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A Phototriggered Molecular Spring for Aerobic Catalytic Oxidation Reactions

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The creation of homogeneous catalysts for the selective oxidation of organic compounds under mild conditions using molecular oxygen as the terminal oxidant remains an elusive goal. In this regard, the reactivity of photoactive iron porphyrins is of interest, owing to the ability of these systems to utilize O_2 for oxidation reactions without the need for an external co-reductant.[1−9] The general catalytic cycle for such processes involves photocleavage of the thermally inert Fe−O bonds of bisiron(III) μ-oxo porphyrins to generate a reactive intermediate capable of oxygenating substrate with the concomitant formation of 2 equiv of reduced iron(II) porphyrin. Reaction of the two separate ferrous porphyrin subunits with O_2 reforms the bisiron(III) μ-oxo complex for re-entry into the catalytic cycle.

Oxygen-atom transfer from a porphyrin platform is preferred for the side-on approach of substrate to the metal−oxygen bond.[10] This side-on model extends beyond porphyrins and is consistent with a wide variety of reactivity patterns involving terminal metal−oxo compounds.[11−13] Notwithstanding, all photooxidation reactions with iron porphyrins to date have been carried out using simple monomeric macrocycles where the reaction coordinate for substrate attack is undirected. For this reason, bisiron(III) μ-oxo porphyrins bearing a single Pacman pillar are intriguing because the architecture of the cleft can sterically confine substrate attack to the electronically favored side-on geometry. Traditional cofacial bisporphyrin systems, however, have little vertical flexibility (ca. 1 Å),[14−16] and consequently they pose the complication that the photogenerated terminal metal oxo will readily reform the inert bisiron(III) μ-oxo species before substrate can attack. To circumvent this problem, we sought to test the structural limits of pocket size and extend the vertical flexibility of the Pacman motif and related constructs.[17−19] Toward this end, we recently synthesized two novel cofacial bisporphyrins bearing xanthene (DPX) and dibenzofuran (DPD) spacers,[20−22] which exhibit unprecedented vertical flexibility. For example, the metal−metal distance of the bisiron(III) μ-oxo DPD complex is 3.5 Å, whereas the metal−metal distance of the relaxed DPD pocket is >7.5 Å. The vertical flexibility of the DPD platform suggests that the bisiron(III) μ-oxo complex will spring open to present the terminal metal oxo upon photon absorption. We reasoned that the "molecular spring" action of the scaffold would (i) hinder the regeneration of the bisiron(III) μ-oxo precatalyst and (ii) dictate a side-on reaction coordinate for oxygen-atom transfer by presenting the terminal metal−oxo species within the cofacial platform.

We now present the first photocatalytic oxidation reactions with cofacial bisporphyrins. Bisiron(III) μ-oxo complexes of both DPD and DPX are active catalysts for the aerobic photoinduced oxygenation of dimethyl sulfide (DMS) under mild conditions. A comparative reactivity study of these compounds with a bisiron(III) μ-oxo etioporphyrin containing no bridge reveals that the concept of a spring-loaded oxygen-atom transfer can lead to the design of efficient photocatalytic oxygenation cycles.

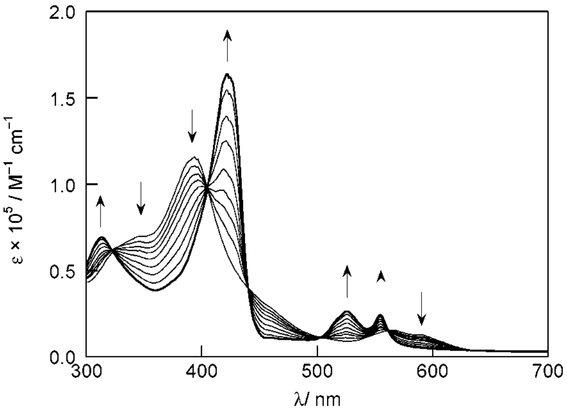
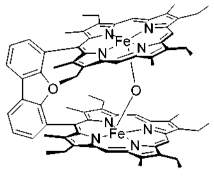


Figure 1. The absorption profiles demonstrate the conversion of benzene solutions of $Fe_2O(DPD)$ **1** (ca. 10^{-6} M) in the presence of dimethyl sulfide (DMS, ca. 0.2 M) at 293 K. The arrows indicate the disappearance of **1** and the appearance of $Fe_2(DPD)(DMS)_2$. Spectra were recorded over the span of 2 h at ~15 min intervals.



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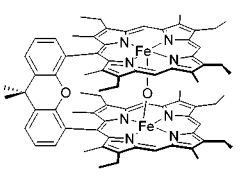

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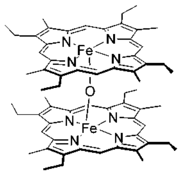

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Bisiron(III) μ-oxo porphyrins $Fe_2O(DPD)$ (**1**), $Fe_2O(DPX)$ (**2**), and $Fe_2O(Etio)_2$ (**3**) are obtained in excellent yields (>90%) by reaction of the corresponding free-base porphyrins with $FeBr_2$ and 2,6-lutidine followed by exposure to air and treatment with basic alumina. Complexes **1**−**3** are thermally inert to DMS. However, irradiation of benzene solutions of **1**−**3** (λ_{exc} > 360 nm, O−Fe LMCT transition) in the presence of excess DMS under anaerobic conditions leads to prompt absorption spectral changes. Consistent with a LMCT photochemistry, the photoreaction efficiency decreases significantly (ca. 10^2-fold) as the irradiation wavelength is shifted into the Soret spectral region (λ_{exc} > 400 nm). Figure 1 shows the evolution of the absorption profiles for the photolysis of **1** under such conditions. Analogous photoreactions with **2** and **3** behave similarly. Well-anchored isosbestic points maintained throughout the irradiation attest to a clean and quantitative photoreaction. With the appearance of the final absorption spectrum, no additional changes are observed with continued irradiation. Also, no photochemistry is observed upon irradiation of solutions containing only DMS or porphyrin. For each photolysis reaction,

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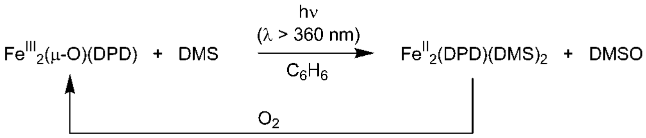
Table 1. Product Quantum Yields (Φ_p) for Stoichiometric Photoreactions[a] and Sulfoxide (DMSO) and Sulfone ($DMSO_2$) Turnover (TO) Numbers[b] for Catalytic Photoreactions of Bisiron(III) μ-oxo Porphyrins **1**−**3** with Dimethyl Sulfide (DMS) at $\lambda_{exc} >$ 360 nm

	Φ_p	DMSO/TO	$DMSO_2$/TO
Fe_2O(DPD) (**1**)	2×10^{-5}	610 ± 31	68 ± 3
Fe_2O(DPX) (**2**)	1×10^{-8}	280 ± 14	16 ± 1
$Fe_2O(Etio)_2$ (**3**)	1×10^{-4}	350 ± 18	47 ± 2

[a] The quantum yield experiments were performed in benzene at 293 K containing 0.2 M DMS under anaerobic conditions. [b] The catalytic experiments were performed for 20 h on solutions of the same composition as used in (a) under 1 atm of O_2. Turnover numbers were determined by analysis of the product yields for sulfoxide and sulfone by using GC−MS and ^{1}H NMR spectroscopy.

a single porphyrin product is isolated with an electronic absorption spectrum identical to that of an independently prepared iron(II) porphyrin complex with axial sulfide ligands (e.g., $Fe_2(DPD)(DMS)_2$).[23] Moreover, each photoreaction yields a stoichiometric amount of dimethyl sulfoxide (DMSO) as determined by ^{1}H NMR and GC−MS. These results establish a formal two-electron photoreduction of the bisporphyrin attendant to the oxygenation of the DMS substrate.

Table 1 lists the product appearance quantum yields (Φ_p) for the photoreactions of complexes **1**−**3** with DMS. Strikingly, the efficiencies for stoichiometric oxygen-atom abstraction span over 4 orders of magnitude. The dibenzofuran-bridged **1** and unbridged **3** complexes have similar quantum efficiencies ($\Phi_p = 2 \times 10^{-5}$ and 1×10^{-4}, respectively); in contrast, xanthene derivative **2** is much less active ($\Phi_p = 1 \times 10^{-8}$). The photocatalytic oxidation of DMS with **1**−**3** can be carried out in the presence of 1 atm of O_2 under similar conditions as those employed for the stoichiometric reactions. Notably, no oxidation occurs upon irradiation under O_2 without substrate or catalyst, and thermal reactions are negligible under these conditions. The total substrate turnover numbers (TO) and selectivities for the sulfoxide (DMSO) and sulfone ($DMSO_2$) products generated in the photoreactions of **1**−**3** are also displayed in Table 1. The most efficient catalyst is **1**, which produces almost twice as much sulfoxide product (610 ± 31 TO) as complexes **2** (280 ± 14 TO) and **3** (350 ± 18 TO). All three complexes exhibit high selectivities (88 to 95%) for DMSO over $DMSO_2$. The results establish the following overall catalytic sequence,



$$\begin{tikzcd} \mathrm{Fe^{III}_2(\mu\text{-}O)(DPD)} + \mathrm{DMS} \arrow[r, "h\nu\ (\lambda > 360\ \mathrm{nm})", "\mathrm{C_6H_6}"'] & \mathrm{Fe^{II}_2(DPD)(DMS)_2} + \mathrm{DMSO} \arrow[l, bend left, "\mathrm{O_2}"] \end{tikzcd}$$

where the aerobic reoxidation of the iron(II) porphyrin complex proceeds quantitatively. We note that independently prepared iron(II) porphyrins in the absence of DMS also generate the bisiron(III) μ-oxo porphyrins quantitatively upon reaction with O_2.

Our findings clearly demonstrate that the vertical Pacman flexibility of the catalyst structure is manifested in multielectron reactivity. We have exploited this vertical flexibility to uncover new modes of reactivity for cofacial bisporphyrin systems, namely the first catalytic, multielectron oxidation of substrates using dioxygen as the terminal oxidant. These oxygen-atom transfer reactions proceed under mild conditions (ambient temperature and pressure) without the need for an external co-reductant. The stoichiometric oxygenation reactions suggest that the superior efficiency of the DPD complex **1** over its DPX counterpart **2** is due to its ability to serve as a molecular spring that can be phototriggered to afford a splayed species upon photon absorption and to promote Fe−O activation via facile side-on oxygen abstraction by the DMS substrate. Remarkably, DPD-bridged complex **1** has a comparable quantum efficiency to unbridged complex **3** even though the back reaction for reclamping in the former occurs by an intramolecular process. The photocatalytic oxidation reactions show that spring-loaded Pacman porphyrins can yield superior catalysts to unbridged analogues. With the synthetic ability to tailor the cofacial pockets of DPD and DPX,[24] we are now poised to construct new scaffolds for multielectron transformations with enhanced selectivity and reactivity. Current studies are aimed at mechanistic characterization of the reactive photointermediates and expanding the scope of multielectron, atom-transfer reactions with cofacial porphyrin architectures and related platforms.

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