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Relationships between Electron-Transfer Rate Constants of Bis(ligated)(octaethylporphinato)iron(III) Perchlorate and the Presence of a Spin Equilibria

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Abstract: Heterogeneous electron-transfer rate constants were measured for a series of bis(ligated)iron(III) octaethylporphyrin and tetraphenylporphyrin complexes in CH_2Cl_2 (0.1 M TBAP). The former series of complexes exist in a spin equilibria while the latter are predominantly low spin at room temperature. Values of the magnetic moment were calculated for each complex and comparisons made between this μ_{eff} and the $k°$ and $E_{1/2}$ of the electron-transfer process Fe(III) $\rightleftarrows$ Fe(II). Both μ_{eff} and the $k°$ and $E_{1/2}$ varied as a function of ligand pK_a for the complexes of $(OEP)Fe(L)_2{}^+ClO_4$. Contrary to expectation, however, no substantial changes were observed in $k°$ as a function of spin state. This was true for comparisons of the $(OEP)Fe(L)_2{}^+$ and $(TPP)Fe(L)_2{}^+$ series as well as for intercomparisons between the high- and low-spin complexes of $(OEP)Fe(L)_2{}^+$.

In recent years numerous papers have been published that characterize the physical properties and structural characteristics of iron(III) and iron(II) metalloporphyrins as a function of the central metal spin state.[1] These spin states may be high, low, or intermediate, depending on the type of porphyrin ring and axially complexed ligand. However, one relationship that has never been investigated for iron porphyrins is how spin conversion of one spin state (either Fe(III) or Fe(II)) effects the standard redox potential and electron-transfer rate for the reaction Fe(III) $\rightleftarrows$ Fe(II). Studies of these types are important in order to better understand electron-transfer processes involving Fe(III) and Fe(II) in biological systems such as cytochrome P-450, myoglobin, or hemoglobin where two electronic states of differing spin multiplicity are in thermal equilibrium with one another.[2-5]

In this work we report the first electron-transfer rate constants for an iron porphyrin spin-equilibria system. The complexes examined in this study are the (octaethylporphyrin)bis(ligated)iron(III) derivatives $(OEP)Fe(L)_2{}^+ClO_4{}^-$, where L = 3-chloropyridine (3-ClPy), pyridine (Py), 4-aminopyridine (4-NH_2Py), and 1-methylimidazole (1-MeIm). These compounds are ideal because there are no changes in coordination during the Fe(III) $\rightleftarrows$ Fe(II) redox process and because the spin equilibria between the low-spin iron(III) ($S = {}^1/_2$) and high-spin iron(III) ($S = {}^5/_2$) has been well characterized in the solution and the solid states.[6-8] The iron tetraphenylporphyrin derivatives with the same ligands were also included in this study because they allow us to gain information on how small structural differences in the porphyrin π systems would affect the spin state of the central metal ion as well as the electron-transfer rate for the electrooxidation/reduction. In solutions containing 1 M ligand, both (TPP)Fe and (OEP)Fe also form bis(ligand) complexes, and the electrode reaction can be represented as

$$PFe(L)_2{}^+ + e \rightleftarrows PFe(L)_2 \qquad (1)$$

where P = TPP or OEP.

Experimental Section

(TPP)FeCl (with some oxo dimer contamination) was synthesized by the method of Adler et al.,[9] converted to $((TPP)Fe)_2O$ by passage through an alumina column, and then quantitatively reconverted to TPPFeCl by hydrolysis/extraction with 10^{-1} M HCl. $(TPP)FeClO_4$ was prepared by metathesis of (TPP)FeCl, with $AgClO_4$ as per the method of Reed et al.[10] $(OEP)FeClO_4$ was prepared by using the same procedure. Both were recrystallized from hot toluene solution by addition of dry heptane and cooling to 10 °C. Purity was ascertained by comparison of visible spectra with literature spectra and by the lack of extraneous current waves due to dimer formation or other (TPP)FeX and (OEP)FeX species formed during the course of the cyclic voltammetric experiments.

Tetrabutylammonium perchlorate (TBAP, Eastman Chemicals), used as supporting electrolyte, was recrystallized once from ethyl acetate/pentane and stored until use under reduced pressure at 40 °C. The ligands, 3-ClPy, 4-NH_2Py, Py, 1-MeIm (Aldrich Chemicals), were used as received. CH_2Cl_2 was freshly prepared from distilling reagent-grade CH_2Cl_2 over P_2O_5 prior to each experiment. Solutions of $(OEP)Fe(L)_2{}^+ClO_4{}^-$ were prepared by dissolving $(OEP)FeClO_4$ or $(TPP)FeClO_4$ in CH_2Cl_2 or $CDCl_3$ that contained 1 M of each ligand and, for some experiments, tetrabutylammonium perchlorate (0.1 M TBAP).

Cyclic voltammetric measurements were obtained with a three-electrode system using either an IBM EC/225 Voltammetric Analyzer or a PAR Model 173 potentiostat, coupled with a PAR Model Universal Programmer and a Houston Instruments Model 2000 recorder or a storage oscilloscope for fast scan rates. No differences were observed between the two instruments. The working electrode was a platinum button, and a platinum wire served as the counterelectrode. A commercial saturated calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass bridge. The current-voltage curves for fast-scan cyclic voltammograms were taken from an oscilloscope with a C-5A oscilloscope camera (Tektronix). Measurements of electron-transfer rate constants were obtained by the method of Nicholson using cyclic voltammetry.[11]

Because of the high resistance of dichloromethane, special precautions must be taken when utilizing this solvent in order to eliminate or minimize potential shifts due to uncompensated iR loss. For this study a Luggin capillary was employed, and positive feedback (which was built into each potentiostat) was utilized. In addition, a small Pt electrode (area = 0.80 mm^2) and low porphyrin concentrations were utilized in order to minimize the peak current and thus the iR loss. The uncompensated solution resistance was determined by monitoring the increase in ΔE_p at a constant high scan rate as a function of porphyrin concentration between 0.29 and 1.05 mM and was approximately 350 Ω. The rate constant for the Fc^+/Fc couple was also measured under the same solution conditions and was approximately 0.1 cm s^{-1}.

Results and Discussion

Table I lists the effective magnetic moments of $(OEP)Fe(L)_2{}^+ClO_4{}^-$ and $(TPP)Fe(L)_2{}^+ClO_4{}^-$ measured by the Evans method in the presence and absence of supporting electrolyte. The measurements were made only at room temperature and were necessary to ensure that the magnetic moments under our experimental conditions (where the solutions contained 0.1 M TBAP

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Table I. Magnetic Moments (μ_B) of $(OEP)Fe(L)_2^+$ and $(TPP)Fe(L)_2^+$ in $CDCl_3$ and CH_2Cl_2 at 293 ± 0.5 K

			$\mu = 0.10^a$		$\mu = 0.00$		
complex	ligand, L	ligand pK_a	$CDCl_3$[b]	CH_2Cl_2[b]	CH_2Cl_2[b]	$CDCl_3$	solid
$(OEP)Fe(L)_2^+$	3-ClPy	2.8	5.1	4.7	5.1, 4.5[d,e]	4.0,[c] 4.5[d,f]	5.0,[g] 4.7[d,h]
	Py	5.3	4.0	3.9	4.2	2.7[c]	3.7[g]
	4-NH_2Py	9.2	2.9	2.6	2.9	3.0[c]	3.6[g]
	1-MeIm	7.3	3.0	2.5	3.1	2.1[c]	2.4[g]
$(TPP)Fe(L)_2^+$	3-ClPy	2.8	3.8	3.3	3.4		2.7[d]
	Py	5.3	3.6	2.9	2.9		
	4-NH_2Py	9.2	2.4	2.0	1.9		
	1-MeIm	7.3	2.5	2.7	2.8		

[a] Solutions contained 0.1 M TBAP. [b] Solutions contained 1 M ligand; estimated error: ±0.2 μ_B. [c] Taken from Figure (a) in ref 6. [d] Taken from ref 8. [e] Measurement was made at 303 K in the absence of excess ligand. [f] Measurement was made at 313 K in the absence of excess ligand. [g] Taken from Figure (b) in ref 6. [h] Measurement made at 294 K.

Table II. Electrochemical Data Used in Calculation of Rate Constants for Reduction of $(OEP)Fe(3\text{-}ClPy)_2^+$ in CH_2Cl_2, 0.1 M TBAP[a]

porphyrin concentration	scan rate, V, s	i_p, μA	$E_{p,c}$, V	E_{pa}, V	ΔE_p,[b] mV	ψ[c]	$k°$, cm s^{-1}
0.29 mM	0.5	0.83	−0.078	0.000	78	1.32	2.4×10^{-2}
	1.0	1.19	−0.080	0.004	84	1.01	2.6×10^{-2}
	2.0	1.68	−0.086	0.012	98	0.60	2.2×10^{-2}
	3.0	1.97	−0.091	0.015	106	0.49	2.2×10^{-2}
	4.0	2.08	−0.093	0.020	113	0.43	2.3×10^{-2}
1.05 mM	0.5	2.91	−0.077	0.001	78	1.32	2.4×10^{-2}
	1.0	4.35	−0.079	0.007	86	0.92	2.4×10^{-2}
	2.0	6.14	−0.087	0.015	102	0.53	2.0×10^{-2}
	3.0	6.90	−0.090	0.020	110	0.45	2.1×10^{-2}
	4.0	7.66	−0.093	0.025	118	0.38	2.0×10^{-2}

[a] Rate constants were calculated by using an experimentally determined diffusion coefficient of 5.7×10^{-6} cm^2 s^{-1}. [b] Experimentally determined values. The differences in ΔE_p between the two concentrations at high scan rates is due to uncompensated resistance (~350 Ω) and leads to an apparent decrease in $k°$ with scan rate. This decrease does not occur at the lower concentration where the contribution of uncorrected resistance to ΔE_p is negligible. [c] Reference 11.

and 1 M ligand) were the same (within experimental error) as had been reported in the literature.[6-8]

As seen in this table, μ_{eff} for a given complex of $(OEP)Fe(L)_2^+$ is relatively constant from laboratory to laboratory, although differences do occur. Generally, differences between measured μ_{eff} in this study and those in previous studies may be assigned to differences in supporting electrolyte, ionic strength, and solution conditions. This has been discussed in the literature.[6-8] Hill et al.[6] reported that μ_{eff} of $(OEP)Fe(L)_2^+X^-$ changed little upon addition of excess ligand to solution and that only small differences existed between values in the solid and the solution states. He also reported that only small differences in μ_{eff} were observed between complexes in the solid state when X^- was PF_6^- and when it was ClO_4^-. The conclusion that similar values of μ_{eff} are obtained between the solid and solution states was also reached by Scheidt et al.[8] in a more recent study of the 3-Clpy derivative of $(OEP)Fe(L)_2^+$. Data from this study is also included in Table I.

Under all experimental conditions the systematic trend of the magnetic moment as a function of axial ligand is always the same. For the complexes of $(OEP)Fe(L)_2^+$, the magnetic moment directly depends on the ligand pK_a. This is shown graphically in Figure 1a for the three pyridine ligands. $(OEP)Fe(1\text{-}MeIm)_2$ is not shown in this plot because of the known differences in linear free energy relationships between series of substituted pyridines and imidazoles. When considering only the pyridines, it is seen that the larger the ligand pK_a, the smaller the magnetic moment of the Fe(III) complex. This trend has been suggested for other metalloporphyrin complexes[13] and is due to the stronger ligand field strength of the ligand with increase in pK_a, which splits the energy levels of the central metal to a greater extent and favors the low-spin form. This changeover in spin state as a function of bound ligand is not observed for complexes of $(TPP)Fe(L)_2^+$ in Table I where all complexes are predominantly in the low-spin state.[14] As seen in Figure 1, however, some small changes in the measured room-temperature magnetic moment do occur with changes in ligand pK_a.

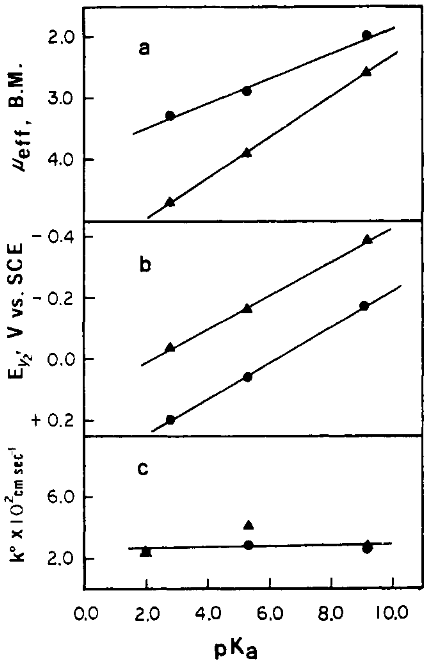

Figure 1. Plot of (a) μ_{eff}, (b) $E_{1/2}$, and (c) $k°$ vs. ligand pK_a for the reduction of $(OEP)Fe(L)_2^+$ (▲) and $(TPP)Fe(L)_2^+$ (●) in CH_2Cl_2–0.1 M TBAP containing 1 M ligand. Only the three pyridine ligands are shown in this figure.

A typical cyclic voltammogram of 0.29 mM $(OEP)Fe(3Cl\text{-}Py)_2^+$ is illustrated in Figure 2. Similar current–voltage curves were obtained between 0.29 and 1.05 mM porphyrin concentration.

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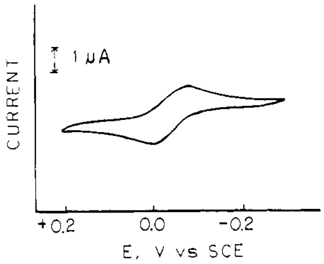


Figure 2. Cyclic voltammogram of 0.29 mM $(OEP)Fe(3\text{-}ClPy)_2^+$ in CH_2Cl_2–0.1 M TBAP. Scan rate = 1.0 V s^{-1}.

Table III. Heterogeneous Electron-Transfer Rate Constant and Potentials for Reduction of $(OEP)Fe(L)_2^+$ and $(TPP)Fe(L)_2^+$ in CH_2Cl_2 Containing 0.1 M TBAP and 1 M Ligand at 293 ± 0.5 K

complex	ligand, L	pK_a	μ_{eff}	$k°$,[b] cm s^{-1}	$E_{1/2}$, V (vs. SCE)
$(OEP)Fe(L)_2^+$	3-ClPy	2.8	4.7	2.3×10^{-2}	−0.04
	Py	5.3	3.9	4.1×10^{-2}	−0.16
	$4\text{-}NH_2Py$	9.2	2.6	2.7×10^{-2}	−0.39
	1-MeIm	7.3	2.5	4.0×10^{-2}	−0.39
$(TPP)Fe(L)_2^+$	3-ClPy	2.8	3.3	2.3×10^{-2}	+0.20
	Py	5.3	2.9	2.8×10^{-2}	+0.06
	$4\text{-}NH_2Py$	9.2	2.0	2.6×10^{-2}	−0.17
	1-MeIm	7.3	2.7	4.0×10^{-2}	−0.16

[a] Estimated error: ±0.2 μ_B. [b] Determined by the Nicholson technique; see ref 11.

In all cases the peak separation $E_{pa} - E_{pc}$ increased as a function of scan rate. For the specific compound in Figure 2, ΔE_p varied between 78 mV at 0.5 V s^{-1} to 118 mV at 4 V s^{-1}. This is shown in Table II, which lists values of ΔE_p at several scan rates as well as the Nicholson parameter ψ and the calculated heterogenous electron-transfer rate constant. The constancy of $k°$ as a function of scan rate at the lower concentration as well as the invariance of ΔE_p with increase in porphyrin concentration from 0.29 to 1.05 mM at 0.5 V s^{-1} indicates a minimal contribution from uncorrected solution resistance and lends credence to the calculated values of $k°$. The differences in ΔE_p between the two concentrations at high scan rates is due to uncompensated resistance and leads to a value of $k°$ that appears to decrease by about 10% at higher scan rates when the $(OEP)Fe(3\text{-}ClPy)_2^+$ concentration is 1.05 mM. A slight but smaller decrease in $k°$ was also observed at high scan rates when the porphyrin concentration was 0.50 and 0.79 mM. At the lowest concentration of 0.29 mM, contributions to ΔE_p from uncorrected resistance are neglible and lead to insignificant changes in the calculated $k°$.

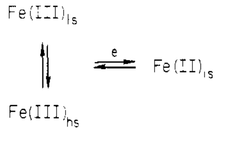
A summary of the electron-transfer rate constants for all eight complexes in Table I is listed in Table III. Also listed in this table are the measured half-wave potentials and the magnetic moments of each complex under the same experimental conditions. Unexpectedly, no real change in $k°$ was observed despite a change from the predominantly high-spin $(OEP)Fe(3\text{-}ClPy)_2^+$ to the predominantly low-spin $(OEP)Fe(4\text{-}NH_2Py)_2^+$. This lack of change with spin state was also observed on going from $(OEP)Fe(3\text{-}ClPy)_2^+$ to $(TPP)Fe(3\text{-}ClPy)_2^+$ (see Figure 1c) and suggests that there is little effect of the porphyrin ring on the heterogeneous rate of electron transfer. At the same time, however, the increase in ligand pK_a did change the potentials for both series of complexes in a manner consistent with an increasing ligand field stabilizing the Fe(III) state more than the Fe(II) state of each complex (Figure 1b).

In a study of electron-transfer rate constants involving the same types of ligands bound to iron protoporphyrin IX chloride, Constant and Davis[15] found that both the standard potential and electron-transfer rate constant changed with the ligand pK_a. This study was carried out in Me_2SO and DMF, and in the former solvent, values of $pk°$ ranged between 2.10 and 0.42 and were linearly related to the ligand pK_a. No values of magnetic moments were calculated, however, and it now appears that the observed large differences in $k°$ with changes in complexed ligand were due to the competing effects of solvent and the Cl^- counterion. A rate study of $(p\text{-}X)(TPP)FeCl$ complexes, published at about the same time, by the laboratories of Davis and Kadish[16] indicated that $pk°$ ranged between 2.08 and 3.10 and that the rate of electron transfer was dependent upon the electron density at the central metal. For the reaction Fe(III) ⇄ Fe(II), larger rate constants were obtained for complexes containing electron-donating ring substituents. However, these results again seem to be dependent upon solvent and counterion effects since a third study in DMF gave opposite effects, that is a larger rate constant for reduction of (TPP)FeCl than for (OEP)FeCl.[17] Rate constants in DMF were measured as 4.0×10^{-3} cm s^{-1} and 1.0×10^{-3} cm s^{-1} for the (TPP)FeCl and (OEP)FeCl complex, respectively. In all three previous studies there appears to be no spin equilibrium involved with the product or the reactant, and the reactions most likely involved high-spin Fe(III) and Fe(II) as well as a change of solvent and/or counterion coordination upon reduction.

It has been known for some time that spin state may account for the effect of ligands on the rates of electron transfer and that the most rapid electron transfer is obtained for reactions in which the electrons in the system are undisturbed during the redox process.[18,19] As a general rule, providing all other factors for a given couple are invariant, the rates (both heterogeneous and homogeneous) are generlly expected to decrease according to the following order: low spin/low spin > high spin/high spin ≫ low spin/high spin. Differences in heterogeneous electron-transfer rate constants, as a function of spin state, have been discussed by Kadish and Jordan[20] for the hypothetical electrode reactions of cytochrome *c*, hemoglobin, and myoglobin. For these systems, the largest rate constant was calculated for the oxidation/reduction of cytochrome *c* where both the Fe(II) reactant and Fe(III) product are low spin.

The conclusion that faster rates are obtained for electrooxidation/reduction of low-spin complexes when compared to similar high- or mixed-spin complexes was also reported by Yasuda et al.[21] This conclusion was based on a study of variable-spin tris(*N*,*N*-disubstituted-dithiocarbamato) Fe(III) complexes using galvanostatic techniques. A similar conclusion was also reached earlier by Kadish and Davis for electroreduction of several synthetic porphyrin complexes.[22] This conclusion, however, was based on limited data in which not a great deal was known about the actual iron spin state in solution and for complexes in which there may have been a change of coordination number upon reduction.

In our present study, the spin states of the reactants $(OEP)Fe(L)_2^+$ are in a well-defined spin equilibrium and it is rather certain that no changes of coordination number occur during the redox reaction. Additionally, the spin state of the Fe(II) product appears to be low spin ($S = 0$) for all of the complexes investigated in this study. Thus, the electron-transfer process can be written as



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Since no trend is present in rates of electron transfer for the $(OEP)Fe(L)_2^+$ complexes as a function of spin state and values of k° are virtually identical with those for $(TPP)Fe(L)_2^+$ where the reaction is $Fe(III)_{ls} \rightleftarrows Fe(II)_{ls}$, one can only conclude that spin conversion to low-spin Fe(III) occurs before the electron-transfer process and that this rate is faster than the electron-transfer step itself.

Using an average electron-transfer rate constant of 2×10^{-2} cm s^{-1} and a closest approach of the porphyrin to the electrode of 10–15 Å would yield a first-order rate of spin conversion between 3×10^5 s^{-1} and 2×10^5 s^{-1}. Unfortunately we are unable to determine the actual closest approach of the porphyrin to the electrode surface since we do not know the initial site of electron transfer or the orientation of the porphyrin ring with respect to the electrode surface. Assuming that electron transfer occurs via the periphery of the porphyrin ring would lead to a conservative estimate of 10–15 Å (the radius of the porphyrin is ~9 Å). On the other hand, if electron transfer occurs directly at the iron center via the bound ligand and the porphyrin ring is oriented parallel to the electrode, a closest approach of 5–10 Å might be possible. In this case a first-order rate constant as large as 6.0×10^5 s^{-1} would be calculated. All of these values are slower than the first-order exchange rate of $>10^7$ s^{-1} determined by Dose et al.[3] for ferric myoglobin hydroxide using the laser Raman temperature jump technique but are close to the lower limit of 2×10^5 s^{-1} estimated by Beattie and West[23] using conventional capacitive-discharge T jump.

It is of some interest to compare the heterogeneous electron-transfer rates of synthetic $(TPP)Fe(L)_2^+$ and $(OEP)Fe(L)_2^+$ to that for electrooxidation/reduction of low-spin, six coordinate cytochrome *c*. Heterogeneous electron-transfer rates of cytochrome *c* have been measured under a variety of experimental conditions and at a variety of electrodes. Until recently, almost all studies on gold, platinum, nickel, or mercury electrodes showed large ranges of rate constants, all of which appeared to be irreversible.[24,25] More recent investigations, however, indicated that revresible cyclic voltammograms could be obtained by using modified gold electrodes,[26,27] tin oxide optically transparent electrodes (OTEs),[28] or doped indium oxide OTEs.[29,30] In addition, the actual rate will depend significantly on the purity of the cyctochrome *c* with the fastest rates being obtained for the most pure preparation.[29,30] Under the best conditions, values of k° obtained by cyclic voltammetry at an indium oxide OTE were between 1.7 (±0.3) $\times 10^{-3}$ and 8.1 (±0.4) $\times 10^{-4}$ cm s^{-1}.[30] These are still a full order of magnitude slower than the (1.5–2.0) $\times$ 10^{-2} cm s^{-1} calculated for cytochrome *c* using ac impedance methods.[25,26] This latter value is within experimental error of our k° values listed in Table III for $(OEP)Fe(L)_2^+$ and $(TPP)Fe(L)_2^+$. In our systems the measurements were made in CH_2Cl_2 while for cytochrome *c* values of k° were determined in buffered aqueous media.[24-30]

Scheidt et al.[8] have characterized the structural properties of the high- and low-spin forms of $(OEP)Fe(3\text{-}ClPy)_2^+$. Although the average decrease of the iron-ligand bond distance is 0.13 Å upon changing from high-spin Fe(III) to low-spin Fe(III), they conclude that movement of the iron atom with respect to the porphinato plane is not required. This is consistent with the rapid and identical rates we have observed in this study for complexes undergoing a spin equilibria.

In summary, we have measured magnetic moments, electron-transfer rate constants, and half-wave potentials for a series of Fe(III) porphyrin complexes differing mainly in spin state in order to determine how a spin equilibrium effects heterogeneous electron-transfer rate constants for the reaction $Fe(III) \rightleftarrows Fe(II)$. We are now able to conclude that, with proper selection of a ligand, it is possible to generate a spin-equilibrium porphyrin complex as well as to "fine-tune" the position of the standard potential. We cannot, however, fine-tune the heterogeneous electron-transfer rate constant as had been previously suspected.

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Registry No. $(OEP)Fe(3\text{-}ClPy)_2^+ClO_4^-$, 71414-31-8; $(OEP)Fe(Py)_2^+ClO_4^-$, 71414-34-1; $(OEP)Fe(4\text{-}NH_2Py)_2^+ClO_4^-$, 71414-33-0; $(OEP)Fe(1\text{-}MeIm)_2^+ClO_4^-$, 71414-35-2; $(TPP)Fe(3\text{-}ClPy)_2^+ClO_4^-$, 72318-32-2; $(TPP)Fe(Py)_2^+ClO_4^-$, 70936-34-4; $(TPP)Fe(4\text{-}NH_2Py)_2^+ClO_4^-$, 84027-63-4; $(TPP)Fe(1\text{-}MeIm)_2^+ClO_4^-$, 70936-45-7.

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