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Substituent Effect on the Redox Potential of meso-Substituted Octaethylporphyrins and their Zinc and Copper Complexes[+]

Guo-Zhang Wu, Hiu-Kwong Leung (Xiaoguang Liang)*, Wei-Xing Gan
(Institute of Photographic Chemistry, Academia Sinica, Beijing 100012, China)

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Abstract - meso-Substituent effect on the redox properties of octaethylporphyrin and its zinc(II) and copper(II) complexes are investigated with cyclic volatmmetry. The $E_{1/2}$ values were observed to correlate linearly with Hammett's σ_p constant for the first and second oxidation reaction and the first reduction reaction in the metallo-OEP series, with ρ values an order of magnitude larger than that of the TPP series. For the free base OEP series, steric effect has to be taken into consideration when discussing the meso-substituent effect of OEP's in addition to electronic effect.

Introduction

The degree and mode of transmission of electronic effects from various points on the ring to the extended conjugated system of porphyrin rings has been a subject of intense investigation.[1] In non-aqueous media, porphyrins as well as their metal complexes may be oxidized in single-electron transfer

[+] Dedicated to the 80th birthday of Professor Wang You
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steps to yield π-cation radicals and dications or reduced in single electron-steps to π-anion radicals and dianions.[2-4] For metalloporphyrins with metal of oxidation states +2, +3 and +4, the thermodynamic redox potentials for anion and cation radical formation are a function of the type and electronegativity of the central metal as well as the basicity of the porphyrin ring.[5]

Hammett linear free energy relationship[6]

$$\log (K^X/K^H) = \sigma\rho' \qquad (1)$$

has been successfully used to quantitate substituent effects on shifts of electronic absorption spectra,[7] relative spectral intensities[8] and equilibrium constants for the addition of one or two axial ligands to the central metal of metalloporphyrins.[9,10] Equation (1) was further modified to treat data on electrochemical redox potentials[11,12]

$$\Delta E_{1/2} = \sigma\rho \qquad (2)$$

where, σ, a substituent constant, a measure of the electron-donating or electron-withdrawing characteristics of substituent X and ρ, the "reaction constant", a measure of the sensitivity of the electron-donating or electron-withdrawing characteristics to the process studied. In equation 2, ρ was given in volts, which depends on the composition of the supporting electrolyte and temperature.[11] Since $E_{1/2}$ is approximately equal to E^0 if measured by cyclic voltammetry[13] and $E^0 = 0.059 \log K_{eq}$ at 25°, it can be easily demonstrated that $\rho \doteq (0.059\ V)\rho'$.[12]

With this method, Kadish and coworkers have studied the electronic effect on the redox potential of a series of H_2(p-X)TPP (TPP = tetraphenylporphyrin; X = OMe, Me, H, F, Cl, COOMe, CN, NO_2). A linear relationship was obtained between $E_{1/2}$ and Hammett σ values, with ρ values in the order of 6×10^{-2}.[12] In the Co(p-X)TPP series, the ρ values increases up to 1×10^{-1},[10] while in the Fe(p-X)TPP series the ρ value remains of the same order as that of the free base.[14] Rillema and coworkers[15] obtained similar results on their study with p-substituted tetraphenylporphine carbonyl complexes of Ruthenium (II), with values around 0.04-0.06 for the first and second oxidation potential and the first reduction potential. It has also been reported that the substituent effect on $E_{1/2}$ for oxidation or reduction of the central metal to be always smaller than that of the ring.[10,16]

Due to the fact that the electron cloud of the phenyl ring being orthogonal to the porphyrin ring, thus diminishing to a large extent the resonance effect of the substituents on the porphyrin ring, the ρ values obtained in these studies are generally low. Jordan and coworkers[16] have reported the β-substituent effect on the electroreduction of porphyrins and metalloporphyrins. The polarographic half-wave potential correlated linearly with the Hammett's σ^- values with the ρ values in the order of 0.30. Kadish and coworkers[12] have briefly mentioned also that the ρ value for the first oxidation potential of meso-substituted octaethylporphine can reach 0.5, but no detail of the study has been presented.

In this paper,[17] we would like to report our recent findings on the meso-substituent effect on the redox properties of octaethyporphyrin and its zinc and copper complexes.

Experimental Section

Materials Preparation and purification of octaethylporphyrin (OEP) were performed according to the procedure of Dolphin and coworkers.[18] meso-Substitution of OEP was carried out according to electrolytic method developed in this laboratory[19] or chemical methods from the literature. The synthesized meso-substituted OEP's were purified by chromatography on alumina column until homogeneous by tlc (neutral silica gel plate) and then recrystallized from chloroform-methanol mixture. The compounds were analysed by UV-visible spectroscopy (Hitachi 340), infrared spectroscopy (Nicolet 20-SX or Perkin-Elmer 983, potassium bromide plate), proton nuclear magnetic resonance spectroscopy (Varian EM-360L, FT-80A or XL-400, with $CDCl_3$ as solvent and TMS as internal standard) and fast atom bombardment mass spectrometry [Scientific Instrument (China) Model KYKYZhP-5A double focusing high resolution instrument equipped with KYQ fast atomic gun].

Zinc(II)-octaethylporphyrin (ZnOEP) Insertion of zinc(II) ion was done by literature method.[20] Analysis data: tlc [neutral silica plate with chloroform/petroleum ether (1:1) as eluent], $R_f = 0.54$; UV-vis (dichloromethane), λ_{max} (nm) (ϵ), 401 (3.19×10^5), 532 (4.23×10^4), 569 (5.77×10^4).

Zinc(II)-5-nitro-octaethylporphyrin ($ZnOEPNO_2$) was prepared by electrolytic method. Electrolysis was carried out in a separate-compartment cell with a three electrode system (working and counter electrode, platinium plate; reference electrode, SCE). In the cathode compartment was placed 40 mL of a 0.1 Molar solution of Et_4NClO_4 in CH_2Cl_2-CH_3OH (4:1) mixture. In the anodic compartment was placed ZnOEP (179 mG, 0.003 Molar) and sodium nitrite (saturated) in 100 mL of the above mentioned solution. Electrolysis was carried out with the anodic potential controlled at +0.60V (vs. SCE). The reaction was monitored with tlc [neutral silica plate with $CHCl_3$-petroleum ether (1:1) as eluent]. After three hours, the anodic solution was worked up with water and the organic solution was dried over anhydrous sodium sulphate. After evaporation of the solvent, the residue was subjected to chromatography on a neutral silica gel column. Elution with dichloromethane-petroleum ether (30^o-60^o) yielded firstly ZnOEP (~10 mG, 6%) and then $ZnOEPNO_2$ (150 mG, 78%): UV-vis (CH_2Cl_2), (ϵ), 399 (189000), 533 (11000), 572 (14100); HNMR (δ), 1.73 (m, 24H), 3.77 (m, 16H), 9.16 (s, 1H), 9.64 (s, 2H); IR (cm^{-1}), 1529, 1370; FABMS, (m+1)/z, 643. All the analytical data were identical to that of an authentic sample prepared by a chemical method reported in literature.[21]

Elution of the column with CH_2Cl_2 yielded $ZnOEP(NO_2)_2$ (a mixture of 5,10- and 5,15-dinitro isomer, 28 mG, 14%): tlc, R_f, 0.21; UV-vis (CH_2Cl_2), (relative ε), 404 (1.00), 537 (0.028), 574 (0.095); IR, 1530, 1370; HNMR, 1.68 (m, 24H), 3.65 (m, 16H), 8.85 (s, 0.5H), 9.79 (s, 1.5H); FABMS, 688.

Zinc(II)-meso-dinitro-octaethylporphyrin [$ZnOEP(NO_2)_2$] was prepared by electrolysis with set-up and conditions similar to that of the previous section, except $ZnOEPNO_2$ (47 mG, 0.0007 Molar) was used as the precursor this time. After electrolysis for six hours with the anodic potential controlled at +0.97V (vs SCE). Chromatography of the crude product on neutral alumina column yielded $ZnOEPNO_2$ (14 mG, 30%) and $ZnOEP(NO_2)_2$ (21 mG, 42%). All the Analysis data were identical to that reported in the previous section.

5-Chloro-octaethylporphyrin (OEPCl) was prepared by electrolytic method. The set-up was similar to that reported in the previous section. To the cathodic compartment was placed 40 mL of Et_4NClO_4 (0.06 Molar) in dichloromethane solution. To the anodic compartment was added 100 mL of a dichloromethane solution containing ZnOEP (85 mG, 0.0015 Molar), Et_4NClO_4 (0.1 Molar) and Et_4NClO_4 (0.06 Molar). Electrolysis was carried out for six hours with the anodic potential controlled at +0.60V (vs. SCE). The anodic solution was then reduced to 50 mL by evaporation of the solvent. To the organic solution was added 1 mL of conc. HCl and the mixture was stirred at room temperature for 15 min. The organic solution was worked up with 400 mL water and the organic phase was washed respectively with saturated sodium bicarbonate solution (100 mL) and water (50 mL x 2). The residue obtained after evaporation of the dried (anhydrous sodium sulphate) solution was subjected to chromatography on a neutral alumina column. Elution with $CHCl_3$/petroleum ether (1:1) mixture yielded $OEPCl_2$ (30 mG, 35%): UV-vis (CH_2Cl_2) (relative ε), 409 (1.00), 510 (0.0686), 544 (0.0173), 583 (0.0222), 636 (0.0032); HNMR, 1.85 (m, 24H), 4.10 (m, 16H), 10.10 (s,, 2H); FABMS, 605; followed by OEPCl (39 mG, 48%): UV-vis (CH_2Cl_2), (relative ε), 402 (1.00), 502 (0.092), 536 (0.0329), 537 (0.0348), 627 (0.0099); HNMR, 1.90 (m, 24H), 4.15 (m, 16H), 10.01 (s, 1H), 10.23 (s, 2H) (identical to that reported in literature[21,22]); FABMS, 569 and OEP (11 mG, 14%). Cutting down the reaction time would decrease the yield of $OEPCl_2$ at the expense of the total % conversion. meso-Di-chloro-octaethylporphyrin ($OEPCl_2$) was the major product if the anodic potential was controlled at +0.65V. From 78 mG of ZnOEP, $OEPCl_2$ (44 mG, 57%), OEPCl (14 mG, 17%) and OEP (10mG, 11%) were isolated after similar treatment as the previous section. From data of HNMR, it seems only one isomer was obtained for the di-substituted compound.

5-Cyano-octaethylporphyrin (OEPCN) was prepared by electrolytic method. Set-up was similar to that of the previous section. To the cathodic compartment was added 40 mL of Et_4ClO_4 (0.06 Molar) in dichloromethane solution. To the anodic compartment was added a solution (100 mL) containing ZnOEP (100 mG), Et_4NClO_4 (0.06 Molar) and Et_4NCN (0.01 Molar). Electrolysis was carried out for 6 hours with the anodic potential controlled at +0.65V. Work-up as the previous section yielded the crude product which was subjected to chromatography on a neutral alumina column. Elution with chloroform/petroleum ether (1:1) mixture yielded traces of ZnOEP, followed by ZnOEPCN (61 mG, 56%): UV-vis (CH_2Cl_2) (relative ε), 405 (1.00), 548 (0.046), 588 (0.119). To a solution of ZnOEPCN (61 mG) in chloroform (30 mL) was added a solution of conc. HCl (1.5 mL) in methanol (5 mL), and the mixture was stirred for 20 min. at room temperature. The reaction mixture was poured into water (400 mL). The organic solution was washed with water (50 mL x 2) and dried over anhydrous sodium sulphate. Evaporation of the solvent yielded a crude product which was subjected to chromatogrpahy on a neutral alumina column. Elution with CH_2Cl_2/petroleum ether (1:1) mixture yielded OEPCN (52 mG, 95%): UV-vis (CH_2Cl_2) (relative ε), 399 (1.00), 510 (0.067), 548 (0.089), 579 (0.040), 635 (0.086); HNMR, 1.86 (m, 24H), 4.02 (m, 16H), 10.0 (s, 1H), 10.05 (s, 2H); IR, 2211; FABMS, 560. Analysis data identical to that reported in literature.[21]

5-Nitro-octaethylporphyrin ($OEPNO_2$) Demetallation of $ZnOEPNO_2$ was achieved by 10% H_2SO_4-CF_3COOH.[21] The title compound was obtained in 87% yield: UV-vis (CH_2Cl_2) (ε), 393 (108000), 500 (10800) 533 (7400), 569 (5000), 621 (39000); HNMR, 1.88 (m, 24H), 4.05 (m, 16H), 10.04 (s, 1H), 10.24 (s, 2H); IR, 1525, 1368; FABMS, 580. Analysis data were identical to that of authentic sample prepared by literature method.[21]

meso-Dinitro-octaethylporphyrin [$OEP(NO_2)_2$] Demetallation of $ZnOEP(NO_2)_2$ was achieved by 10% H_2SO_4 in CH_3COOH according to literature procedure.[21] The title compound was obtained in 71% yield: UV-vis (CH_2Cl_2) (relative ε), 380 (0.98), 396 (1.00), 504 (0.124), 534 (0.084), 576 (0.066), 626 (0.049); HNMR, 1.78 (m, 24H), 3.74 (m, 16H), 10.08, 10.37 (2s, 2H), IR, 1535, 1365; FABMS, 625.

Zinc-5-Chloro-octaethylporphyrin (ZnOEPCl) Insertion of Zn(II) ion into the porphyrin cavity was performed as previously described in 87% yield: UV-vis (CH_2Cl_2) (relative ε), 410 (1.00), 540 (0.055), 576 (0.035); FABMS, 633.

Zinc-*meso*-dichloro-octaethylporphyrin ($ZnOEPCl_2$) Insertion of Zn(II) ion was performed as previously described in 90% yield: UV-vis (CH_2Cl_2) (relative ε), 420 (1.00), 552 (0.0565), 594 (sh, 0.167); FABMS, 667.

Zinc-5-cyano-octaethylporphyrin (ZnOEPCN) Insertion of Zn(II) ion was performed as previously described: UV-vis (CH_2Cl_2) (relative ε), 412 (1.00), 552 (0.053), 592 (0.128); HNMR, 1.67 (m, 24H), 3.83 (m, 16H), 10.15 (s, 1H), 10.20 (s, 2H); IR, 2212; FABMS, 622.

Zinc-5-amino-octaethylporphyrin ($ZnOEPNH_2$) To a solution of $ZnOEPNO_2$ (148 mG) in THF (50 mL) was added Pd/C (5% Pd) and a solution of sodium boronhydride (400 mG) in methanol (40 mL). The reaction mixture was stirred at room temperature for thirty min.. Tlc indicated that the reaction was complete. The Pd/C was filtered off. Evaporation of the solvent yielded the crude product, which was washed with water and then extracted into ether. The ethereal solution was dried over anhydrous sodium sulphate. After evaporation of the solvent, the residue was subjected to chromatography over a neutral alumina column. Elution with chloroform yielded the title compound (90%): UV-vis (CH_2Cl_2) (relative ϵ), 418 (1.00), 544 (0.105), 602 (0.066); IR, 3480, 3405; FABMS, 611.

5-Amino-octaethylporphyrin ($OEPNH_2$) Demetallation was achiceved by H_2SO_4-CF_3COOH (1:9): UV-vis (CH_2Cl_2) (relative ϵ), 415 (1.00), 520 (0.073), 556 (0.038), 590 (0.025), 649 (0.040); HNMR, 1.79, (m, 24H), 3.78 (m, 16H), 6.14 (bs, 2H), 9.25 (s, 1H), 9.60 (s, 2H); IR, 3410, 1620; FABMS, 551. The analysis data were identical to that of authentic sample prepared by literature method[23] or by reduction of $OEPNO_2$ with Pd/C and sodium boronhydride as described in the previous section.

Zinc-meso-tetranitrooctaethylporphyrin [$ZnOEP(NO_2)_4$][24] By known method, the title compound was prepared in 57% yield: UV-vis (CH_2Cl_2), 365 (45000), 431 (102400), 564 (b, 13800) 590 (sh, 9600); HNMR, 1.37 (m, 24H), 3.40 (m, 16H), no meso-H signal; IR, 1526, 1370; FABMS, 779.

meso-Tetranitro-octaethylporphyrin [$OEP(NO_2)_4$] Demetallation was carried out with 25% HCl as previously described. The title compound was isolated in 50% yield: UV-vis (CH_2Cl_2), 432 (80000), 533 (10100), 613 (4700), 676 (1200); IR, 1533, 1339; FABMS, 715.

Copper(II)-octaethylporphyrin (CuOEP) Insertion of Cu(II) ion was performed simliar to that of the insertion of Zn(II). The title compound was isolated in 97% yield: UV-vis. (CH_2Cl_2) (relative ϵ), 396 (1.00), 524 (0.109), 560 (0.193).

Copper(II)-5-formyl-octaethylporphyrin (CuOEPCHO)[20,24] meso-Formylation of OEP was carried out according to a known procedure. The title compound was isolated in 64% yield): UV-vis (CH_2Cl_2), 404 (232000), 526 (16200), 566 (20200), 640 (sh); IR, 1701; FABMS, 623.

5-Formyl-octaethylporphyrin (OEPCHO) Demetallation was achieved by 10% H_2SO_4 in CF_3COOH as previously described. The title compound was isolated in 54% yield: UV-vis (CH_2Cl_2) (relative ϵ), 404 (1.00), 503 (0.0664), 536 (0.0489), 572 (0.0471), 624 (0.0293), 662 (0.0186); HNMR, 1.85 (m, 24H), 4.00 (m, 16H), 9.86 (s, 1H), 10.0 (s, 2H), 12.7 (s, 1H); IR, 1696; FABMS, 563.

Zinc(II)-5-formyl-octaethylporphyrin (ZnOEPCHO) Insertion of Zinc(II) ion was performed as previously described. The title compound was obtained in 88% yield: UV-vis (CH_2Cl_2), (relative ϵ), 405 (1.00), 535 (0.048), 537 (0.055), 630 (0.01).[24]

5-Methyl-octaethylporphyrin ($OEPCH_3$)[25] Reduction of CuOEPCHO was performed according to known procedure, except tetra-tert-butylammonium boronhydride was used instead of tetra-n-butylammonium boronhydride. Demetallation was achieved by 10% H_2SO_4 in CF_3COOH as previously described. The title compound was obtained in 76% yield: UV-vis (CH_3Cl) (relative ϵ), 406 (1.00), 504 (0.073), 540 (0.032), 576 (0.031), 628 (0.008); HNMR, 2.07 (m, 24H), 4.15 (m, 16H), 4.70 (s, 3H), 9.95 (s, 1H), 10.15 (s, 2H); FABMS, 549.

Zinc(II)-5-methyl-octaethylporphyrin ($ZnOEPCH_3$) Insertion of Zinc(II) ion was performed as previously described to give the title compound: UV-vis

(CH_2Cl_2) (relative ε), 410 (1.00), 540 (0.053), 574 (0.034); FABMS, 611.

Cyclic Voltammetric Study The cyclic voltammograms were obtained from a Jinan No.4 Factory, Model 79-1 instrument. A closed cell with a three electrode system was used. The working electrode is glassy carbon. The counter electrode is a platinum wire coiled around the working electrode. The reference electrode is Ag/AgCl,KCl (sat.), isolated from the sample solution with a Luggin capillary salt bridge. Concentration of the porphyrin was maintained at 3×10^{-3} Molar. The supporting electrolyte used was tetra-*n*-butyl-ammonium perchlorate (0.1 Molar). The solvent used was AR grade dichloromethane from Beijing Chemical Company, pretreated with anhydrous potassium carbonate and redistilled. Temperature of the system was maintained at 25±1 °C. The solution was deaerated by bubbling nitrogen or argon through for 15 min before experiment. The voltammogram was done with the instrument scanning between +1.7V and -1.7V at an usual rate of 100 mV/sec. All the data reported were in volts vs Ag/AgCl (saturated).

Results and Discussion

The electrode reactions we studied can be summarized by equation (3)-(6):

$$\text{MOEP} \rightleftharpoons \text{MOEP}^{+\cdot} + e \qquad E_{1/2}^{ox}(1) \qquad (3)$$

$$\text{MOEP}^{+\cdot} \rightleftharpoons \text{MOEP}^{++} + e \qquad E_{1/2}^{ox}(2) \qquad (4)$$

$$\text{MOEP}^{-\cdot} \rightleftharpoons \text{MOEP} + e \qquad E_{1/2}^{red}(1) \qquad (5)$$

$$\text{MOEP}^{--} \rightleftharpoons \text{MOEP}^{-\cdot} + e \qquad E_{1/2}^{red}(2) \qquad (6)$$

Shown in Figure 1 is a typical cyclic voltamogram of the system we studied. In this case, the compound we studied was $ZnOEPNO_2$. There are two electrode reactions in the region 0-+1.6V, corresponding to equation (3) and (4). Since Zinc is not involved in the redox reaction within this region, we assign these two reactions to be the first and second oxidation reaction of the extended conjugation of the porphyrin ring. Both reactions show very symmetrical oxidation and reduction peak, indicating that the electrode reactions are reversible and the dication and the cation radical formed are stable. This is not necessarily true in other cases. The reduction peak of the reaction (4) for free base OEP's is not obvious. Raising the scanning speed to 1000 mV/s does not make significant improvement. This phenomenon suggests that the dication of free base OEP is not stable and chelation with zinc(II) or copper(II) ion increases the stability significantly.

The voltammogram between 0--1.6V is generally much more complicated. Most of them show very large reduction current, but with very small oxidation current correspondingly. This again indicates the anion radicals or dianions to be unstable. This data agree with the general observation that the anion of porphyrins to be chemically very reactive species.[26]

The average of the anodic peak potential E_p^a and the corresponding cathodic peak potential E_p^c is taken as the half-wave potential $E_{1/2}$. The half-wave potential [vs. Ag/AgCl (saturated)] of the meso-substituted OEP's observed is listed in Table. In order to study the meso-substituent effect of the porphyrin system, the data were examined with the Hammett linear free energy relationship:

$$\Delta E_{1/2} = \rho \cdot \sigma_p$$

The $E_{1/2}$-σ_p plot for different electrode reaction of the meso-substituted-OEP series and its zinc(II) and Cu(II) complexes are listed in Figure 2-4.

For the Zn(II)-meso-substituted-OEP series (Figure 2), the $E_{1/2}$ values for the first and second oxidation reaction are linearly related to the substituent constant, σ_p[27], with $\rho_1 = 0.22$ [coefficient of correlation (r) = 0.99] and $\rho_2 = 0.23$ (r = 0.94). For substituent, $-NH_2$, $-CH_3$, -H, -Cl, -CN, the linear relationship between the first reduction reaction and σ_p is good, with $\rho_3 = 0.29$ (r = 0.85). But for the formyl- or nitro-substituted compounds, $E_{\frac{1}{2}}^{red}(1)$ falls off from this linear relationship significantly. We attribute this to the reduction of the substituent[28], rather than that of the π-system of the prophyrin ring as in the other cases.

Similar phenomenon for the Cu(II)OEP series is observed for the first and second oxidation reaction and the first reduction reaction although the number of points obtained is much less. (Figure 3)

Shown in Figure 4 are the Hammett plots of the free base OEP series. For the monosubstituted compounds, the linear relationship of $E_{1/2}$ with σ_p is acceptable for the first and second oxidation reaction and the first reduction reaction. The reaction constant are $\rho_1 = 0.42$ (r = 0.96), $\rho_2 = 0.38$ (r = 0.92), $\rho_3 = 0.42$ (r = 0.97), respectively, around double that of the zinc complexes. In other words, the electrode processes are more sensitive to the substituent effect in free base porphyrin than in the zinc complexes. However, we would like to point out that in order to obtain a good linear relationship for the first and second oxidation reaction, points corresponding to disubstituted and tetrasubstituted compounds are dropped. Taking these points into consideration also, there are two linear relationships occurring. The first one includes the electron-pushing $-NH_2$, $-CH_3$ and the parent OEP, which has a ρ value of 0.65 (r = 1) and the second one includes parent OEP, and electron-withdrawing -CHO, -Cl, -CN, $-NO_2$, $-(NO_2)_2$ and $-(NO_2)_4$ substituted compounds, with a ρ value of 0.21 (r = 1.0) (broken line in the first oxidation curve). Compared with that of the ZnOEP series which has a linear relationship from the most electron-pushing amino- to the most electron-withdrawing tetranitro-substituted compound studied (Figure 2, first oxidation curve), it is obvious that some factor other than electronic factor is playing a role in the free base series.

Hursthouse and Neidle[29] have reported the X-ray structure of 5-benzoyloxyoctaethylporphyrin. They demonstrated that introduction of a meso-substituent, in their case a benzoloxy-group, may cause significant ruffling

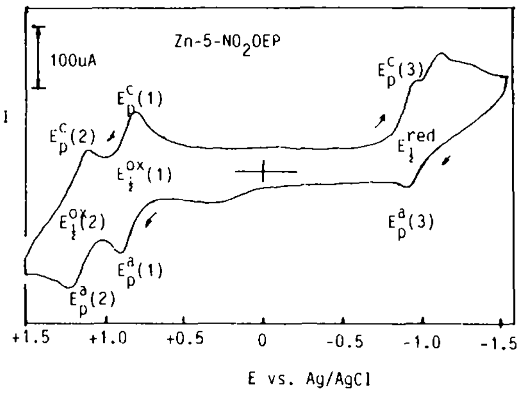

Fig. 1. Cyclic Voltammogram of $ZnOEPNO_2$

Table Redox Potentials of some <u>meso</u>-Substituted Octaethylporphyrins and their Zinc and Copper Complexes

Porphyrin	$E_{1/2}^{ox}(2)$	$E_{1/2}^{ox}(1)$	$E_{1/2}^{re}(1)$	$E_{1/2}^{re}(2)$	[Volts vs. Ag/AgCl(sat)]
$OEPNH_2$	+0.92	+0.55	-1.30		
$OEPCH_3$	+1.17	+0.84	-1.39		
OEP	+1.39	+0.94	-1.36		
$OEPCH_2OH$	+1.15	+0.94			
OEPCHO	+1.30	+1.03	-0.93	-1.18	
OEPCl	+1.27	+1.01	-1.18		
OEPCN	+1.44	+1.12	-1.06	-1.31	
$OEPNO_2$	+1.50	+1.16	-0.81	-1.53	
$OEP(NO_2)_2$	+1.53	+1.34	-0.50	-1.09	
$OEP(NO_2)_4$		+1.62	-0.25	-0.62	
$ZnOEPNH_2$	+0.88	+0.56	-1.49		
$ZnOEPCH_3$	+0.89	+0.62	-1.49		
ZnOEP	+1.04	+0.72	-1.33	-1.51	
$ZnOEPCH_2OCH_3$	+0.93	+0.73	-1.51		
ZnOEPCHO	+1.04	+0.80	-0.84	-1.51	
ZnOEPCl	+1.00	+0.77	-1.15	-1.60	
ZnOEPCN	+1.22	+0.88	-1.20	-1.59	
$ZnOEPNO_2$	+1.24	+0.90	-0.87	-1.00	
$ZnOEP(NO_2)_2$	+1.31	+1.03	-0.76	-1.60	
$ZnOEP(NO_2)_4$		+1.38	-0.24	-0.85	-1.14
CuOEP	+1.32	+0.81	-1.37	-1.50	
CuOEPCHO	+1.29	+0.92	-0.86	-1.30	-1.60
CuOEPCN	+1.39	+0.99	-1.16	-1.49	
$CuOEPNO_2$	+1.45	+1.04	-0.84	-1.34	

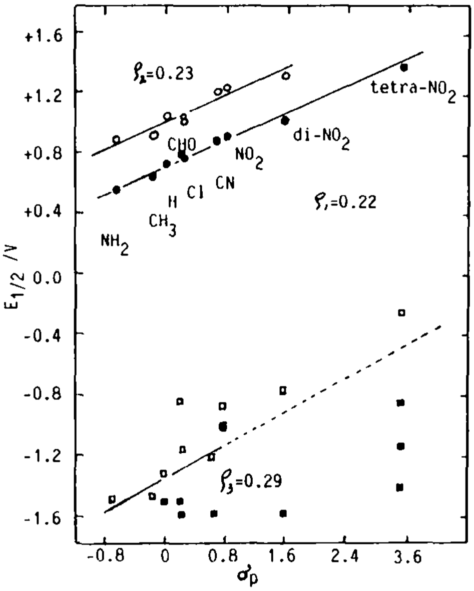

Fig. 2. Hammett plots of $E_{\frac{1}{2}}$ vs. σ_p for ZnOEP's. $E_{\frac{1}{2}}^{ox}(1)$, ●; $E_{\frac{1}{2}}^{ox}(2)$, ○; $E_{\frac{1}{2}}^{re}(1)$, □; $E_{\frac{1}{2}}^{re}(2)$, ■.

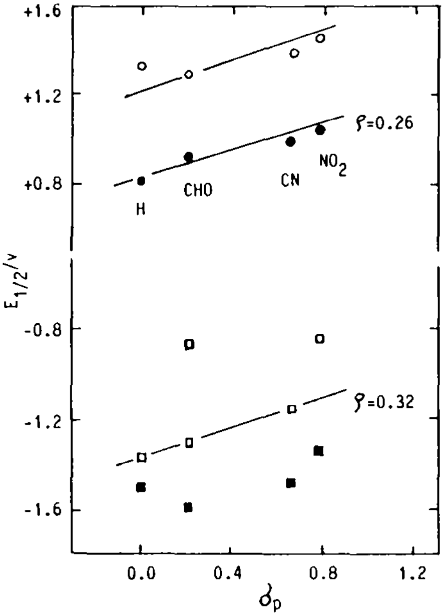

Fig. 3. Hammett plots of $E_{\frac{1}{2}}$ vs σ_p for CuOEP's. $E_{\frac{1}{2}}^{ox}(1)$, ●; $E_{\frac{1}{2}}^{ox}(2)$, ○; $E_{\frac{1}{2}}^{re}(1)$, □ ; $E_{\frac{1}{2}}^{re}(2)$, ■.

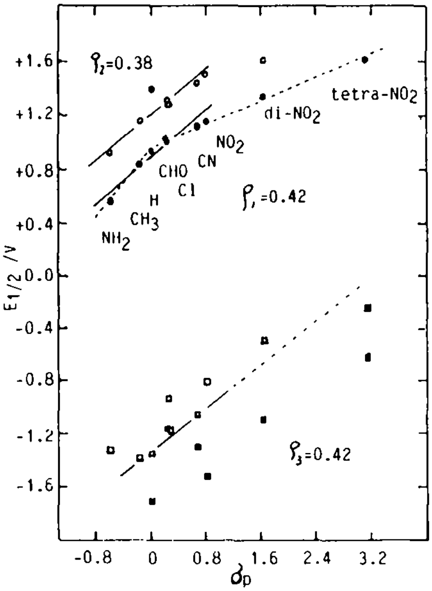

Fig. 4. Hammett plots of $E_{\frac{1}{2}}$ vs. σ_p for free base OEP's. $E_{\frac{1}{2}}^{ox}(1)$, ●; $E_{\frac{1}{2}}^{ox}(2)$, ○; $E_{\frac{1}{2}}^{re}(1)$, □; $E_{\frac{1}{2}}^{re}(2)$, ■.

of the porphyrin skeleton together with an alteration in geometry of the central 'hole' of the porphyrin ring. From data on the metallo-OEP and the TPP series (free base and metal complexes)[9,10,12-16], it is obvious that electron-pushing group tends to raise the energy level of HOMO and electron-withdrawing group tends to act otherwise. It seems distortion of the ring is raising the HOMO level generally, irrespective of the nature of the *meso*-substituent(s) and its effect is additive to the electronic effect. The net result is the two linear dependency of $E_{1/2}$ to σ_p. Due to the disturbance of the nitro group in the reduction reaction, the steric effect on the LUMO of porphyrin ring cannot be estimated similarly. Further work along this line is in progress and results on the *meso*-substituent effect on photophysical properties of porphyrin as well as X-ray structure determination of some *meso*-substituted OEP's will be reported in due course.

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