In summary, we have demonstrated that *cis*-$[Pt(NH_3)_2Cl_2]$ reacts with the self-complementary oligonucleotide, $[d(ApGpGpCpCpT)]_2$, to yield a structure with an intrastrand cross-link between two N7 atoms of adjacent guanine residues. Substantial conformational changes accompany this binding. The platinated hexanucleotide does not form a duplex structure.

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Registry No. *cis*-$[Pt(NH_3)_2Cl_2]$, 15663-27-1; d(ApGpGpCpCpT), 83026-06-6.

Photodisproportionation of (μ-Oxo)bis[(tetraphenylporphinato)iron(III)]

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Strategies for photochemical solar energy conversion in solution have relied almost exclusively on the generation of long-lived charge-transfer excited states that undergo bimolecular redox quenching.[1-4] This approach precludes the choice of potential photocatalysts whose excited states are either nonemitting (and hence short lived) or dissociative. Unfortunately, most transition-metal complexes appear to fall into one or both of these categories.[5,6]

We propose an alternative strategy in which the photocatalyst dissociates from an excited state that may react in the strong coupling limit[7] or even predissociate. The key requirement for uphill thermodynamics is that one photoproduct be either a stronger oxidant or a stronger reductant than the starting compound. The requirement for the potential to recycle as a catalyst is that the products not be reactive radicals. A reaction likely to meet these criteria is a photodisproportionation[8] of the form

$$\text{M-O-M} \xrightarrow{h\nu} \text{M=O} + \text{M}$$

We report here the first recognized example of this mechanism for potentially storing energy.

Several transition metals exhibit the M-O-M[10-14] structure, and many of these have known complexes of both M and M=O forms.[15-19] Recently Balch and co-workers have postulated the ferryl complex of tetraphenylporphine (FeOTPP),[16,17] and the ferrous complex (FeTPP) is well-known and characterized in many solvents.[18,19] Bartocci and co-workers have recently demonstrated that alcohol complexes of Fe^{III} porphyrins do photochemistry[20] that, according to Brault and co-workers, originates with O → Fe charge transfer.[21] One might expect analogous photochemistry from the title compound, $(FeTPP)_2O$,[16] where the alcoholic R group is replaced by FeTPP.

Irradiation into the Soret band of a rigorously degassed benzene or pyridine solution of $(FeTPP)_2O$ leads to no observable spectral changes in the UV-visible or infrared spectrum.[22] If an excess

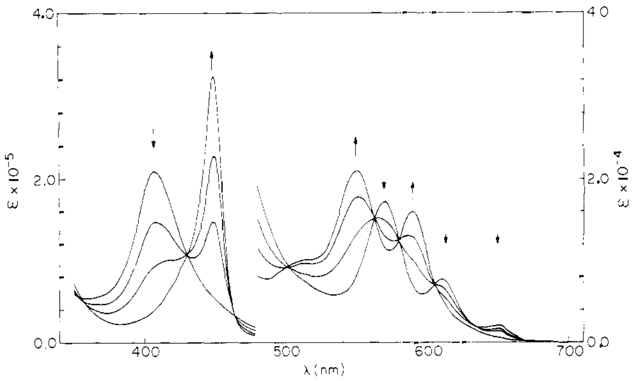

Figure 1. Spectral changes of a benzene solution of 0.2 M PPh_3, and 9×10^{-6} M $(FeTPP)_2O$ upon irradiation with a 450-W medium-pressure Hg lamp fitted with a Corning 0-51 cutoff filter. Spectra taken at t = 0, 15, 30, and 158 min.

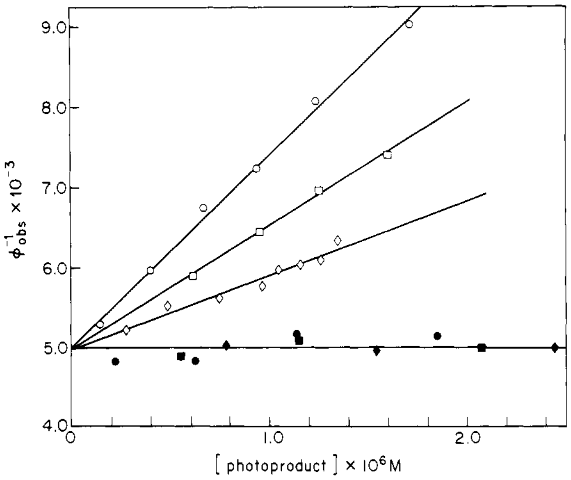

Figure 2. Inverse of the observed quantum yield for appearance of photoproduct vs. photoproduct concentration at $I_0 \simeq 2 \times 10^{-9}$ einstein and initial $[(FeTPP)_2O] \cong 9 \times 10^{-6}$ M: (○) $[PPh_3]$ = 0.1 M; (□) $[PPh_3]$ = 0.15 M, (◇) $[PPh_3]$ = 0.25 M in benzene; (●) $[PPh_3]$ = 0.1 M; (■) $[PPh_3]$ = 0.15 M; (◆) $[PPh_3]$ = 0.2 M in pyridine. Pyridine data points go to 4×10^{-6} M but are truncated for purpose of display. All lines are least-squares fits.

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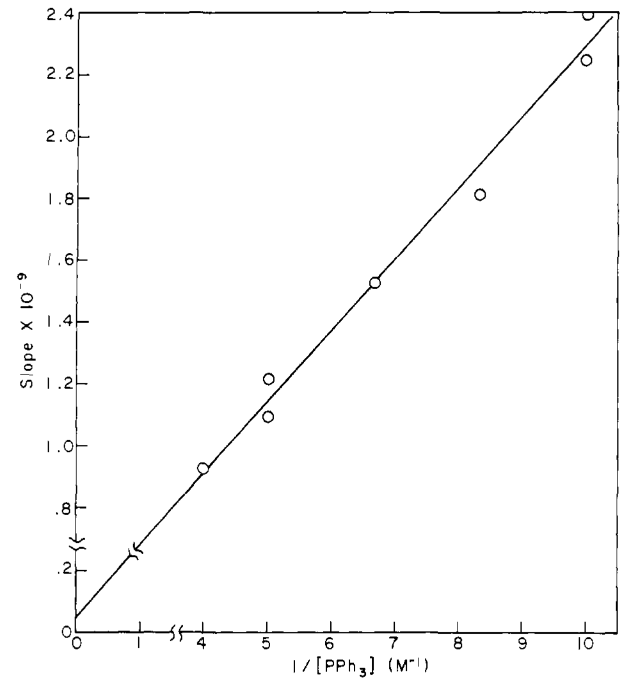

Figure 3. Slope of ϕ_{obsd}^{-1} vs. [(PPh$_3$)FeTPP] plots in benzene vs. 1/[PPh$_3$]. The *y* intercept, within experimental error, equals the theoretical value of zero.

of triphenylphosphine (PPh$_3$) is added, the solution is thermally inert.[17] When irradiated, however, this solution exhibits spectral changes consistent with the formation of (Py)$_2$FeTPP in pyridine and (PPh$_3$)FeTPP in benzene. Exposing the photoproduct to oxygen leads to regeneration of (FeTPP)$_2$O over time.[17] The visible spectral changes have isosbestic points at 548, 475, 446, and 404 nm in pyridine and at 605, 580, 562, 498, 464, and 430 nm in benzene. Similar changes are observed in pyridine if PPh$_3$ is replaced by either AsPh$_3$ or SbPh$_3$; however, the changes are substantially smaller (PPh$_3$ > AsPh$_3$ > SbPh$_3$) at equivalent intensities. Photolysis of an N$_2$ deoxygenated solution of (Fe(TPP)$_2$O and PPh$_3$ in an IR cell leads to the growth of peaks at 1194 and 1122 cm^{-1}, consistent with triphenylphosphine oxide (OPPh$_3$).[24] The rate of molar production of the Fe(II) complex is twice the rate of loss of Fe(TPP)$_2$O and twice the rate of gain of OPPh$_3$.

The visible spectral changes accompanying irradiation at 409 nm of (FeTPP)$_2$O plus PPh$_3$ in benzene are shown in Figure 1. The inverse of the quantum yield for appearance of (PPh$_3$)FeTPP in benzene is not constant with time but rather varies in a Stern–Volmer relationship with respect to the photoproduct being produced (Figure 2). Moreover, the slope of such plots shows an inverse relationship with respect to the PPh$_3$ concentration (Figure 3) while maintaining a common intercept of 5.0×10^3. In pyridine, on the other hand, the quantum yield is constant with time, shows no variation with the concentration of PPh$_3$, and has the same value of ϕ_{obsd}^{-1} at $t = 0$ of 5.0×10^3.

Four potential mechanisms have been considered to explain the observed results: (1) electron transfer from phosphine to iron; (2) formation of a precursor complex; (3) dissociation to Fe$^{\text{III}}$OTPP$^-$ and Fe$^{\text{III}}$TPP$^+$; (4) dissociation to Fe$^{\text{IV}}$OTPP and Fe$^{\text{II}}$TPP. Of these mechanisms three may be eliminated on the basis of experimental results. Electron transfer is inconsistent with Figure 2 since this would require a variation of ϕ_{obsd}^{-1} with increasing concentration of PPh$_3$. No such variation is observed at $t = 0$. Furthermore, this would require a long-lived excited state, yet (FeTPP)$_2$O shows no emission in solution below 740 nm ($\phi < 10^{-4}$) at room temperature and none is reported at lower temperature. Both UV–visible and infrared spectra show no changes upon addition of PPh$_3$, so we eliminate the possibility of a precursor complex having phosphine coordinated to iron or oxygen.

Dissociation of the excited state to form Fe$^{\text{III}}$OTPP$^-$ + Fe$^{\text{III}}$TPP$^+$ can be ruled out by two arguments. First, Balch et al.[17] found no thermal reaction of PPh$_3$ with FeTPPCl or B$_2$FeTPP$^+$, and we observe none with FeTPP(CH$_3$CO$_2$) or FeTPPClO$_4$. Second, only PPh$_3$FeTPP quenches the photochemistry, and it does so by producing (FeTPP)$_2$O. PPh$_3$FeTPP is thermally inert toward OPPh$_3$, so quenching can only occur by reaction of PPh$_3$FeTPP with FeOTPP.[25]

The case for photodisproportionation is strong. Recently Balch et al.[17] have given convincing evidence for the existence of the ferryl complex Fe$^{\text{IV}}$OTPP and demonstrated its ability to oxidize PPh$_3$ to OPPh$_3$. Accordingly, we propose the mechanism given in eq 1–7, where B represents PPh$_3$ in benzene and pyridine in pyridine.

$$(\text{FeTPP})_2\text{O} \overset{h\nu}{\rightleftharpoons} (\text{FeTPP})_2\text{O}^* \tag{1}$$

$$(\text{FeTPP})_2\text{O}^* \xrightarrow{k_2} \text{FeOTPP} + \text{FeTPP} \tag{2}$$

$$\text{FeOTPP} + \text{FeTPP} \xrightarrow{k_3} (\text{FeTPP})_2\text{O} \tag{3}$$

$$\text{FeOTPP} + \text{PPh}_3 \xrightarrow{k_4} \text{FeTPP} + \text{OPPh}_3 \tag{4}$$

$$\text{FeTPP} + \text{B} \xrightarrow{k_5} \text{BFeTPP} \tag{5}$$

$$\text{BFeTPP} + \text{B} \xrightarrow{k_6} \text{B}_2\text{FeTPP} \tag{6}$$

$$\text{BFeTPP} + \text{FeOTPP} \xrightarrow{k_7} (\text{FeTPP})_2\text{O} + \text{B} \tag{7}$$

At low intensities, the k_3 pathway is negligible. In benzene we assume[26] $k_6 = 0$ and steady-state concentrations of (FeTPP)$_2$O*, FeTPP, and FeOTPP, to obtain eq 8, where ϕ_0 is

$$\frac{1}{\phi_{\text{obsd}}} = \frac{1}{2\phi_0} + \frac{[\text{BFeTPP}]k_7}{4\phi_0 k_4[\text{PPh}_3]} \tag{8}$$

the photodisproportionation quantum yield and ϕ_{obsd} is the measured quantum yield for production of (PPh$_3$)FeTPP. In the case of pyridine (a much stronger base than PPh$_3$) k_6 is likely to be large,[18] making the k_7 step negligible. Assuming additionally a steady-state concentration of BFeTPP leads to $\phi_{\text{obsd}} = 2\phi_0$, where ϕ_{obsd} is the measured quantum yield for production of (Py)$_2$FeTPP. This then leads to a straightforward analysis of Figures 2 and 3. From Figure 2 we obtain $\phi_0 = 1.0 \times 10^{-4}$, and from Figure 3, $k_7/k_4 = 9.5 \times 10^4$. Finally, eq 3 should grow in importance at high intensity, causing eq 8 to break down. This is observed.

While the trapping reaction (steps 1–7) is not thermodynamically uphill, it establishes photochemistry (steps 1 and 2) that is uphill. Thus we have demonstrated the use of visible light to initiate a dissociation reaction that leads not merely to decomposition but to the generation of a high-energy[28] and potentially useful oxidizing agent. We intend to pursue wavelength dependence, flash photolysis, substrates other than PPh$_3$, and water soluble porphyrins.

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Registry No. (FeTPP)$_2$O, 12582-61-5; PPh$_3$, 603-35-0; py, 110-86-1; (py)$_2$FeTPP, 16999-25-0; (PPh$_3$)FeTPP, 83026-05-5; benzene, 71-43-2.

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