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Electrode Reactions of μ-Oxo Iron(III) Porphycene Dimers. Formation of Stable $[[(\mathrm{Pc})\mathrm{Fe}]_2\mathrm{O}]^n$ Complexes Where $n = -4$ to $+4$

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This paper reports the first detailed electrochemistry of iron(III) μ-oxo porphycene dimers. The investigated compounds are represented as $[(\mathrm{Pc})\mathrm{Fe}]_2\mathrm{O}$ where Pc = the dianion of octaethylporphycene (OEPc), etioporphycene (EtioPc), tetrapropylporphycene (TPrPc) or tetra-*tert*-butylporphycene (TBuPc). Each derivative undergoes four reversible one-electron reductions and four reversible one-electron oxidations, and this data is compared to that of the related iron(III) porphyrin μ-oxo dimers which in non-aqueous media may undergo up to four one-electron oxidations but only a single reversible one-electron reduction. The site of electroreduction during the first two one-electron transfers of $[(\mathrm{Pc})\mathrm{Fe}]_2\mathrm{O}$ was evaluated utilizing thin-layer UV–visible spectroelectrochemistry and indicated the stepwise addition of two electrons to the conjugated π-ring system of the porphycene rather than to the Fe(III) metal ions of the μ-oxo dimer. Comparisons are made between the electrochemistry and UV–visible spectra of electroreduced $[(\mathrm{EtioPc})\mathrm{Fe}]_2\mathrm{O}$ and a related μ-oxo porphycene dimer possessing the same macrocycle but electroinactive metal ions, $[(\mathrm{EtioPc})\mathrm{Al}]_2\mathrm{O}$, as well as between dimeric $[(\mathrm{OEPc})\mathrm{Fe}]_2\mathrm{O}$ and monomeric (OEPc)FeCl. This data is self-consistent and clearly indicates that the first two reductions of $[(\mathrm{Pc})\mathrm{Fe}]_2\mathrm{O}$ occur at the porphycene macrocycle rather than at the Fe(III) center as has been suggested for iron μ-oxo porphyrin dimers. The difference in reductive electrochemistry between $[(\mathrm{Pc})\mathrm{Fe}]_2\mathrm{O}$ and $[(\mathrm{P})\mathrm{Fe}]_2\mathrm{O}$ (where P = the dianion of a porphyrin ring) is interpreted in terms of different sites of electron transfer and a lowering of the LUMO energy level.

Introduction

A variety of metalloporphyrin dimers have been investigated as to their redox properties in non-aqueous media.[2–31] These include "face-to-face" type dimers,[3–8,20–22] "edge-to-edge" type dimers and dimers with a variety of orientations with respect to each other.[18–31] The most studied have been those with a face-to-face orientation in which the two macrocycles are linked to each other either with covalent bridges[3–8,20–22] or via a single-atom or multiatom bridge connecting the two metal centers.[10–19] Many of the complexes have been synthesized with an aim of obtaining multielectron transfer[26–27] while others have been prepared with the goal of examining the nature of interactions which might occur between two closely-spaced redox centers such as in the case of cytochromes.[32,33]

The most easily accessible iron porphyrin dimers are those with μ-oxo bridges, and these compounds have been studied as to both their electrooxidation and electroreduction in a variety of non-aqueous solvents.[2] The oxidation proceeds via four one-electron abstractions, the first of which generates a porphyrin π-cation radical.[11,12] A similar behavior is seen for μ-oxo iron dimers of chlorins and isobacteriochlorins,[13] and these latter two

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(1) (a) University of Houston. (b) Université de Bourgogne. (c) Universität zu Köln.

(2) Kadish, K. M. *Prog. Inorg. Chem.* **1986,** *34,* 435–605.

(3) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Tabard, A.; Guilard, R.; Seok, W. K.; Ibers, J. A.; L'Her, M. *J. Am. Chem. Soc.* **1992,** *114,* 9869–9877.

(4) Uemori, Y.; Nakatsubo, A.; Imai, H.; Nakagawa, S.; Kyuno, E. *Inorg. Chem.* **1992,** *31,* 5164–5171.

(5) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984,** *106,* 2725–2726.

(6) Liu, H. Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985,** *89,* 665–674.

(7) Ni, C. L.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1987,** *91,* 1158–1166.

(8) Collman, J. P.; Hendricks, N. H.; Leidner, C. R.; Ngameni, E.; L'Her, M. *Inorg. Chem.* **1988,** *27,* 387–393.

(9) Cosmo, R.; Kautz, C.; Meerholz, K. H.; Heinze, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 604–607.

(10) Wollmann, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1977,** *4,* 723–733.

(11) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1979,** *101,* 7641–7643.

(12) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982,** *104,* 6026–6034.

(13) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981,** *103,* 4763–4778.

(14) Kadish, K. M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1985,** *24,* 2148–2156.

(15) Kadish, K. M.; Rhodes, R. K.; Bottomley, L. A.; Goff, H. M. *Inorg. Chem.* **1981,** *20,* 3195–3200.

(16) Lançon, D.; Kadish, K. M. *Inorg. Chem.* **1984,** *23,* 3942–3947.

(17) Chang, D.; Cocolios, P.; Wu, Y. T.; Kadish, K. M. *Inorg. Chem.* **1984,** *23,* 1629–1633.

(18) Kadish, K. M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1985,** *24,* 2148–2156.

(19) Scheidt, W. R.; Cheng, B.; Safo, M. K.; Cukiernik, F.; Marchon, J.-C.; Debrunner, P. G. *J. Am. Chem. Soc.* **1992,** *114,* 4420–4421.

(20) Brookser, B. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1991,** *113,* 4208–4218.

(21) Karaman, R.; Blasko, A.; Almarsson, O.; Arasasingham, R. D.; Bruice, T. C. *J. Am. Chem. Soc.* **1992,** *114,* 4889–4878.

(22) Mest, Y. L.; L'Her, M.; Hendricks, N. H.; Kim, K.; Collman, J.-P. *Inorg. Chem.* **1992,** *31,* 835–847 and references cited therein.

(23) Smith, P. D.; James, B. R.; Dolphin, D. *Coord. Chem. Rev.* **1981,** *39,* 295–383.

(24) Felton, R. H.; Owen, A. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J. *Ann. N.Y. Acad. Sci.* **1973,** *206,* 504–515.

(25) Kadish, K. M.; Larson, A.; Lexa, D.; Momenteau, M. *J. Am. Chem. Soc.* **1975,** *97,* 282–288.

(26) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980,** *102,* 6027–6036.

(27) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983,** *105,* 2710–2718.

(28) Collman, J. P.; Hutchison, J. E.; Lopez, M. A.; Guilard, R. *J. Am. Chem. Soc.* **1992,** *114,* 8066–8073.

(29) *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980.

(30) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978.

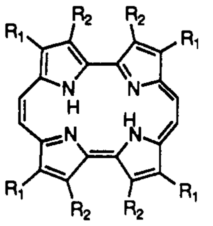
(31) Chang, C. K.; Wang, C. B. In *Binuclear Porphyrin Complexes in Electron Transport and Oxygen Utilization*; Chein, H., Ed.; Elsevier: Amsterdam, 1982; p 237.

(32) Caughey, W. S. *Adv. Chem. Ser.* **1971,** *100,* 248–259.

(33) Der Vartanian, D. V.; LeGall, J. *Biochem. Biophys. Acta* **1974,** *346,* 79–99.

0020-1669/94/1333-0471$04.50/0

Chart 1



$R_1 = R_2 =$ Et; H_2OEPc
$R_1 =$ Et; $R_2 =$ Me; H_2EtioPc
$R_1 =$ *n*-Pr; $R_2 =$ H; H_2TPrPc
$R_1 =$ *t*-Bu; $R_2 =$ H; H_2TBuPc

compounds undergo a single one-electron reduction as is the case for all but one μ-oxo porphyrin dimer. The single exception is $[(CN)_4TPP)Fe]_2O$ which undergoes four reversible one-electron reductions but no oxidation within the potential range of the solvent.[18]

Recently several laboratories have begun to investigate the properties of porphycenes,[34–37] structural isomers of the porphyrins. One such property is their electrochemistry which, in the case of monomers, may differ substantially from that of the related metalloporphyrins having the same central metal ions.[38,39] However, the detailed electrochemistry of μ-oxo porphycene dimers has yet to be described in the literature, and it was therefore not known how their redox properties might differ from that of the related iron μ-oxo porphyrin dimers. This is examined in the present manuscript which reports the electrochemistry of four iron(III) porphycene μ-oxo dimers, one iron(III) porphycene monomer and one μ-oxo porphycene dimer containing electroinactive Al(III) metal ions. The investigated compounds are represented as $[(Pc)Fe]_2O$, $[(EtioPc)Al]_2O$, and (OEPc)FeCl, where Pc = the dianion of octaethylporphycene (OEPc), etioporphycene (EtioPc), tetrapropylporphycene (TPrPc) or tetra-*tert*-butylporphycene (TBuPc). These macrocycles differ by the substituents on the ring periphery and have the structures shown in Chart 1.

Experimental Section

Chemicals. Benzonitrile (PhCN), obtained from Aldrich Chemicals was distilled over P_2O_5 under reduced pressure.[40] Tetra-*n*-butyl ammonium perchlorate (TBAP), obtained from Eastman Chemicals, was recrystallized from ethanol and then dried in vacuo at 40 °C.

Synthesis of $[(EtioPc)Fe]_2O$. (EtioPc)FeCl was prepared by the reaction of $(EtioPc)H_2$[41] with $FeCl_2 \cdot 2H_2O$ in DMF. The μ-oxo dimer, $[(EtioPc)Fe]_2O$, was obtained by treating (EtioPc)FeCl with NaOH (10%) in CH_2Cl_2 and then purified on a basic alumina column using CH_2Cl_2 as eluent after which it was recrystallized from benzene. The mass spectrum revealed a molecular ion peak at 1080 (calculated 1081). ^1H NMR ($CDCl_3$): δ 6.8 (br s, 8H, H-9,10,19,20), 6.8 (br s, 8H, α-CH_2), 6.6 (br s, 24H, α-CH_3), 4.8 (br s, 8H, α'-CH_2), 1.7 (br s, 24H, β-CH_3). IR (KBr): 2961, 2928, 2869, 1493, 1123, 848, 801 cm^{-1}. UV–visible (CH_2Cl_2), λ_{max}, nm: 344, 367, 429, 632.

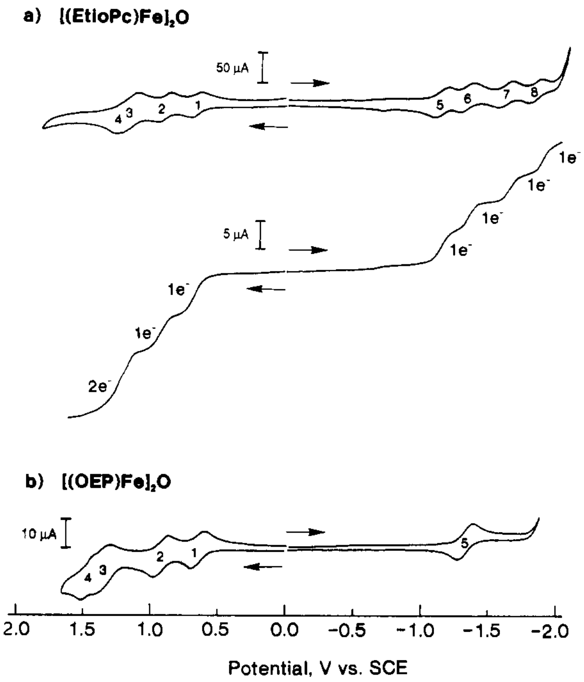


Figure 1. (a) Cyclic voltammogram (scan rate = 0.1 V/s) and rotating disk voltammogram (rotation rate = 500 rpm; scan rate = 0.1 V/s) of $[(EtioPc)Fe]_2O$ in PhCN containing 0.1 M TBAP and (b) cyclic voltammogram of $[(OEP)Fe]_2O$ under the same experimental conditions.

Synthesis of $[(Pc)Fe]_2O$, Where Pc = OEPc, TPrPc, or TBuPc. The μ-oxo iron(III) porphycene dimers of TPrPc, OEPc, and TBuPc were synthesized from the corresponding free base porphycenes[34,35] with iron(III) acetylacetonate in boiling phenol. Conventional workup and recrystallization gave the μ-oxo complexes in 70–80% yields. $[(TPrPc)Fe]_2O$; mp 266–268 °C. ^1H NMR ($CDCl_3$): δ 14.40 (br s, 8H, H-3,6,13,16), 6.91 (br s, 8H, H-9,10,19,20), 6.65 (br s, 8H, α-CH), 5.41 (br s, 8H, α-CH), 2.47 (br s, 16H, β-CH_2), 1.37 (br s, 24H, CH_3). EIMS, *m/z*; 1080, 24%, M^+; 532, 100%, $[M - Fe(TPrPc)O]^+$. IR (CsI): 2957, 2929, 2868, 1466, 968, 844, 812 cm^{-1}. UV–vis (CH_2Cl_2), λ_{max} nm (ϵ): 342 sh (86 100), 367 (99 600), 427 sh (23 600), 632 (55 500). $[(OEPc)Fe]_2O$: mp 274–276 °C. ^1H NMR ($CDCl_3$): δ 6.83 (br s, 8H, H-9,10,19,20, H-3a,6a,13a,16a), 6.14 (br s, 4H, H-3a,6a,13a,16a), 5.89 (br s, 4H, H-2a,7a,12a,17a), 4.78 (br s, 4H, H-2a,7a,12a,17a), 1.68 (br s, 24H, H-2b,7b,12b,17b, H-3b,6b,13b,16b). EIMS, *m/z*: 1192, 20%, M^+; 588, 100% $[M - Fe(OEPc)O]^+$. IR(CsI): 2959, 2925, 2866, 1487, 1093, 998, 872 cm^{-1}. UV–vis (CH_2Cl_2) λ_{max}, nm (ϵ): 375 (112 100), 452 sh (25 000), 587 sh (31 800), 637 (69 700). $[(TBuPc)Fe]_2O$: mp >300 °C. ^1H NMR ($CDCl_3$): δ 14.39 (br s, 8H, H-3,6,13,16), 7.29 (br s, 8H, H-9,10,19,20), 2.50 (br s, 72H, CH_3). EIMS, *m/z*: 1192, 48%, M^+; 588, 100%, $[M - Fe(TBuPc)O]^+$. IR (CsI): 2963, 2909, 2871, 1464, 1039, 1010, 976, 902 cm^{-1} UV–vis (CH_2Cl_2) λ_{max}, nm. (ϵ): 370 (123 000), 430 sh (21 000), 580 sh (31 600), 628 nm (89 000). Additional details on the synthesis and molecular structure of these μ-oxo dimers will be published elsewhere.[42] (OEPc)FeCl was synthesized using a procedure similar to that described in the literature.[38]

Synthesis of $[(EtioPc)Al]_2O$. The μ-oxo bis(etioporphycene) aluminum(III) dimer, $[(EtioPc)Al]_2O$, was prepared by heating the precursor, (etioporphycinato)aluminum(III) hydroxide, (70 mg, 0.13 mM) at 350 °C under reduced pressure. The dark green powder was recovered by sublimation (42 mg) and found to be the desired $[(EtioPc)Al]_2O$ product (yield 60%). ^1H NMR ($CDCl_3$): δ 9.7 (s, 8H, H-9,10,19,20), 3.83 (q, 16H, α-CH_2), 3.36 (s, 24H, α-CH_3), 1.7 (t, 24H, β-CH_3). Mass spectrum DCI $(M + 1)^+ = 1023$. UV–visible (CH_2Cl_2) λ_{max}, nm: 390, 568, 608.

Instrumentation and Methods. Cyclic voltammetry was carried out with an EG&G Model 173 potentiostat and an IBM Instruments Model EC 225 voltammetric analyzer. Current–voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. A three-electrode system was used and consisted of a platinum or glassy-carbon-button working electrode, a platinum-wire counter electrode, and a saturated calomel electrode (SCE) as reference. The reference electrode was

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(34) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257–259.

(35) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928–931.

(36) Waluk, J.; Müller, M.; Swiderek, P.; Köcher, M.; Vogel, E.; Hohlneicher, G.; Michl, J. *J. Am. Chem. Soc.* **1991**, *13*, 5511–5527.

(37) Berman, A.; Michaeli, A.; Feitelson, J.; Bowman, M. K.; Norris, J. R.; Levanon, H.; Vogel, E.; Koch, P. *J. Phys. Chem.* **1992**, *96*, 3041–3047.

(38) Gisselbrecht, J. P.; Gross, M.; Köcher, M.; Lausmann, M.; Vogel, E. *J. Am. Chem. Soc.* **1990**, *112*, 8618–8620.

(39) Kadish, K. M.; Van Caemelbecke, E.; Boulas, P.; D'Souza, F.; Vogel, E.; Kisters, M.; Medforth, C. J.; Smith, K. M. *Inorg. Chem.* **1993**, *32*, 4177–4178.

(40) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: New York, 1980.

(41) Vogel, E.; Koch, P.; Hou, X.-L.; Lex, J.; Lausmann, M.; Kisters, M.; Guilard, R.; Aukauloo, A.; Richard, P. *Angew. Chem.* **1993**, *105*, 1670–1673.

(42) Vogel, E.; Lausmann, M.; Zimmer, I.; Lex, J.; Lueken, H.; Wieghardt, K. Manuscript in preparation.

Table 1. Half-Wave Potentials (V vs SCE) for Oxidation and Reduction of Investigated μ-Oxo Iron(III) Dimers in PhCN

			oxidation[a]				reduction[a]			
macrocycle	compound	Fe-O-Fe angle, deg	4th	3rd	2nd	1st	1st	2nd	3rd	4th
porphyrin	$[(OEP)Fe]_2O$	172[b]	1.46	1.35	0.93	0.67	−1.35			
porphycene	$[(EtioPc)Fe]_2O$	–c–	1.22[d]	1.16[d]	0.94	0.71	−1.14	−1.33	−1.63	−1.86
	$[(OEPc)Fe]_2O$	180[e]	1.22	1.15	0.97	0.75	−1.09	−1.30	−1.62	−1.78
	$[(TBuPc)Fe]_2O$	179[e]	1.21[f]	1.21[f]	1.03	0.84	−1.01	−1.20	−1.51	−1.70
	$[(TPrPc)Fe]_2O$	145[e]	1.39	1.25	1.04	0.82	−0.99	−1.10	−1.50	−1.74

[a] Measured in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s. [b] Reference 19. [c] Structure not known. [d] Values determined by differential pulse voltammetry. Pulse amplitude = 25 mV. Pulse period = 300 ms. Scan rate = 5 mV/s. [e] Reference 42. [f] Overlapping third and fourth oxidations.

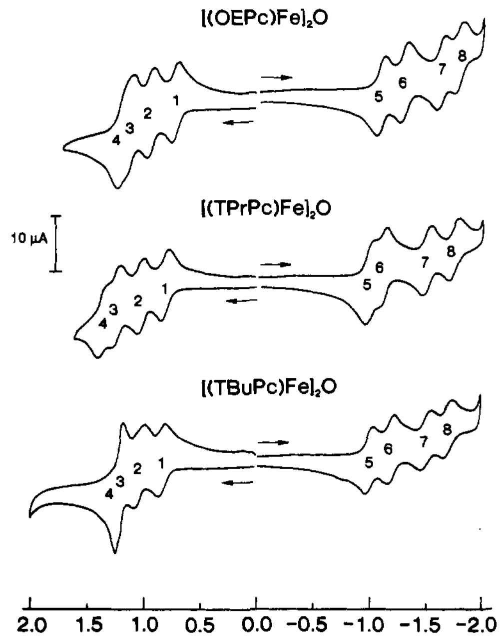

Figure 2. Cyclic voltammograms of $[(Pc)Fe]_2O$ (Pc = OEPc, TPrPc or TBuPc) in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

separated from the bulk of the solution by a fritted-glass bridge filled with the solvent and supporting electrolyte. Solutions containing the supporting electrolyte and the metalloporphycene were first deoxygenated by a stream of nitrogen for at least 10 min and then protected by a nitrogen blanket during the experiment. Rotating disk electrode (RDE) voltammetry was performed with an MSR speed control unit (Pine Instrument Co.). A platinum RDE of area 0.198 cm^2 was employed as the working electrode. All potentials are referenced to the SCE.

Spectroelectrochemical experiments and thin-layer coulometry were preformed at a platinum thin-layer electrode whose design is described in the literature.[43] Potentials were monitored with an IBM Instruments Model EC 225 voltammetric analyzer. Time-resolved UV–visible spectra were recorded with a Tracor Northern Model 6500 rapid spectrophotometer/multichannel analyzer.

Results and Discussion

Electrochemistry of $[(Pc)Fe]_2O$. Figure 1a shows cyclic and rotating disk (RDE) voltammograms of $[(EtioPc)Fe]_2O$ in benzonitrile containing 0.1 M TBAP. The compound undergoes eight one-electron oxidation/reduction reactions and this is best illustrated by the RDE voltammogram which shows four one-electron abstractions (reactions 1–4) and four one-electron additions (reactions 5–8), indicating that all overall nine different oxidation states can be obtained. The first two oxidations and all four reductions are well-separated in potential while the third and fourth oxidations involve two overlapping processes. The combined current for reactions 3 and 4 is double that of the other six one-electron transfer processes at the RDE, consistent with the global abstraction of two-electrons. However, it was still possible to evaluate separate potentials for the overlapping processes by differential pulse voltammetry and these are located at E_p = 1.16 and 1.22 V. The values of $E_{1/2}$ measured at the RDE are given in Table 1 and are superimposable with those obtained by cyclic voltammetry, thus indicating that each electrode reaction is associated with the initial dimer and not due to a chemical side-product.

It is of interest to compare the electrochemistry of the μ-oxo porphycene dimer to that of a μ-oxo porphyrin dimer and this is done in Figure 1 for the case of $[(EtioPc)Fe]_2O$ and $[(OEP)Fe]_2O$ (OEP = the dianion of octaethylporphyrin). The current–voltage curves are similar for oxidation of the two compounds and both agree with data for other porphyrin, chlorin, or isobacteriochlorin iron(III) μ-oxo dimers, all of which undergo four one-electron oxidations under similar solution conditions.[13] Similar electrochemical behavior is also observed for $[(OEPc)Fe]_2O$, $[(TPrPc)Fe]_2O$, and $[(TBuPc)Fe]_2O$, all of which show four reversible one-electron oxidations and four reversible one-electron reductions and give no indication for cleavage of the dimeric unit on the cyclic voltammetric timescale. A summary of half-wave potentials for oxidation and reduction of the four compounds is given in Table 1 and cyclic voltammograms of these species are illustrated in Figure 2. Each of the eight electrode reactions are reversible at a scan rate of 0.1 V/s and each involves the transfer of one electron to a dimeric unit.

An examination of the redox potentials in Table 1 reveals that the four investigated μ-oxo porphycene dimers are easier to reduce by 210–360 mV as compared to $[(OEP)Fe]_2O$. On the other hand, the first oxidation of the porphycene dimers occurs at 40–170 mV more positive potentials than for the porphyrins, thus making the overall HOMO–LUMO energy gap smaller. Among the investigated compounds, $[(TPrPc)Fe]_2O$ has the smallest potential separation between the first and second reductions (0.11 V) and this compound also shows the smallest HOMO–LUMO gap, i.e., the smallest difference in potential between the first reduction and the first oxidation (1.81 V) as compared to data for the other three porphycene dimers where these values average 0.20 and 1.85 V, respectively. A variation in these two values between the four different porphycenes might arise from different ring substituent effects, different degrees of solvation in the electrooxidized or electroreduced species, or different degrees of interaction between the two macrocycles which might in turn also depend upon the orientation between the two rings with respect to each other in solution.

An X-ray crystallographic study shows that two of the neutral dimers, $[(OEPc)Fe]_2O$ and $[(TBuPc)Fe]_2O$, have Fe-O-Fe bond angles of 180° while $[(TPrPc)Fe]_2O$ has a substantially different angle of 145° in the solid state (Table 1).[42] The same angles may or may not be present in solution and these values might change upon oxidation or reduction of the various complexes. However, it is interesting to note that the smaller potential separation between the first and second reductions (0.11 V) and that between the first reduction and first oxidation of $[(TPrPc)Fe]_2O$ (1.81 V) as compared to values for the other two structurally characterized dimers both suggest that the degree of interaction between the two rings of each $[(Pc)Fe]_2O$ complex will govern at least in part the various $E_{1/2}$ values for oxidation or reduction of the complexes.[19,22,44,45] On the other hand, as already mentioned,

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(43) Lin, X. Q.; Kadish, K. M. *Anal. Chem.* **1985**, *57*, 1498–1501.

Table 2. UV–Visible Spectral Data[a] for Some of the Investigated Metalloporphycene Complexes and Their Anions in Benzonitrile Containing 0.1 M TBAP

compound	wavelength, nm ($\epsilon \times 10^{-5}$)					
$[(OEPc)Fe]_2O$	372 (0.86)	427^{sh} (0.32)	560^{sh} (0.16)	643 (0.56)		
$\{[(OEPc)Fe]_2O\}^-$	342 (0.82)		545 (0.16)	648 (0.37)	753 (0.13)	854 (0.13)
$\{[(OEPc)Fe]_2O\}^{2-}$	341 (0.79)		538 (0.16)		764 (0.21)	854 (0.13)
$[(TPrPc)Fe]_2O$	372 (0.85)	433^{sh} (0.23)	560^{sh} (0.15)	636 (0.55)		
$\{[(TPrPc)Fe]_2O\}^-$	340 (0.72)		536 (0.17)	640 (0.30)	745 (0.17)	844 (0.15)
$\{[(TPrPc)Fe]_2O\}^{2-}$	340 (0.70)		514 (0.15)		744 (0.22)	840 (0.22)
$[(EtioPc)Fe]_2O$	376 (1.47)	435 (0.41)	560^{sh} (0.20)	638 (0.69)		
$\{[(EtioPc)Fe]_2O\}^-$	353 (1.36)		543 (0.22)	639 (0.53)	747 (0.22)	837 (0.19)
$[(EtioPc)Al]_2O$	393		571^{sh}	613		
$\{[(EtioPc)Al]_2O\}^{2-}$	373		553		743	850
$\{[(EtioPc)Al]_2O\}^{4-}$	350					
$(OEPc)FeCl$	373 (0.67)	480^{sh} (0.08)		623 (0.36)		
$(OEPc)Fe^{II}$	373 (0.51)	484^{sh} (0.05)	569^{sh} (0.17)	623 (0.32)		
$[(OEPc)Fe^{II}]^-$	352 (0.37)	383^{sh} (0.37)	561 (0.14)	609 (0.16)	746 (0.09)	851 (0.09)

[a] Key: sh = shoulder.

additional factors such as degree of solvation and substituent effects are also known to substantially affect the redox potentials of metalloporphyrins and related macrocycles[2] and a complete analysis of the electrochemical data on $[(Pc)Fe]_2O$ must therefore await structural characterization of the various oxidized and reduced porphycene dimers.

Spectroelectrochemistry and Site of Electroreduction. Singly oxidized μ-oxo porphyrin dimers have been characterized as Fe(III) π-cation radicals[11,12] and the similarity in their electrochemistry to that of the presently investigated iron(III) porphycene μ-oxo dimers suggests a similar oxidation site in both of the two series of compounds. However, less can be said about the site of electroreduction where relatively little is known regarding the μ-oxo porphyrin dimers. Most iron(III) μ-oxo porphyrin dimers are unstable after reduction in non-aqueous media but an Fe(III)/Fe(II) transient has been suggested as an intermediate prior to decomposition of singly-reduced $[(TPP)Fe]_2O$ in DMF.[25] A higher stability is observed in CH_2Cl_2 or PhCN, and under these conditions, the same μ-oxo porphyrin dimer undergoes only a single reversible one-electron reduction.[2] This is also the case for $[(OEP)Fe]_2O$ in PhCN and this contrasts with $[(EtioPc)Fe]_2O$ which shows four one-electron reductions under the same solution conditions (see Figure 1).

The electrochemistry of $[(OEP)Fe]_2O$ and $[(EtioPc)Fe]_2O$ are thus dramatically different from each other upon reduction and the spectral properties for three of the reduced porphycenes were therefore investigated in order to ascertain the initial site of electroreduction in these compounds. The resulting data are summarized in Table 2 while Figure 3 reproduces the UV–visible spectra obtained during the first and second reversible one-electron reductions of $[(OEPc)Fe]_2O$ in a thin-layer cell. As the first reduction proceeds, the 372, 427, and 643 nm bands of the neutral dimer decrease in intensity while new absorptions suggesting a π-anion radical appear at 342, 545, 753, and 854 nm (see Table 2). These latter near-IR bands increase in intensity during the second one-electron reduction and, at the same time, the visible absorption band at 550 nm undergoes a blue shift of 8–10 nm. The spectral changes are all reversible and stepping the potential back to 0.0 V leads to a complete recovery of the original μ-oxo dimer spectrum.

The spectral properties of $[(OEPc)Fe]_2O$, $[(EtioPc)Fe]_2O$, and $[(TPrPc)Fe]_2O$ are similar to each other and the same types of spectral changes are seen during the first and second one-electron reductions of these three compounds (see Table 2). The UV–visible data are similar after the first and second reductions, and this suggests formation of porphycene π-anion radicals after the addition of either one or two electrons to $[(Pc)Fe]_2O$. This is also the conclusion reached when one compares this spectral data to that obtained after controlled-potential reduction of (OEPc)FeCl or $[(EtioPc)Al]_2O$ by two electrons under the same experimental conditions. The former compound undergoes a well-defined Fe(III)/Fe(II) process prior to π-anion radical formation while the latter, which contains two electroinactive metal ions, can only be reduced at the porphycene π-ring system.

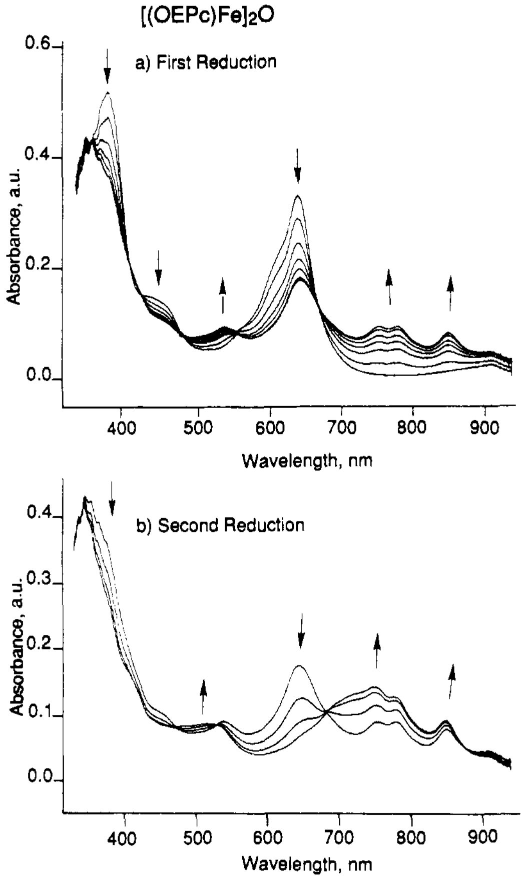

Figure 3. Thin-layer spectral changes obtained during the first two reversible reductions of $[(OEPc)Fe]_2O$ in PhCN, 0.1 M TBAP.

(OEPc)FeCl undergoes three one-electron reductions in PhCN, 0.1 M TBAP, as was earlier demonstrated for (TPrPc)FeCl in CH_2Cl_2.[38] These are labeled as processes 1–3 in Figure 4a and occur at $E_{pc} = -0.51$ and $E_{1/2} = -1.06$ and -1.42 V for a scan

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(44) DeWulf, D. W.; Leland, J. K.; Wheeler, B. L.; Bard, A. J.; Batzel, D. A.; Dininny, D. R.; Kenney, M. E. *Inorg. Chem.* **1987**, *26*, 266–270.

(45) Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 3415–3425.

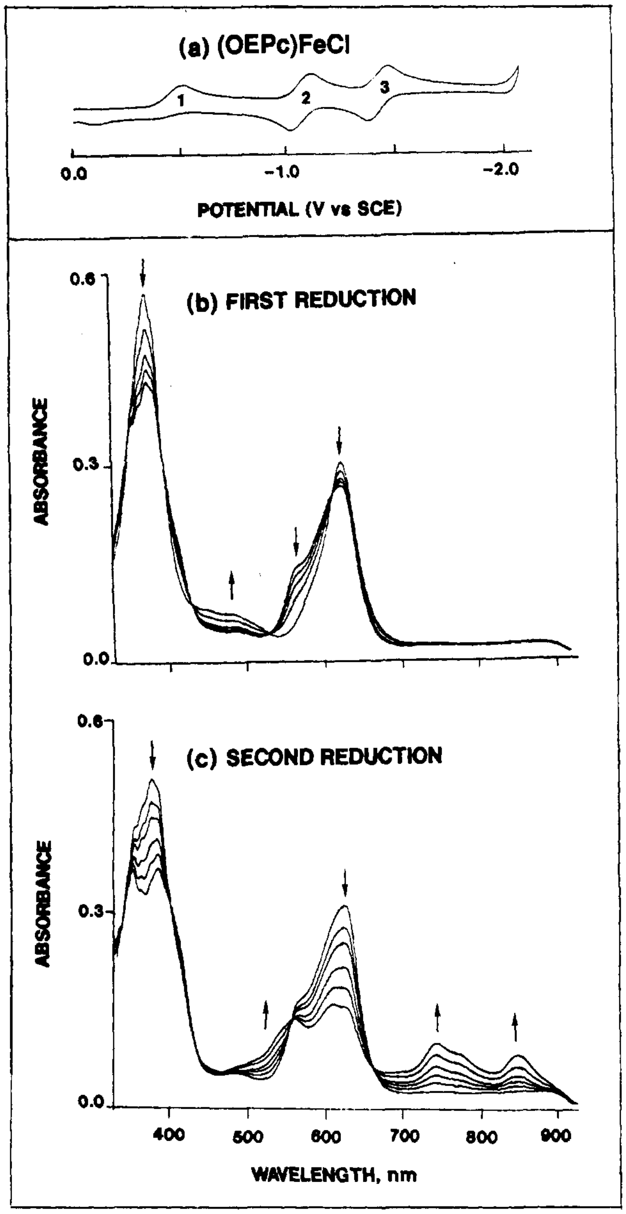

Figure 4. (a) Cyclic voltammogram of (OEPc)FeCl in PhCN containing 0.1 M TBAP and associated spectral changes observed during the controlled potential electrolysis at (b) −1.10 V (first reduction) and (c) −1.35 V (second reduction).

rate of 0.1 V/s. Process 1 is assigned to the Fe(III)/Fe(II) transition and is irreversible as is also the case for reduction of numerous monomeric iron(III) porphyrins containing a halide axial ligand. In these cases, the mechanism has been interpreted in terms of halide loss after electroreduction in noncoordinating solvents which leads to a four-coordinated Fe(II) species that is then oxidized at a more positive potential.[2] This oxidation process is also seen after the irreversible reduction of (OEPc)FeCl and occurs at E_{pa} = −0.05 V under the conditions shown in Figure 4a.

The spectral changes observed during the first one-electron reduction of (OEPc)FeCl are shown in Figure 4b. The near UV (Soret) band at 373 nm and the visible band at 625 nm both decrease in intensity as the iron(II) porphycene is generated in the thin-layer cell. No new absorption bands are seen over the whole UV–visible/near-IR spectral range, consistent with generation of an Fe(II) species.

The second reduction of (TPrPc)FeCl was proposed to involve formation of a porphycene π-anion radical rather than lead to generation of the Fe(I) complex,[38] and the spectral data in Figure 4c support this same assignment in the case of doubly-reduced

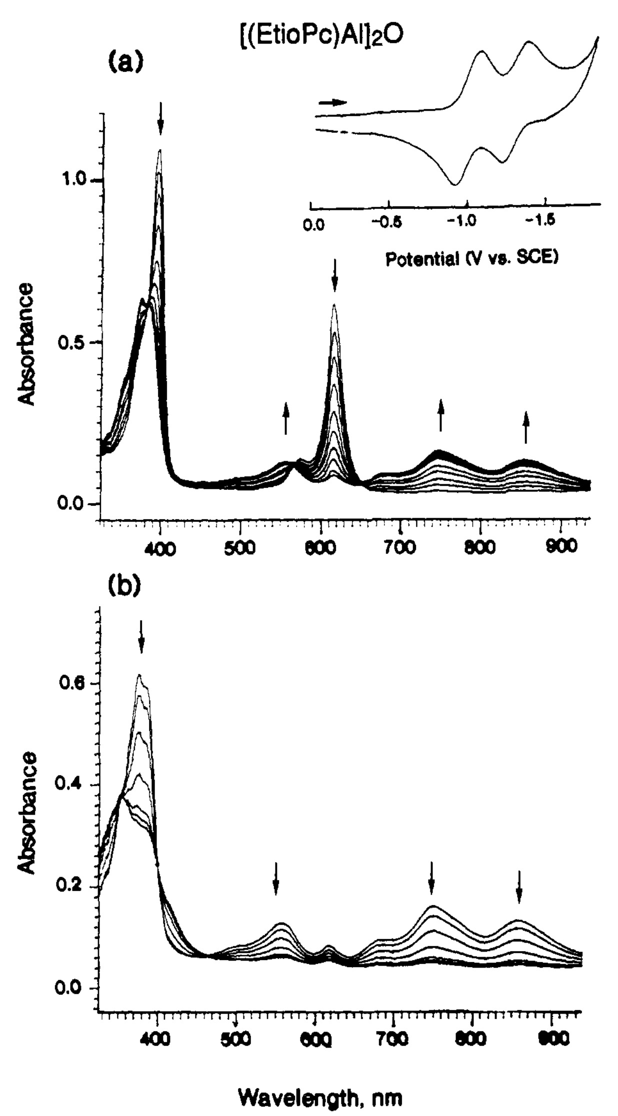

Figure 5. Thin-layer spectral changes obtained during (a) the first and (b) second one-electron reduction of $[(EtioPc)Al]_2O$ in PhCN containing 0.1 M TBAP. A cyclic voltammogram of the dimer is shown in the figure inset.

(OEPc)FeCl. As seen in this figure, the bands at 373 and 623 nm both decrease in intensity while new absorptions appear at 561, 746, and 851 nm. Similar bands have been reported for other metalloporphycene π-anion radicals.[46,47] The spectral pattern for doubly-reduced (OEPc)FeCl is also similar to that for singly- and doubly-reduced $[(Pc)Fe]_2O$ (see Figure 3a and Table 2) and this further suggests formation of porphycene π-anion radicals after the first two reductions of the four iron(III) μ-oxo dimers. However, the most definitive evidence for formation of porphycene π-anion radicals comes from spectroelectrochemical studies of a related μ-oxo dimer which contains electroinactive metal ions, $[(EtioPc)Al]_2O$. This compound can only be reduced at the conjugated macrocycle and undergoes two reversible diffusion controlled reductions which in PhCN are located at $E_{1/2}$ = −0.94 and −1.25 V vs SCE (see Figure 5 inset). Each involves a global transfer of two electrons, i.e., a simultaneous reduction of the two monomeric entities. The appearance of two, rather than four, reductions contrasts with results for the iron(III) porphycene dimers and is consistent with a lack of interaction between the two macrocycles of the $[(EtioPc)Al]_2O$ complex.

A detailed study of $[(EtioPc)Al]_2O$ will be published elsewhere in conjuction with data on other $(EtioPc)Al^{III}$ complexes con-

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(46) Kadish, K. M.; D'Souza, F.; Boulas, P.; Aukauloo, A.; Guilard, R.; Vogel, E. Manuscript in preparation.

(47) Renner, M. W.; Forman, A.; Wu, W.; Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1989**, *111*, 8618–8621.

taining both σ-bonded and anionic axial ligands. However, of relevance to this present work are time-resolved UV–visible spectra obtained during the first and second reductions of this dimer since an evaluation of the π-anion radical spectra will be of help to assign the site of electron transfer in the related μ-oxo iron porphycene dimers. This spectroelectrochemical data is shown in Figure 5. The initial absorption bands at 393 and 613 nm for $[(EtioPc)Al]_2O$ decrease in intensity during the first reduction as new bands appear at 553, 743, and 850 nm (Figure 5a). Because the metal ions of $[(EtioPc)Al]_2O$ are electroinactive, the spectral changes in this figure can only be accounted for by addition of one electron to each of the two conjugated macrocycles. The second reduction leads to a porphyrin dianion where each of the rings has been reduced by two electrons and this is evidenced by the broad 350-nm absorption band of $\{[(EtioPc)Al]_2O\}^{4-}$ which is characteristic of other monomeric metalloporphycene dianions.[46] The spectral changes shown in Figure 5 are reversible (as is also the case for the cyclic voltammogram shown in the figure inset) and stepping the potential back to 0.0 V leads to a complete recovery of the initial absorption spectrum for unreduced $[(EtioPc)Al]_2O$. Finally, it should be noted that the UV–visible spectrum obtained after the first reduction of $[(EtioPc)Al]_2O$ is quite similar to the one obtained for electrogenerated $[(OEPc)Fe^{II}]^{\bullet-}$ (Figure 4c) and this spectral patterns seems to unambiguously be that of a porphycene π-anion radical.

The remarkable difference in cathodic electrochemistry between $[(Pc)Fe]_2O$ and most previously investigated μ-oxo porphyrin dimers might also be due to the different HOMO–LUMO energy levels for these two classes of dimers in addition to the different sites of electroreduction. The lower LUMO level of the μ-oxo porphycene dimers leads to further electroreductions, unlike in the case of porphyrin μ-oxo dimers where the LUMO's lie much higher in energy. The substitution of electron-withdrawing groups onto the porphyrin periphery will also result in a lowering of the LUMO energy and thus might also allow further electroreductions. This would explain the reductive behavior of $[((CN)_4TPP)Fe]_2O$ which is the only porphyrin μ-oxo dimer known to undergo four one-electron ring-centered reductions without breaking the dimeric unit.[18]

In conclusion, the four investigated μ-oxo iron(III) porphycene dimers can exist as stable complexes in up to nine different oxidation states on the cyclic voltammetric time scale. The first two reduced forms of $[(Pc)Fe]_2O$ are also quite stable upon reduction in a thin-layer cell, and this is also the case for doubly reduced $[(EtioPc)Al]_2O$. The spectral data indicate that all five investigated dimers are reduced at the conjugated π-ring system. This may be an additional reason for the multielectron transfers and the higher stability of the reduced species with respect to the related electroreduced metalloporphyrins. Further studies are now in progress to isolate and structurally characterize these partially reduced dimeric species.

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