

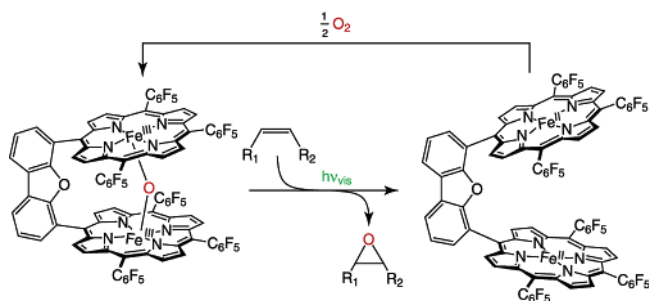
Aerobic Catalytic Photooxidation of Olefins by an Electron-Deficient Pacman Bisiron(III) μ -Oxo Porphyrin

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The synthesis and oxygen atom transfer (OAT) photoreactivity of a diiron(III) μ -oxo *meso*-tripentafluorophenyl bisporphyrin appended to a dibenzofuran spacer are presented. Reaction of 4,6-diformyldibenzofuran under standard Lindsey conditions furnishes the parent cofacial porphyrin architecture in a single step. These cofacial porphyrins photocatalyze the oxidation of sulfides and olefins using visible light and molecular oxygen as the terminal oxidant. High turnover numbers reflect the enhanced stability of the electron-deficient diiron(III) μ -oxo bisporphyrin core appended to a dibenzofuran spacer under aerobic conditions.

Diiron bisporphyrins may utilize O_2 for substrate oxidation without the need for an external co-reductant.^{1–8} The overall cycle relies on a photon to cleave the thermally inert Fe–O bonds of a diiron(III) μ -oxo bisporphyrin to generate a geminal PFe^{II}/PFe^{IV}=O pair (P = porphyrin). The active catalyst, the ferryl intermediate, is capable of oxygenating substrates with the concomitant formation of two equivalents of reduced iron(II) porphyrin. Reaction of the two separate ferrous porphyrin subunits with O_2 reforms the diiron(III) μ -oxo complex^{9–11} for re-entry into a photocatalytic cycle.

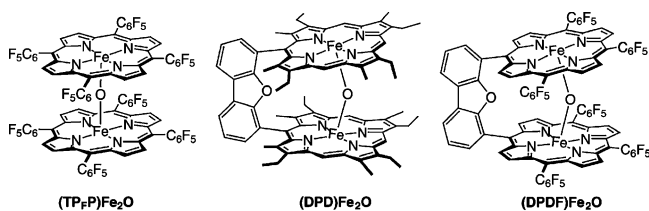
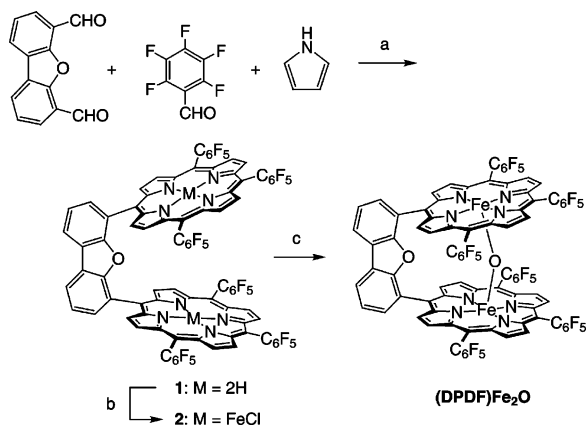
Oxygen atom transfer (OAT) from porphyrin¹² as with other metal–oxo platforms^{13–15} is preferred for the side-on approach of substrate to the metal–oxygen bond. The architecture of the cofacial cleft, formed from attaching the diiron(III) μ -oxo bisporphyrins to a single rigid pillar, can sterically confine substrate attack to the electronically favored side-on geometry. Traditional cofacial bisporphyrin systems, however, have little vertical flexibility (ca. 1 Å),^{16,17} and consequently pose the complication that the photogenerated terminal metal oxo is difficult to access by substrate. To circumvent this problem, we have synthesized cofacial bisporphyrins bearing a dibenzofuran (DPD) spacer,^{18–20} which exhibits significant vertical flexibility.^{21,22} X-ray crystallography establishes that the diiron(III) μ -oxo DPD complex, (DPD)Fe₂O, is a clamped spring;^{23,24} the metal–metal distance of the (DPD)Fe₂O complex is 3.5 Å whereas the metal–metal distance of the relaxed DPD pocket is >7.5 Å. We have shown by transient absorption spectroscopy²⁵ that the strongly clamped DPD Pacman is opened by photocleavage of the Fe–O bond, induced by excitation of the Fe^{III}–O–Fe^{III} core. A superior photocatalytic activity of the DPD framework, as compared to traditional xanthene or anthracene bridged Pacman porphyrins (ca. 10000-fold) is derived from the presentation of an extended cofacial cleft, enabling the ferryl intermediate to be accessed easily by substrate from a side-on approach. To date, the photocatalytic cycle has been turned over with easily oxidized substrates (e.g., phosphines and sulfides) owing to the modest redox potential of the etioporphyrin ferryl subunit.^{26,27}

It is known that the oxidizing power of metalloporphyrins can be increased by introducing electron-withdrawing groups onto the porphyrin periphery.^{28,29} Toward this

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CHART 1

SCHEME 1^a

^a Key: (a) (1) BF₃·OEt₂, CH₂Cl₂, (2) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); (b) (1) FeBr₂, CH₃CN, reflux, (2) aq HCl; (c) 2N NaOH.

end, we now describe the synthesis and characterization of an electron-deficient DPD platform appended with *meso*-pentafluorophenyl porphyrins (DPDF) (Chart 1). The photooxidation chemistry of Fe₂O(DPDF) is compared to that of (DPD)Fe₂O and nonpillared tetrakis(pentafluorophenyl) bisporphyrin, (TPF-P)Fe₂O. We show that the (DPDF)Fe₂O complex is an active catalyst for the photoinduced aerobic oxygenation of sulfides and olefins under mild conditions and with the highest turnover numbers (TONs) yet achieved for a cofacial bisporphyrin photocatalyst.

The synthesis of the (DPDF)Fe₂O is outlined in Scheme 1. The triptafluorophenyl cofacial bisporphyrin (DPDF)H₄ (**1**) is obtained in one step by reacting 4,6-diformyldibenzofuran with pyrrole and pentafluorobenzaldehyde under standard Lindsey conditions.³⁰ The major byproduct, tetrakis(pentafluorophenyl)porphyrin, is separated from **1** by column chromatography. Iron insertion into **1** with FeBr₂ followed by treatment with HCl furnishes the corresponding (dichloro)diiron(III) complex **2** (91%). The (DPDF)Fe₂O complex is obtained in 93% yield by metathesis in benzene with 2 N NaOH.

Figure S1 (Supporting Information) compares the ground-state electronic absorption spectrum of (DPDF)Fe₂O to its nonfluorinated DPD parent complex, (DPD)Fe₂O. The prominent Soret absorption of (DPDF)Fe₂O at 402 nm is energetically comparable to that of (TF₅PP)Fe₂O³¹ but red-shifted from that of (DPD)Fe₂O (λ_{\max} = 392 nm); the energies of the Q-bands for all three compounds are similar. The overall red-shift of the absorption profile of (DPDF)Fe₂O as compared to (DPD)Fe₂O

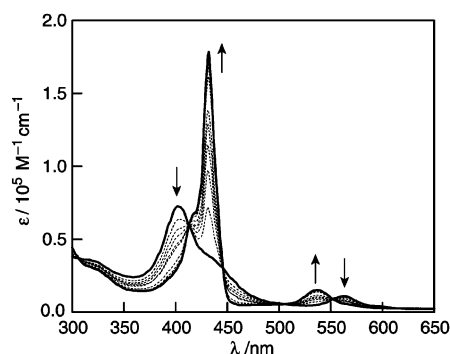


FIGURE 1. Changes in the absorption profile for the photolysis ($\lambda_{\text{exc}} > 425$ nm) of benzene solutions of (DPDF)Fe₂O (ca. 10⁻⁶ M) in the presence of DMS (ca. 0.2 M) at 293 K. The arrows indicate the disappearance of (DPDF)Fe₂O and the appearance of (DPDF)Fe₂(DMS)₂. Spectra were recorded over the span of 30 min at ~5 min intervals.

TABLE 1. Turnover Numbers and Conversion Yields for Photocatalytic DMS Oxidation^a

catalyst	photoproduct	
	DMSO TON (% yield)	DMSO ₂ TON (% yield)
(TPF-P)Fe ₂ O	750 ± 25 (96%)	32 ± 4 (4%)
(DPDF)Fe ₂ O	9635 ± 165 (~100%)	trace
(DPD)Fe ₂ O ^b	620 ± 31 (90%)	68 ± 3 (10%)

^a Determined for a 4 h photolysis ($\lambda_{\text{exc}} > 425$ nm) of solutions under 1 atm of O₂ (298 K) but otherwise of the same composition as those used in stoichiometric photolysis experiments. ^b Reference 26.

is consistent with the more electron-withdrawing perfluorinated phenyl periphery of the porphyrin platform. Consistent with these spectral trends, the photooxidation chemistry of (DPD)Fe₂O is promoted with λ_{exc} = 360–380 nm whereas the photochemistry of (DPDF)Fe₂O proceeds smoothly with λ_{exc} = 420–460 nm.

Although (DPDF)Fe₂O is thermally inert in dry benzene (~10⁻⁶ M), a prompt photoreaction is observed when the compound is photolyzed ($\lambda_{\text{exc}} > 425$ nm) in the presence of dimethyl sulfide (DMS) (0.2 M). As shown in Figure 1, isobestic points are maintained during the course of the photoreaction (Figure 1); no spectral changes are observed with continued irradiation at times longer than that for which the final trace is shown. The photoproduct spectrum is identical to that of (DPDF)Fe₂(DMS)₂, which was independently prepared by the Na/Hg reduction of (DPDF)Fe₂Cl₂ in benzene in the presence of DMS ($\lambda_{\text{abs,max}}$ = 416, 526, 554(sh) nm). The organic oxidation photoproduct was identified as DMSO by GC/MS analysis.

The photooxidation ($\lambda_{\text{exc}} > 425$ nm) of DMS by (DPDF)Fe₂O in benzene solutions becomes catalytic when performed in the presence of O₂. Turnover numbers (TONs) for a given photolysis period and overall conversion yields for DMS photooxidation performed under 1 atm of O₂ are listed in Table 1. The TON for DMS photooxidation by (DPDF)Fe₂O is more than an order of magnitude greater than that obtained for (DPD)Fe₂O and unbridged (TPF-P)Fe₂O photocatalysts. Moreover, (DPDF)Fe₂O is selective for the oxidation of DMS to DMSO; no dimethyl sulfone (DMSO₂) was observed by GC/MS analysis. For comparison, 10% DMSO₂ is produced by the (DPD)Fe₂O photocatalyst. The increased catalytic efficacy of (DPDF)Fe₂O is attributed to the increased stability of the *meso*-substituted photocatalyst, as (DPDF)Fe₂O remained

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TABLE 2. Turnover Numbers and Conversion Yields for Olefin Oxidation Using (DPDF)Fe₂O as the Photocatalyst^a

substrate	product	TON	% yield
cyclohexene	cyclohexene oxide	89 ± 17	15
	2-cyclohexen-1-ol	69 ± 12	12
	2-cyclohexen-1-one	437 ± 74	73
styrene	styrene oxide	37 ± 6	2
	benzaldehyde	1609 ± 340	87
	acetophenone	150 ± 27	8
	phenylacetaldehyde	54 ± 11	3

^a Determined for a 4 h photolysis ($\lambda_{\text{exc}} > 425$ nm) of solutions under 1 atm of O₂ (298 K) but otherwise of the same composition as those used in stoichiometric photolysis experiments.

active under photocatalytic conditions more than twice as long as the (DPD)Fe₂O. The latter is susceptible to decomposition by hydroxylation of the unsubstituted meso-positions of the porphyrin ring;^{32–34} this pathway is circumvented by the presence of the ancillary pentafluorophenyl groups of (DPDF)Fe₂O, which lower the susceptibility of the porphyrin to oxidative damage.^{35–37} Additionally, the DPD spacer and meso-substituents result in increased steric congestion about the ferryl oxygen. Hence, if a second Pacman molecule is considered as a potential substrate, it is not surprising that the rate of oxidative decomposition is reduced dramatically for (DPDF)Fe₂O as compared to the unbridged congener.

The increased electrophilicity of the ferryl intermediate of (DPDF)Fe₂O prompted us to consider the more challenging task of olefin oxidation. A prompt photoreaction is observed upon irradiation ($\lambda_{\text{exc}} > 425$ nm) of (DPDF)Fe₂O ($\sim 10^{-6}$ M) in deaerated, dry benzene containing either styrene or cyclohexene (1.0 M) and *tert*-butyl isonitrile (1.5×10^{-7} M) as a capping ligand for the Fe(II) photoproduct. The time course for the absorption profile for this photoreaction is virtually identical to that shown in Figure 1 for DMS oxidation. For pyridine solvent, a clean photoreaction is observed in the absence of external capping ligand.

Photocatalytic epoxidation of cyclohexene and styrene was accomplished in a fashion similar to that described for DMS photooxidation. Table 2 lists the TON for photoepoxidation of the two substrates. We note that no photoreaction is observed in the absence of (DPDF)Fe₂O photocatalyst. Cyclohexene photoconversion proceeds with modest turnover but multiple products are obtained as a result of OAT (cyclohexene oxide) and allylic oxidation (cyclohexen-1-ol and 2-cyclohexen-1-one). Cyclohexene is generally susceptible to radical chain autoxidations that can give rise to yields of 2-cyclohexen-1-ol and/or 2-cyclohexen-1-one that exceed the amount of epoxide product.³⁸ The product distribution shown in

Table 2 is consistent with an autoxidation process and no different than that typically obtained for other cofacial porphyrin photocatalysts.^{5,6} It might be expected that the lack of easily abstracted hydrogen atoms in styrene would lead to simpler photoproduct mixtures. However, as shown in Table 2, large amounts of benzaldehyde, as well as acetophenone and phenylacetaldehyde, are obtained along with the epoxide product. This product distribution parallels that previously observed for the stoichiometric oxidation of styrene derivatives by electron rich Fe^{IV}=O intermediates produced by nonphotochemical methods.³⁹ The products are derived from a carbon radical, which is postulated to form from the reaction of the ferryl intermediate with alkene.

Figure 2 adapts this mechanism to (DPDF)Fe₂O photocatalysis. Epoxide and aldehyde photoproducts form along separate paths with photogenerated benzylic radical **I** as a common origin. The epoxide is produced from direct carbon–oxygen ring closure of **I**; the (DPDF)Fe₂O photocatalyst reforms from reaction of oxygen with the cofacial bisporphyrin photoproduct. Competing with ring closure to give the epoxide, oxygen attack of **I** yields **II**, which presumably converts to benzaldehyde via the oxetane. (DPDF)Fe₂ is converted to (DPDF)Fe₂O most likely by a Balch-type mechanism.^{10,40–42} While it is possible that a μ -peroxo intermediate, formed from the reaction of O₂ with (DPDF)Fe₂, could act as an oxidant toward substrate, it is more likely that the unimolecular O–O bond ruptures to give the *bis*-ferryl Pacman intermediate occurs under catalytic conditions (i.e., inert solvent at room temperature). Indeed, in the absence of substrate, (DPDF)Fe₂ is converted quantitatively to (DPDF)Fe₂O upon addition of 0.5 equivalents of O₂, indicating that substrate is not necessary to effect μ -oxo formation from the presumed μ -peroxo intermediate.

Electron transfer from olefin substrate to the highly oxidizing ferryl accounts for the other products of styrene oxidation. Ketones have been observed for styrene oxidation by dioxygen using redox active rhodium⁴³ and palladium⁴⁴ catalysts. Although electron transfer is most effectively promoted by an Fe^{IV}=O porphyrin cation radical, it is likely that the highly electron deficient nature of the DPDF platform enables the charge-transfer chemistry that leads to the observed acetophenone and phenylacetaldehyde oxidation products. Indeed, the fact that no ketone oxidation product has been previously reported for stoichiometric styrene oxidation by the more electron rich (TMP)Fe^{IV}=O oxidant,³⁹ lends credence to this contention.

(DPDF)Fe₂O does not oxidize *cis*-cyclooctene or *cis/trans*-stilbene under photocatalytic conditions. We attribute this lack of reactivity to the inability of bulky substrates to access the sterically hindered cleft of the tetra-*meso*-substituted Pacman architecture. Time-re-

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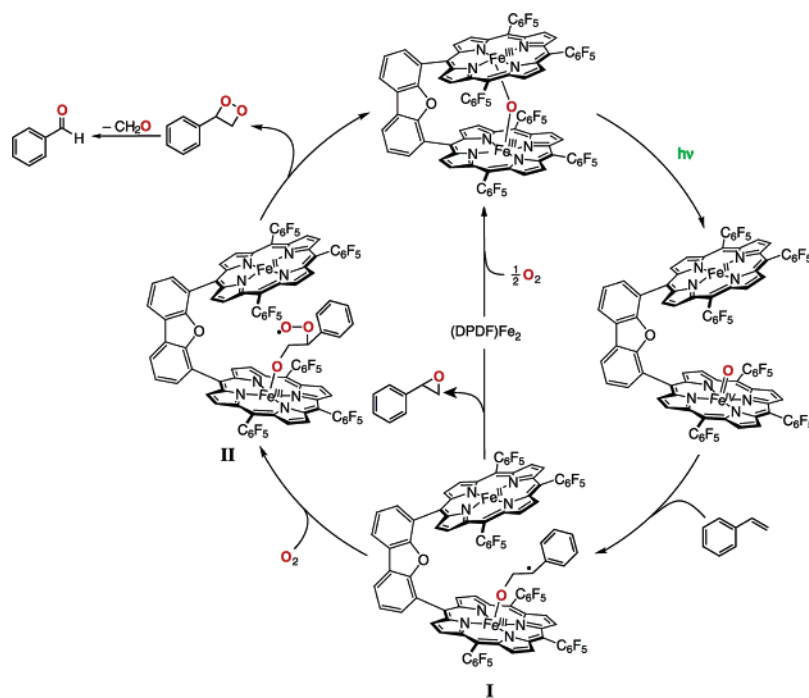


FIGURE 2. Photocycle for styrene oxidation by (DPDF) Fe_2O that accounts for epoxide and aldehyde photoproduction.

solved transient absorption studies of phosphine oxidation by bis-iron(III)- μ -oxo Pacman catalysts have shown that the rate and efficiency of OAT decrease as the steric demand of phosphines increase,²⁵ illustrating the importance of substrate access to the short-lived ferryl photo-intermediate. For the DPDF Pacman, amine photooxidation (i.e., trimethylamine, pyridine, etc.) is not observed. The cone angle of trimethylamine is 132° .⁴⁵ Previous studies of phosphine oxidation establish that substrates possessing cone angles in the range of 130° have access to the DPD Pacman cleft.²⁷ Accordingly, the lack of substrate oxidation appears to be of thermodynamic and not of kinetic origin.

As has been done previously for transition metal oxo species,^{46–50} the overall OAT reaction may be partitioned into the following simple thermodynamic steps:



The approximate strength of the iron–oxygen bond of the photochemically generated ferryl intermediate (species **A** in eq 2) may be determined (ΔH_2) with the enthalpic expressions for O–O bond homolysis and substrate (X) oxidation in place. Enthalpic values for the oxidation of a number of organic oxygen atom acceptors

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TABLE 3. Thermodynamic Reactivity Scale and X–O Bond Energies for $\text{X}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{XO}(\text{g})$ ⁵¹

X	XO	ΔH (kcal/mol) $\text{X}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{XO}(\text{g})$
Ph_3P	Ph_3PO	–133
Me_2S	Me_2SO	–86
styrene	styrene oxide	~ –86
Me_3N	Me_3NO	–67
O	O_2	–59

are collected in Table 3. Using the thermodynamic cycle, the opposing OAT reactivity displayed by DMS and styrene versus trimethylamine allows us to bracket the approximate $\text{Fe}^{\text{IV}}=\text{O}$ BDE between 65 and 85 kcal/mol. Although OAT to substrates that would be expected to be thermodynamically favorable such as stillbene and cyclooctene is not observed, it must be concluded that the barrier to these oxidations is kinetic in origin and related to the sterically restricted molecular cleft.

In summary, we have shown that the multielectron oxidation photocatalysis of olefins may be achieved using an electron-deficient Pacman bisporphyrin (DPDF) Fe_2O and molecular oxygen without the need for an external coreductant. The electron deficiency of this bisporphyrin photocatalyst is reflected in our ability to drive the photochemistry using relatively long-wavelength light in the visible region.

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Supporting Information Available: Experimental methods and procedures and absorption spectra of (DPDF) Fe_2O and (DPD) Fe_2O . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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