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Electrostatically Paired Porphyrin and Phthalocyanine: Equilibria and Electrochemical Oxidation

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Electrostatically Paired Porphyrin and Phthalocyanine: Equilibria and Electrochemical Oxidation

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April 24, 1991

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Abstract

A synthetic model system for the special pair in the photosynthetic reaction center of bacteria has been prepared from electrostatically paired porphyrin and phthalocyanine molecules. Use of rigorously dry propylene carbonate as the solvent allowed complex formation to occur between tetra-(N-methyl-4-pyridyl)porphyrin hexafluorophosphate ($H_2TMPyP(PF_6)_4$) and tetraphenylphosphonium tetrasulfatophthalocyanine $(Ph_4P)_4H_2TSPc$ molecules. The stoichiometry of the complex was determined to be 1:1 by Job's method and the pair formation constant K_1 was estimated to be 1×10^8. The dependence of K_1 on ionic strength was studied at various concentrations of tetra-*n*-butylammonium tetrafluoroborate Bu_4NBF_4. With increasing ionic strength K_1 decreases as expected according to the Debye-Hückel limiting law. Using an ionic strength of 2 mM (Bu_4NBF_4) in PC, the extent of pairing was found to be almost 100%. Under these conditions tetrasulfatophthalocyanine and the electrostatically paired complex were oxidized at $E_{1/2}$'s of 0.453 and 0.350 V vs SCE (aq), respectively. From evaluation by the Nernst equation of the measured potential difference between paired and unpaired tetrasulfatophthalocyanine, the ratio of $[C]K_2 / [C^+]K_1$ is estimated to be 55. K_2 is the equilibrium constant for the formation of the singly-oxidized pair. The significance of the value of the ratio leads to an estimate of $K_2 = 6 \times 10^9$ at an ionic strength of 2.0 mM.

Introduction

The Special Pair

The biological importance of porphyrin based compounds has been established for many years. Recently, great interest has been shown in porphyrin pairing systems due to the recent elucidation of the structure of reaction centers in photosynthetic bacteria.[1]

Photosynthesis in these bacteria begins in complexes called reaction centers located in bacterial membrane. The structure of the reaction center of *Rhodopseudomonas viridis*, a purple sulfur bacterium, has been recently determined at atomic resolution from the X-ray crystallographic analysis of Johann Deisenhofer, Hartmut Michel, and Robert Huber.[1] The reaction center consists of two main systems: the protein and the donor-acceptor complex. The protein portion has four polypeptides: L (31 kd), M (36 kd), and H (28 kd) subunits and a *c* -type cytochrome (Figure 1).

The cytochrome contains four covalently attached heme groups. The donor-acceptor complex, embedded primarily in the L and M components, contains four bacteriochlorophyll *b* molecules (BChl-b) (structure shown in Figure 2). Two bacterio-chlorophyll *b* molecules, known as the special pair, form the primary donor of electrons. The remaining two bacteriochlorophyll *b* molecules are referred to as the bridging or accessory bacteriochlorophylls (Figure 3). Also associated with the L and M subunits are two bacteriopheophytin *b* molecules (BPh-b), two quinones (Q_A and Q_B), and a ferrous ion, which together with BChl-b form an electron transfer chain.[2]

BChl-b (special pair) $\longrightarrow$ BChl-b $\longrightarrow$ BPh-b $\longrightarrow$ Q_A $\longrightarrow$ Q_B

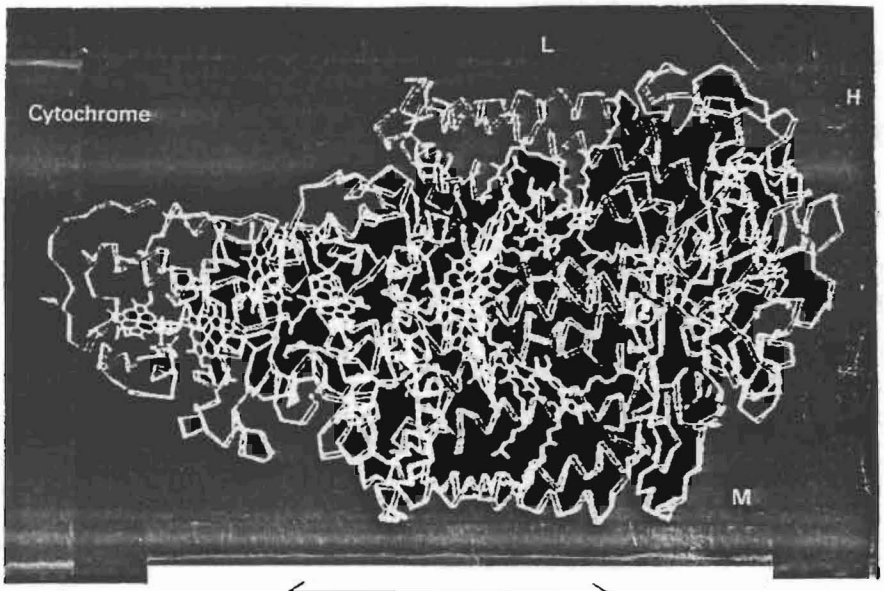


Figure 1.

The three-dimensional structure of the photosynthetic reaction center of *Rhodopseudomonas viridis*, a purple sulfur bacterium. The reaction center consists of four subunits: a cytochrome, L, M, and H. (Reference 2)

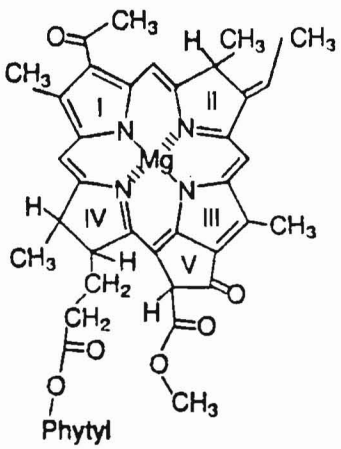


Figure 2.

The structure of a bacteriochlorophyll *b* molecule. (Reference 3)

In *R. viridis*, the special pair absorbs maximally at 960 nm. Upon photon excitation, the special pair is oxidized as one electron is transferred from $(BChl\text{-}b)_2$ through the chain to Q_A which is reduced to Q_A^- . Next, the cytochrome molecule binds to the reaction center and the hemes of the cytochrome subunit reduce $(BChl\text{-}b)_2^+$ to the ground state. A second photon of light can induce a second electron to transfer to Q_A^-. The doubly reduced Q_A^{2-} then picks up two protons from the cytoplasm and is released as QH_2 from the reaction center. This reduced quinone (QH_2) gives up its electrons and protons to a cytochrome bc_1 protein located in the hydrophobic part of the bacterial membrane, and provides enough energy to release four protons on the outside of the membrane under some redox conditions. As a result, an electrical potential gradient is formed across the membrane. The energy stored in this proton gradient is sufficient for the synthesis of ATP in bacteria[3]. The orientation of these molecules in bacterial membrane is shown in Figure 3 .

The structural basis of one electron oxidation of the special pair lies in the cofacial orientation of the two bacteriochlorophyll molecules (Figure 4), which allows the close proximity of the π-electrons in the porphyrin rings. Upon oxidation, one of the π-electrons is released, resulting in a cationic radical. This cofacial orientation was first suggested by Stoll[4] in 1932, supported by ESR and ENDOR data,[5,6] and recently confirmed by X-ray crystallography.[7]

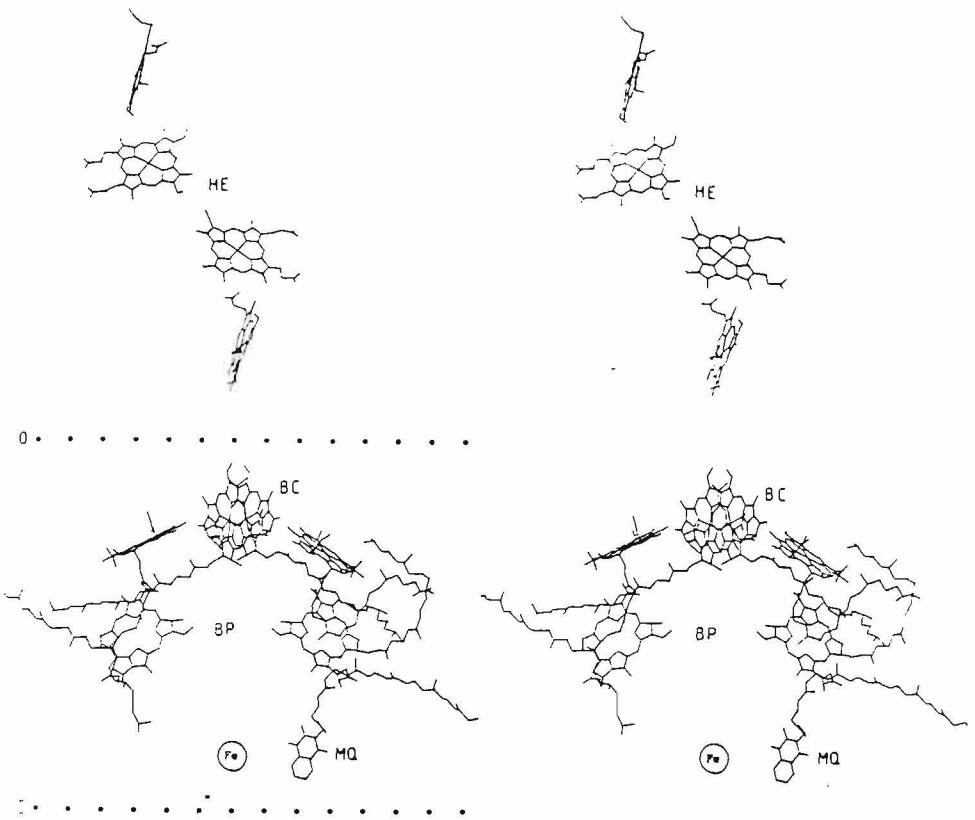


Figure 3.

The prosthetic groups of the photosynthetic reaction center in bacterial membrane of the purple bacterium *Rhodopseudomonas viridis* as determined by X-Ray diffraction. The dotted lines marked O and I indicate the presumed approximate outer and inner membrane surfaces of the bacterial cell. (Reference 7)

BC - The Special Pair Bacteriochlorophyll *b* Molecules

Fe - Non-heme Iron MQ - Quinone

BP - Bacteriopheophytin *b* HE - Heme groups

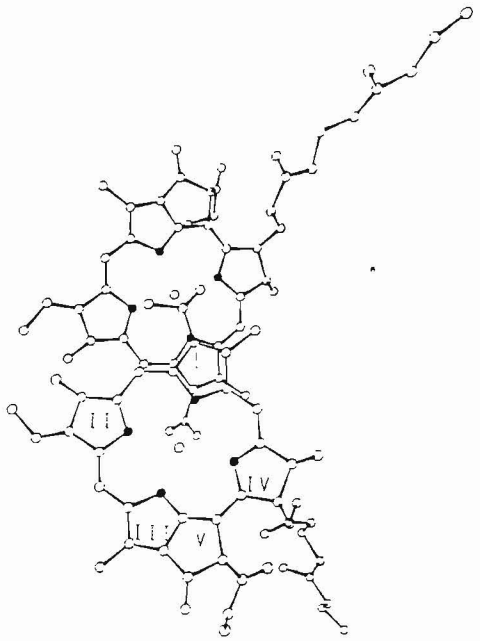


Figure 4.

The cofacial orientation of the special pair. The central local symmetry axis runs horizontally between the BChl-bs. Ring numbers are indicated in one BChl-b. Phytyl chains are truncated. (Reference 7)

The two BChl-b molecules of the special pair are thought to be linked noncovalently. The force that holds the two molecules together is not specified[7]. Studies on electron density of BChl-b reveal that one protein side chain, histidine of either L or M subunit, is bound to the magnesium ion of each BChl-b as a ligand. The pyrrole ring I of each BChl-b in the special pair stacks on top of each other and is the site of the closest interaction. The interplanar distance between the two closely associated bacterialchlorophyll *b* molecules is about 3 Å and Mg···Mg distance about 7 Å.[7] The acetyl groups of rings I are in direct contact with the Mg atoms of the other BChl-b in the pair, the nature of this interaction

is not yet understood, but water molecule does not seem to be involved as it was previously believed.[8]

Synthetic Model Systems

Synthetic systems that contain cofacially oriented porphyrins have been the subjects of several recent studies due to their structural analogies to the special pair and as they serve as a basis for understanding π interactions in general. One type of model system consists of binuclear metalloporphyrin covalently linked by multi-atomic bridges between the central metals,[9] or binuclear phthalocyanines cavalently linked by a triatomic bridge on a rigid naphthalene framework on one of the peripheral sulfato group.[10] The other consists of electrostatically paired species, which consist of two porphyrin or porphyrin-phthalocyanine species having oppositely charged substituent groups.[11-16]

The doublet state for dimeric bacteriochlorophylls is well studied. In this state, the dimer is singly oxidized and there is full delocalization of the radical electron over two ring systems.[11] Even though porphyrin systems are synthetic structural analogues of the natural chlorophylls, when they are oxidized, dicationic species are likely to be formed. It has been reported that rapid electron transfer is seen in Cu(II) porphyrin-Cu(II) porphyrin radical species.[17] In another study using ESR technique,[12] the oxidation of Zn(II) porphyrin-Cu(II) porphyrin dimer gives rise to two cationic radicals $[ZnP]^+$ and $[CuP]^+$ (P stands for porphyrin) and there is a strong preferential interaction between the two species. Further oxidation of the ZnP and CuP mixture results in the removal of a second electron from $[ZnP]^+$ and produces $[CuP\text{-}CuP]^{2+}$.

Covalently attached systems are not ideal model systems for the special pair because of the difficulty in synthesis and weak π-interactions apparently restricted by their interplanar geometries.[10] As the special pair is thought to be a noncovalently linked dimer, the use of electrostatic pairs as models is particularly attractive. The electrostatic driving force for heterodimer formation of the highly charged pair of ions allows the observation and study of an electrostatic pair in strongly coupled, singly-oxidized state instead of a homo-dimer dication. Geiger and Kelly[18] reported formation constants of four porphyrin-phthalocyanine combinations in 50% ethanol to be around 2×10^5. Reports of other studies on the aggregation behavior[13,14] and solution structure and dynamics[16] of these electrostatically paired species have also appeared.

The Proposed Model

A new model system containing (tetra-(N-methy-4-pyridyl)-porphinato)zinc(II)/ (tetrasulfatophthalocyaninato)zinc(II) was established by Goodwin and Caccitolo.[19] Their preliminary studies using UV-vis spectroscopy and differential pulse voltammetry indicated that a complex is formed between $[ZnTMPyP]^{4+}$ and H_2TSPc^{4-} molecules and that the complex undergoes a one electron oxidation in propylene carbonate. However, many unanswered questions remained upon completion of their studies. The aggregation problem of H_2TSPc^{4-} which has been reported,[20] was ignored, the ionic strength dependence of the pair formation was not investigated, and the species present in the electrolysis cell were not clearly defined. Without careful analysis of these factors, which are important in understanding the model system, the preliminary results were questionable.

The current work focuses on the solution equilibria and redox properties of a similar system consisting tetra-(N-methyl-4-pyridyl)-porphyrin and tetrasulfatophthalocyanine free base salts. In the previous study, a solubility problem of metallophthalocyanine salt in propylene carbonate was observed and a suitable alternative was to use free base phthalocyanine salt. In addition, it has been observed for some redox-neutral electrostatic pairs that there is a tendency to form higher aggregates due to the coordination of the central metal ions[15]. To avoid potential solubility problem of the porphyrin in propylene carbonate at high concentrations and any potential aggregation upon oxidation, free base salt of porphyrin instead of metalloporphyrin salt was chosen for the current model.

Propylene carbonate ($C_4H_6O_3$) remains the solvent system for spectroscopic and electrochemical studies. The combined features of its strong polarity with a dielectric constant of 64.4[21](structure see Figure 5) with a resulting ability to dissolve highly charged porphyrin and phthalocyanine species, and its inactivity upon electrochemical oxidation (potential limits from 2.1 to -2.5 V vs NHE) make it a very suitable solvent for our purposes. The electrolyte is tetra-*n*-butylammonium tetrafluoroborate.

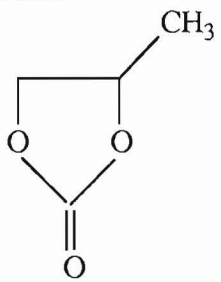


Figure 5.
Structure of propylene carbonate.

An electrostatically paired complex is expected to form between the two free base salts. This free-base derivative is also expected to undergo one-electron oxidation as outlined in Figure 6.

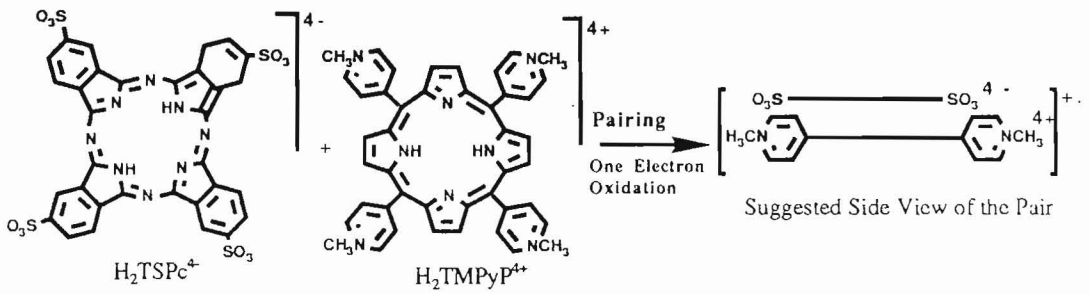


Figure 6.
The proposed structure of the electrostatically paired H_2TSPc^{4+} and H_2TMPyP^{4+} and its oxidation scheme.

As it has been mentioned earlier, H_2TSPc^{4-} tends to aggregate to form a dimer. Since this dimer formation is a competing equilibrium to the pair formation, it would be important to estimate the dimer association constant. Measurement of deviations from Beer's law was used for this evaluation under the dry conditions used for the studies of complex formation and the electrochemistry of the complex. The suggested equilibria are shown as below.

$$H_2TMPyP^{4+} + H_2TSPc^{4-} \overset{K_1}{\rightleftharpoons} \text{Complex}$$

$$+$$

$$H_2TSPc^{4-}$$

$$\Updownarrow K_D$$

$$(H_2TSPc^{4-})_2$$

The ionic strength dependence of the pair formation was studied to explore the possibilities of carrying out electroanalytical chemistry of the pair. On one hand with high electrolyte concentration the dimer formation of tetrasulfatophthalocyanine is preferred to the complex formation between the phthalocyanine and the porphyrin molecules. This would hamper the electrochemical oxidation of the proposed complex. On the other hand, high enough electrolyte concentration is required for the differential pulse voltammetry technique. A proper balance between the ionic strength and the complex formation was studied.

The porphyrin π-system has the ability to undergo redox reactions. Studies in this area have demonstrated two types of redox reactions: metal centered and ring centered electron transfers.[22,23] In *R. viridis*, as mentioned earlier, the special pair loses one electron upon oxidation and results in a π-cation radical $(BChl\text{-}b)_2^+$, which has a transient presence in the physiological environment as it is reduced by cytochrome with in about 270 nanoseconds. Much attention is given to this type of ring centered reversible electron transfer reaction of metalloporphyrins. That is, upon oxidation, a π-cation radical is formed by losing electron(s) without interrupting the π-conjugation,[24] which implies little conjugative interaction between the metal and the ring.

Electrochemical studies could suggest the presence of a singly-oxidized state and the sites of oxidation process. Compared with simple porphyrin dimers, which tend to disproportionate in solution leaving doubly-oxidized pair and unoxidized monomers, "electrostatically paired" complex could undergo one electron oxidation and produce a singly-oxidized radical product.[16,18] Confirmation of this singly-oxidized state could provide us some insight into the relative stability of the complex and

its radical, which is related to the π-π interaction in the pair in the singly oxidized state.

This may also lead to understanding the role of the center metal, as the case in some studies[10] in which binuclear metalloporphyrin complexes have been developed. The two macrocycles are joined together by a multiple metal-metal bond. The porphyrin macrocycle is rigid in nature and requires a planar or nearly planar geometry about each metal center, thus allows the variation of the metal-metal bond orders in these complexes. Redox properties of these dimers inferred from a combination of cyclic voltammetry and NMR techniques suggest variations of the bond order induced by oxidation in the metalloporphyrin dimer.

Experimental Procedures

Preparation of Tetraphenylphosphonium Tetrasulfatophthalocyanine

Tetraphenylphosphonium tetrasulfatophthalocyanine ($(Ph_4P)_4H_2TMPyP$) was precipitated from the mixture of equivalent amounts of tetraphenyl phosphonium bromide ($Ph_4P^+Br^-$) (Aldrich) and tetrasulfatophthalocyanine sodium salt (Midcentury) in aqueous solution. The solids were collected by centrifugation on a Clay Adams Physicians compact Centrifuge and dried in an Abderhalen apparatus under vacuum at 140 °C with phosphoric anhydride (Merck, Reagent) for a minimum of 3 hours. The dried salts were stored in a nitrogen-filled glove-box (refurbished LABCONCO).

Preparation of Tetra-(N-methy-4-pyridyl)porphyrin Hexafluorophosphate

Tetra-(N-methy-4-pyridyl)porphyrin hexafluorophosphate was precipitated from the mixture of equivalent amounts of potassium hexafluorophosphate (Aldrich) and tetra-(N-methyl-4-pyridyl) porphyrin (Midcentury) in aqueous solution. The precipitates were treated the same way as the phthalocyanine free base salts.

Purification of Propylene Carbonate

Three procedures for purifying propylene carbonate were explored. The first procedure was distillation of propylene carbonate (PC) (Aldrich) under vacuum on a Schlenk line at 110 °C. The second variation was a distillation of PC with calcium hydride (Fisher Scientific, Purified) under vacuum as above in an attempt to dry the solvent more carefully. The third approach, which was ultimately adopted for use, was a modification of the

procedures from Srivastava and Mukhorjee[25] and Izutsu et al.[21] Propylene carbonate (Baxter, Burdick and Jackson) was distilled first with 0.2 g/l *p*-toluenesulfonic acid (TSA) (Fisher Scientific, Certified) under vacuum on the Schlenk line and then redistilled with 10 g/l 3 Å activated molecular sieves (Fisher Scientific) under vacuum. For all procedures, distilled PC was collected in a Schlenk flask. At the end of distillation, the Schlenk flask containing the distilled PC was filled with purified nitrogen gas, sealed, and then transferred into the glove box. This purified PC is now referred simply as PC unless specified. Nitrogen gas (Linde Dry Grade, distributed by Illini TEC) was dried with a column of anhydrous $Mg(ClO_4)$.

Recrystallization of Tetra-n-butylammonium Tetrafluoroborate

Into a 50 ml beaker, 5.016 g of tetra-n-butylammonium tetrafluoroborate (Bu_4NBF_4) (Aldrich) was weighed out and 10 ml of ethyl acetate (Fisher Scientific) was added. The solution was heated on a hot plate and stirred for 10 minutes until all Bu_4NBF_4 was dissolved. The solution was cooled to room temperature and 5 ml of hexane (Fisher Scientific) was added. The solution became cloudy and was cooled in an ice bath for 30 minutes. The precipitate was collected by suction filtration and dried in Abderhalen apparatus under vacuum overnight. Dried Bu_4NBF_4 was stored in a desiccator.

Preparation of Solutions

All solutions were prepared in the glove box. The concentrated stock solution of the desired free base salt was prepared by dissolving as much of the desired salt as possible into 15 ml of PC in a beaker. The solution was then transferred into a 25 ml volumetric flask and was filled with PC to the mark. A 1:25 diluted stock solution for each concentrated solution was prepared in another 25 ml volumetric flask. All solutions taken out of the glove box were contained in volumetric flasks with septum stoppers. The diluted solutions were taken out of the glove box and their absorbances were measured by syringing 3 ml of the stock solution into a 1-cm cell (Fisher Scientific 282 or 283) with a septum stopper. Spectra were recorded from 900 to 315.1 nm on a Perkin-Elmer Model 559 UV-vis Spectrophotometer with a scan rate of 120 nm/min and recording scale of 20 nm/cm These conditions were maintained through-out all experiments. The concentration of the diluted solution was calculated using the literature extinction coefficient values[20, 21](see discussion). Solutions of desired concentrations were then prepared by proper dilution of the concentrated stock solutions.

Spectral Evidence of Electrostatic Interaction of H_2TMPyP^{4+}/H_2TSPc^{4+} Pair

Two diluted solutions of 10 ml each were prepared: one contained 3.0×10^{-6} M of H_2TMPyP^{4+} in PC and the other 2.9×10^{-6} M H_2TSPc^{4-} in PC. The spectrum of each solution was taken. Then 1.5 ml of each solution was syringed into a 1-cm cell with septum stopper and the spectrum of the mixture was taken. Finally, the two original solutions were syringed into two separate cells. The two cells were then placed in

series in the spectrophotometer. The spectrum of this combination was also taken.

Determination of the Stoichiometry of the Complex by Job Titration

Two solutions of H_2TMPyP^{4+} and H_2TSPc^{4-} were prepared with concentrations of 4.3×10^{-6} M and 4.9×10^{-6} M respectively. From these two stock solutions, eleven solutions of constant total molarity of $(4.6 \pm 0.2) \times 10^{-6}$ M were prepared with mole fraction of $H_2TMPyP^{4+}/H_2TSPc^{4-}$ ranging from 0.0 to 1.0 with 0.10 mole fraction increments. Spectra of the eleven solutions was recorded.

Verification of Beer's Law Behavior at Low Concentrations of H_2TSPc^{4-}

Two solutions of H_2TSPc^{4-} at concentrations of 3.6×10^{-5} M and 3.6×10^{-6} M in PC were prepared. The spectra of 26 solutions with a concentration range from 2.0×10^{-8} M to 1.2×10^{-6} M were recorded. These solutions were prepared by additions of proper amounts of the two stock solutions with a 500-µl syringe into either a 1-cm or 10-cm cell containing proper amount of PC. The stock solution concentrations were calculated from the concentration of the lowest dilution of 2.0×10^{-8} M, assuming that only the monomeric form was present at such a low concentration.

Ionic Strength Dependence on Pair Formation

Two diluted stock solutions were prepared, with equal concentration H_2TMPyP^{4+} and H_2TSPc^{4-} of 6.1 x 10^{-6} M in both solutions, and with electrolyte (Bu_4NBF_4) concentration of 0.10 M and 0.010 M each. A third stock solution containing equal concentration of H_2TMPyP^{4+} and H_2TSPc^{4-} at 4.9 x 10^{-6}M without electrolyte was also prepared. By proper mixing of the three stock solutions, solutions containing the electrostatically paired complex at 6.1 x 10^{-6} M and at the following added electrolyte concentrations were obtained: 0.10, 0.070, 0.040, 0.010, 0.0050, 0.0020, and 0.0 M. The spectra of these solutions were recorded.

Electrochemical Studies

Electrochemical oxidation was performed via differential pulse voltammetry (DPV) with a Princeton Applied Research Model 174 A Polaragraphic Analyzer with a Hewlett Packard Model 7040 A X-Y Recorder. Both the working and counter electrodes were platinum electrodes. The reference electrode is a saturated calomel electrode. Diagrams of the reference electrode and the experimental set-up are shown in Figure 7. The solutions prepared in glove box were: 1.22 x 10^{-5} M H_2TSPc^{4-} and 1.22 x 10^{-5} M H_2TMPyP^{4+}, each containing 2.0 mM (0.0165 g) Bu_4NBF_4; and 2.0 mM (0.0165 g) Bu_4NBF_4 in PC. About 15 ml of the electrolyte solution was syringed into a dried electrolysis cell and kept under a constant flow of purified nitrogen gas. A DPV scan was performed and recorded from 0 to 1 .5 V vs SCE (aq) at a scan rate of 2 mV/sec and a sensitivity of 0.1 mA full scale setting. These conditions were maintained for all the DPV scans. About 9 ml of the H_2TSPc^{4-}

solution was syringed into the cell. Another DPV scan was recorded. Then about 9 ml of solution was syringed into the cell, the DPV scan for this mixture was also recorded. The cell was emptied, rinsed thoroughly, and dried in oven (110 °C) for half an hour. The DPV scan for H_2TMPyP^{4+} was performed similarly with 15 ml of electrolyte solution and 9 ml of H_2TMPyP^{4+} solution A small amount of ferrocene (Fisher Scientific) was added into the porphyrin-electrolyte mixture and another DPV scan was also recorded.

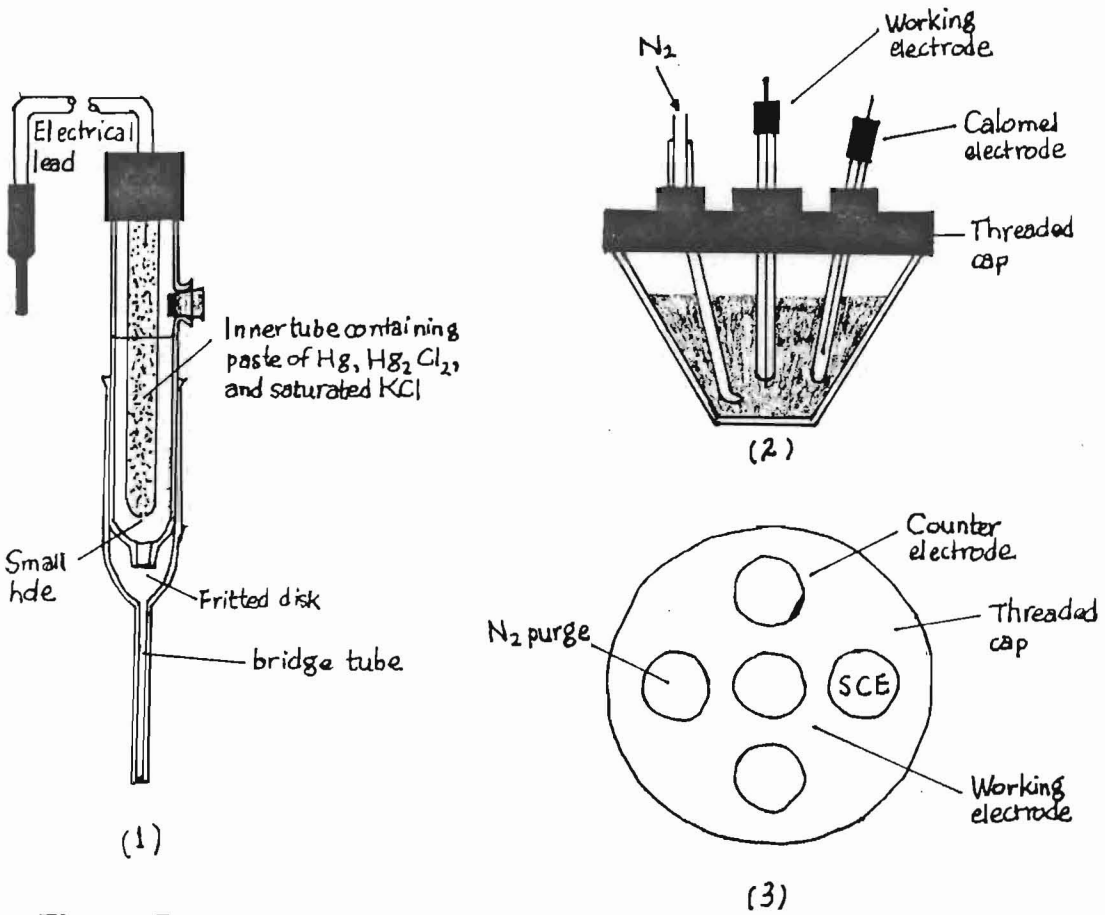


Figure 7.

The experimental arrangement for differential pulse voltammetry. (1) Diagram of the saturated calomel electrode, (2) cross-sectional view of the voltammetric cell, (3) top view of the cap of the cell.

Results and Discussion

UV-vis Spectroscopy

The wavelength of maximum absorbance (the Soret band) of H_2TMPyP^{4+} is 422 nm, a blue shift of 26 nm from that of $[ZnTMPyP]^{4+}$ reported by Goodwin and Caccitolo.[19] The monomeric form of H_2TSPc^{4-} absorbs maximally at 688 nm and the dimeric form at 610 nm. The molar absorption coefficients of the monomer ε_M (9.98×10^4 $M^{-1}cm^{-1}$ at 697 nm) and of the dimer ε_D (8.59×10^4 $M^{-1}cm^{-1}$ 632 nm) have been reported to be independent of the solvent and the value of ε_M obtained in 50% aqueous ethanol is in good agreement with that for DMSO solvent.[20] These values are taken as the literature values for our solvent system. The visual spectra of the monomeric and dimeric forms of phthalocyanine are shown in Figure 8 .

The extinction coefficient of H_2TMPyP^{4+} was taken as 8.0×10^4 $M^{-1}cm^{-1}$ estimated from the Job titration of $CuTSPc^{4-}$ and H_2TMPyP^{4+} in DMSO system reported by Gaspard.[26] This value is believed to be valid for our system. The visual spectrum of this porphyrin free base is shown also in Figure 8.

The maximum absorption wave lengths for both H_2TMPyP^{4+} and the monomeric form of H_2TSPc^{4-} in dried PC are observed to vary within a range of 4 nm. Since the variation is very small , it is considered as systematic error. Therefore, all measured absorbance values were recorded at the wave lengths of 422 and 688 nm the maxima for H_2TMPyP^{4+} and H_2TSPc^{4-} monomers respectively.

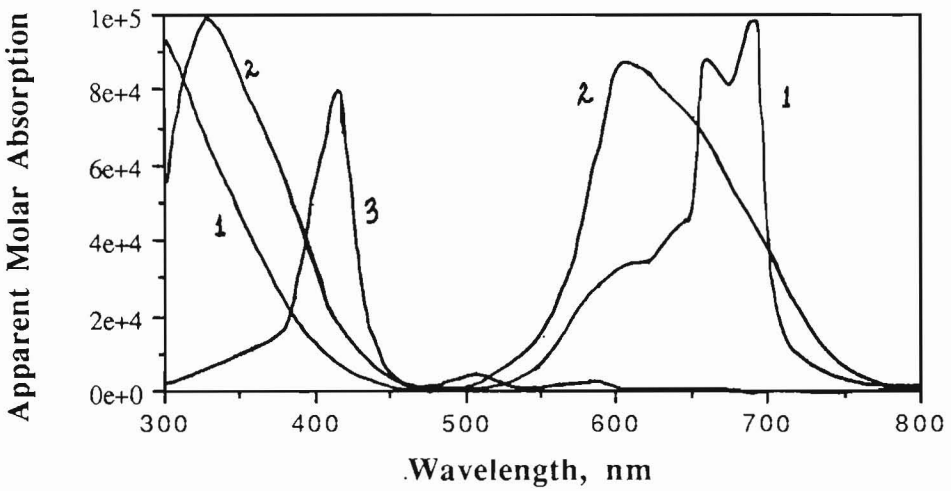


Figure 8.

Visual spectra of (1) the monomeric form of H_2TSPc^{4-} in dried PC (3.2×10^{-6} M), (2) the dimeric form of H_2TSPc^{4-} in undried PC (3.2×10^{-6} M), and (3) H_2TMPyP^{4+} in dried PC (1.6×10^{-5} M). Cell pathlength is 1 cm. No electrolyte was present.

Tetrasulfatophthalocyanine Homo-Aggregation

The formation of dimeric free base H_2TSPc^{4-} in PC was found to be very sensitive to contaminant water. In the presence of trace water (actual concentration is unknown), the dimeric form is preferred to the monomeric form as indicated by broad absorbance at 610 nm. *In situ* water removal was attempted by direct addition of drops of acetic anhydride into the cell containing tetrasulfatophthalocyanine dimer solution. As more acetic anhydride was added, the absorbance at 688 nm began to increase, while the absorbance at 610 nm started to decrease. These changes are direct evidence for a water-dependent equilibrium of dimer formation and are not justified by the dilution resulting from the addition of acetic anhydride.

This sensitivity to water contamination at very low concentration suggests a molecular complex formation with water. Since the acetic acid generated from the reaction of trace water and acetic acid did not contribute to dimer formation as water did, we may speculate that the water molecules may serve as a hydrogen-bonded bridge between sulfonato-groups on the H_2TSPc^{4-}. The hypothetical structure is shown is Figure 9.

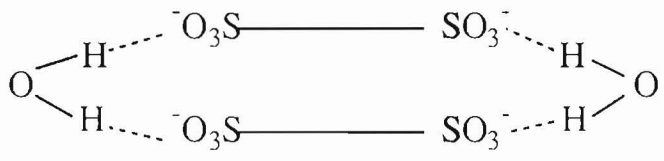


Figure 9.
Hypothetical water-bridged dimer structure of H_2TSPc^{4-}. Two more out-of-plane water-bridges between the two tetrasulfatophthalocyanine are not shown in this diagram.

The dimer formation was initially thought to interfere with the pair formation between the porphyrin and the phthalocyanine molecules. A quick test of this intererence was performed by taking the spectrum of phthalocyanine dimer and porphyrin solution mixture. Due to an error in calculation, 1:10 mole ratio of phthalocyanine dimer: porphyrin were mixed instead of 1:2. This test has not been repeated and the effect of dimer formation of phthalocyanine on the pair formation is not yet determined.

Using rigorously dry solvent (solvent purification procedure number 3) H_2TMPyP^{4+} and H_2TSPc^{4-} allowed the formation of a complex (Figure 10).

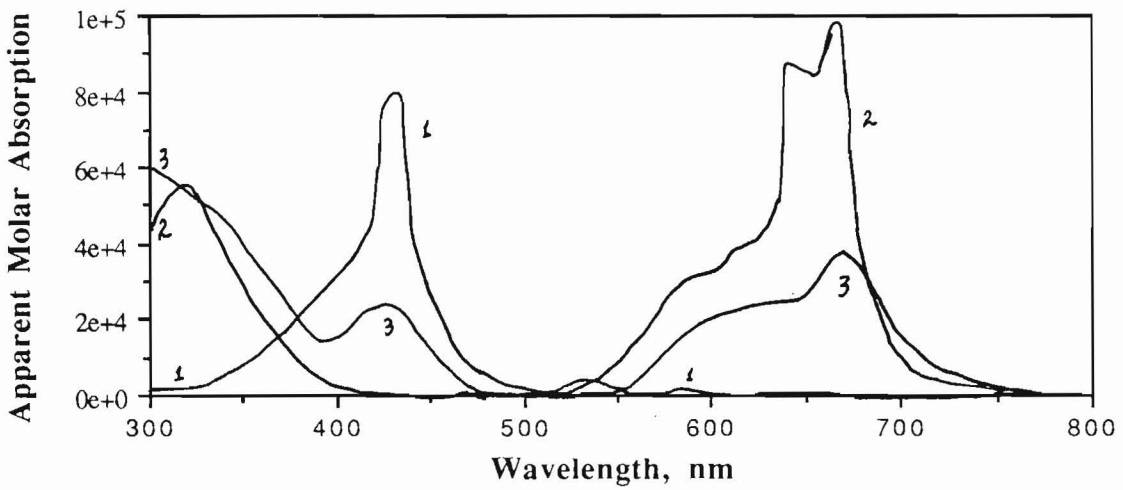


Figure 10.

Spectral Evidence of Pair Formation. Visual spectra of (1) H_2TMPyP^{4+} (3.0×10^{-6} M), (2) H_2TSPc^{4-} monomer (2.9×10^{-6} M), and (3) 1:1 mixture of H_2TSPc^{4-} and H_2TMPyP^{4+} (complex concentration: 1.5×10^{-6} M).

The absorbance of the 1:1 mixture of showed a marked decrease which is characteristic of electrostatically interacting species at low ionic strength.[27-29] It suggests that the electrostatic force results in a large association constant and that these free base molecules have interacting π-electronic structures indicating a cofacial orientation in PC. Similar spectra due to this type of cofacial structure have been observed before.[16]

Stoichiometry of the Complex

The stoichiometry of the complex was determined by Job's method. The data were summaried in Table 1. Due to the scatter of the data, the usually simple graphic analysis of constructing tangents to the curves and identifying the intersection was unsatisfactory, hence, the data were numerically analyzed by Los Alomos nonlinear least-squares program.

This program could give estimations of the unknown parameters to fit the data. The derivation of equations for the program and the detailed analysis are described in the Appendix. The best fitting curve computed is shown in Figure 11 , which supports the 1:1 stoichiometry of the complex. K_1 is estimated to be 1 x 10^8 and ε_c, (3 $\pm$ 2) x 10^4 $M^{-1}cm^{-1}$. The large standard deviation of ε_c reflects the near-complete association at this concentration, the scatter in the data and the small number of data points.

The two tangents drawn from the first and the second half of the curve can almost be superimposed on the best fitting curve, which indicates very small amount of unpaired tetrasulfatophthalocyanine mononers. The estimation of K_1 and ε_c based on the numerically determined best fitting curve are not very reliable. The fitting program did not actually reach convergence at the values reported. Further work to determine these values more precisely is warranted. The most direct method for this determination is analysis of Beer's law deviation in solutions of the pair at various concentrations. Nonlinear least squares analysis could be used to determined both K_1 and ε_c.

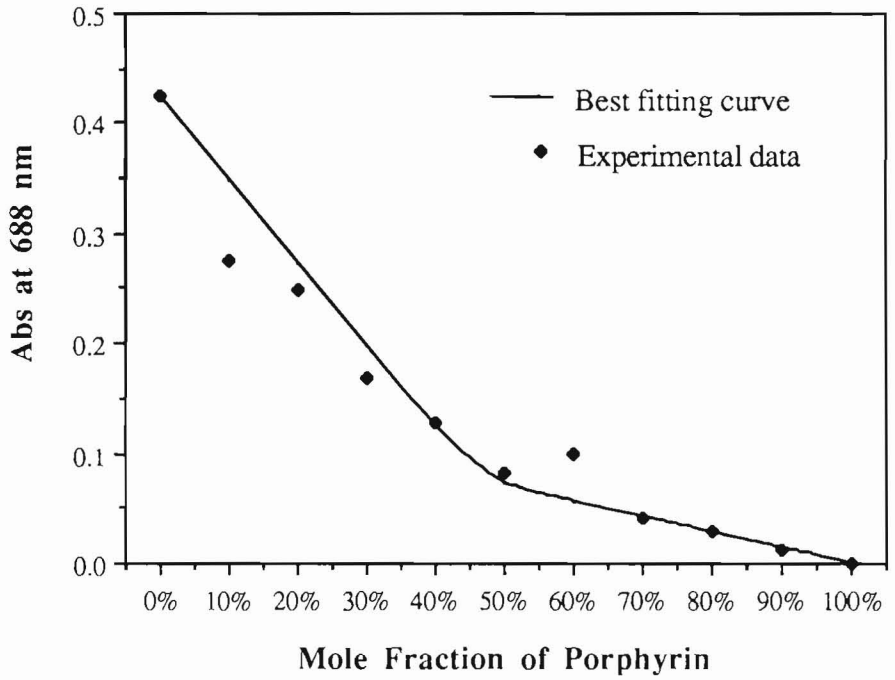


Figure 11.

Job Plot: 1:1 Pairing of H_2TSPc^{4-} and H_2TMPyP^{4+}.

Table 1. Absorbance Values for Job Titration in Dried PC with a Total Concentration of 4.6×10^{-6} M.

Abs at 686 nm	Abs at 422 nm	$[Ph]_o$ ($\times 10^6$ M)	[Por] ($\times 10^6$ M)
0.425	0.040	4.3	0.00
0.275	0.030	3.8	0.49
0.249	0.050	3.4	0.99
0.170	0.062	3.0	1.5
0.129	0.083	2.6	2.0
0.082	0.072	2.1	2.5
0.100	0.140	1.7	3.0
0.042	0.140	1.3	3.5
0.030	0.215	0.85	4.0
0.013	0.285	0.43	4.4
0.000	0.395	0.00	4.9

The Dimer Association Constant of H_2TSPc^{4-} in Dried PC

The dimer association constant of H_2TSPc^{4-} at low ionic strength was assessed by examining the deviations from Beer's law. The data are summaried in Table 2 and the results are shown in Figure 12. As can be seen, the absorbances at 688 nm is proportional to the concentrations of H_2TSPc^{4-} and no significant deviation was observed. That is, within the concentration range under study, H_2TSPc^{4-} is present in monomeric form and the dimer does not exist at a significant level to interfere the pair formation. The lack of deviation from linearity up to a concentration of 1 x 10^{-6} M indicates that the dimer association constant must be smaller than 1 x 10^4 in rigorously dry solvent.

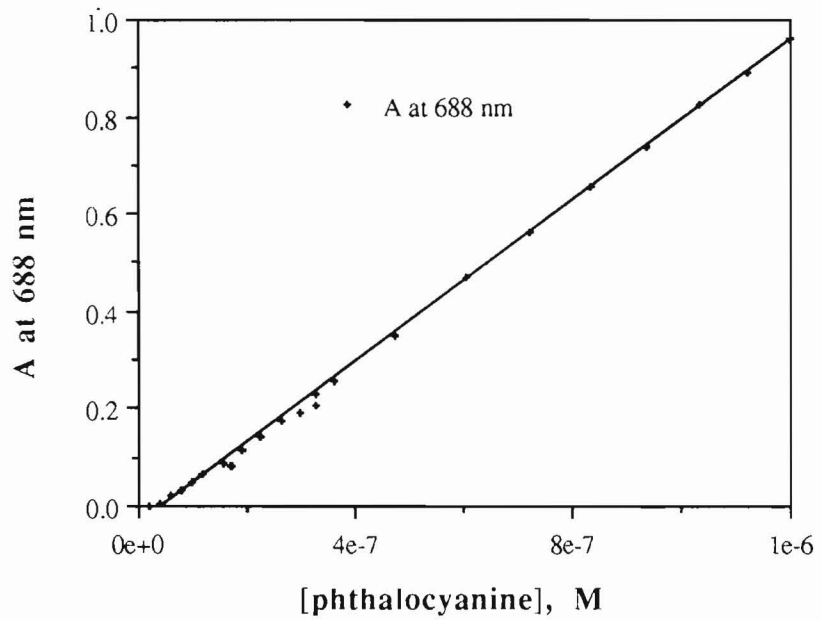


Figure 12.
Examination of the deviation of H_2TSPc^{4-} from Beer's law at low concentrations in dried PC. Cell pathlength is 1 cm.

Table 2. Raw Data and Calculated Data for the Deviation from Beer's Law of H_2TSPc^{4-} at Low Concentration in PC.

Trial	Concentration of H_2TSPc^{4-} ($x10^8$ M)	Absorbance[a]
1	2.0	0.020
2	4.0	0.063
3	6.0	0.211
4	8.0	0.346
5	10.0	0.494
6	11.7	0.632
7	15.4	0.879
8	17.2	0.080
9	19.0	1.140
10	22.6	1.440
11	26.1	1.740
12	29.5	1.890
13	32.9	2.090
14	32.9	0.220
15	36.2	2.420
16	47.2	0.340
17	60.3	0.462
18	72.4	0.562
19	83.5	0.654
20	93.8	0.733
21	103	0.822
22	112	0.888
23	120	0.940

a Trial 1-7, 9-13, and 15 were measured in 10 cm cell, the rest in 1 cm cell.

Ionic Strength Dependence on Pair Formation

The dependence of K_1 on ionic strength was studied by measuring the absorbance of the complex solution at various concentrations of tetra-*n*-butylammonium tetrafluoroborate Bu_4NBF_4. The formation constant K_1 of the complex at a specific ionic strength can be calculated as followed:

$$K_1 = \frac{[C]}{[Ph][Por]} \qquad (1)$$

$$[Ph] = [Ph]_o - [C] \qquad (2)$$

$$[Por] = [Por]_o - [C] \qquad (3)$$

where $[Ph]_o$ and $[Por]_o$ are the analytical concentrations of the phthalocyanine and the porphyrin present in the electrolyte solution. [C] is the concentration of the electrostatically paired complex, which can be obtained by rearranging Equation (4) and (5) into Equation (6):

$$A_{Total} = \varepsilon_{ph}[Ph]\, d + \varepsilon_c[C]\, d \qquad (4)$$

$$[Ph] = [Ph]_o - [C] \qquad (5)$$

$$[C] = \frac{A_{Total} - \varepsilon_{ph}[Ph]_o\, d}{-(\varepsilon_c - \varepsilon_{ph})\, d} \qquad (6)$$

where d is the cell pathlength, are the extinction coefficients of the complex and the tetrasulfatophthalocyanine respectively. ε_{ph} is a known value, whereas ε_c is estimated from Los Alomos nonlinear least-squares program.

The calculated results are summarized in Table 3 and the representative spectra are shown in Figure 13.

The dependence can be analyzed by Debye-Hückel limiting law:

$$\log K_1 = \log K_1^{o} + \frac{2AZ_AZ_B\,\mu^{1/2}}{1 + Ba\mu^{1/2}} \qquad (7)$$

where K_1^{o} is the formation constant of the complex at zero ionic strength which approximates K_1 estimated from Los Alomos program. Z_AZ_B is equal to the product of the respective charges on the complexes. The parameter A is calculated to be 0.558 from the following equation:[30]

$$A = \frac{e^3N_o^2}{4\pi\varepsilon_oDRT}\left(\frac{\rho_o}{2000\varepsilon_oDRT}\right) \qquad (8)$$

where $e = 1.60219 \times 10^{-19}$ C,

$N_o = 6.022 \times 10^{23}$ mole^{-1}

$\varepsilon_o = 8.85419 \times 10^{-12}$ J^{-1}C^{2}m^{-1}

$D = 64.4$

$R = 8.314$ Jmole^{-1}K^{-1}

$T = 294.75$ K

$\rho_o = 1.204 \times 10^3$ kgm^{-3}

Due to the unavailability of literature values of parameter B for propylene carbonate, the nonextended form of the Debye-Hückel limiting law was used for analysis:

$$\log K_1 = \log K_1^{o} + \frac{2AZ_AZ_B\,\mu^{1/2}}{1+\mu^{1/2}} \qquad (9)$$

A Debye-Hückel plot of log K_1 vs $\mu^{1/2}/(1+\mu^{1/2})$ was constructed and is shown in Figure 14. A straight line was obtained from this plot with a slope of -17. The factor $2AZ_AZ_B$ equals to -17.9. Therefore, this dependence is highly consistant with the Debye-Hückel limiting law. The contributions of dimerization at the high ionic strength limits have not been determined, however. Additionally, the extent of ion pairing of the supporting electrolyte has not been evaluated.

Table 3. Ionic strength dependence of the electrostatic pairing constant K_1 in propylene carbonate for the association of H_2TSPc^{4-} and H_2TMPyP^{4+}.

Ionic Strength mM[b]	Absorbance[a] at 688 nm	K_1	Cal'cd. Extent of pairing,[c] fraction
0.0	0.178	$1x10^8$	1
2.0	0.195	$1x10^7$	1
5.0	0.280	$3x10^6$	0.8
10.0	0.370	$5x10^5$	0.6
40.0	0.452	$2x10^5$	0.4
70.0	0.575	$2x10^4$	0.08

a Cell pathlength is 1 cm.

b The electrolyte is Bu4NF4.

c The fraction of pairing was calculated from the following equation:

$$\text{fraction of pairing} = [C] / [Ph]_0 \quad (10)$$

where [C] could be calculated from Equation (6)

$[Ph]_o = [Por]_o = 6.1 \times 10^{-6}$ M

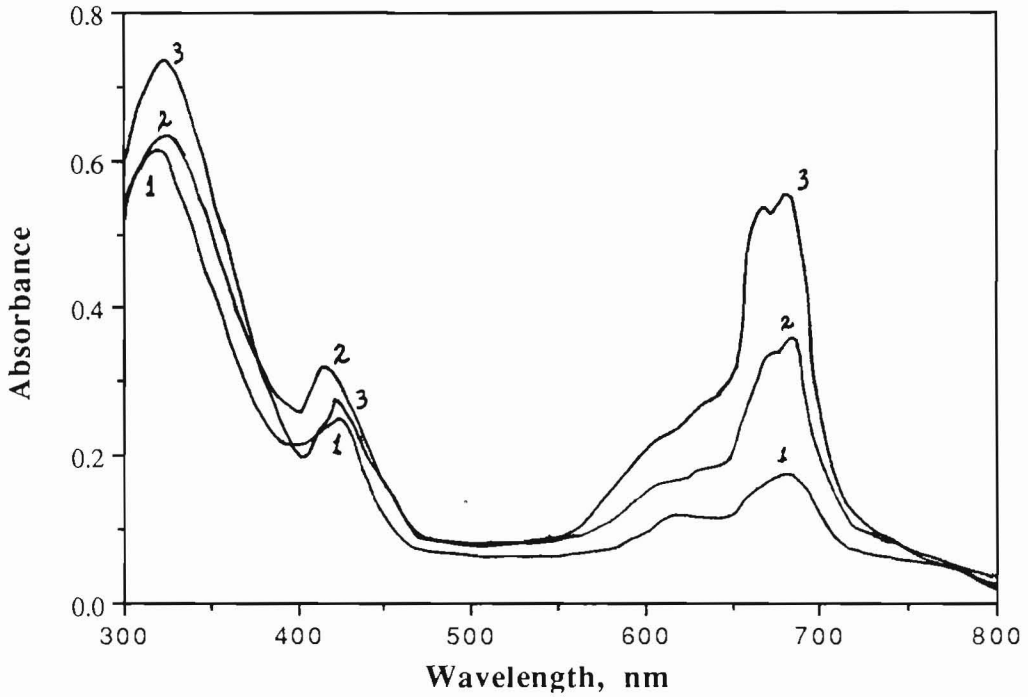


Figure 13.

Dependence of pair formation on ionic strength. The concentrations of electrolyte Bu4NBF4 are (1) 0.0 mM, (2)10.0 mM, and (3) 70.0 mM. The concentration of the complex is 5.89 x 10^{-6} M in all trials shown. Cell pathlength: 1 cm.

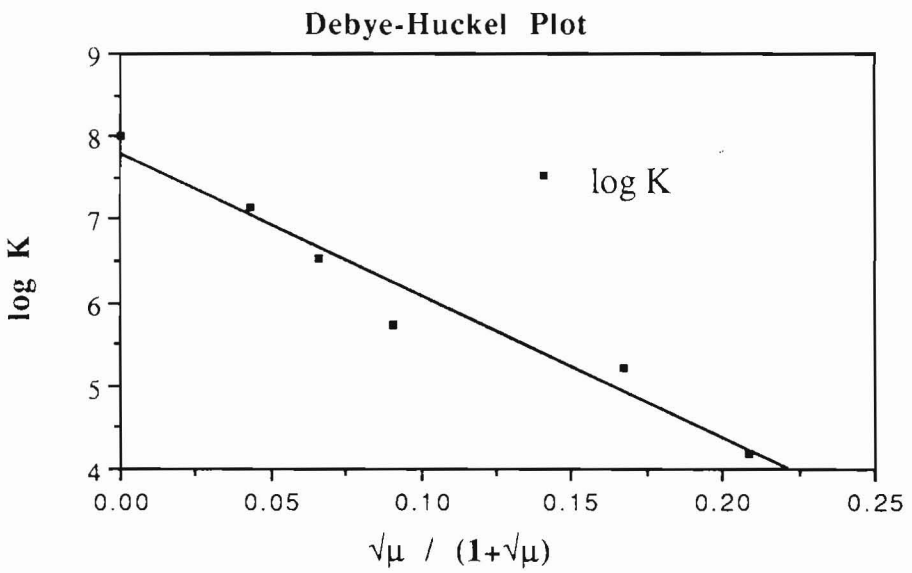


Figure 14. Debye-Hückel plot.

The function of the straight line is: $\log K_1 = 7.8 - 17\,\mu^{1/2} / (1 + \mu^{1/2})$

Electrochemical Oxidation of the Complex and Its Implications The electrolyte concentration of 2.0 mM was chosen for the electrochemical oxidation of the complex by differential pulse voltammetry with the porphyrin and phthalocyanine concentration held at 3.3 x 10^{-7}M. Preliminary studies on the electrochemistry of our model system have shown that phthalocyanine and the complex were oxidized at half wave potentials of 0.453 and 0.350 V vs SCE (aq), respectively (Figure 15); while porphyrin was not oxidized within the range from 0 to 3.0 V vs SCE (aq). This result is supported by the electrochemical characterization of (meso-tetrakis(1-methyl-pyridinium-4-yl)porphinato)nickel(II) (TMPyP)Ni(ClO_4)$_4$ in dimethylformamide by Kadish et al.[31] The dc polarograms of (TMPyP)Ni(ClO_4)$_4$ complex show that the complex does not undergo any oxidations within the potential range of the solvent. This can be attributed to the positive charge of the porphyrin ring the pyridyl substituent group.

The half wave reduction potentials for tetrasulfato-phthalocyanine and the complex in our experiments are different from those obtained by Caccitolo,[19] which are 0.835 and 0.915 V vs SCE. The voltammagraphs from Caccitolo were also amibiguous in that two oxidation curves were observed from the phthalocyanine voltammograph. This may be an indication of the problems proposed earlier: the species being oxidized might have been the tetrasulfatophthalocyanine dimer instead of the mononer. The "complex" he studied might be of a different nature from the 1:1 porphyrin-phthalocyanine hetero-dimer.

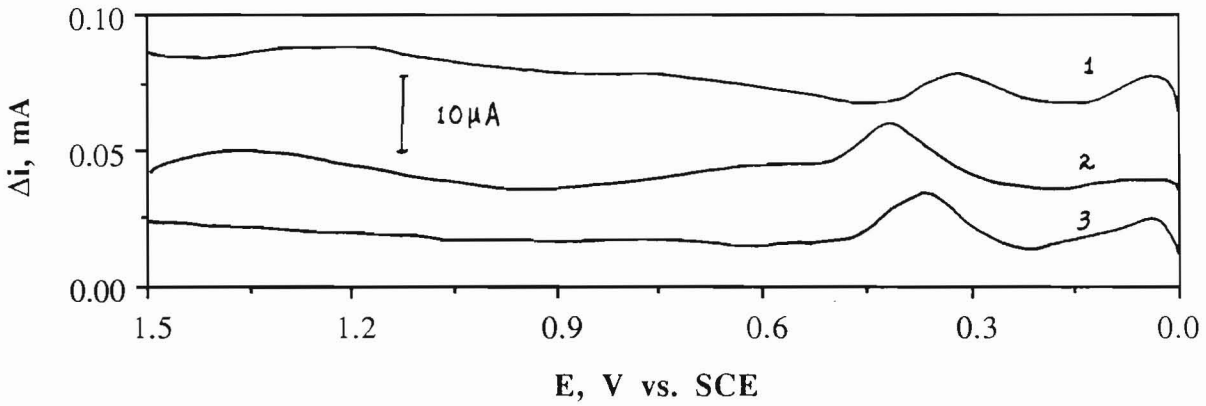


Figure 15.

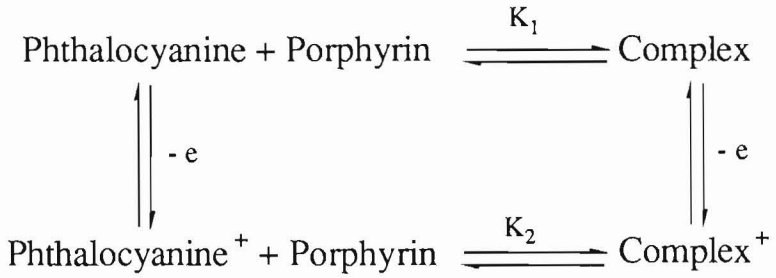
Differential pulse voltammetry scans. $E_{peak} = E_{1/2} - 0.050$ mV/2.

1. $H_2TMPyP^{4+}/H_2TSPc^{4-}$ complex (3.3×10^{-6} M)
2. H_2TSPc^{4-} monomer (4.6×10^{-6} M)
3. H_2TMPyP^{4+} (4.6×10^{-6} M) with trace amount of ferrocene

Electrolyte: Bu_4BF_4 (2.0 mM)

Ferrocene in electrolyte solution containing porphyrin was oxidized at an $E_{1/2}$ of 0.390 V vs SCE, characteristic of ferrocene. Ferrocene is used as a standard internal reference since it is known to undergo one electron oxidation. The half width of the oxidation curve is inversely proportional to the number of electrons transfer in the redox process.[32] The half width of the ferrocene oxidation wave is 105 mV, indicating one electron loss. The half widths of phthalocyanine and the $H_2TMPyP^{4+}/H_2TSPc^{4-}$ oxidation waves are 105 mV and 100 mV respectively. This supports our proposed one electron oxidation scheme of our model system.

The suggested equilibria in the experimental system are shown as below:



The following equations can be established for the above equilibria:

$$K_1 = \frac{[C]}{[Ph][Por]} \tag{11}$$

$$K_2 = \frac{[C^+]}{[Ph^+][Por]} \tag{12}$$

$$\frac{[Ph]}{[Ph^+]} = \frac{[C]\,K_2}{[C^+]K_1} \tag{13}$$

$$E_{measured} = E_{ph} - \frac{RT}{nF} \ln \frac{[Ph]}{[Ph^+]} \tag{14}$$

Substituting Equation 13 into the Nernst equation for tetrasulfato-phthalocyanine (Equation 14), the following ratio is obtained:

$$\frac{[C]\,K_2}{[C^+]\,K_1} = 55$$

Since $[C]/[C^+]$ is unknown, some assumptions may be made to make use of this result. One can analyze it in two different situations. First, if K_2

and K_1 are approximately the same, $[C]/[C^+]$ can be estimated to be 55. Substituting this value into the Nernst equation for the electrostatically paired complex (Equation 15), the standard reduction potential of the complex can be calculated to be 0.452 V. This would mean that the complex and tetrasulfatophthalocyanine have the same reduction potential.

$$E_{measured} = E^{o}_{complex} - \frac{RT}{nF} \ln \frac{[C]}{[C^+]} \qquad (15)$$

This is unrealistic description since it ignores the physical meaning of peak potential in the DPV experiment. The ionic strength has been adjusted to allow ~ 100% complexation, the peak potential results mainly from the 1:1 ratio of the complex and the complex radical; i.e., $[C]/[C^+] = 1$.

In the second situation, if $[C]/[C^+]$ appoaches unity, then K_2/K_1 would equal to 55 and $E^{o}_{complex}$ is the measurement value of 0.350 V. The estimate of K_2 is 6×10^9. This means that the oxidized complex is more stable than the unoxidized and is easier to oxidize than tetrasulfatophthalocyanine.

This would suggest a stabilization of the pair due to the single π-electron vacancy. This supports the stabilization which occurs in doubly oxidized pairs of nonionic porphyrins such as octaethylporphinatozinc(II).[33] However, recent X-ray diffraction studies of crystalline octaethylporphinatonickel(II) dimer have shown that it does undergo one electron oxidation and is stable in the solid state as a cationic radical dimer. In contrast, octaethylporphinatozinc(II) dimer does not undergo one electron oxidaiton, instead it tends to disproportionate in

solution leaving doubly-oxidized pair and unoxidized monomers.[34-36] The central metal seems to play an important role in the stability of the complex radical. Systematic investigations of this nature have not been pursued to our knowledge. Most of the investigation in electrochemical studies of porphyrins deal with covalently linked metalloporphyrin systems and their serial redox processes.[10,37]

Conclusion

Careful assessments of this model system are leading a well-defined solution system. This has permitted an evaluation of the solution phase stability of the electrostatically paired radical of a free base porphyrin and phthalocyanine. Considering previous observations of the relative stabilities of metal complexes and their oxidized derivatives suggests that the metal may play an important role in determining the relative stability of the radical pair and therefore will control its tendency to disproportionate. Further studies with metal derivatives based on this model system are planned.

Future Studies

To complete the examination of the current model system, a few more aspects of the system have to be studied. The effect of ionic strength on the competing equilibrium of dimer formation of phthalocyanine will be studied. The deviation from Beer's law for the complex formation will be examined for better evaluation of K_1 and ε_c.

As discussed earlier, refinements to the approximation of $[C] = [C^+]$ in the electroanalytical study would require direct measurement of [C] and $[C^+]$ during oxidation. Techniques of spectroelectrochemistry using optically transparent thin layer electrode (OTTLE) cells can be an effective approach to carry out this study. In this technique, spectral measurements on the solution adjacent to the electrode are made simultaneously with the oxidation process that occurs at the electrode by the removal of one electron. Since the electrogenerated radical usually has a different absorption spectrum from the unoxidized species,[37] the radical can be characterized by spectroscopy and the remaining unoxidized species can be quantified as well.

Appendix

Curve Fitting by Los Alomos Nonlinear Least-Squares Program

For the eleven solution prepared in Job titration, the absorbance of each solution at 688 nm can be expressed as followed:

$$A_{Total} = \varepsilon_{ph}[Ph]d + \varepsilon_c[C]d \quad (1)$$

$$[Ph] = [Ph]_o - [C] \quad (2)$$

where d is the cell pathlength, ε_{ph} and ε_c are the extinction coefficients of the tetrasulfatophthalocyanine and the electrostatically paired complex respectively. $[Ph]_o$ is the analytical concentration of tetrasultatophthalocyaine, and [C] is the concentration of the complex.

In substituting (2) into (1) Equation (3) is obtained:

$$A_{Total} = \varepsilon_{ph}[Ph]_o d - (\varepsilon_c - \varepsilon_{ph})[C]d \quad (3)$$

The formation constant K_1 of the complex is expressed as follow:

$$K_1 = \frac{[C]}{[Ph]^m[Por]^n} \quad (4)$$

Since

$$[Por] = [Por]_o - [C] \quad (5)$$

$$[Ph] = [Ph]_o - [C] \quad (6)$$

where $[Ph]_o$ and $[Por]_o$ are the analytical concentrations of the phthalocyanine and the porphyrin in the solution. In substituting Equation (5) and (6) into (4), Equation (4) can be rewritten as:

$$K_1 = \frac{[C]}{([Ph]_o - [C])^m([Por]_o - [C])^n} \qquad (7)$$

If m = n = 1, in rearranging the above equation, the expression of [C] can be obtained:

$$K_1[C]^2 - \{1 + K_1([Ph]_o + [Por]_o)\}[C] + K_1[Ph]_o[Por]_o = 0 \qquad (8)$$

$$[C] = \frac{1 + K_1([Ph]_o + [Por]_o)}{2K_1} - \frac{\sqrt{\{\{1 + K_1([Ph]_o + [Por]_o)\}^2 - 4K_1^2[Ph]_o[Por]_o\}}}{2K_1} \qquad (9)$$

In equation (3) , ε_c and K_1 are the two unknown parameters. The partial derivatives of equation (3) in respect to ε_c and K_1 are expressed in equation (10) and (11) respectively:

$$\frac{\partial A_{Total}}{\partial \varepsilon_c} = [C] \qquad (10)$$

$$\frac{\partial A_{Total}}{\partial K_1} = \frac{(\varepsilon_{ph} - \varepsilon_c)\, d}{2K_1^2} \times \left(1 + \frac{1 + K_1([Ph]_o + [Por]_o)}{\sqrt{\{\{1 + K_1([Ph]_o + [Por]_o)\}^2 - 4K_1^2[Ph]_o[Por]_o\}}}\right) \qquad (11)$$

To start the Los Alomos program, equations (3), (10), and (11) were compiled into the Fortran Program. The data of the absorbances of the eleven solutions and initial estimates of ε_c and K_1 were entered into the computer. The Los Alomos program will calculate the corresponding absorbance values for the eleven solutions based on the estimated ε_c and K_1. A comparison was made between the calculated values and the experimental data. If the deviation is larger than a certain assigned fractional limit, the

program will give new estimates of ε_c and K_1 according to their partial derivatives. Then it will go through the calculation and comparison again. This whole process will be repeated until either it finds the best fitting estimates of ε_c and K_1, or the number of iteration is larger than 2000. In our case the values of ε_c and K_1 are estimates after 2001 iterations and the best fitting curve is constructed based on these two estimates.

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ELECTROSTATICALLY PAIRED PORPHYRIN AND PHTHALOCYANINE: EQUILIBRIA AND ELECTROCHEMICAL OXIDATION

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