)
73225-MS-II.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is 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

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Sefaattin Tongay
UU	UU	UU	UU		19b. TELEPHONE NUMBER 480-727-4301

RPPR Final Report
as of 28-Jan-2020

Agency Code:

Proposal Number: 73225MSII **Agreement Number: W911NF-18-1-0381**
INVESTIGATOR(S):

Name: Ph.D. Sefaattin Tongay
Email: Sefaattin.Tongay@asu.edu
Phone Number: 4807274301
Principal: Y

Organization: **Arizona State University**
Address: ORSPA, Tempe, AZ 852876011
Country: USA
DUNS Number: 943360412 EIN: 860196696
Report Date: 31-Aug-2019 Date Received: 24-Jan-2020
Final Report for Period Beginning 01-Sep-2018 and Ending 31-May-2019
Title: Understanding Quantum Effects in 2D polymeric Systems
Begin Performance Period: 01-Sep-2018 **End Performance Period:** 31-May-2019
Report Term: 0-Other
Submitted By: Ph.D. Sefaattin Tongay Email: Sefaattin.Tongay@asu.edu
Phone: (480) 727-4301
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: **STEM Participants:**

Major Goals: Two-dimensional polymers (2DPs) consist of covalently bonded molecular tiles (ligands) that extend across two dimensions to form layered van der Waals (vdW) materials similar to graphene and other 2D inorganic materials (MoS2, WSe2, h-BN, etc.). While quantum effects are well-established for inorganic vdW solids, properties of 2DPs remain largely unknown. This is mainly due to difficulties in 2DPs sample preparation, characterization, as well as instrumentation inadequacies. Thus, studies are often restricted to simulations or thick polymers. However, true merits of 2DPs lie in two-dimensions when quantum effects become prominent. For example, theoretical studies predict and our preliminary experimental findings hint many exciting properties and quantum phenomena on 2DPs at the nanoscale.

Precisely focused on these merits, the scientific objective of this Short Term Innovative Research (STIR) project is to enable, discover, and understand emergent optical and electronic behavior of optically active 2DPs. The project will systematically investigate material behavior of 2DPs from bulk to monolayers to capture quantum confinement effects. Studies will help to test thoretical predictions and unravel novel quantum phenomena at nanoscale. If successful, this research effort will 1) offer the first look at electronic, optical properties of 2DPs, 2) provide atomic resolution insight into crystallographic properties of 2DPs, and 3) establish how material behavior of 2DPs changes when quantum size confinement effects become dominant.

Accomplishments: Please see the attached

Training Opportunities: PhD student Kedi Wu has been trained on polymeric synthesis. The student currently works at Applied Materials, California
PhD student Mark Blei has been trained on polymeric synthesis and spectroscopy. The student is currently at PhD program at ASU with Prof Tongay

Results Dissemination: Published Advanced Materials article (in press). Advanced Materials adma. 201907364R1

Honors and Awards: 2019 Presidential Early Career Award for Scientists and Engineers (PECASE) awards.
2019 Ten Outstanding Young Persons of the World – Academic Leadership and Accomplishment
2019 Highly Cited Researchers of 2019 by Web of Science and Clarivate Analytics

Protocol Activity Status:

RPPR Final Report
as of 28-Jan-2020

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: Kedi Wu
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Mark Blei
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

A. Updates on 2D Perovskite Based Polymers

1. The synthesis of 2D layered perovskites

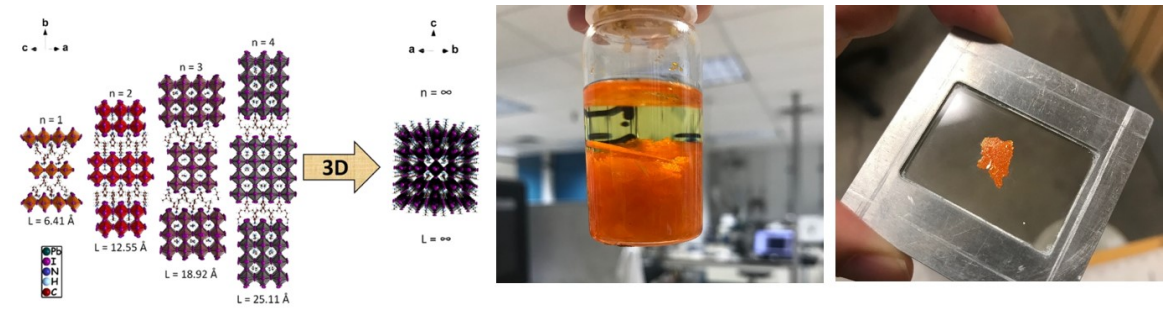

Figure A1 a. Schematic of layered perovskites **b-c.** typical vdW perovskites collected after the synthesis

In a typical growth, we have used lead (II) oxide (PbO, 99.9%), hydrobromic acid (HBr, 48% w/w aq), hydro-phosphorous acid (H_3PO_2, 50% w/w aq), 1-butylammine (BA, 99%) from Alfa Aesar. Methylammonium bromide (MABr, 98%) from Sigma-Aldrich. All chemicals are used without further purification.BA_2PbBr_4 (n=1 material): 2.15 mL HBr and 0.425 mL H_3PO_2 are mixed together in a glass vial. 279 mg PbO (1.25 mmol) is added to the mixture. In a separate vial, 140 µL BA is added dropwise in 1.075 mL HBr in an ice bath to produce BABr solution. The content of both vials is then mixed and put in an autoclave for hydrothermal synthesis. The reaction temperature is raised in four hours till 110 ^oC, kept for 2 hours, cooled to 50 ^oC in four hours,

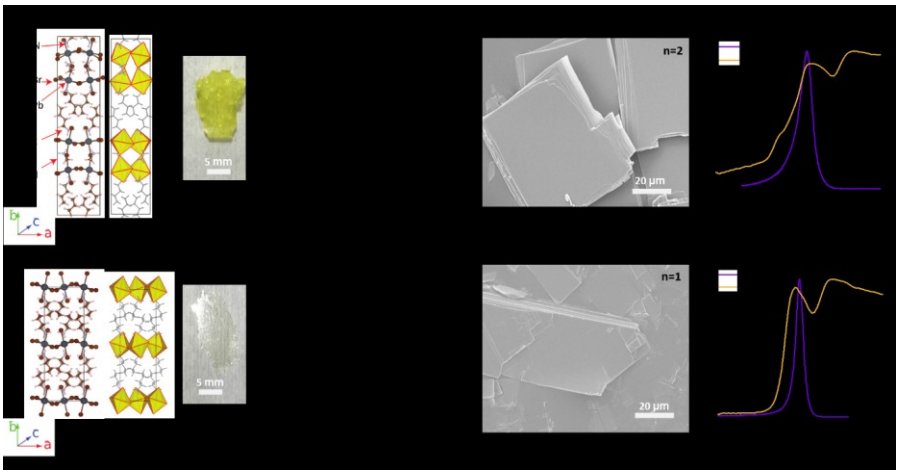

Figure A2 Characterization of 2D perovskite a. Crystal structure of vdW perovskite **a.** $(BA)_2(MA)PbBr_7$ (n=2) **and** $(BA)_2PbBr_4$ (n=1). **c-d)** XRD datasets **e-f.** SEM images and g-h. PL and absorption spectra of these layers.

and further cooled to room temperature in 16 hours.

$BA_2MAPb_2Br_7$ (n=2 material): 2.15 mL HBr and 0.425 mL H_3PO_2 are mixed together in a glass vial. 279 mg PbO (1.25 mmol) and 70 mg MABr (0.625 mmol) is added in the mixture. In a separate vial, 87 µL BA is added dropwise in 1.075 mL HBr in an ice bath to produce BABr solution. The content of both vials is then mixed and put in an autoclave for hydrothermal synthesis. The reaction temperature is raised in four hours till 110 ^oC, kept for 2 hours, cooled to 50 ^oC in four hours, and further cooled to room temperature in 16 hours. Typical products are shown in Figure A1 and characterization results are summarized in Figure A2.

2. Understanding the effect of interlayer coupling on the excitonic properties of 2D perovskites

To monitor the effects of applied pressure on the $(BA)_2(MA)PbBr_7$ (*n*=2) sheets, ultra-thin sheets (lateral sizes ~30 microns and ~100nm thickness) were loaded into our DAC chamber using sodium chloride (NaCl) as the pressure media. The rationale behind NaCl over ethanol-methanol liquid solution is to eliminate the detrimental effects of the solution itself on

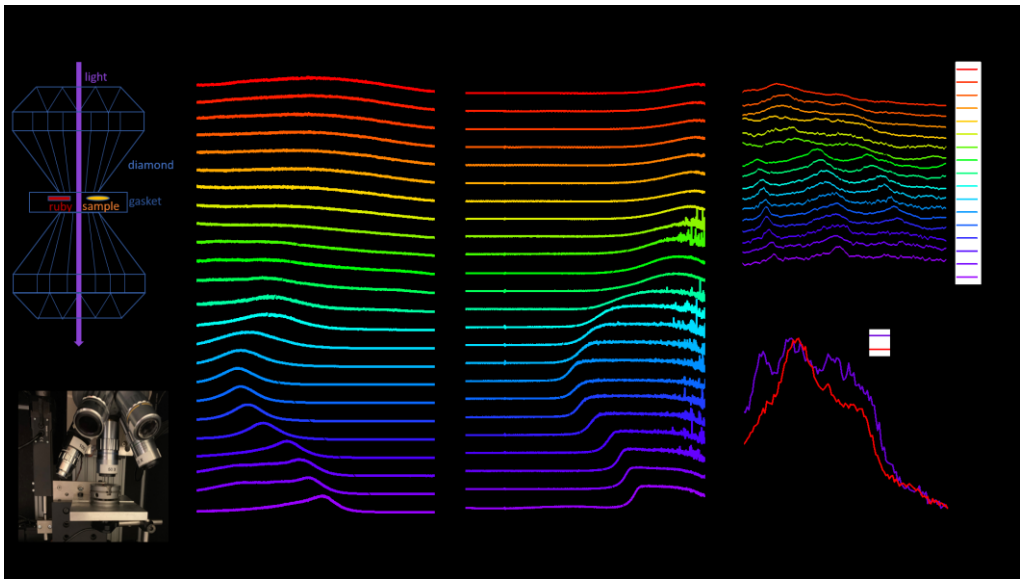

Figure A3 $(BA)_2(MA)PbBr_7$ (n=2) Phase transition at high pressure a. Schematic Diamond Anvil Cell **b.** Diamond anvil cell under home-made Raman spectroscopy. **c.** Photoluminescence stacking with respect to pressure from 0 GPa to 15.1 GPa. **d.** Micro absorption stacking plot from 0 GPa to 15.1 GPa. **e.** Raman shift of perovskite from 0 GPa to 15.1 GPa. **f.** Raman spectrum obtained at 2.6 GPa and 3.4 GPa.

$(BA)_2(MA)PbBr_7$ (*n*=2) sheets. When pressure studies were performed using NaCl media, the material properties remained unchanged after full compression and decompression cycle without any permanent impact on the material properties. Unlike methanol-ethanol media, the use of NaCl also enabled us to apply uniaxial pressure[29] which is best suited for probing structural and physical changes related to interlayer distance and interaction strength. In our studies, we have applied pressures up to 15 GPa around which Raman, PL, and micro-absorption spectra became unmeasurably weak and the data analysis became unreliable. The pressure was measured using well-established ruby fluorescence technique in close proximity to loaded RPP perovskite sheets (see schematic in Fig.2a), and the optical spectroscopy

measurements were performed using our home-made setup integrated with the DAC chamber (Fig.A3b).

Results in Figure A3 shows that the band gap variation of 2D layered perovskites show a unique and completely different band renormalization. The band gap first red-shifts followed by strong blue shift. These behavior was observed both in PL as well as absorption spectra. Interestingly, a closer inspection shows that absorption spectra and PL shows rather different band gap values at high pressures (Pressure 4-12GPa) as shown in Figure A4a which is related to high

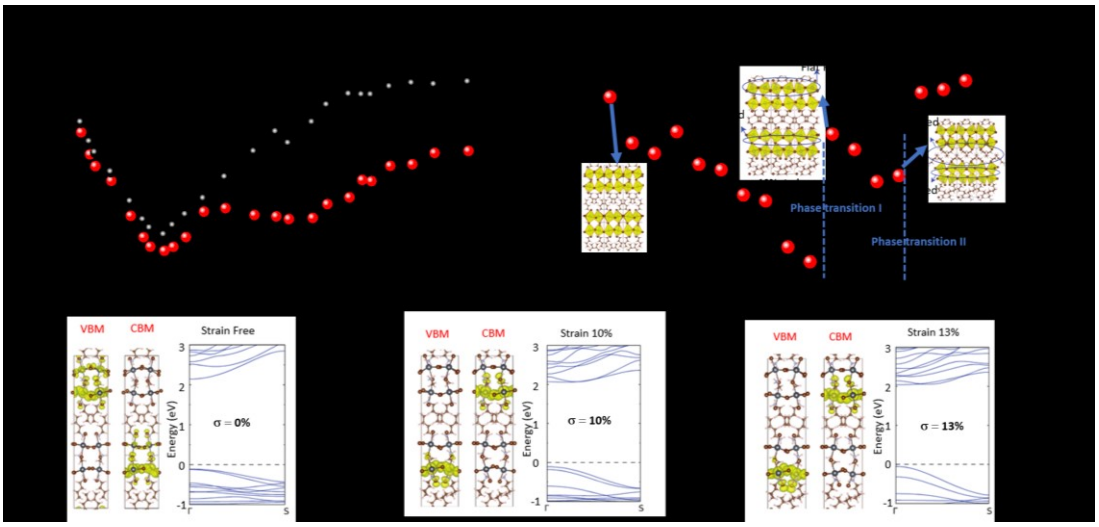

Figure A4 a. PL emission (red) and absorption edge (black) behavior under high pressure in **$(BA)_2(MA)PbBr_7$**. **b.** Calculated band gap behavior with strain along b axis(stacking direction). **c.** VBM, CBM and band structure at 0%, 10% and 13% strain.

transition (Figure A4b-c)

Our preliminary studies suggest that there is a significant phase transition at high pressures and the exciton binding energy reaches to world record 400 meV in layered perovskite systems. At the moment, the valleytronic, excitonic, and optical properties in this high excitonic binding energy (high pressure phase) is completely unknown and future studies are absolutely needed to under the their fundamental properties.

3. Exciting observations and future needs

- The presence of unique phase transition in 2D perovskite systems and world record exciton binding energy observation
- More studies needed in this high pressure regime to elucidate on if there is a novel excitonic and spintronic properties.
- More studies are needed on n=1, 3, and others.
- More studies are needed 2D perovskites involving Lanthanide metals (as opposed to Pb) to enable strongly correlated interactions through f orbital interactions.

B. Updates on 2D HAB Based Polymers

1. Studied 2D HAB based polymeric material systems

In our studies, our goal was to focus on hexaminobenzene (HAB) based polymers specific metal linkers such as Co, Ni, etc. and layered perovskite and PbBr6BAMA based halide organics. *The rationale behind selecting these 2DPs was three folds:* ***i)*** our established synthesis methods results in highly-crystalline, environmentally and energetically stable HAB and BAMA based 2DPs. This helps us to characterize them without material degradation during the course of measurements, ***ii)*** Their lateral sizes can reach to ~100 um^2 with great control over its thickness (~0.5–50 nm), ***iii)*** they show direct band gaps with high light absorption and emission rates which are technologically most relevant to DoD applications. These characteristics also enable us to use nanoscale electron energy loss spectroscopy (nano-EELS), PL, and micro-absorption measurements to acquire information on their properties.

2. The synthesis of M-HAB (M=Ni and Co)

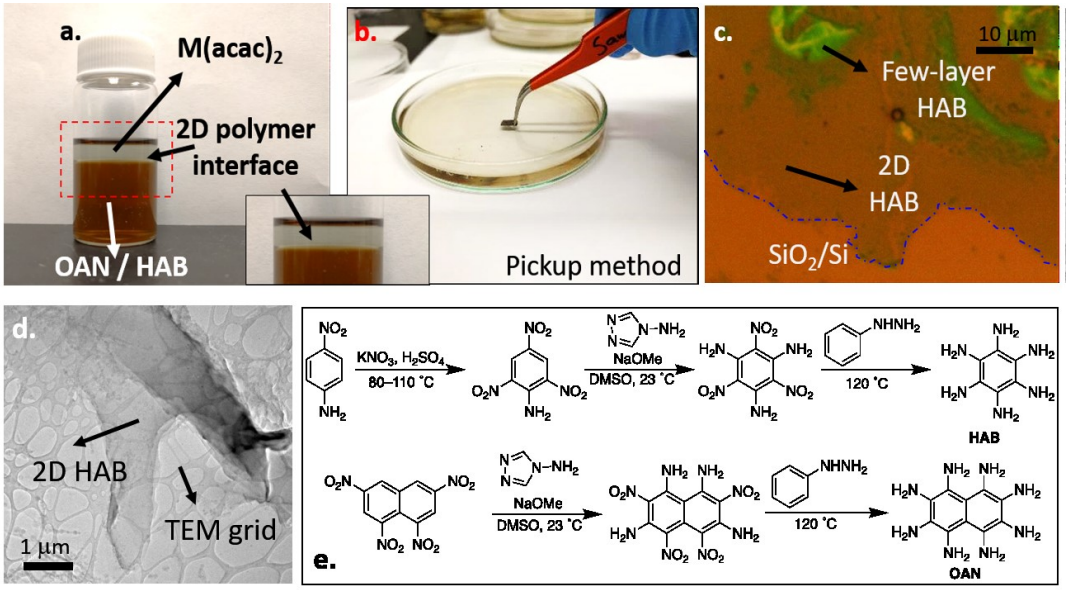

Figure B1 a. Schematic of two-phase 2D polymer synthesis **b.** Conventional pick-up method for depositing 2D HAB onto **c.** SiO_2/Si or **d.** TEM grids **e.** proposed synthesis routes for HAB and OAN 2DPs

Based on the reaction mechanism elucidated above in Figure B1e, we have synthesized few-layered M-HAB sheets onto SiO2/Si or sapphire substrates. The image above shows our standard approach (pick up method to deposit 2D polymeric materials onto desired substrates. The SEM and EDS spectra shows the presence of Ni and Co linker in our synthesized polymeric systems in Figure B2.

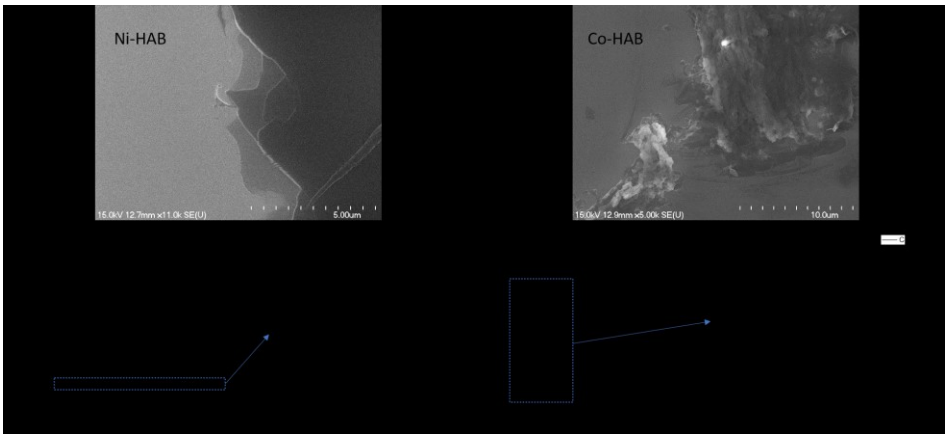

Figure B2 The SEM images collected from Ni-HAB and Co-HAB polymeric sheets deposited onto SiO2/Si substrates. These layers exhibit firm layers and presence of C, N, and Co/Ni metal linkers.

3. The preliminary magnetic studies on M-HAB (M=Ni and Co)

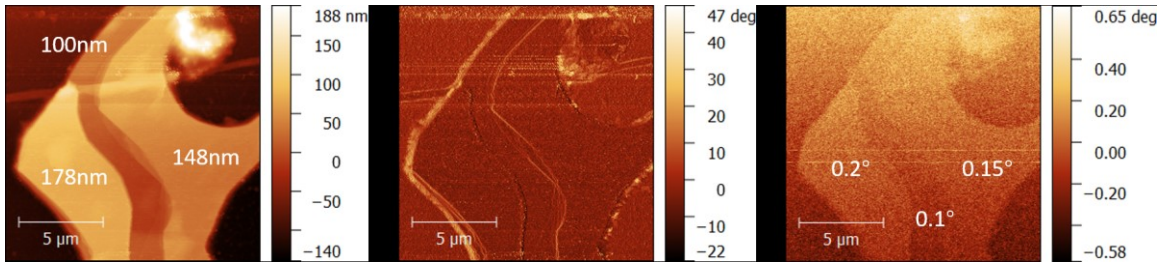

Figure B3 AFM and MFM images collected from Ni-HAB sheets on SiO2/Si substrates.

We have carried out preliminary magnetic force microscopy (MFM) and kelvin probe force microscopy (KPFM) studies/measurements in these synthesized and deposited 2D polymeric layers. Below are some of the images collected from M-HAB layers.

Figure B3 shows that the MFM datasets exhibit finite phase shift depending on the layer thickness. Overall observed magnetism is rather minimal and the presence of 2D magnetic order remains uncertain at this time. In contrast, Co-HAB sheets exhibit rather large magnetism as shown in the Figure B4.

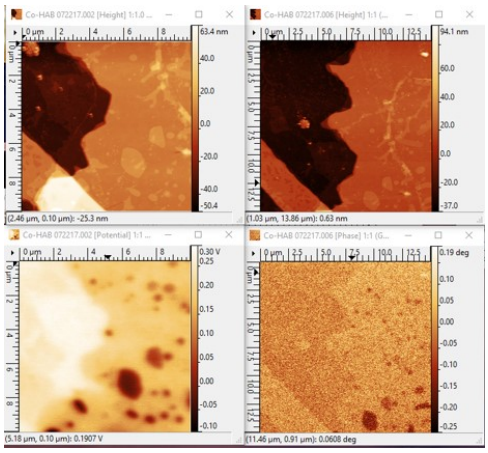

Figure B4 KPFM (left) and MFM (right) images collected from Co-HAB sheets on SiO2/Si substrates.

Figure B4 shows that Co-HAB shows strong electron affinity or work function variation as proven by KPFM measurements and in these certain thickness of materials there exist significant magnetic phase shift. This shows that Co-HAB layers possess some degree of magnetic order. Future studies are needed going far beyond this preliminary 6 months effort to understand

the magnetic properties of these 2D M-HAB layers.

4. The stability of 2D M-HAB layers

Prior to our optical characterization, we have carried our systematic studies to understand the

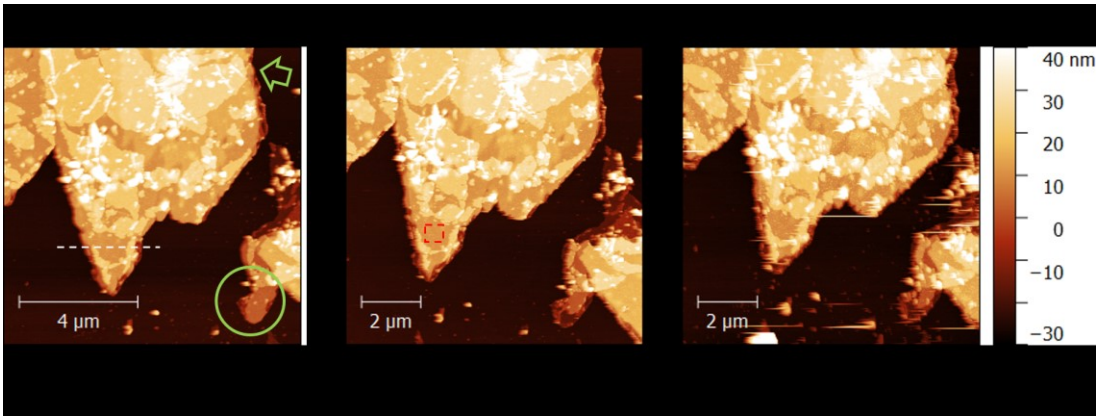

Figure B5 AFM images collected from Co-HAB samples on the 1st, 4th, and 7th day after the

stability of our 2D M-HAB layers under optical excitation. Unfortunately, these layers were highly unstable under photo-excitation which has significantly prohibited our team to collect any meaningful optical signals.