

Direct Oxidations of *meso*-Tetrakis(pentafluorophenyl)porphyrin: Porphotrilactones and Entry into a Nonbiological Porphyrin Degradation Pathway

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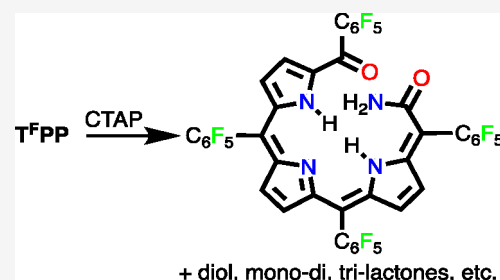


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ABSTRACT: The direct oxidations of *meso*-tetrakis(pentafluorophenyl)-porphyrin using cetyltrimethylammonium permanganate (CTAP), RuCl₃/Oxone/base or Ag⁺/oxalic acid each generate distinctive product mixtures that may contain, inter alia, porpho-mono-, di-, and trilactones. The CTAP and RuCl₃/Oxone/base oxidations also generate a unique open chain tripyrrin derived from the degradation of a porpholactone oxazolone moiety. Thus, its formation and structure are distinctly different from all biological or nearly all other nonbiological biliverdin-like linear porphyrinoid degradation products that are derived from ring cleavages between the pyrrolic building blocks.



Pyrrole-modified porphyrins (PMPs) are porphyrinoids containing one, or more, nonpyrrolic heterocycle(s).¹ One example, azuliporphyrin **1** was prepared by total synthesis from monopyrroles and analogues (Figure 1).² Alternatively, morpholinochlorin **2** was prepared by multistep conversion of a pyrrolic building block within a preformed *meso*-tetraarylporphyrin.³

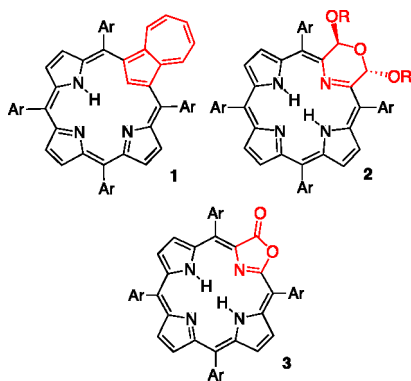


Figure 1. Examples of the literature-known pyrrole-modified porphyrins (PMPs).

meso-Arylporpholactone **3** is one of the earliest examples of a PMP made by conversion of *meso*-tetraarylporphyrins.⁴ For instance, Gouterman and co-workers adventitiously generated porpholactone **3** and a number of dilactone isomers (or corresponding silver complexes) by oxidation of one or two β,β' -double bonds of *meso*-tetrakis(pentafluorophenyl)-porphyrin (TFPP), respectively, while attempting to form the porphyrin silver complex using AgNO₃/oxalate.^{4b} Multiple

other direct or stepwise oxidation pathways to access porpho-mono-, di-, and even trilactones have become known since.⁵ Especially tetrakis(pentafluorophenyl)porpholactone metal complexes and their reduced derivatives found utility as, e.g., catalysts,⁶ photosensitizers in biological applications,^{5i,7} or optical cyanide or high-pH chemosensors.⁸

Two other oxidation methods have become known to directly convert porphyrins to porpholactones: Zhang's RuCl₃/Oxone/base methodology^{5d} and a cetyltrimethylammonium permanganate (CTAP)-mediated oxidation featured by us.^{5h} In terms of yield and ease of isolation of porpholactone **3**, as well as substrate scope, Zhang's methodology proved to be superior.^{5d,9} This is in large part because this reaction is characterized by the absence of the formation of a plethora of intractable 'overoxidation' products that are notably formed in the CTAP-mediated oxidations.^{5h} However, we later learned that a trifluoroacetic acid (TFA) wash of the crude product mixture from a superstoichiometric CTAP oxidation of chlorin- β -polyols rendered many previously insoluble or very polar products to become tractable; this allowed us to isolate the unprecedented trilactones.^{5j}

Now having all isomers of the mono-, tri-, and trilactones, in addition to related derivatives, at hand, we felt well-equipped to reinvestigate all three known oxidation methodologies of TFPF. Focus of this investigation was the screening of the

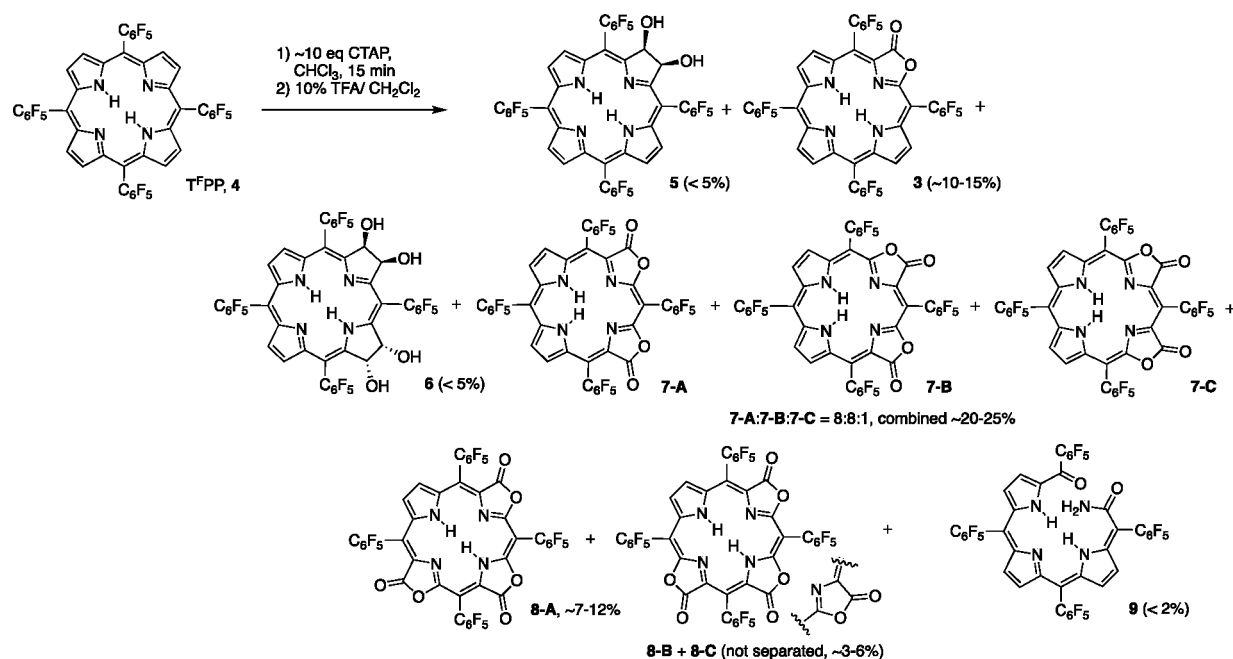
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Scheme 1. Products Identified Resulting from the Super-stoichiometric Permanganate (CTAP)-Mediated Oxidation of *meso*-Tetrakis(pentafluorophenyl)porphyrin 4


product portfolios formed for known and novel compounds, especially when using large quantities of oxidant and/or longer reaction times. Specifically, we hoped to find products that would provide fundamental insight into the oxidative chemistry of porphyrins, in general, or PMPs, in particular. The salient findings of these T^FPP oxidation studies are reported here.

When oxidizing T^FPP (4) in CH₂Cl₂ at ambient temperature with a larger stoichiometric excess of CTAP than used in the chlorin diol oxidations reported earlier,^{Se,h,j} all of the porphyrin was, as per TLC, consumed within 20–25 min (Scheme 1). The crude reaction mixture was treated with TFA and separated into low and high polarity fractions by column chromatography. We isolated the majority of products formed by using preparative plate chromatography.

As expected, significant amounts of porpholactone 3 were found (10–15%). The largest fraction (up to 25% yield) was the mixture of isobacteriodilactones 7, distributed over all three regioisomers. The regioisomer distribution was identical to that observed for the CTAP oxidation of tetrahydroxyisobacteriochlorin 6.^{Sh} The presence of dihydroxychlorin 5 and tetrahydroxyisobacteriochlorin 6 in the reaction mixture suggests that β,β' -dihydroxylations—as opposed to, for instance, ketol formation (expected for reaction of MnO₄[−] with a cyclic olefin)¹⁰—is the first step in these oxidations, followed by diol to lactone oxidations, with no observable intermediate in the latter conversion.^{Se,h,j} Notably absent in the reaction mixture were any tetrahydroxybacteriochlorins or bacteriodilactones.^{Sh} Thus, the direct CTAP-mediated oxidations of free base T^FPP, as well as of porpholactone 3 (verified in independent oxidation experiments), show a different regioselectivity than the OsO₄-mediated dihydroxylation or other free base chlorin modification reactions that are biased toward the generation of bacteriochlorins.¹¹

A considerable fraction (~15%) of a mixture of the three pyrrocorphine trilactones 8 was also formed. As observed previously,^{Sj} isomer 8-A was the most abundant (~2/3 of this

fraction) and could be readily separated; isomers 8-B and 8-C were analyzed as a mixture. The trilactones were also found to be present in the same isomer ratio under equivalent CTAP-mediated oxidation conditions of bacterio-^{Sf,h} and isobacterio-^{Sh} regioisomeric mixtures, albeit accompanied by fewer side products.

Among the multiple polar minor fractions present in the reaction mixture, compound 9 attracted our attention because of its unusual bright blue color. Its UV–vis spectrum is, with its two broad biliverdin-like bands, suggesting the presence of a conjugated but nonaromatic and possibly open-chain chromophore (Figure 2) (for details to all spectroscopic analyses, see Supporting Information).¹²

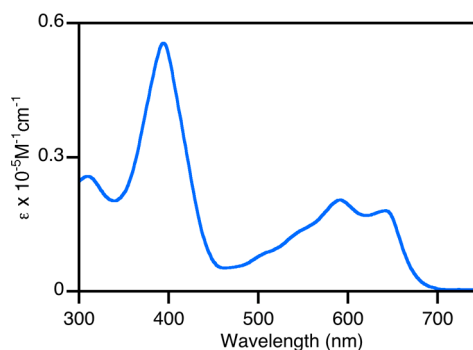


Figure 2. UV–vis spectrum (CH₂Cl₂) of blue tripyrrin compound 9.

The ¹H NMR spectrum of 9 showed the presence of an asymmetric product with six nonequivalent β -protons (6.3–6.8 ppm) and a sharp upfield signal at ~5.1 ppm, exchangeable with D₂O, assigned to be an amide NH, as well as a pair of exchangeable protons at 12.3 and 12.0 ppm, assigned to pyrrole-type NHs. The latter low-field NH signals are hallmarks of nonaromatic oligopyrrolic compounds, especially when intramolecular H-bonds are present. The ¹³C{¹H} NMR

spectrum of **9** showed the presence of two carbonyl carbon atoms. The parent ion peak in the ESI+ HR-MS spectrum of **9** suggested the composition of $C_{41}H_{11}F_{20}N_4O_2$ (for $[M + H]^+$). When compared to the composition of the starting porphyrin **4**, the composition of **9** arises from the addition of two oxygen atoms and the loss of three carbon atoms. A biliverdin-like ring cleavage between two pyrrolic building blocks of a porphyrin is concomitant with the addition of two oxygen atoms and the possible loss of the *meso*-carbon.^{12–14} The loss of three carbon atoms without the loss of fluorine atoms indicates that at least two of these atoms were derived from a pyrrolic moiety, pointing toward a unique structure for this pigment. A single crystal X-ray analysis of **9** provided certainty of its connectivity (Figure 3).

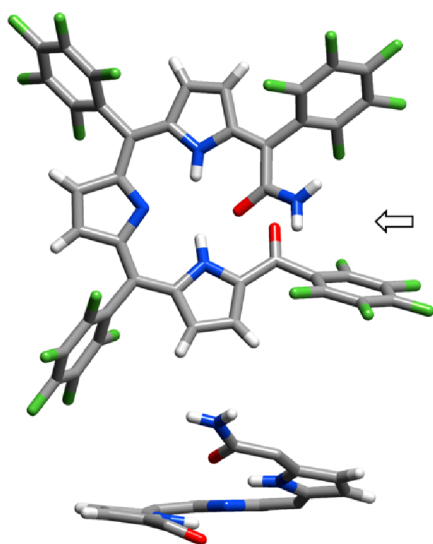


Figure 3. Stick representation of top (top) and side (bottom) views of the single-crystal X-ray structure of tripyrrin **9**. Arrow indicates view direction in the front view. All *meso*-substituents were removed in side view; only one of the two independent molecules in the unit cell is shown, and all disorder and solvents were removed for clarity. For details, see the [Supporting Information](#).

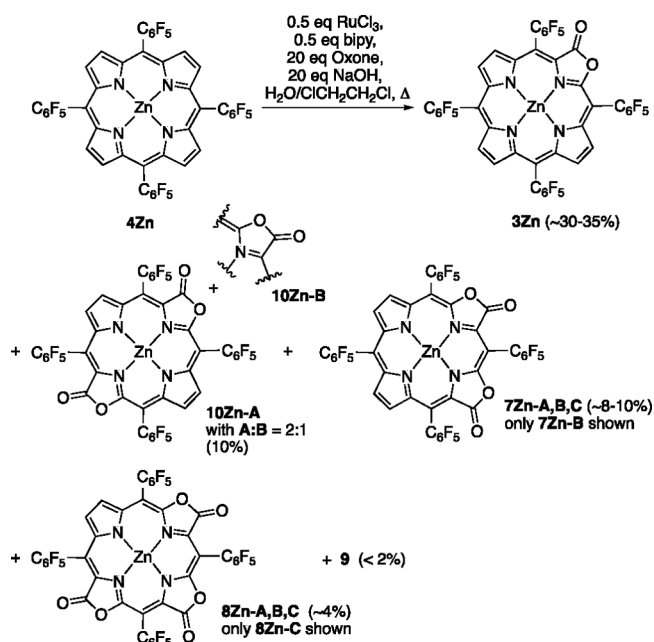
Compound **9** is a linear, conjugated tripyrrolic compound of the tripyrrin class carrying all four *meso*-carbon atoms with their (pentafluorophenyl) substituents. Like other biliverdins¹² or analogues,^{14d} this compound adopts an overall (chiral) helimeric conformation. Also similar to a typical biliverdin-type porphyrin cleavage product, carbonyl groups terminate the carbon atom chain at the ring cleavage sites. Unlike any other biliverdin or tripyrrolic analogues (such as the uroerythrins/biotripyrrins),^{12,14d,15} however, the cleavage site is not located between two pyrrolic moieties. Instead, a pyrrolic moiety was degraded: one α - and both β -carbon atoms were lost, and the remaining *meso*- and α -carbon atoms were functionalized by carbonyl oxygen atoms.

We are not aware of any other structurally characterized linear oligopyrrolic compound that was derived from a *meso*-arylporphyrinoid by degradation of a pyrrolic moiety.¹⁶ To be sure, other porphyrinic macrocycles with ring-opened pyrrolic units have become known,¹⁷ but these products did not form open-chain compounds. Structurally closest to **9** is a tripyrroloxazole derived from the pyrrole-opening and rearrangement of an octa- β -alkylporphyrin-5-formyloxime.^{16a,18}

We can only speculate about the mechanism of formation of **9**. However, because the major products of the CTAP-mediated oxidation of T^FPP are porpholactones, we surmise that it was derived from the breakup of an oxazolone moiety. Thus, this product highlights to which degree the chemistry of the porpholactones varies from those of porphyrins of similar architecture and electronic properties.^{5e} A recent paper by Zhang and co-workers also highlighted the chemistry of the porpholactones in which the lactone moiety opened up, though this breakup reaction also yielded a macrocyclic compound.^{17h}

Studies toward the possible generalization of this degradation chemistry of porpholactones are ongoing. In fact, we already found this product not to be exclusive to the CTAP-mediated oxidation of T^FPP: When the $RuCl_3$ /Oxone/base-oxidation protocol of porphyrins described by Zhang and co-workers^{5d} is applied twice to the same sample of the zinc complex of T^FPP, **4Zn**, an increase of the fraction of dilactones and other ‘overoxidized’ products can be observed, including the formation of a trace of **9** (Scheme 2). We also note that the

Scheme 2. Products Formed during the $RuCl_3$ /Oxone-Mediated Oxidation of [*meso*-Tetrakis(pentafluorophenyl)porphyrinato]zinc **4Zn**



$RuCl_3$ /Oxone-mediated oxidation does not show any regioselectivity and forms bacterio- (as reported)^{5d} and isobacteriodilactones and even trilactones. When compared to the CTAP oxidation, this reaction generates fewer products overall, and thus tripyrrin **9** is more readily isolated from this process. Irrespective of this improvement, neither method to produce **9** is of true preparative value.

We also re-examined the Gouterman oxidation of T^FPP to see whether any trilactones had also formed, but had been overlooked previously.^{4b,19} However, even careful MS- and TLC-based screens of the complex reaction mixtures arising from the treatment of T^FPP (**4**), or its zinc complex **4Zn**, under Gouterman's conditions did not indicate the presence of any trilactones (or their silver/zinc complexes). We inferred that should any trilactones have formed in these reactions, they

would have to be derived from the oxidation of a dilactone precursor. We therefore simplified the reaction by subjecting [bacteriodilactonato]zinc(II) **10Zn-A/B**^{5h} to Gouterman oxidation conditions. Again, multiple hard to separate new compounds formed, but none possessed the diagnostic composition of a trilactone (as per ESI[±] HR-MS). Instead, their complex mass spectra suggested that (multiple) nitration reactions had taken place; neither X-ray diffractometry or ¹H/¹³C NMR spectroscopy could resolve the number or connectivity of isomers present in a mononitrated dilactone fraction (see [Supporting Information](#)).

In conclusion, we demonstrated that the direct oxidations of T^FPP (**4**) or its zinc complex **4Zn** may generate, based on the methodology chosen (Ag⁺/oxalic acid, RuCl₃/Oxone and CTAP), porpholactone **3**, some or all of the five isomers of the dilactones **7** and **10**, or three isomers of the pyrrocorphin-trilactones **8**. Each oxidation protocol generated a unique set of products, providing insight into the regiochemical preferences of these direct porphyrin to porpholactone conversions. Only the CTAP and RuCl₃/Oxone oxidations are capable of forming trilactones, rendering these reactions the first direct porphyrin-to-trilactone conversions reported.^{5j} Most significantly, a unique tripyrrolic, open chain compound **9** was formed under CTAP and RuCl₃/Oxone-oxidation conditions. We derived this tripyrrolic to be the product of the degradation of an oxazolone moiety. This feature distinguishes the formation of this compound from previous biological and nonbiological biliverdin-like linear oligopyrrole degradation products of the *meso*-tetraarylporphyrinoids that were exclusively derived from oxidative ring cleavage between the pyrrolic building blocks.^{12–14,20} In all other cases, in which (modified) pyrrolic building blocks were broken up, the resulting products remained macrocyclic.^{16b,17} Thus, tripyrrolic product **9** highlights new and drastic consequences that can result from the modification of the β,β'-bond of porphyrins. This contrasts with the finding of others that, for example, N-confused and a regular porphyrin showed identical oxidative ring-opening reactions.²⁰

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.4c00283>.

Experimental procedures, spectroscopic data, reproduction of the key spectra, and details of all novel compounds, as well as illustrations of the X-ray single crystal structural determinations reported ([PDF](#))

FAIR data, including the primary NMR FID files, for compound **9** ([ZIP](#))

Accession Codes

CCDC 2209823 and 2300192 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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