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**RPPR Final Report**  
as of 10-Jan-2023

Agency Code: 21XD

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**Agreement Number: W911NF-15-1-0435**

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**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

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**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](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

Project Contribution:

National Academy Member: Y

**Funding Support:**

**Participant Type:** Staff Scientist (doctoral level)

**Participant:** Thomas Magnera

**Person Months Worked:** 6.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**Participant Type:** Graduate Student (research assistant)

**Participant:** Milena Jovanovic

**Person Months Worked:** 12.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**Participant Type:** Undergraduate Student

**Participant:** Jared Bozzone

**Person Months Worked:** 12.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**Participant Type:** Undergraduate Student

**Participant:** Victoria Schlutz

**Person Months Worked:** 6.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**RPPR Final Report**  
as of 10-Jan-2023

**Partners**

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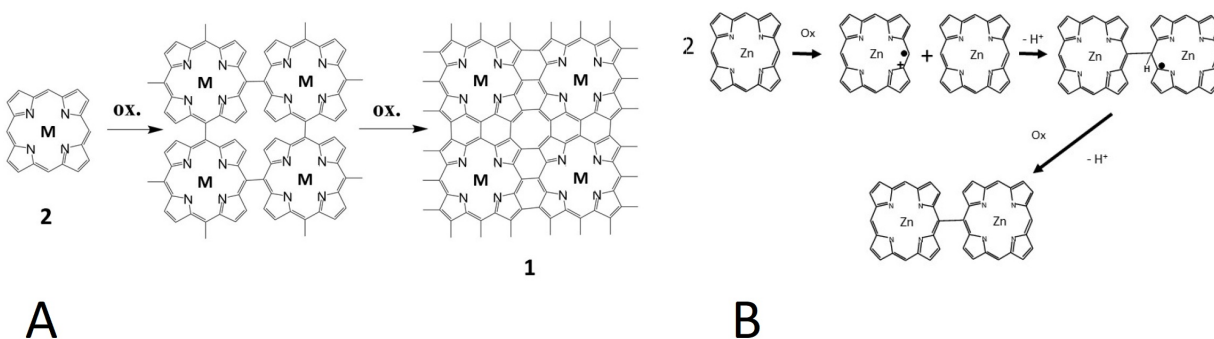
I certify that the information in the report is complete and accurate:

Signature: Josef Michl

Signature Date: 7/16/22 8:30AM

**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- $\beta$  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<sup>1</sup> 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.

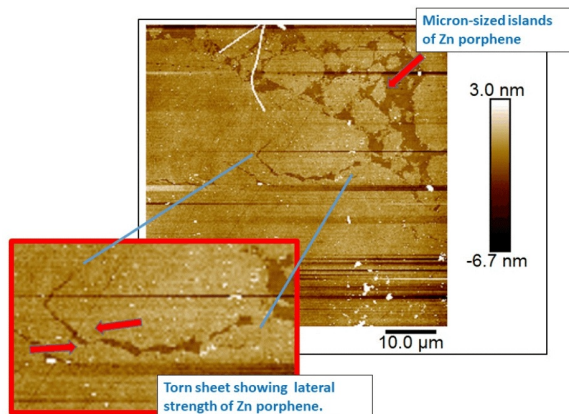


**Figure 1.** A: Oxidative coupling of **2** to **1**, M = Zn. B: Proposed mechanism of oxidative dimerization of **2**.

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  $\sim 70 - 100 \text{ \AA}^2$ . 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  $\sim 50 \text{ \AA}^2$ , 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,<sup>2</sup> and are often studied diluted by an immiscible second component<sup>3</sup> or derivatized with alkyl side chains<sup>4</sup> to improve their spreading and organizational characteristics.

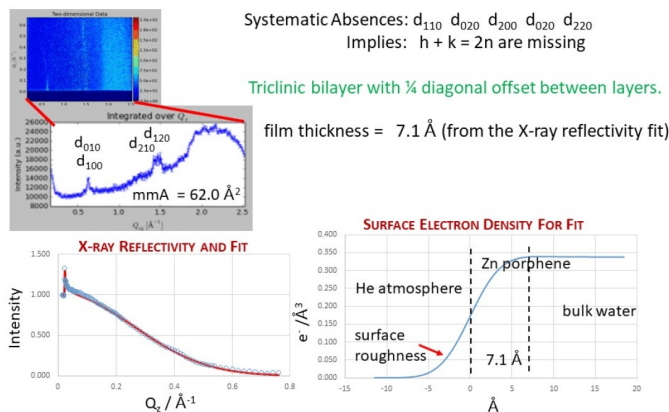
The oxidants used by Osuka to prepare dimers and other small fragments of **1** (the Ag<sup>+</sup> cation to couple the meso positions followed by DDQ and Lewis acid catalysis to couple the  $\beta$

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.

a monolayer of **1** exactly, but it still is rather erratic and unconvincing, especially since GIXD requires 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.

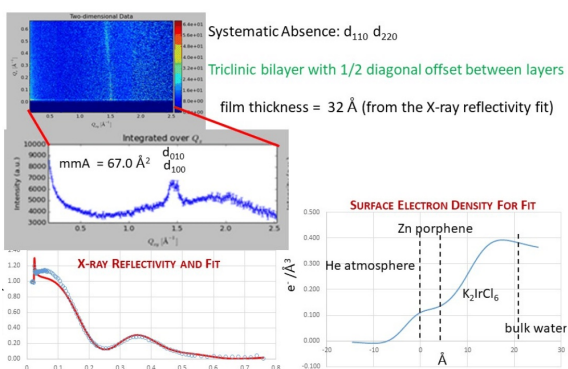


**Figure 3.** In situ GIXD and X-ray reflectivity of **2** on aqueous subphase.

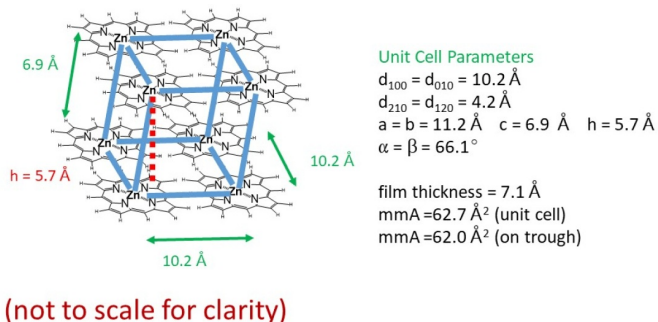
containing subphase. An XPS measurement showed that they were absent after transfer to a solid substrate. However, to simplify the structural description, we show them as still present.

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<sup>5</sup> 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 step increase of the isotherm is observed is larger,  $\sim 70 \text{ \AA}^2$ , and would fit

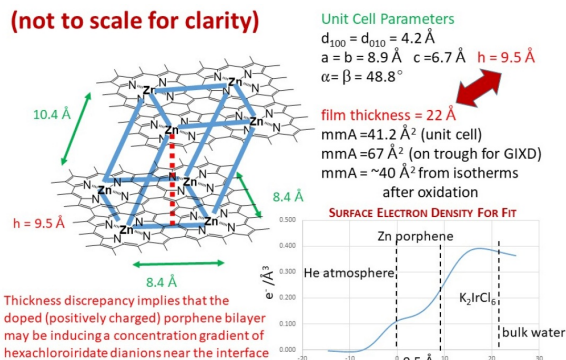
Grazing incidence X-ray diffraction (GIXD), recorded at a nominal mma of  $67 \text{ \AA}^2$  for uncoupled **2** (Figure 3<sup>2</sup>) and for **1** after oxidative coupling (Figure 4), was analyzed by methods described previously.<sup>6</sup> The positions of peaks observed and the absence of others yielded the bilayer unit cells for the assembly of **2** (Figure 5<sup>2</sup>) 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-



**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.



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

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

For **2** the side of the 4 Zn square is 10.2 Å, the two layers are shifted (probably diagonally) by  $\sim 1/4$  of the unit cell, and the footprint of the unit cell is 104.4 Å<sup>2</sup>. 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<sup>2</sup>, 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.<sup>7</sup> 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.

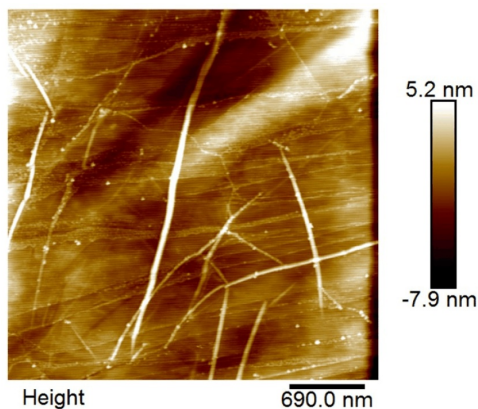
Additional detail about the analysis of the GIXD patterns follows.

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  $0.5 \times 4.2 \times 10.2 = 21.4$  Å<sup>2</sup> for a unit cell with a basis of two, clearly too small. An mmA of  $0.5 \times 4.2 \times 4.2 = 8.8$  Å<sup>2</sup> 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<sup>-1</sup> has an off-axis component  $q_x = 0.52$  Å<sup>-1</sup> whereas the other two peaks ( $q = 0.62$  and  $1.50$  Å<sup>-1</sup>) have their maximum intensity near  $q_x = 0$  Å<sup>-1</sup>. A close-packed 2-D crystal with tilted **2** will have an

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  $I \propto |F(\mathbf{Q})|^2$ , with

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

where  $\mathbf{Q}$  is the scattering vector,  $\mathbf{G}_{hkl}$  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  $\pi$  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 to 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  $\gamma = 90^\circ$  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<sup>2</sup> and effective  $mmA$  is 35.3 Å<sup>2</sup> 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<sup>8</sup> 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.<sup>8</sup>

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