Porphene and Porphite: Porphyrin Analogs of Graphene and Graphite

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Summary: Two-dimensional (2D) organic materials offer atomic precision for optoelectronics and energy-efficient nanoelectronics, but most are not easily patterned and tuned. The long-sought porphene \([\text{C}_{20}\text{N}_4\text{H}_2]^+\) has now been prepared in a hole-doped form from the zinc salt \(\text{C}_{20}\text{N}_4\text{H}_{12}\text{Zn}\) (Zn-1) by oxidative polymerization on aqueous surface accompanied by loss of zinc ions. After hole removal by excess reductant in the subphase, metal ions can be introduced to form Zn-porphene, \((\text{C}_{20}\text{N}_4\text{Zn})_n\) (Zn-1, Figure 1), or other metalloporphenes. Reversible insertion of metal ions promises painting on an atomic canvas with distinct metal ions and ligands without removing any \(\pi\) centers from conjugation. The bond pattern in 1 and Zn-1 is deduced from in-situ and ex-situ spectra and images. Early GGA DFT computations for a perfect sheet of Zn-1 predicted a \(P4mm\) \((D_{4h})\) square unit cell and metallic conductivity, but hybrid DFT predicts it to be a semiconductor with two slightly rectangular antiaromatic \(P2mm\) \((D_{2h})\) unit cells containing deformed planar cyclooctatetraene, analogous to “Kekule” structures of a 2×2 fragment of Zn-1 and planar \([4n]\)annulenes, cf. a vast physics literature on 2D-Peierls distortions. The polymer sheet was transferred to solid substrates, producing multilayers of 1 (porphite) and semiconducting Zn-1 (Zn-porphite), analogous to graphite.
27 **Main Text**

Initial approaches to two-dimensional (2-D) organic polymers at liquid interfaces\textsuperscript{32,33} or surfaces\textsuperscript{34,35,36,37} were disappointing; the products were either many atoms thick\textsuperscript{32,33} or small and irregular.\textsuperscript{34,35} Only the method they introduced for surface-to-surface transfer by coating with a

![Diagram of Zn porphyrin (Zn-2), Zn porphene (Zn-1), Zn z-isoporphene, and Zn s-isoporphene.]

**Figure 1.** Optimized DFT/PBE50 structures and (in red) symmetries of Zn salts of porphyrin (Zn-2), z-isoporphene, s-isoporphene, and \textit{P2mm} and \textit{P4mm} forms of porphene (Zn-1); in parentheses, energies (kcal/macrocycle); Bond lengths in Å. Black, green, and red circles are $\alpha$, $\beta$, and meso carbon atoms, respectively; nitrogen atoms are blue. In Zn salts, larger purple circles are Zn atoms. In free bases 1 and 2, they represent two diagonally disposed H atoms. Red lines define unit cells: Zn-1: 8.26 Å $\times$ 8.36 Å (\textit{P2mm}) or 8.29 Å $\times$ 8.29 Å (\textit{P4mm}).
thin layer of polystyrene, dissolved after transfer,\textsuperscript{34,35} is still in use.\textsuperscript{38} More recently, sizeable 2-D polymer sheets have been prepared successfully on liquid surfaces.\textsuperscript{39,40,41,42,43,44}

Our preparation of porphene (1) by oxidative polymerization of zinc porphyrin (Zn-2) in a Langmuir layer was inspired by the groups of Osuka\textsuperscript{45,46,47,25} and of Vorotyntsev and Devillers.\textsuperscript{48,49} The former oxidatively fused derivatized Zn-porphyrins into tape- and square-shaped fragments of 1 with stabilized edges, and the latter anodically oxidized Mg-2 in bulk solution to a thick layer of charge-transporting polymer of undetermined structure.

In spite of the intriguing metallic conductivity and superconductivity predicted for the fully conjugated 2-D sheets of 1 and Zn-1,\textsuperscript{17} we are not aware of prior attempts to prepare them. Oxidative coupling of 2 or its metal salt requires the generation of 12 C-C bonds around the periphery of every porphyrin unit, each with a loss of two protons. At first sight, the coupling\textsuperscript{48,49} is likely to produce an irregular 3-D cross-linked jumble of variously connected porphyrins. Osuka constrained fusion to a limited number of directions through blocking selected edges of starting porphyrins with substituents, but in the synthesis of 1 all four sides of each macrocycle must be free to couple. The mechanism implied by his group’s work\textsuperscript{45} is initial formation of a radical cation, followed by reversible aromatic substitution\textsuperscript{50,51,52} on an uncharged neighbor, loss of a proton, oxidation of the resulting radical to a cation, and another deprotonation. Similar possibly irreversible events then establish the remaining bonds that finally fuse the edges. Given the reversibility of the initial C-C coupling,\textsuperscript{53} we hoped that the anticipated 2-D confined reactions in a preorganized layer would offer only limited choices to each additional molecule of 2, favoring planarity and repair of defects.

Randomness is a threat even in a 2-D product, because oxidative porphyrin dimerization by edge-to-edge fusion often follows two competing pathways, “m-m + 2×β-β” (three new C-C
bonds in a dimer) and “β-β + 2×β-m” (two new C-C bonds in a dimer),\textsuperscript{45} sometimes in a random sequence of fusion modes.\textsuperscript{54} Formation of 1 requires m-m + 2×β-β fusion at all four edges. Our DFT calculations suggest that regular fusion via m-m + 2×β-β at two opposite edges and β-β + 2×β-m at the other two will be followed by a strongly exothermic Woodward-Hoffmann allowed electrocyclic reaction forming two 7-membered rings and two allylic CH bonds, susceptible to oxidative loss of two more hydrogens to yield many isomers of 1, such as s-isoporphene with straight stripes of Zn-Zn connectors, z-isoporphene with a zig-zag pattern (Figure 1), and others with more complex connector patterns and larger unit cells. A β-β + 2×β-m fusion at all four edges would produce a highly strained non-planar isomer. It is unlikely to proceed to the end and such polymer would remain partially hydrogenated, in contrast to what we observe.

**Results and Discussion**

In a day or less, fresh 0.01 - 10 mM K$_2$IrCl$_6$ in the aqueous subphase converts a Langmuir bilayer of Zn-2 or Zn-2-$d_{12}$ into a monolayer of 1 with a loss of all zinc (Figure 2) and nearly all CH or CD bonds (Figures 3 and E5), and without detectable formation of isoporphenes. Full removal of CH or CD bonds takes time (see below). Old or more dilute solutions leave some of the zinc inside. In the absence of an oxidant, no loss of zinc is observed from the bilayer of Zn-2. We refer to the use of fresh aqueous 0.035 mM K$_2$IrCl$_6$ for 24 h as “standard conditions”.

Like graphene, 1 is gray (Figure E9), sturdy (Figure E12), transferable (cf. the ex situ section below), self-supporting (Figure 4), and after transfer to solid substrates builds multilayers analogous to graphite (Figure 4). We have not detected the metallic conductivity predicted\textsuperscript{17} for a perfect infinite sheet but conductivity was induced by reversible doping with I$_2$ in hexanes (Figure E1).
Structural evidence for oxidative polymerization of Zn-2 was obtained (i) in situ (on water) to form 1, using UV-visible spectroscopy (UV-vis, Figure E9), grazing incidence X-ray diffraction (GIXD, Figure E5), and X-ray reflectivity (XR, Figure E5), and after conversion to Zn-1, also Langmuir isotherms and Brewster angle microscopy (BAM, Figure E2), and (ii) ex situ (after Zn reintroduction and transfer to form Zn-porphite), using ultraviolet-visible-infrared (UV-vis-IR, Figure E9), infrared (IR, Figures 3 and E5), resonance Raman (Figure 3), and X-ray photoelectron spectroscopy (XPS, Figure E11), and atomic force (AFM, Figure E12) and transmission electron (TEM, Figure 4) microscopy.

Like all previous cyclic boundary condition periodic DFT calculations for porphenes, ours suffer from the use of a single reference configuration at or near $P4mm$ geometries where at least two are called for. However, a hybrid functional with >25% exact exchange and a geometry optimized to rectangular $P2$ (Figure 1) nevertheless provides overall compatibility with experimental observations, including vibrational spectra (Figure 3) and particularly, the absence of metallic conductivity (Figure E1).

Details of the structural proof are provided in Supplementary Information.

(i) In Situ Polymerization Monitoring. UV-vis. Figure E2A provides evidence for a slow chemical transformation in the LB layer of Zn-2 by $K_2IrCl_6$ in the subphase. The Soret band is first replaced by broad absorption at lower energies expected for edge-fused porphyrins, some of which disappears again at very long times (see ex-situ studies below).

LB Isotherms (Figure E2B). Porphyrins usually yield poorly defined Langmuir isotherms (surface pressure as a function of mean area per molecule, mmA). On pure water, the isotherm of Zn-2 rises perceptibly above baseline at mmA of 80 - 90 $\text{Å}^2$ and steeply at mmA of ~50 $\text{Å}^2$. Calculated molecular footprints are ~108 $\text{Å}^2$ with molecules flat on the surface and ~35 $\text{Å}^2$ when
nearly perpendicular to it (Figure E3). Most likely, at high dilution Zn-2 molecules lie flat on the surface and upon compression slide over each other until they produce a full bilayer, which resists further compression. BAM reveals small highly scattering islands, presumably Zn-2 microcrystals, moving slowly independently of each other, probably due to air currents. After polymerization to 1, they are still present and are interspersed with large zones of reduced contrast, but their motions are correlated, all as expected for a surface covered with large rigid sheets (Figure E2C).

After polymerization, the onset of a steep rise upon compression is poorly reproducible. For both 1 and Zn-1 it occurs at mmA 65-105 Å², presumably depending on how the large sheets happen to pack. The mmA/macrocycle value expected at perfect monolayer packing both from GIXD and DFT is 71 Å². It is thus highly unlikely that 1 could be present as a bilayer, for which a steep rise should occur at mmA of ~35 Å², a value much smaller than any observed in numerous experiments.

Figure 2. Top, GIXD at air/water interface: Zn-2 and 1 unit cells (orange balls: IrCl₆⁻²). Bottom, top view of a sheet of 1/IrCl₆⁻².
GIXD and XR (Figures 2 and E4). Analysis by previously described methods\textsuperscript{56} showed that the dominant phase occurs in single crystalline domains. Zn-2 forms pre-organized crystalline bilayer domains with a 3.5 Å interlayer spacing, an almost orthogonal (θ = 84.4°) primitive 2-D unit cell (9.3 x 10.1 Å; P1, domain size 38 nm), and slightly twisted (14.4°) fully metallated Zn-2 macrocycles lying nearly flat (tilt angle 24.8°). The upper layer is offset by 0.5 and 0.08 of the unit cell length along the short and long directions, respectively. The mmA of 46.5 Å\textsuperscript{2}/molecule at perfect packing calculated from the unit cell is slightly smaller than the ~50 Å\textsuperscript{2}/molecule found from the Langmuir isotherm, a difference attributable to a minor amount of Zn-2 microcrystals observed by BAM, or of other unknown material.

For 1 an examination of many possible structures identified only one unit cell that fits the observed GIXD (Figure E4F) pattern well, is compatible with all other evidence, and positions macrocycle centers 8 - 9 Å apart as required by the one or more CC bonds connecting their edges. Others were dismissed because they disagreed with the XR results or required a bilayer of 1, which would contradict the LB isotherm. The acceptable solution we found is a chiral superlattice of a square or approximately square grid monolayer of 1 with a unit cell of 8.4 ± 0.1 Å length (90°, P4mm, domain size, 123 nm), containing a single macrocycle, located 3.6 Å above a second square lattice with a 26.5 Å unit cell (90°, P4mm, domain size, 19 nm), containing two rotationally disordered IrCl\textsubscript{6}\textsuperscript{2-} ions. The lattice vectors of the two cells are not aligned and the Bravais lattice is monoclinic. The best fit is found if the anion lattice is non-primitive and 2-D body centered with one corner offset relative to the polymer unit cell by (0.5,0) and twisted by 18.5° (Figure 2). The footprint is 73.0 Å\textsuperscript{2} mmA/macrocycle. This solution agrees with the observed XR (Figure E4H) and with the LB isotherm (Figure E2B). We cannot tell how the -NH- and =N- groups are arranged in the free-base macrocycles nor how many macrocycles
are oxidized to radical cations. If the \( \text{I/} \text{IrCl}_6^{2-} \) superlattice is electroneutral, the oxidized fraction is 40%. If the superlattice carries a net charge, it will be compensated by disordered ions in the nearby layer of solution. Precedents for such situations exist.\(^{57,58}\)

*DFT geometry optimizations* (Figure 1) were performed for Zn-1 and the results depend on the functional used (Supporting Information). Calculations without any exact exchange, known to exaggerate delocalization,\(^{59}\) agree with earlier reports\(^ {16,17}\) and yield a single \( P4mm \) minimum (8.42 Å × 8.42 Å for PBE) with partially filled bands, suggesting metallic conductivity. For hybrid functionals with >25% of Hartree-Fock exchange, there are two potential energy minima at mutually perpendicular slightly rectangular \( P2mm \) geometries (8.26 Å × 8.36 Å for PBE50), and the band structure is that of an indirect band semiconductor. Both results agree with the structure deduced from the in-situ GIXD pattern within its uncertainty limits (the PBE calculated interlayer separation is excessive, 4.0 Å). It is presently not known whether the heavy hole doping and the presence of water and counterions affect the observed structure.

At the \( P2mm \) geometry, optimized with functionals containing >25% of exact exchange, 1 is calculated to be a few kcal/mol below the \( P4mm \) geometry and the difference increases as the amount of exact exchange grows. The results for 1 and Zn-1 are similar and those obtained with an atomic and a plane wave basis set agree (Table E3).

**(ii) Ex Situ Polymerization Monitoring.** Oxidative polymerization of Zn-2 was monitored by performing the NaI quench at various times after the reaction was launched or by varying the concentration of \( \text{K}_2\text{IrCl}_6 \), keeping the reaction time constant. Concentrations up to 0.21 M and reaction times up to 120 h were used to obtain complete conversion (Figure 3). Similar experiments were performed with Zn-2-\( d_{12} \). To optimize the signal to noise ratio, the Zn-1 monolayer was transferred to substrates at a surface pressure high enough to convert it into small
domains of bilayers and multilayers (porphite and Zn-porphite). The IR spectra (Figures 3 and E5) also allow us to follow the loss and reinsertion of Zn$^{2+}$ in 1, using its NH stretch at 3340 cm$^{-1}$ (cf. 3309 cm$^{-1}$ in 2) and NH pyrrole deformation at 1227 cm$^{-1}$ (cf. 1223 cm$^{-1}$ in 2). For details, see Supplementary Information.

Figure E5 shows the IR and Figure E6 the resonant Raman spectra of incompletely oxidized samples. Figure E7 compares the Raman spectra obtained starting with Zn-2-$h_{12}$ and with Zn-2-$d_{12}$. Figure E8 contains the DFT optimized structure of the most common defect due to incomplete oxidation. As deduced from peak positions and integrated intensities in the vibrational spectra, it is a porphyrin macrocycle that still has 10 of its original 12 C-H or C-D bonds, is only attached to two of its neighbors at two opposed meso positions, and is twisted nearly perpendicular to the porphene plane. The overall observed and DFT calculated UV-vis-NIR-IR absorption can be seen in Figure E9, where difference spectroscopy yields the visible spectrum of the defects. DFT calculations on a simple nine-porphyrin model for the defect accounts for this spectrum well and computed transition densities collected in Figure E10 clearly distinguish excitations localized on the twisted macrocycle from those localized in its immediate vicinity where edge fusion failed to occur and which have also kept a total of ten C-H or C-D bonds.

The key peaks used for the observation of residual C-H or C-D bonds, identified by their large isotopic shifts, were the stretches at 3034 cm$^{-1}$ ($C_m$H) and 3110 cm$^{-1}$($C_p$H) in the IR$^{60,61}$ and the in-plane bends at 1158 cm$^{-1}$ ($C_m$H) and 1060 cm$^{-1}$ ($C_p$H) in Raman$^{60,61}$ (Table E4). The standard polymerization conditions (fresh 0.035 mM K$_2$IrCl$_6$ for 24 h) were chosen as those under which IR spectra no longer showed any residual C-H or C-D bonds, although Raman spectra still did.
Given the level of noise in the IR spectrum, the ratio of fully incorporated to defective porphyrin macrocycles is at least 40 (3.5 ×10^{12}/cm^{2}) under the standard synthetic conditions. Under the most forcing conditions, when not even the resonant Raman spectra show any C-H or C-D bonds, and based on the noise level, the ratio is at least 400 and the defect density is at most 3.5×10^{11}/cm^{2}. These results for identified defects compare well with defect densities observed in other 2-D materials (10^{15}/cm^{2} in fully disordered graphene^{62} and 10^{13}/cm^{2} in MoS_{2}^{63}). The presence of other types of defects that are spectroscopically silent cannot be excluded.

Vibrational spectra demonstrate the absence of CH bonds in the polymer and limit its structure to Zn-2 and zinc isoporphenes (Figure 1). GIXD rules out the latter (Figure E4).

**Figure 3.** Vibrational spectra of Zn-1: (A) Calculated IR. (B) IR observed on a Ge internal multireflection plate (red; in black, spectrum of Zn-2). (C) Calculated Raman. (D) Raman observed on CaF_{2} (orange, sample polymerized under standard conditions; green, sample polymerized exhaustively; blue, spectrum of Zn-2). Black arrows mark defect peaks and red arrows emphasize the absence of CH stretching vibrations.

XPS (Figure E11) provides independent evidence for the transformation of 1 into Zn-1. The Zn(2p) peak of Zn-1 is absent after polymerization, which forms 1, and is presumably present
after zinc is reinserted to produce Zn-1, but it remains obscured by ZnCl₂ impurity even after repeated rinsing. We therefore focus on the N(1s) binding energies,⁶⁴ which show a strong increase relative to monomeric porphyrins (Table E5, cf. previous reports for 2⁶⁵ and for Zn salts of substituted porphyrins⁶⁶). A 2.5 eV binding energy difference between Zn-1 and Zn-2 is well reproduced by our DFT calculation, which yields 2.2 eV for the rectangular P2₁mm form. A calculation for the square P4mm form gives a very large value of 4.7 eV, which is perhaps not surprising considering that this form is calculated to be metallic, providing very effective hole screening. Next to the observation of low electrical conductivity of undoped Zn-1, the much better agreement between the observed and calculated N(1s) binding energy difference for the rectangular than the square form provides further evidence for a rectangular unit cell and a semiconductor, and shows that the use of more than 25% of exact exchange in the DFT functional is justified.

AFM (Figure E12). Transfer to a solid substrate permits AFM imaging of porphite. It illustrates the mechanical strength of the 2-D sheets draped over steps in HOPG, and demonstrates their large size, up to many scores of μm. The conformity of the edges of some of the neighboring patches shows that they were torn by shearing forces in transfer and remained intact thereafter.
TEM of Zn-1 converted to Zn-porphite by transfer at high surface pressure shows overlapping lattices and moiré patterns in a disordered mass of small crystalline domains of Zn-1 multilayers (Figure 4). The white box in Figure 4 matches the unit cell expected for Zn-1 with a (0.5,0.5) offset between neighboring layers. An analysis of Zn-Zn distances at various angles of electron incidence agrees with the dimensions determined in-situ by GIXD and provides an independent confirmation of the prevalence of m-m + 2×β-β coupling in the formation of 1 from Zn-2. The thinnest free-standing layers were rapidly degraded in a 200 keV e-beam of an HRSTEM instrument.

**Figure 4.** (A) TEM image of Zn-porphite polymerized under standard conditions and transferred to Au mesh. (B) An enlargement of the white box shown in panel A, with a 8.4 × 8.4 Å² unit cell deduced for 1 from GIXD and a (0.5,0.5) offset between layers. Inset shows FFT of B.

**Electrical Conductivity.** This probably is the most immediately interesting of all material properties of a new family of 2D materials. At the moment, we have only examined room-temperature conductivity of multilayer Zn-1 and found that the undoped material is an insulator
and follows Ohm’s law after doping with I₂ (Figure E1). It loses conductivity when the dopant is removed.

Possible Antiaromaticity. The antiaromaticity of a substituted 2×2 fragment of porphene has been discussed\textsuperscript{25} and it appears that it can be extended to an infinite polymer sheet. In spite of the weakness related to the use of a single reference configuration, the present periodic boundary condition calculations credibly suggest the existence of a striking difference between the antiaromatic porphenes with two potential energy surface minima in a primitive unit cell and the aromatic graphene with one. If confirmed by higher level calculations and less ambiguous experimental tools, this suggests a general classification of fully conjugated two-dimensionally infinite π-electron systems. Like aromatic annulenes and many more complicated polycyclic molecules, aromatic 2D polymers would be built from units possessing a single equilibrium structure described by a superposition of two strongly interacting Kekule resonance structures. Antiaromatic 2D polymers would be built from two (and possibly more) distinct units, each corresponding primarily to one Kekule structure, interacting only weakly with the other. In Zn-1, the source of antiaromaticity is the cyclooctatetraene ring, but it is possible that the presence of a heptalene structure in the presently unknown Zn isoporphenes (Figure 1) might make them antiaromatic, too. The lower energy of the latter isomers may be primarily due to reduced strain in their σ skeleton. It is noteworthy that the polymerization of Zn-2, whose first steps most likely are reversible, permitting the formation of a highly regular structure, nevertheless in the end yields the less stable isomer.

The square to rectangle distortion of the unit cell observed in our calculations on porphene is a form of two-dimensional Peierls distortion, much studied by physicists on graphene, e.g.\textsuperscript{28,29,30,31}

Reversible Metal Ion Complexation. Ordinarily, metal ions enter porphyrin macrocycles
readily and a low pH is required to remove them. The loss of Zn$^{2+}$ ions into the subphase during oxidative polymerization is however not induced by acid,$^{67}$ but by the oxidant (bulk pH is ~6 and is not perturbed significantly by the small number of protons produced by the slow surface oxidative polymerization). Since it initiates polymerization by converting Zn-2 into a radical cation, the oxidant surely also injects positive charges into the more extensively conjugated Zn-1, lowering the binding constant of Zn$^{2+}$ ions. After charge removal with excess NaI, addition of metal cations converts 1 to Zn-1 and other metalloporphenes readily (ZnCl$_2$ is used at pH ~3 to avoid hydrolysis). The method of metallization of 1 appears to be general judging by IR and XPS results obtained when FeCl$_2$ or CuCl$_2$ are used instead of ZnCl$_2$.

The reversible insertion of metal ions into the macrocycles in 1 offers 2-D patterning without jeopardizing mechanical strength. About 60 different elements have been inserted into monomeric porphyrins,$^{68}$ (almost all metals and some non-metals), and many can attach two, one, or zero additional ligands. These could be bidentate, stitching two or more sheets into multilayers analogous to metal-organic frameworks. A layer-by-layer fabrication would allow aperiodic variation of dopants and separation of neighboring layers by different functionalized ligands, hence patterning in the third dimension and access to programmable solids.$^{69,70}$

Conclusions

Spectroscopy and imaging show that porphene (1), a heterocyclic sibling of graphene, is produced by 2-D oxidative polymerization of Zn-2 on water surface. This synthetic approach confines porphyrin ring polymerization to two dimensions to produce planar sheets and gives rise to structurally homogeneous graphene-like material by consistent formation of 12 C-C bonds around the periphery of every porphyrin ring. Selection of the porphene metal ion opens up new
possibilities to realize mechanical, electronic, optical, magnetic and spintronic functionality. As selected metal ions provide opportunities to coordinate one or two axial ligand orthogonal to the porphene plane, new opportunities arise for material processing, patterning in three dimensions, and developing novel interfacial compositions with other 2D semiconducting and conducting structures.

Many issues remain to be addressed, such as the effects of the choice of metal attached to the binding site of the monomer on the polymerization, its detailed mechanism, detection and characterization of additional kinds of defects, definitive proof of the presence of rectangular valence tautomers and their thermal, tunneling, and photochemical interconversion and the statistical mechanics and phase behavior associated with antiaromaticity, and a full investigation of electrical and thermal conductivity and other material properties.

References and Notes


Acknowledgements: We thank Dr. Binhua Lin (University of Chicago) and the ChemMAT/CARS Sector 15 facility, supported by NSF/CHE-1834750, for assistance with GIXD and XR at APS, an Office of Science User Facility operated for DOE by ANL and supported by DOE under DE-AC02-06CH11357. We thank Dr. Sadegh Yazdi at CU Boulder FEMM for access to TEM and useful discussions, Prof. Daniel Dessau and Ms. Peipei Hao for initial XPS measurements, Mr. Jonathan Bair, Mr. Edward Tortorici, Ms. Olivia Krohn, and Ms. Victoria Schlutz for technical assistance, Dr. Eric Buchanan for assistance with computations, and Professors Frank Barnes and Charles Rogers (CU Boulder), and Gian-Marco Rignanese (Catholic University Louvain, Belgium), for insightful discussions and support.

Funding:

Army Research Laboratory and Army Research Office grant W911NF-15-1-0435 (TFM, JPD, MJ)
National Science Foundation grant CHE 1900226 (TFM, JPB)
DARPA grant HR00111810006 (TFM)
University of Colorado Boulder Research Computing Group, funded by National Science Foundation grants ACI-1532235 and ACI-1532236, and Colorado State University
University of Colorado Boulder (TFM, PID, JPB, MJ)
Institute of Organic Chemistry and Biochemistry, RVO: 61388963 (IR, JM)
The Czech Science Foundation grant 20-03691X (IR)
Czech Ministry of Education, Youth and Sports grant e-INFRA CZ, ID:90140 (IR)
Wallonia-Brussels International Excellence Grant (IR)
Department of Energy Office of Science, BES, Division of Chemical Sciences, Geosciences and Biosciences, Solar Photochemistry (EMM). The views expressed in the article do not necessarily represent the views of the Department of Energy or the U.S. Government. 

Alliance for Sustainable Energy, LLC, operating NREL for Department of Energy grant DE-AC36-08GO28308 (EMM).

**Author Contributions:** JM and TFM conceived, supervised, and wrote up the project, TFM and JPB developed the synthetic procedure, TFM, PID, and WB performed measurements at the synchrotron and TFM analyzed the data, MJ and IR performed calculations, TFM measured most of the spectra, and EMM measured XPS.

**Competing interests:** Authors declare that they have no competing interest.

**Additional Information:**

**Supplementary Information** is available for this paper.

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