REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)
16-07-2022

2. REPORT TYPE
Final Report

3. DATES COVERED (From - To)
1-Aug-2015 - 31-Jul-2019

4. TITLE AND SUBTITLE
Final Report: Porphene: A Regular Heterocyclic Analog of Graphene

5a. CONTRACT NUMBER
W911NF-15-1-0435

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Colorado - Boulder
3100 Marine Street, Room 481
572 UCB
Boulder, CO 80303 -1058

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)
66509-CH.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			Josef Michl
UU	UU	UU	UU		19b. TELEPHONE NUMBER 303-492-6428

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR Final Report
as of 10-Jan-2023

Agency Code: 21XD

Proposal Number: 66509CH
Agreement Number: W911NF-15-1-0435

INVESTIGATOR(S):

Name: Ph.D. Josef Michl
Email: josef.michl@colorado.edu
Phone Number: 3034926428
Principal: Y

Organization: **University of Colorado - Boulder**
Address: 3100 Marine Street, Room 481, Boulder, CO 803031058
Country: USA
DUNS Number: 007431505
EIN: 846000555
Report Date: 31-Oct-2019
Date Received: 16-Jul-2022
Final Report for Period Beginning 01-Aug-2015 and Ending 31-Jul-2019
Title: Porphene: A Regular Heterocyclic Analog of Graphene
Begin Performance Period: 01-Aug-2015
End Performance Period: 31-Jul-2019
Report Term: 0-Other
Submitted By: Ph.D. Josef Michl
Email: josef.michl@colorado.edu
Phone: (303) 492-6428
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 3 **STEM Participants:** 2

Major Goals: The synthesis of porphene, a regular heterocyclic analog of graphene, at the air-water interface through oxidative coupling of zinc porphyrin.

Accomplishments: See upload.

Training Opportunities: Three students were trained during the reporting period:

Milena Jovanovic, graduate student
Victoria Schlutz, undergraduate student
Jared P. Bozzone, undergraduate student

Results Dissemination: Nothing to Report

Honors and Awards: Hammond Award, I-APS, 2015

Neuron Foundation Award, Czech Republic, 2016

Award, Czechoslovak Society for Arts and Sciences, Prague Section, 2017

Fellow of the I-APS, 2017

Fellow of the Royal Society of Chemistry, 2019

Medal of the Learned Soc. Czech Rep., 2019

Symposium in honor of 80th birthday, IOCB, Czech Acad. Sci., Prague, Czech Rep., 2019

Member, Sigma Xi, 2021

Josef Michl Festschrifts for 80th birthday: (i) J. Phys. Chem. A 2021, 125, 1802-1808, https://pubs.acs.org/page/jpcafh/vsi/michl-festschrift; (ii) Chemistry 2021, 3, 440-443, https://www.mdpi.com/journal/chemistry/special_issues/for_Josef_Michl

RPPR Final Report
as of 10-Jan-2023

Protocol Activity Status:

Technology Transfer: Michl, J.; Magnera, T. F. Zinc Porphene a Heterocyclic Analog of Graphene and Methods of Making and Using the Same. US. Provisional Patent Application No. 62/775,322, Dec. 4, 2018.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Josef Michl
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: Y

Participant Type: Staff Scientist (doctoral level)
Participant: Thomas Magnera
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Milena Jovanovic
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Jared Bozzone
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Victoria Schlutz
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Partners

,

I certify that the information in the report is complete and accurate:
Signature: Josef Michl
Signature Date: 7/16/22 8:30AM

Final report for USARO grant W911NF-15-1-0435
Grant period: August 1, 2015 - July 31, 2019
Principal Investigator: Josef Michl

Technical Report. After years of effort, we learnt how to convert parent Zn porphyrin (**2**, M = Zn) into macroscopic (0.1 - 0.01 mm across) sheets of Zn or free-base porphene (**1**, M = Zn or 2H, Figure 1), a periodic fully conjugated porphyrin network (Zn ions tend to get lost from the positively doped sheet during synthesis). At this point, it was likely that the regular meso-meso coupling in the structure shown in Figure 1A is contaminated with defects due to occasional meso-β coupling or is even less regular. It is considered likely that the sheets are double but could be separated into single and also made much larger. Initial measurements suggested that **1** is a semiconductor, doped with holes provided by the aqueous oxidant.

The results have been submitted for patent application by the University of Colorado[1] but the US patent office has since determined that the application contained too much material and requested that it be separated into several applications. This process is still underway. More recently, considerably updated results were also submitted for open publication and the manuscript is now in the peer review process in Nature Communications.

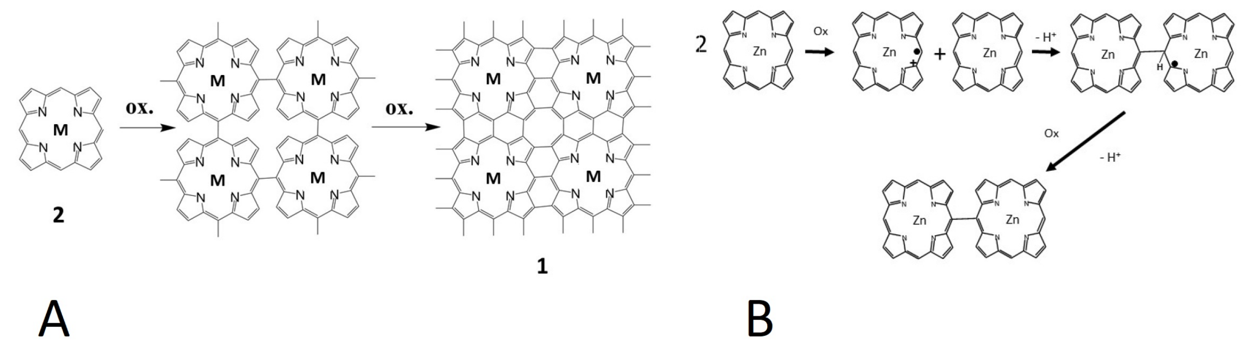

Figure 1. A: Oxidative coupling of **2** to **1**, M = Zn. B: Proposed mechanism of oxidative dimerization of **2**.

The oxidation of **2** (M = Zn) is performed in a Langmuir-Blodgett trough under conditions where the porphyrin planes are parallel to the surface of an aqueous subphase containing an oxidant. The isotherms of monomeric **2** that has been spread on the aqueous subphase and then immediately compressed after the addition of the oxidant increase gradually and somewhat erratically starting at mean molecular areas (mmA) smaller than ~70 - 100 Å^2. The latter value fits the expected footprint of **2** lying flat on the water surface. In absence of the oxidant, the isotherm starts to climb steeply at mmA of ~50 Å^2, suggesting the formation of a bilayer of **2**. Nonstandard isotherm shapes have been often observed for simple porphyrins that have turned on their edge or collapsed to multilayer films. Simple monomeric porphyrins are actually notorious for their non-ideal Langmuir surface film behavior,[2] and are often studied diluted by an immiscible second component[3] or derivatized with alkyl side chains[4] to improve their spreading and organizational characteristics.

The oxidants used by Osuka to prepare dimers and other small fragments of **1** (the Ag^+ cation to couple the meso positions followed by DDQ and Lewis acid catalysis to couple the β positions) failed on the surface of water. We had to develop an alternative and found that K_2IrCl_6 works well. Figure 2, obtained after vertical Blodgett transfer to a solid substrate of germanium, demonstrates the structural strength of the resulting **1**, which is only slightly disturbed by tearing. A similar result is obtained on HOPG, with **1** draping across terraces.

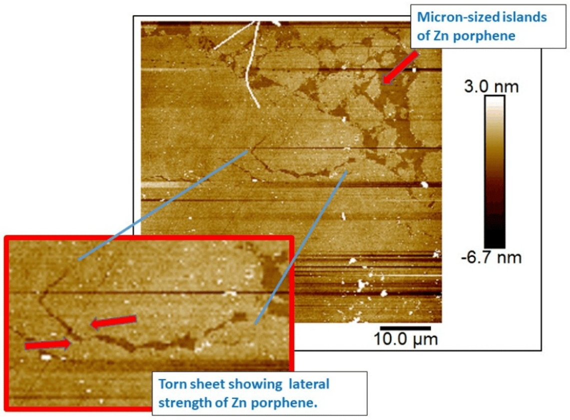

Figure 2. AFM of **1** on Ge substrate.

UV-vis spectrum measured at grazing incidence during the oxidative coupling shows a gradual disappearance of the Soret band of **2** and a gradual increase of poorly structured absorbance in the visible region, as might be expected from the spectra obtained by Osuka[5] for fused porphyrin oligomers, especially in the presence of doping with positive holes. A similar decrease in the Soret band occurs in the vis-NIR spectrum of a LB film of partially oxidized monolayers of **1**. After the oxidation process is complete, the mmA value per macrocycle at which a steep increase of the isotherm is observed is larger, ~70 Å^2, and would fit a monolayer of **1** exactly, but it still is rather erratic and unconvincing, especially since GIXD requiers a bilayer, as we shall see below. If **2** has fused into **1** as suggested by the vis-NIR spectrum, the erratic behavior of the mmA could reflect the random nature of the packing of irregularly shaped large sheets of **1**. At this point it was not definitive whether a monolayer or a bilayer of **1** has been formed and we were inclined to favor a bilayer. Since that time, further investigations showed that a bilayer is indeed formed, but that it consists of one layer of **1** and one layer of $IrCl_6^{4-}$ counterions and therefore fits both the mmA value and the GIXD results. This was not known at the end of 2019.

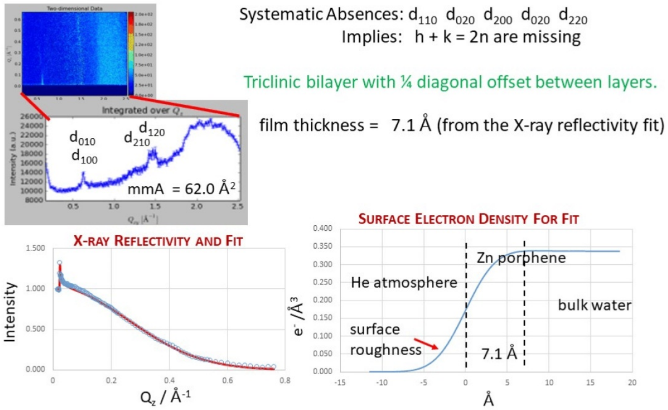

Figure 3. In situ GIXD and X-ray reflectivity of **2** on aqueous subphase.

Grazing incidence X-ray diffraction (GIXD), recorded at a nominal mma of 67 Å^2 for uncoupled **2** (Figure 3[2]) and for **1** after oxidative coupling (Figure 4), was analyzed by methods described previously.[6] The positions of peaks observed and the absence of others yielded the bilayer unit cells for the assembly of **2** (Figure 5[2]) and for **1** (Figure 6). We cannot tell if the Zn atoms are still present in **1** at the centers of the macrocyclic rings on the aqueous surface or if they were leached out during the many hours of contact between the heavily positively doped **1** and the oxidant-containing subphase. An XPS measurement showed that they were absent after transfer to a solid substrate. However, to simplify the structural description, we show them as still present.

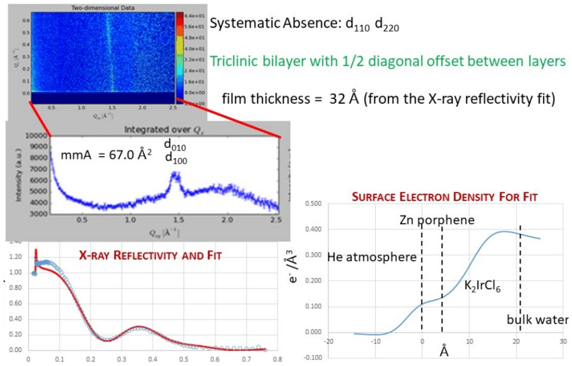

Figure 4. In situ GIXD and X-ray reflectivity of **1** on aqueous subphase.

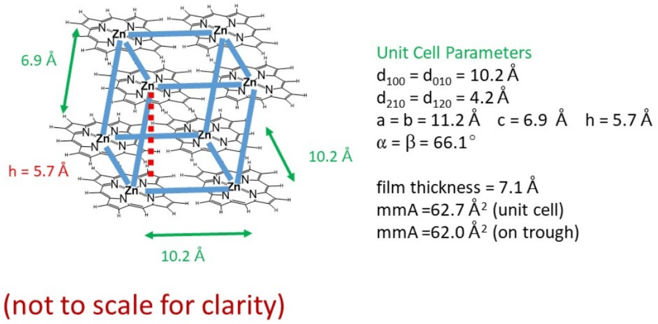

Figure 5. Unit cell structure of a layer of **2** on aqueous subphase from in-situ X-ray data.

For **2**^{2} the side of the 4 Zn square is 10.2 Å, the two layers are shifted (probably diagonally) by ~1/4 of the unit cell, and the footprint of the unit cell is 104.4 Å^2. The bilayer thickness is 6.9 Å. In **1**, the side of the 2 × 2 Zn square is 8.3 Å, the two layers are shifted along a square edge by 0.38 of the unit cell, and the area of the unit cell is 70.6 Å^2, which would agree with the presence of a monolayer and not a bilayer. As noted above, this contradiction, unresolved at the time, has now been solved. The Zn-Zn distance can be compared with 8.5 Å in Osuka's meso-meso,β-β,β'-β' triply linked fused Zn double porphyrins.[7] The bilayer thickness is 2.3 Å when estimated from the intensity maximum of the Bragg rod away from the *xy* plane. From X-ray reflectivity, it is 22 Å, but this number contains an unknown contribution from a layer of anions expected at the interface of water with **1**, surely richly doped with positive holes inserted from the strong oxidant present in the solution.

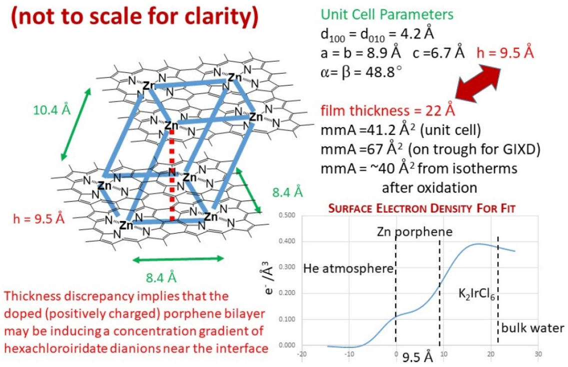

Figure 6. Unit cell structure of **1** on aqueous subphase from in-situ X-ray data.

Additional detail about the analysis of the GIXD patterns follows. Trigonal packing was discarded since it produced unreasonable mmA values. Orienting **2** on its edge with a brick layer offset leads to an estimated mmA of 0.5×4.2×10.2 = 21.4 Å^2 for a unit cell with a basis of two, clearly too small. An mmA of 0.5×4.2×4.2 = 8.8 Å^2 is similarly unphysical for **1**. A bilayer of porphene sheets resulting from coupling of dimers of **2** offers a more reasonable interpretation of the GIXD results. The peak near q = 1.42 Å^{-1} has an off-axis component q_x = 0.52 Å^{-1} whereas the other two peaks (q = 0.62 and 1.50 Å^{-1}) have their maximum intensity near q_x = 0 Å^{-1}. A close-packed 2-D crystal with tilted **2** will have an oblique unit cell with three fundamental peaks indexed as [h,k,l]=[0,1], [1,0] and [1,1], two of which will have off-axis intensity. This is excluded since we only observe a single off-axis peak. Alternatively, the two on-axis diffraction peaks can be assigned to a centrosymmetric orthogonal unit cell with systematic absences at $h + k = 2n+1$ and indexed [1,1] and [2,0], which leaves the off-axis peak to be assigned to scattering intensity normal to the water surface that arises from the tilting of the reciprocal lattice relative to the water surface and allows us to estimate the thickness. This approach requires that **2** be organized as at least a bilayer. The peaks are now no longer considered Bragg rods and are indexed as [h,k,l]. The simplicity of the scattering pattern implies that there is symmetry in the bilayer stacking that leads to systematic absences. This can be formulated as $I \propto |F(\boldsymbol{Q})|^2$, with

$$F(\boldsymbol{Q}) = \sum_{h,k,l\,-\infty}^{\infty} \{1 + \exp[iQ_{xy}a(s_x + s_y)]\exp(iQ_z z_0)\}\delta(\boldsymbol{k} - 2\pi \boldsymbol{G}_{hkl})$$

where $\boldsymbol{Q}$ is the scattering vector, $\boldsymbol{G}_{hkl}$ is a reciprocal lattice point, a is the length of the unit cell base which is assumed to be square, s is the fractional shift vector [s_x,s_y] of the upper layer and z_0 is its vertical spacing. The term in the folded brackets is the scattering phase and vanishes when [$ika(s_x + s_y)$] equals π and $z_0 = 0$ (for $l = 0$). This leads to zero or weak intensities for in-plane scattering peaks [$h,k,0$] and happens generally when $s_x = s_y$ and simultaneously s is a simple fraction such as 1/2 (centered: $h + k = 2n + 1$) or 1/4 (diamond: $h + k = 4n + 2$). An offset bilayer structure whose orientation is strictly constrained to a plane will specifically have missing peaks when those peaks fall outside of the out-of-plane view of the detector or are blocked by the constraining plane, in our case the water surface.

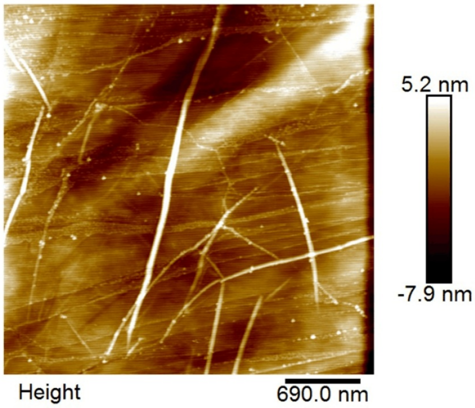

Figure 7. AFM on Ni-porphene nanoropes on HOPG.

This arises due the a rotation of the reciprocal lattice with the lateral shift of the upper lattice. The plane spacings are calculated using the general formula for a triclinic unit cell with $a = b$, $\alpha = \beta$ and $\gamma = 90°$ with an assumed unit cell basis of two. In the case of **1**, both the on-axis and off-axis GIXD intensities can be satisfactorily indexed for either [s_x,s_y]=[1/2,1/2] or [1/2,0] (shown in Figure 6). A bilayer slide just along the unit cell edge leads to a more realistic bilayer thickness of 9.5 vs 2.3 Å, estimated from indexing the peaks with off-axis intensity. The footprint for this unit cell is 70.6 Å^2 and effective mmA is 35.3 Å^2 for the bilayer. Further support for the [1/2,0] shift was provided by GIWAXS of **1** transferred to silicon covered with native oxide.

Remarkably, under similar conditions for oxidative coupling Ni porphyrin produces ropes (Figure 7) with diameters between 23 - 115 Å and lengths exceeding 5 µm. It is not yet known whether these are hollow or filled tubes. The Ni-Ni distance determined from GIXD after coupling is 8.29 Å, and this can be compared to reported values[8] of 8.20 Å for meso-meso,β-β,β'-β' fused zinc diporphyrins and 10.0 Å for the Ni-Ni distance found before coupling. The different response of **2** (M = Ni) to oxidative coupling under otherwise identical conditions is intriguing and is not understood. It may be related to its ruffled shape and to known meso-β coupling during oxidative oligomerization.[8]

References

1. Michl, J.; Magnera, T. F. Zinc Porphene a Heterocyclic Analog of Graphene and Methods of Making and Using the Same. US. Provisional Patent Application No. 62/775,322, Dec.

4, 2018.

2. Bull, R. A.; Bulkowski, J. E. Tetraphenylporphyrin Monolayers: Formation at the Air-Water Interface and Characterization on Glass Supports by Adsorption and Fluorescence Spectroscopy. *J. Colloid Sci.* **1983**, *92*, 1-12.

3. Peng, J. B.; Foran, G.J.; Barnes, G.T.; Crossley, M. J.; Gentle, I. Structures of Mixed Langmuir−Blodgett Films of Tetrakis(3,5-di-tert-butylphenyl)porphinatocopper(II) with Cadmium Arachidate: A Grazing Incidence Synchrotron X-ray Diffraction Study. *Langmuir* **2000**, *16*, 607-611.

4. Lesieur, P.; Vandevyver, M.; Ruaudel-Teixier, A.; Barraud, A. Orientational Studies of Langmuir-Blodgett Films of Porphyrins with Polarized Resonant Raman Spectroscopy. *Thin Solid Films* **1988**, *159*, 315-322.

5. Kim, D.; Osuka, A. Photophysical Properties of Directly Linked Linear Porphyrin Arrays. *J. Phys. Chem. A* **2003**, *107*, 8791-8816.

6. Kaleta, J.; Wen, J.; Magnera, T. F.; Dron, P. I.; Zhu, C.; Michl, J. Structure of a Monolayer of Molecular Rotors on Aqueous Subphase from Grazing-Incidence X-Ray Diffraction. *PNAS* **2018**, *115*, 9373-9378.

7. Tsuda, A.; Furuta, H.; Osuka, A. Syntheses, Structural Characterizations, and Optical and Electrochemical Properties of Directly Fused Diporphyrins. *J. Am. Chem. Soc.* **2001**, *123,* 10304-10321.

8. Tsuda, A.; Nakamura, Y.; Osuka, A. Synthesis of *meso*-β Doubly Linked Porphyrin Tapes. *Chem. Commun.*, **2003**, 1096-1097.