spectrometer was funded through NIH Grant 1 S10 RR02004 and a gift from the Monsanto Co.

Registry No. Fe(PPIXDME)(CN), 59890-73-2; Fe(PPIXDME)$(CN)_2^-$, 64060-98-6; Fe(PPIXDME)(CN)(n-$BuNH_2$), 103836-00-6; Fe(PPIXDME)(CN)($PrNH_2$), 103836-01-7; Fe(PPIXDME)(CN)(i-$PrNH_2$), 103836-02-8; Fe(PPIXDME)(CN)(i-$BuNH_2$), 103836-03-9; Fe(PPIXDME)(CN)(neo-$C_5H_{11}NH_2$), 103836-04-0; Fe(4-MeTPP)(CN)(n-$BuNH_2$), 103836-05-1; Fe(PPIXDME)(CN)($CH_3NH(CH_2)_3CH_3$), 103836-06-2; Fe(PPIXDME)(CN)(1-MeIm), 100473-40-3; Fe(PPIXDME)(CN)(1-$[H_2N(CH_2)_3]$Im) (isomer 1), 103836-07-3; Fe(PPIXDME)(CN)(1-$[H_2N(CH_2)_3]$Im) (isomer 2), 103836-08-4; Fe(PPIXDME)(CN)(5-$[H_2N(CH_2)_3]$Im), 103836-09-5; Fe(PPIXDME)(CN)(5-MeIm), 103836-10-8; Fe(PPIXDME)(n-$BuNH_2)_2^+$, 103836-11-9.

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Synthesis and Characterization of a *meso*-Tetrakis(4-ferrocenylphenyl)porphyrin and Examination of Its Ability To Undergo Intramolecular Photocatalyzed Electron Transfer

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and Thomas C. Bruice*

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Modeling of the light-initiated electron transfer in photosynthesis has received much attention in recent years.[1] A system that has been widely used is a porphyrin with a covalently linked quinone.[2] Upon excitation of the porphyrin to its singlet excited state, an electron can be transferred to the quinone moiety, forming a quinone anion radical and a porphyrin π-cation radical. This high-energy ion pair collapses in a nano- or picosecond time scale to the neutral species.[3] We were interested in a model system where, upon photoinduced electron transfer, a more stable species results. A promising candidate seemed to be a porphyrin with linked ferricenium ions. Electron transfer to the ferricenium ion should quench the porphyrin fluorescence.

In this paper we wish to report the synthesis of a ferrocene-substituted porphyrin, its electrochemistry, and oxidation to the porphyrin ferricenium cation. Also, the fluorescence and phosphorescence of the porphyrin ferricenium compound is investigated. We choose to study *meso*-tetrakis(4-ferrocenylphenyl)porphyrin (**1**). In **1** the phenyl substituents are out of plane with the porphyrin ring so that they serve only as spacer groups allowing rotational freedom to the ferricenium while providing for a rather rigid system with a fixed distance between the donor and the acceptor groups. The center to center distance of 10.4 Å, as calculated from published crystallographic data on *meso*-tetraphenylporphyrin[4] and ferrocene,[5] is ideal for electron transfer.[6]

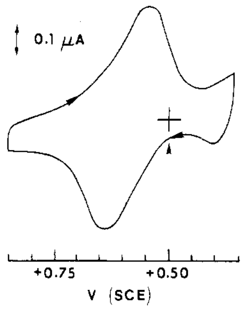
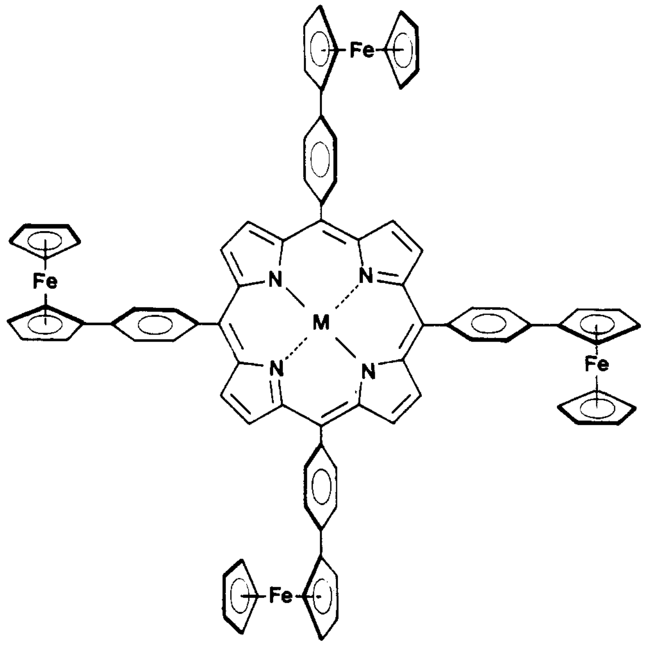


Figure 1. Thin-layer cyclic voltammgram of **1** (1.5×10^{-5} M) in a 1:1 *o*-dichlorobenzene/acetonitrile solution (0.1 M TBAP). Coulometry by integration of the area under the peak heights, after substraction for solvent contribution, indicates that 4 electrons are involved in both anodic and cathodic sweeps. The midpoint potential is at +0.59 V (SCE).

meso-Tetrakis(4-ferrocenylphenyl)porphyrin (**1**) was prepared from 4-ferrocenylbenzaldehyde[7] and pyrrole in 15% yield according to the method of Adler et al.[8] The isolation of **1** was complicated by its low solubility. It is insoluble in almost any solvent except chlorinated aromatic solvents, in which it is slightly soluble. Approximation 10^{-5} M solutions can be obtained in *o*-dichlorobenzene at 25 °C. Protonation at the pyrrole nitrogen atoms made porphyrin **1** fairly soluble in polar solvents. This enabled us to obtain a ^1H NMR spectrum of the diprotonated form in deuteriochloroform/deuteriotrifluoroacetic acid. The structure of product **1** was established beyond doubt by UV–vis spectroscopy, laser desorption Fourier transform mass spectroscopy,[9] and elemental analysis. Contrary to the case of *meso*-tetraferrocenylporphyrin,[10] **1** showed a UV–vis spectrum (see Experimental Section) almost identical with that of *meso*-tetraphenylporphyrin,[11] which indicates that there is little or no electronic interaction between the porphyrin and the ferrocene π-system.



1, M = H_2
2, M = Zn

(*meso*-Tetrakis(4-ferrocenylphenyl)porphinato)zinc (**2**), which was prepared from **1** and zinc acetate[4] in 67% yield, was even less soluble than the free-base species.

The thin-layer cyclic voltammogram of **1** in a 1:1 mixture of *o*-dichlorobenzene and acetonitrile gave an oxidation wave at +0.64 V and a reduction wave at +0.54 V, both of which by

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(1) Boxer, S. G. *Biochem. Biophys. Acta* **1983**, *726*, 265.
(2) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090 and references cited therein.
(3) Wasielewski, M. R.; Niemczyk, M. P.; Svee, W. A.; Pewitt, E. P. *J. Am. Chem. Soc.* **1985**, *107*, 5562.
(4) Smith, V. M., Ed. *Porphyrins and Metalloporphyrins*; Elsevier: Amsterdam, 1975.
(5) Konno, M.; Hyodo, S.; Lijima, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2327.
(6) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043.
(7) Egger, H.; Schloegl, K. *Monatsh. Chem.* **1964**, *95*, 1756.
(8) Adler, A.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
(9) Wilkins, C. L.; Weil, D. A.; Yang, C. L. C.; Ijames, C. F. *Anal. Chem.* **1985**, *57*, 520. Johlman, C. L.; White R. L.; Wilkins, C. L. *Mass Spectrom. Rev.* **1983**, *2*, 389.
(10) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 3079.
(11) Treibs, A.; Haeberle, N. *Justus Liebigs Ann. Chem.* **1968**, *718*, 183.

0020-1669/86/1325-3718$01.50/0

integration correspond to a 4e transition[12] (Figure 1). This indicates that all four ferrocene moieties present in **1** become oxidized in one step, which is not surprising in view of their weak interaction and results reported in the literature on 1,3,5-triferrocenylbenzene.[13] The cyclic voltammogram of the zinc porphyrin (**2**) in *o*-dichlorobenzene showed oxidation waves at +0.64, +0.92, and +1.26 V and reduction waves at +0.43, +0.83, and +1.15 V. The CV of (*meso*-tetraphenylporphinato)zinc(II) was run in *o*-dichlorobenzene as a comparison to the CV of **2**, and it showed two oxidation waves at +0.93 and +1.25 V with reductions at +1.13 and +0.77 V. This shows that the couple at +0.64 V/+0.43 V for **2** pertains to the ferrocene substituents.

The controlled-potential oxidations of **1** and **2** were performed in *o*-dichlorobenzene, since this is the only solvent that has a high dielectric constant (9.93 at 25 °C) and dissolves both compounds. Controlled-potential coulometric oxidation of **1** and **2** at +0.72 V (which is slightly above the ferrocene/ferricenium potential) consumed 4 electrons and led to a completely colorless solution. The oxidized materials being assigned to the tetraferricenium perchlorate salts **1a** and **2a** are completely insoluble in *o*-dichlorobenzene and plated out on the Pt-working electrode. In acetonitrile, dimethylformamide, and dimethyl sulfoxide, however, **1a** and **2a** would be dissolved. It has been observed[14] that ferricenium salts undergo overall solvolysis and reduction in nucleophilic solvents. In acetonitrile, ferricenium salts are reported to stable for several hours.[14] Cyclic voltammetry of freshly prepared solutions of **1a** in acetonitrile, however, indicated the presence of both oxidized and reduced material. Coulometry by controlled-potential reduction of **1a** in acetonitrile at +0.30 V resulted in the plating out of 90% (by UV–vis spectra of the solution) of the reduced species on the Pt working electrode. From the coulometric experiment only 3e rather than 4e were employed in the reduction. These observations lead us to conclude that during the time of the electrolysis (about 25 min) approximately three of the four ferricenium moieties have been reduced. Coulometric oxidation of this reduced solution showed that four electrons were released, which indicates that all four ferrocene moieties are still intact. From these results we draw the conclusion that, on the average, three of the four ferricenium moieties of **1a** remain oxidized. For photocatalyzed intramolecular electron transfer between porphyrin and fericenium moieties, only one of the latter is required.

In solution, the porphyrins **1** and **1a** as well as the Zn porphyrins **2** and **2a** show identical electronic spectra between 350 and 700 nm. This is expected, since both ferrocene and ferricenium ions exhibit comparatively weak absorptions in this region and as has been shown (loc. cit.) there appears to be no electronic interaction between ferrocene and porphyrin π-systems. Fluorescence spectra of matched solutions of **1** and **1a** were recorded at room temperature in a 1:1 mixture of acetonitrile and *o*-dichlorobenzene (5×10^{-6} M). To our surprise the fluorescence intensity ratio of **1a** vs. **1** between 600 and 775 nm was 1.65. Thus, electron transfer from the singlet excited porphyrin to the ferricenium ion can not compete with fluorescence decay. This observation is contrary to results obtained with a *meso*-phenylporphyrin substituted with a quinone in the para position of the phenyl ring[2] and a *meso*-tetraquinonylporphyrin.[15] Two explanations are offered for the present observation. The first is based on an energetic consideration, and the second is based on the rates of electron transfer to metal centers.

Recent experiments[16] have confirmed earlier theories[17] that predicted the existence of an inverted region in a plot of the log of the rate constant for through-space electron transfer vs. $\Delta G°$. This means that at high exothermicity the rate of an electron-transfer reaction falls off. The standard free energy ($\Delta G°$) for an electron transfer from the singlet excited porphyrin to the ferricenium ion **1a** is estimated to be about −1.4 eV.[18] To date, the highest reported $\Delta G°$ values for efficient intramolecular electron transfer from singlet excited porphyrin to quinone are about −0.9 eV. The lack of electron transfer in our system could be due to its high exothermicity. A very similar phenomenon has been observed in the charge recombination of porphyrin quinone zwitterions.[18] An alternative explanation for the lack of fluorescence quenching with **1a** is based on the observation that electron transfer is considerably slowed when the acceptor is metal-centered.[19]

Intersystem crossing from singlet excited porphyrin and metalloporphyrins to the triplet state is a very efficient process. The triplet state lies about 0.5 eV lower in energy than does the singlet state. Phosphorescence quenching with **2a** should not be restricted by the problem of the inverted region. Also, since the triplet state has a much longer life than the singlet state, phosphorescence quenching by slow electron transfer to the ferricenium metal center would be anticipated. Examination of the phosphorescence of **2** and **2a** was carried out in an ethanol glass at 77 K. The zinc derivatives **2** and **2a** were chosen because free-base porphyrins do not exhibit phosphorescence.[20] Both zinc porphyrins showed a broad emission signal centered at 770 nm, which is attributed to phosphorescence.[20] The lack of significant differences in the intensities of the phosphorescence of **2** and **2a** establishes that quenching of the triplet state does not occur with **2a**. At such a low temperature in a glass the rate of electron transfer to the ferricenium may be considerably slowed. Such a situation is to be expected, if the reduction of the ferricenium moiety involves considerable solvent reorganization. In order to test for this phenomenon, phosphorescence measurements would have to be performed in liquid phase at higher temperature. Under such conditions, however, both the ferrocene porphyrin **2** and the ferricenium porphyrin **2a** did not exhibit any detectable phosphorescence.

Experimental Section

The UV–vis spectra were measured on a Cary 118C spectrophotometer. Corrected fluorescence spectra were obtained at room temperature of 5×10^{-6} M aerated solutions of **1** and **1a** in 1:1 acetonitrile/*o*-dichlorobenzene. For phosphorescent measurements *o*-dichlorobenzene was used as solvent with **2** and acetonitrile with **2a**. Measured small aliquots of the two solutions were diluted into 21-mL volumes of ethanol (final concentrations of **2** and **2a** 10^{-6} M) and immediately frozen at 77 K. A Spex Fluorolog II emission spectrophotometer equipped with 2.5-mm slits and a Spex 150 W Xe lamp was employed for the determination of emission spectra. In all experiments the Soret band was excited (420 nm for **1** and **1a** and 428 nm for **2** and **2a**). The ^{1}H NMR spectrum for **1** was recorded on a Nicolet NT-300 spectrometer (300 MHz). Cyclic voltammetry was carried out with a three-electrode potentiostat (Bioanalytical Systems, Model CV-27 voltammograph) connected to a Houston Instruments Model 100 x-y recorder. The electrochemical cell was equipped with a Bioanalytical Systems platinum electrode and an Ag/AgCl reference electrode filled with aqueous tetramethylammonium chloride adjusted to 0.00 V vs. saturated calomel electrode. For thin-layer cyclic voltammetry we employed the Pt-electrode design of Hubbard.[21] The scan rate was 1 mV/s. The number of electrons transferred in a reversible process was determined as described previously.[12] Controlled-potential electrolysis was carried out with a three-electrode coulometer designed by Professor Arthur Hubbard of this department. The working electrode consisted of a 2 × 2.5 cm platinum foil. Laser desorption Fourier transform mass spectra were taken at the Department of Chemistry, University of California, Riverside, CA. Elemental

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(12) Hubbard, A. T. *CRC Crit. Rev. Anal. Chem.* **1973**, *3*, 201. Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *22*, 165.

(13) Pittman, C. U.; Sasaki, Y.; Wilemou, G. *Tetrahedron Lett.* **1973**, 4399. Nakashima, T.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2892.

(14) Schmid, R.; Gutman, V. *Monatsh. Chem.* **1973**, *104*, 864. Prins, R.; Korswagen, A. R.; Kortbeek, A. G. *J. Organomet. Chem.* **1972**, *39*, 335.

(15) Harriman, A.; Hosie, R: J. *J. Photochem.* **1981**, *15*, 163.

(16) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(17) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.

(18) Estimated from electrochemical data on **1** and tetraphenylporphyrin and the energy of the singlet excited state of the latter according to: Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewett, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.

(19) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* (*London*), in press.

(20) Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.

(21) Hubbard, A. T. *CRC Crit. Rev. Anal. Chem.* **1973**, *3*, 210–243. Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *22*, 165.

analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

***meso*-Tetrakis(4-ferrocenylphenyl)porphyrin (1).** A 500-mg sample of 4-ferrocenylbenzaldehyde[7] (1.72 mmol) was heated to reflux in 20 mL of purified propionic acid. Then, 116 mg (1.72 mmol) of freshly distilled pyrrole was added, and refluxing was continued for 30 min. After cooling, the reaction mixture was diluted with 50 mL of *n*-heptane, and the precipitate was separated by filtration. It was washed with 20 mL of dichloromethane and extracted with 5 × 30 mL of chlorobenzene at 80 °C. The solution was concentrated at 30 mL by rotoevaporation. Upon cooling, 87 mg (15%) of porphyrin (**1**) crystallized in the form of purple rods. ^{1}H NMR (300 MHz, $CDCl_3$ containing 1% CF_3CO_2D): δ 4.85 (br s, 20 H, cyclopentadienyl H), 5.23 (br s, 8 H, cyclopentadienyl H), 5.71 (br s, 8 H, cyclopentadienyl H), AA′BB′ system (δ_A 7.65, δ_B 8.28, J_{AB} = 6.0 Hz, 16 phenyl H), 8.53 (s, 8 H, β-pyrrole H). UV–vis (*o*-dichlorobenzene): 425 (ϵ 2.7 × 10^5), 525 (ϵ 1.5 × 10^4), 565 (ϵ 1.5 × 10^4), 600 (ϵ 6 × 10^3), 655 nm (ϵ 7 × 10^3). Mass spectrum: *m/e* 1351 [M^+]. Anal. Calcd for $C_{84}H_{62}Fe_4N_4$: C, 74.69; H, 4.63; Fe, 16.54; N, 4.15. Found: C, 74.41; H, 4.57; Fe, 17.16; N, 3.93.

(*meso*-Tetrakis(4-ferrocenylphenyl)porphinato)zinc (2). To 60 mg (4.40 × 10^{-2} mmol) of porphyrin (**1**) in 400 mL of refluxing chloroform was added 400 mg (1.80 mmol) of $Zn(OAc)_2 \cdot 2H_2O$ in 4 mL of methanol and refluxing continued for 1 h. The solution was concentrated by evaporation to 15 mL, and 20 mL of methanol was added. The formed precipitate was filtered and washed with 2 × 3 mL of methanol. Recrystallization from 10 mL of chlorobenzene afforded 42 mg (67%) of the zinc porphyrin (**2**) as purple rods. UV–vis(*o*-dichlorobenzene) 428 (ϵ 2.7 × 10^5), 555 (ϵ 2.1 × 10^4), 598 nm (ϵ 1.1 × 10^4). Mass spectrum: *m/e* 1414 [M^+]. Anal. Calcd for $C_{84}H_{60}Fe_4N_4Zn$: C, 71.34; H, 4.28; N, 3.96; Fe, 15.80; Zn, 4.62. Found: C, 71.46; H, 4.49; N, 3.75; Fe, 14.18; Zn, 4.01.

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Additions and Corrections

1986, Volume 25

Robert J. Deeth and Michael A. Hitchman*: Factors Influencing Jahn–Teller Distortions in Six-Coordinate Copper(II) and Low-Spin Nickel(II) Complexes.

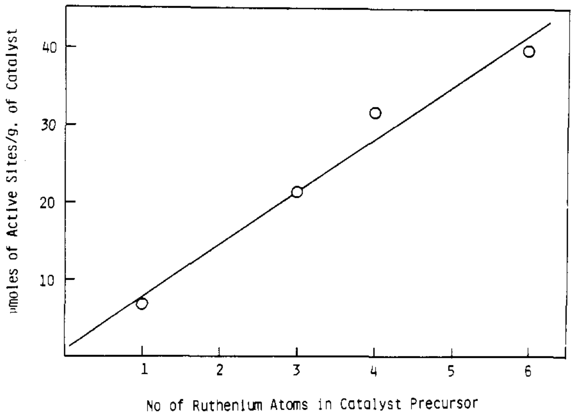
Page 1227. Equation 3 should read

$$\delta_x \approx \frac{nm\Delta'}{12r_0f}$$

All calculations in the paper were carried out by using the correct formula.—Michael A. Hitchman

Donald J. Darensbourg* and Cesar Ovalles: Catalytic Carbon Dioxide Methanation by Alumina-Supported Mono- and Polynuclear Ruthenium Carbonyls.

Page 1606. The ordinate scale in Figure 4 is incorrectly represented. The correct version appears below:



—Donald J. Darensbourg