

Properties of Porphyrin Dimers, Formed by Pairing Cationic and Anionic Porphyrins

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Evidence that closely coupled porphyrin-related structures are involved in bacterial¹ or green plant² photosynthesis has led to much recent work on such associated systems *in vitro*, in which a number of covalently linked porphyrin "dimers" or higher complexes have been synthesized by various means.³ We now report the preparation and some properties of dimeric and aggregated structures formed simply by spontaneous association of cationic and anionic porphyrins.

Mixing aqueous or ethanolic solutions of tetrasodium *meso*-tetrakis(*p*-sulfonatophenyl)porphyrin (TPPS) and *meso*-tetrakis(*p*-trimethylphenyl)ammonio]porphyrin tetraiodide (TTAP), or their metal complexes, produces precipitates which are shown by elementary analysis to be 1:1 porphyrin cation-anion aggregates.⁴ *meso*-tetrakis(methylpyridinio)porphyrin tetraiodide reacts similarly with TPPS. These porphyrin or metalloporphyrin aggregates are slightly soluble, to various degrees, in mixed aqueous-organic media, such as 1:1 water/acetone (WA) or water/ Me_4SO . Figure 1a,b shows absorption spectra of solutions of TPPS, TTAP, and their mixture, all at the same molar concentration of each porphyrin. It is evident that the spectrum of the mixture is not simply the sum of the component monomer spectra. The Soret band is much broadened, extending to both higher and lower energies than that of the monomers, and the peak absorption is blue-shifted by about 540 cm^{-1} . The visible spectrum is also broadened and slightly red-shifted. Cooling to 77 K in a water/acetone/glycerol (1:1:2) solvent does not appreciably sharpen the mixed spectrum.

Addition of inert salt dissociates the complex in solution (Figure 2). In WA, both TPPS and TTAP obey Beer's Law at least over the range 10^{-7} – 10^{-4} M and 0–0.1 M NaClO_4 . Dissociation constants of the complex may thus be conveniently obtained from spectrophotometric measurements on aggregate solutions of varying concentration, using salt addition to establish the final absorption corresponding to total dissociation (Figure 2). Reasonably good ($\pm 10\%$) equilibrium constants are obtained corresponding to simple dimer \leftrightarrow monomer equilibria in solution, over dissociation ranges from 10% to 60%. These results, obtained for a variety of ion pairs (Table I), over substantial dissociation ranges, indicate that higher oligomers contribute relatively little to the equilibria in solution. This conclusion is supported by the very slight solubility of the precipitated aggregates, implying that higher complexes tend toward insolubility.

The behavior of the aggregate solutions indicates appreciable intermolecular interaction. The broadening and blue shift of the Soret band for the free-base dimer appear also, and to about the same extent, in zinc, copper, and the several mixed diporphyrins (Figure 2). The fluorescence of the free-base pair is red-shifted (monomer peaks at 649 nm, dimer at 657 nm), with yield about 20% that of each monomer. It is notable that the fluorescence of free base or zinc porphyrin is strongly quenched when paired with a nonfluorescent copper-complexed monomer, although the free-base absorption extends to the red of the copper porphyrin. Triplet-triplet spectra of the dimers, obtained by flash technique, resemble the corresponding monomer triplets, with peak absorption around 470 nm and weaker, broad absorption extending into the

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(4) (a) TTAP–TPPS aggregate: C, 59.05; N, 8.44; S, 6.44; H, 5.90. Calcd: C/N, 8.33; N/S, 3.00. Found: C/N, 8.16; N/S, 3.00. (b) ZnTTAP–CuTPPS aggregate: N, 8.00; S, 6.43; Cu 3.14; Zn, 3.11. Calcd: N/S, 3.00; Cu/Zn, 1.00. Found: N/S, 2.84; Cu/Zn, 1.00. Analyses by Galbraith Labs., Knoxville. Results are calculated as atom ratios because air-dried precipitates contain 14–16 molecules of water per dimer unit, based on hydrogen analysis.

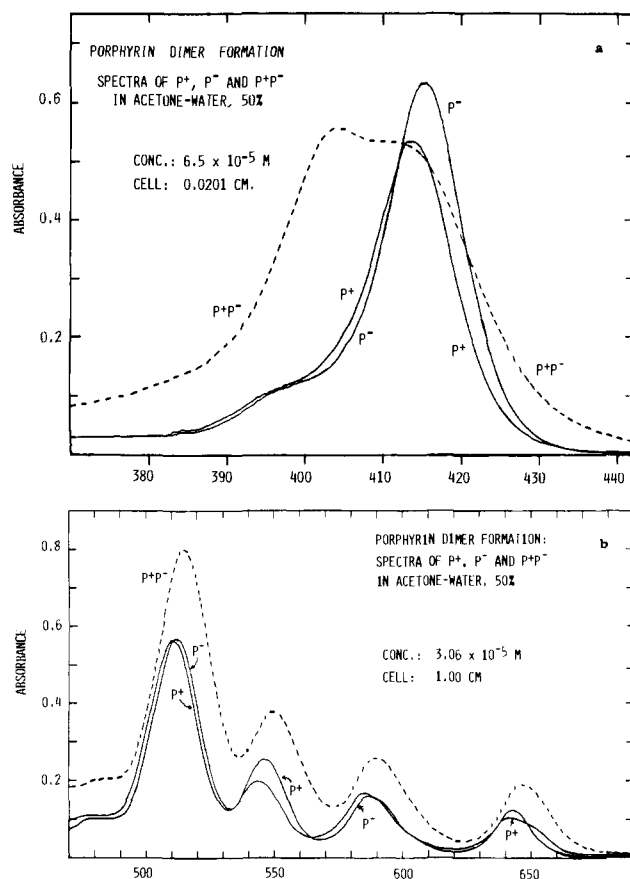


Figure 1. (a) Soret bands of TTAP (P^+) and TPPS (P^-), separately (—) and mixed (···), in 1:1 water/acetone. Concentration of each porphyrin in each solution, 6.5×10^{-5} M. Cell path, 0.020 cm. (b) Spectra in visible region of TTAP (P^+) and TPPS (P^-), separately (—) and mixed (···), in 1:1 water/acetone. Concentration of each porphyrin in each solution, 3.06×10^{-5} M. Cell path, 1.00 cm. The slight far-red shoulder for P^+ , perhaps due to impurity, does not indicate association (see text).

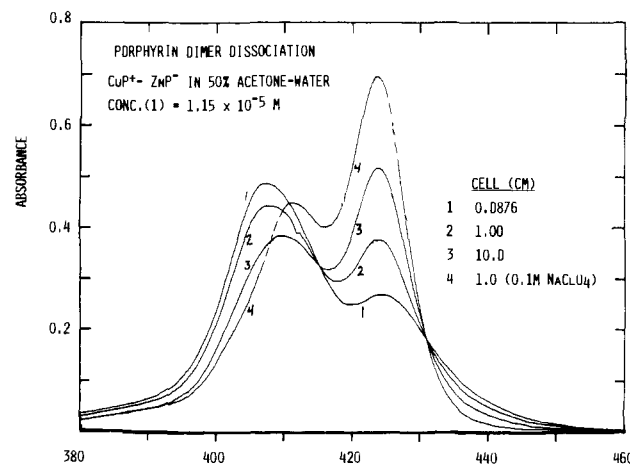


Figure 2. Soret bands of $(\text{CuP}^+)(\text{ZnP}^-)$ at constant concentration-path length product. (1) Path length 0.0876 cm, dimer concentration 1.15×10^{-5} M; (2) 1.00 cm, 1.01×10^{-6} M; (3) 10.0 cm, 1.01×10^{-7} M; (4) solution 2 with added NaClO_4 , 0.1 M. This last spectrum is sum of separate monomer absorptions (CuP^+ , 414 nm; ZnP^- , 423 nm).

red.⁵ Triplet lifetimes are decreased by pair formation. In 1:1 water/glycerol at 77 K, lifetimes (ms) are the following: TTAP, 4.1; TPPS, 7.3; free-base pair, 1.4.

Various effects on absorption, fluorescence, and phosphorescence behavior have been observed for singly linked diporphyrins^{6–9} or

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Table I. Dissociation Constants of Porphyrin Ion Pairs^a

pair	$K \times 10^8, M$
(P ⁺)(P ⁻) ^b	1.1
(P ⁺)(ZnP ⁻) ^c	5.8
(P ⁺)(CuP ⁻)	1.0
(ZnP ⁺)(P ⁻)	1.2
(CuP ⁺)(CuP ⁻)	0.65
(ZnP ⁺)(CuP ⁻)	2.5
(CuP ⁺)(ZnP ⁻)	7.3

^aIn 1:1 water/acetone; room temperature. ^bP⁺ = TTAP; P⁻ = TPPS. ^cWith 5% pyridine.

cofacial structures formed by multiply linked cyclophanes,¹⁰⁻¹² metal-oxo bridges¹³ or association at low temperatures or in films.¹⁴ The effects described here correspond to those seen in cofacial diporphyrins,¹⁰ as expected from the charge distribution of the cationic and anionic monomers. The magnitude of the interactions may of course be limited by steric constraints imposed by noncoplanarity of the phenyl rings.

These systems are evidently well adapted, through their ease of preparation and controllable equilibria, to study phenomena in mixed metalloporphyrin pairs. More detailed reports on ion-paired porphyrins and reduced porphyrins will appear shortly, including studies on magnetic, photophysical, and photochemical behavior.

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Triplet ESR Study of Dimerization of Cationic and Anionic Water-Soluble Porphyrins

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A new class of electrostatically linked porphyrins well suited for spectroscopic study is reported above by Ojadi, Selzer, and Linschitz.¹ These authors show that combination of cationic and anionic water-soluble porphyrins [*meso*-tetrakis(4-(trimethylammonio)phenyl)porphyrin (TTAP) and *meso*-tetrakis(4-sulfonatophenyl)porphyrin (TPPS)] leads to the formation of a stable 1:1 complex (TTAP/TPPS). As part of a systematic study of the spectroscopic properties of these compounds, we report here

(1) Ojadi, E.; Selzer, R.; Linschitz, H. *J. Am. Chem. Soc.*, preceding paper in this issue.

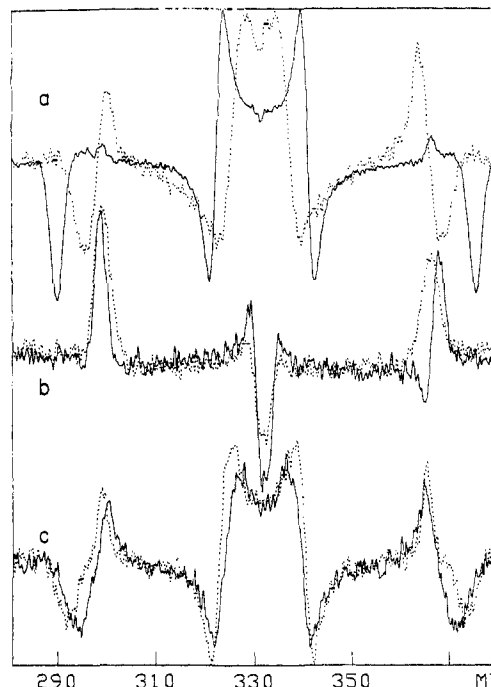


Figure 1. ESR spectra of photoexcited triplets of porphyrins in frozen 1:1 H₂O-glycerol recorded at 10 K. For experimental details see ref 2-4. (a) Solid line TTAP, dotted line TTAP/TPPS; (b) solid line ZnTTAP, dotted line ZnTTAP/ZnTPPS; (c) solid line ZnTTAP/TPPS, dotted line ZnTPPS/TTAP.

Table I. Triplet Zfs Values^a and Decay Rates

system	$D, 10^{-4} \text{ cm}^{-1}$	$E, 10^{-4} \text{ cm}^{-1}$	$k, \text{ s}^{-1}$
TTAP (TPPS) ^b	400	75	110
TTAP/TPPS ^c	343	80	260
ZnTTAP (ZnTPPS) ^b	323	95	
ZnTTAP/ZnTPPS ^c	316	91	
ZnTTAP/TPPS ^c	361	75	150
ZnTPPS/TTAP ^c	380	75	
[TPPS] ₂ ^d	334	80	
TCP ^e	377	79	200
[TCP] ₂ ^e	332	73	200
ZnTCP ^e	298	99	
[ZnTCP] ₂ ^e	291	69	

^aEstimated uncertainty $\pm(5 \times 10^{-4}) \text{ cm}^{-1}$. ^bMonomers. ^cDimers. ^dTPPS dimerization induced by K⁺-18-crown-6 addition.² ^eTCP = *meso*-tetrakis(benzo-15-crown-5)porphyrin, dimerization is induced by K⁺ addition.⁴

results of ESR measurements on photoexcited triplets of dimers and monomer precursors. Comparisons are made with data on other porphyrin dimers,²⁻⁴ and a tentative interpretation of dimerization effects is presented.

Figure 1a shows the ESR spectra of photoexcited TTAP (identical with that of TPPS²) and a 1:1 mixture of TTAP and TPPS. Figure 1b gives the spectra of triplet ZnTTAP (identical with that of ZnTPPS³) and ZnTTAP/ZnTPPS. Finally, in Figure 1c the spectra of ZnTTAP/TPPS and ZnTPPS/TTAP are presented. Values of zero field splitting (zfs) parameters D and E are given in Table I.

There is a striking similarity between dimerization effects observed for systems that contain a free base moiety. This includes dimers studied earlier.²⁻⁴ The value of D is reduced by 10-20% with respect to the monomer free base value, the E values remains unaffected. The effect on D and E of the formation of [TPPS]₂

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