2062 *Inorg. Chem.* **1994,** *33,* 2062–2065

Resonance Light-Scattering Studies of Porphyrin Diacid Aggregates

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Received October 6, 1993

Introduction

In the course of studies of porphyrin aggregation, reviewed by White[1] and Hambright,[2] a rather remarkable spectral feature was noted at low pH both for tris(4-sulfonatophenyl)monophenylporphine,[3] H_2TPPS_3, and tetrakis(4-sulfonatophenyl)porphine,[4] H_2TPPS_4. Under appropriate conditions of porphyrin concentration, pH, and ionic strength, a band of Soret intensity was observed at about 490 nm for both porphyrins in addition to the "normal" Soret at 434 nm. The profile of this long-wavelength absorption was observed to be uncharacteristically narrow, and its intensity was shown to display *specific* electrolyte effects.[3,5] The exact nature of the porphyrin species giving rise to these spectral features remained uncertain. In a recent investigation of the aggregation tendencies of a series of sulfonated porphyrins, one of us[5] provided evidence that the "490-nm absorbing species" is an extended aggregate, in that it can be preferentially removed by passing an acidic mixture containing it as one of the components through a 0.45-μm Millipore filter. Furthermore, a combination of flow-induced dichroism, circular dichroism, magnetic circular dichroism, and polarized fluorescence excitation spectral results have been interpreted as indicating that the species involved are so-called "J aggregates", rodlike assemblies consisting of linear oscillators polarized along the long axis.[6] This putative model can now be tested directly using a nontraditional light-scattering technique.

In a previous paper,[7] we applied a rather unorthodox approach to light-scattering (termed "resonance light-scattering")[8] in which the wavelength dependence of the scattering profile is considered *within* the absorption envelope of chromophores. We have shown that this modification of the standard experimental protocol provides highly sensitive, detailed information about extended aggregates, including the *absorption spectrum of the scattering species.* Porphyrin monomers and small oligomers do not show such enhanced light-scattering profiles. The present report describes the application of resonance light-scattering to the solution properties of various sulfonated porphyrin derivatives in acidic media.

Experimental Section

The various porphyrins used in this study—tetrakis(4-sulfonatophenyl)porphine (H_2TPPS_4, I); tris(4-sulfonatophenyl)monophenylporphine (H_2TPPS_3, II); *cis*- and *trans*-bis(4-sulfonatophenyl)diphenylporphine (*c*- and *t*-H_2TPPS_2, III and IV); tetrakis(4-sulfonatophenyl)porphinatocuprate(II) ($CuTPPS_4$, V); *N*-methyltetrakis(4-sulfonatophenyl)porphine (H(*N*-CH_3)$TPPS_4$, VI); tetrakis(2,6-difluoro-3-sulfonatophenyl)porphine, VII; tetrakis(2,6-dichloro-3-sulfonatophenyl)porphine, VIII; tetrakis(2-chloro-3-sulfonatophenyl)porphine, IX; tetrakis(4-methyl-3-sulfonatophenyl)porphine, X; tetrakis(4-fluoro-3-sulfonatophenyl)porphine, XI; tetrakis(4-methoxy-3-sulfonatophenyl)porphine, XII; beta(octabromo)-tetrakis(4-sulfonatophenyl)porphine, XIII; and 2,4-disulfonatodeuteroporphyrin IX dimethyl ester, XIV—were prepared, purified and analyzed as previously described.[5,9]

Spectral measurements were performed on Nicolet 9420 and Varian 2200 UV/vis spectrophotometers and the light-scattering measurements were conducted on a SPEX F111 spectrofluorimeter employing a synchronous-scan protocol and right-angle geometry.[7]

Results and Discussion

Absorption and resonance light-scattering experiments were conducted for all of the species I–XIV in acidic media at a porphyrin concentration of 1–5 μ M. The solution conditions were adjusted with HCl and NaCl (where needed): (i) pH = 1.2, I = 0.1 M; (ii) pH = 3.0, I = 0.001 M; (iii) pH = 3.0, I = 0.1 M. We begin with the results obtained for species I and II, the two porphyrins first reported as showing anomalous behavior in aqueous acid solution.[3,4] The absorption spectra for these two porphyrins at pH = 1.2 are shown in Figure 1. Their Soret bands are at 434 nm (as contrasted to a λ_{max} of 414 nm for the free-base forms) but notice should be taken of a second feature, much more prominent for II than I, at about 489 nm. This band first attracted our attention some years ago when we tentatively assigned it to porphyrin diacid aggregates.[3,4] Consistent with this interpretation are the resonance light-scattering results also shown in Figure 1. The profiles are dominated by the long wavelength feature even for I for which the absorbance at 489 nm is only about 1% that of the 434-nm band, demonstrating the sensitivity of this method for the detection of extended chromophore aggregates. The light-scattering profiles for these porphyrins also show a detectable dip at about 434 nm (more obvious for I than II) consistent with the absorbing form at this wavelength being either a monomer or a small aggregate. These resonance light-scattering results are completely consistent with our previous assignments and more recent reports;[3–6] the prominent feature at ~490 nm is, from our interpretation of resonance light-scattering, due to an extended aggregate of electronically coupled porphyrins. When conditions ii or iii above are applied to I, no band is observed at 489 nm and no enhanced light-scattering is obtained, underscoring the importance of proton concentration to this aggregation phenomenon. However, whereas II shows no evidence for extended aggregates under condition ii, an absorption band and enhanced scattering at 489 nm is obtained at pH = 3.0 and I = 0.1 M (NaCl). As reported earlier,[3] electrolyte effects can contribute significantly to the aggregation process.

When the central nitrogens of I or II are not available for protonation, no extended aggregates form. Thus, when V, the copper(II) derivative of I is considered, the Soret maximum is at 412 nm at all pH's studied between 1 and 6 with no additional spectral features appearing near 490 nm; the light-scattering shows no evidence for extended aggregates (Figure 2).

None of the species VI–XII show any unusual spectral features in the Soret region other than small shifts in the position of the band and changes in intensity as would be expected for acid–base and/or monomer–small aggregate equilibria. No enhanced scattering is observed for any of these porphyrins at low pH. Porphyrin XIV shows a rather dramatic change in its Soret absorption band at pH 1.2 as compared to pH 3.0 as shown in Figure 3. The pH = 3.0 spectra show a rather broad band centered at about 380 nm, the position and intensity of which are independent of ionic strength. However, when the pH is lowered

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(2) Hambright, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 6.

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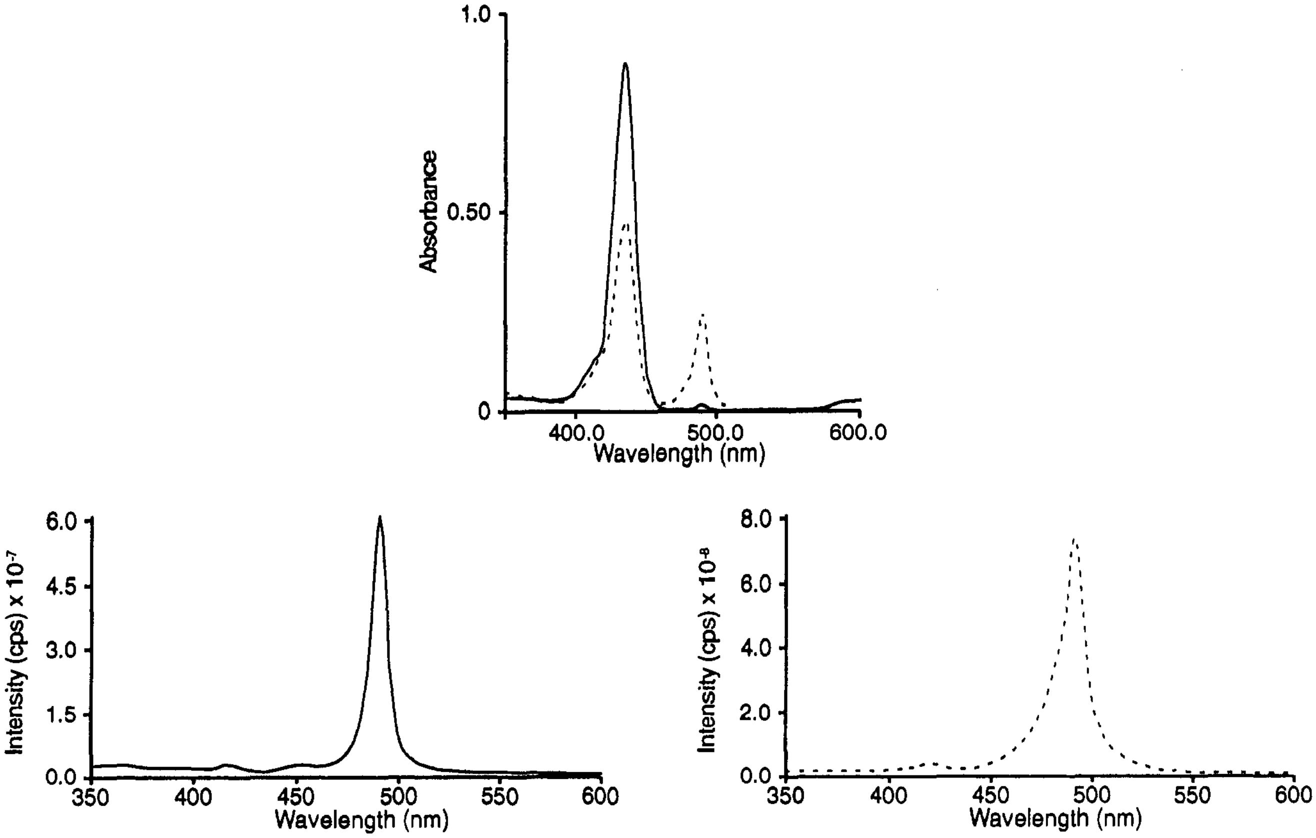

Figure 1. Absorbance and resonance light-scattering results for H_2TPPS_4 and H_2TPPS_3 at pH = 1.2, I = 0.1 M. Top: Absorption spectra for H_2TPPS_4 (—) and H_2TPPS_3 (- - -). Lower left: Resonance light-scattering profile for H_2TPPS_4. Lower right: Resonance light-scattering profile for H_2TPPS_3.

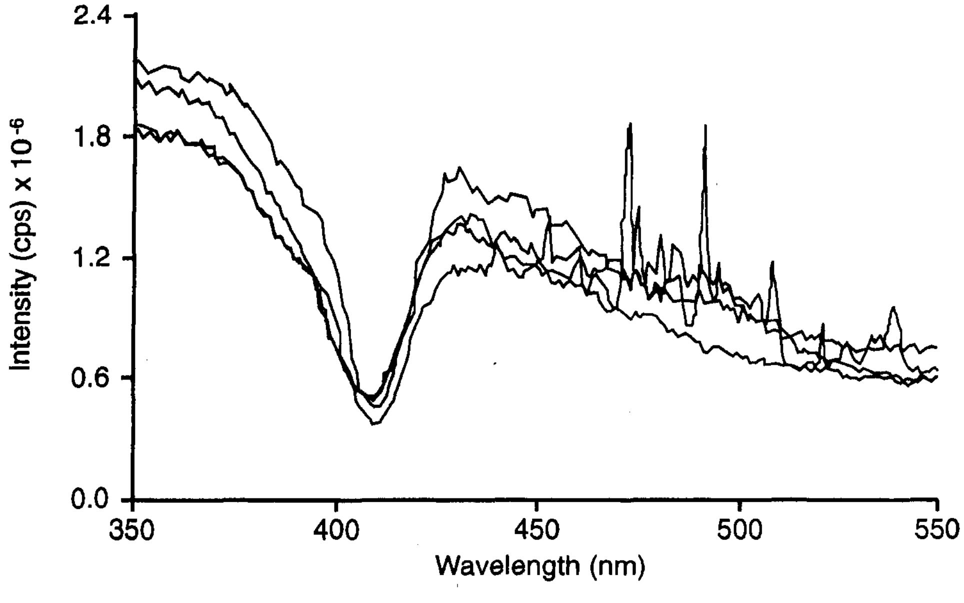

Figure 2. Resonance light-scattering profiles for $CuTPPS_4$ under all conditions investigated (see text).

to 1.2, a new, sharp band appears at 408 nm. This new band is shown *not* to be due to extended-aggregate formation; it does not produce an *enhanced* light-scattering feature (Figure 3). Indeed, the acid–base properties of this porphyrin differ from those of most *meso*-substituted porphyrins in that a stable monoacid form can be detected over a relatively extended pH range.[10] The value of pK_3 was determined as 4.2,[9] and pK_4, for the equilibrium between the mono- and diacid forms, is 0.3.[10] The spectral feature at 408 nm arises not from the formation of an aggregate but from the conversion of monoacid to diacid as the pH is lowered.

All of the species **III**, **IV**, and **XIII** show evidence for the formation of large aggregates under certain of the experimental conditions considered here. As demonstrated for *cationic* porphyrins based upon *N*-methylpyridyl peripheries, the 2:2 derivatives and, in particular, the trans isomer show a much greater tendency to aggregate in aqueous solution than do the 3:1 (charged to uncharged substituent) or 4:0 species.[5,11,12] Figure 4 shows

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[10] Neuberger, A.; Scott, J. J. *Proc. R. Soc. London* **1952**, *A213*, 307; Walter, R. I. *J. Am. Chem. Soc.* **1953**, *75*, 3860. Scott, J. J. *J. Am. Chem. Soc.* **1955**, *77*, 325.

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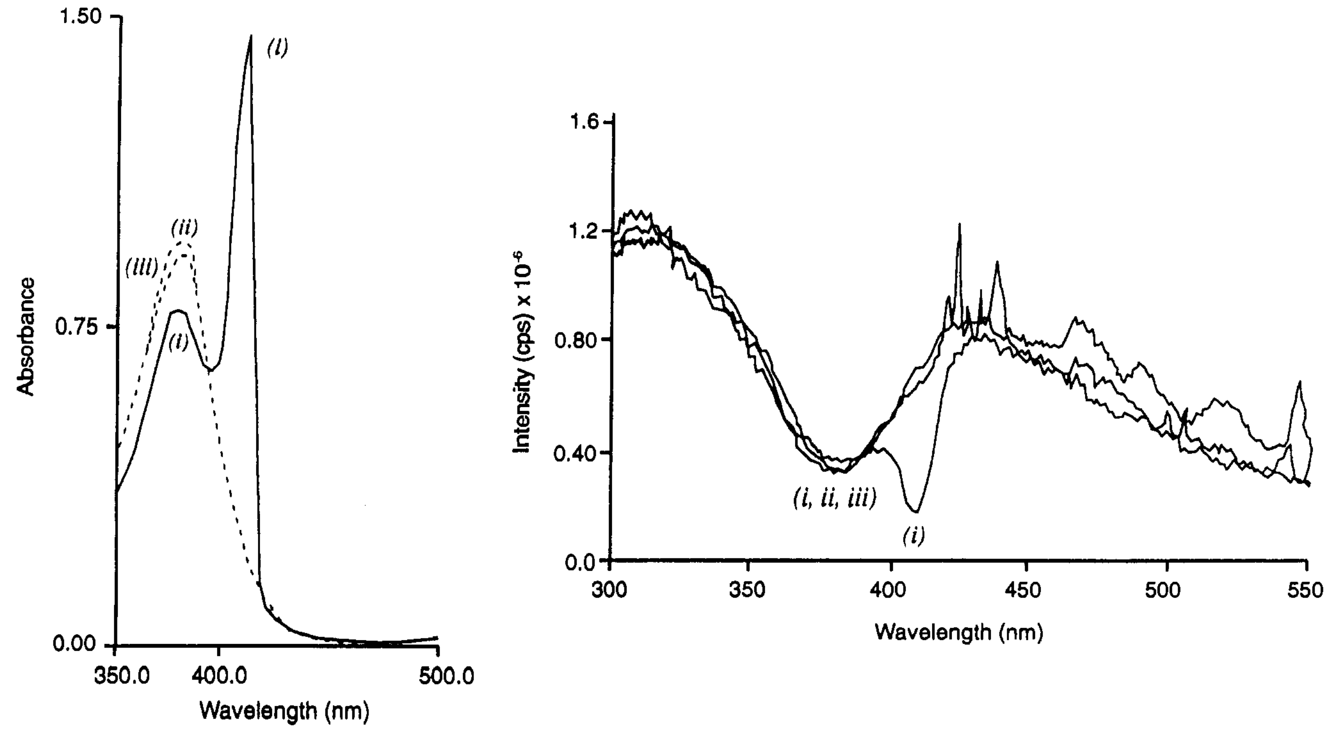

Figure 3. Absorption spectra and resonance light-scattering profiles for 2,4-disulfonatodeuteroporphyrin IX dimethyl ester under conditions defined in the text.

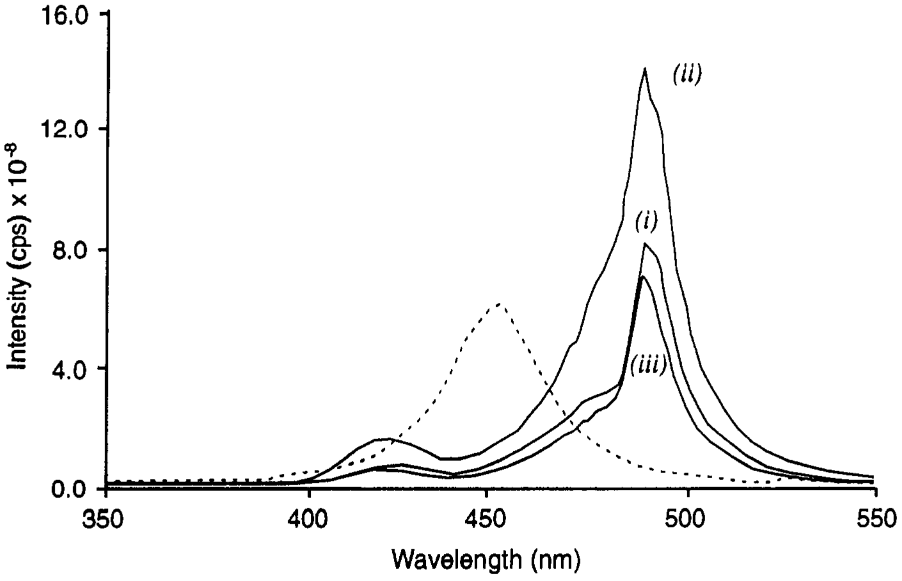

Figure 4. Resonance light-scattering profiles for t-H_2TPPS_2 at (—) conditions defined in the text and (- - -) at pH = 6.0, I = 0.1 M where the porphyrin exists in its free-base form.

the light-scattering results for t-H_2TPPS_2 under each of the various sets of conditions described above and, in addition, also at pH = 6 and I = 0.1 M. The monomer Soret maximum is at 413 nm for the free-base form stable in basic media; in the absence of NaCl, no additional spectral feature of Soret intensity is observed and no enhanced light scattering is obtained. However, at I = 0.1 M, a new band is observed at 450 nm and a large light-scattering feature is seen. In acidic media where the diacid is stable, the aggregate has a Soret maximum at 488 nm, and as shown in Figure 4, it produces enhanced resonance light-scattering.

Finally, species **XIII** (the β-octabromo derivative) has its Soret band at 478 nm in basic media and at 490 nm in acid. The position and intensity of the Soret is identical at pH = 3.0 regardless of whether the ionic strength is 0.001 or 0.1 M (see Figure 5). However at pH = 1.2, a new, sharp band appears at 521 nm, and under these conditions, a light-scattering profile characteristic of an extended aggregate is obtained near this wavelength.

In summary, we have confirmed the existence of extended porphyrin aggregates under certain conditions of concentration, pH and ionic strength. The position and nature of the peripheral substituents on the porphine core play a key role in determining which of these sulfonated porphyrins form such aggregates. In the course of these studies we have further demonstrated the utility of resonance light-scattering[7] as a sensitive and selective probe of extended porphyrin aggregation. In complex mixtures in which absorption spectra show contributions from a variety of species, the resonance light-scattering spectrum is simple, showing

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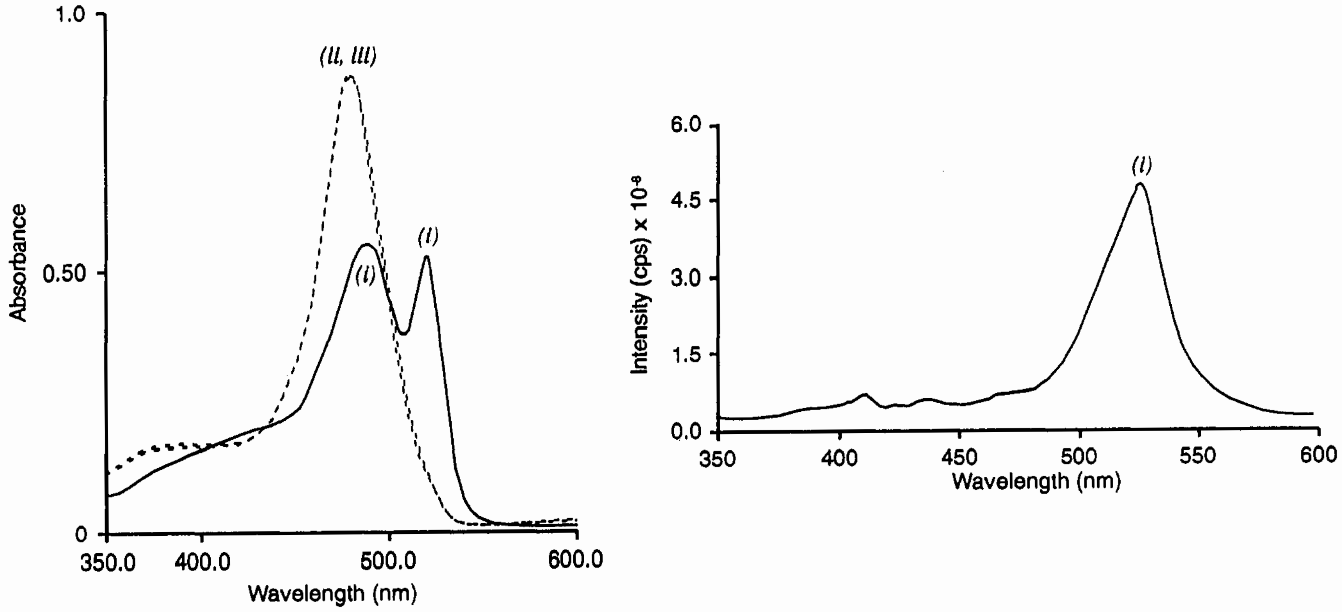

Figure 5. Left: Absorption spectra of β-octabromotetrakis(4-sulfonatophenyl)porphine under conditions defined in the text. Right: Resonance light-scattering profile for this porphyrin at pH = 1.2, I = 0.1 M.

features from large aggregates only. The technique thus lends itself to analytical investigations involving such chromophore arrays because of its sensitivity; it compares a high intensity signal against a "dark" reference.

The present work adds to our investigations elucidating the usefulness of this approach to porphyrin and metalloporphyrin[7] aggregates as well as to extended chlorophyll arrays.[13] Resonance light-scattering shows great promise as a fundamental tool to probe light-harvesting assemblies of both natural and synthetic types.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (CHEM-8915264), the Howard Hughes Medical Institute, and the Wolfson Fund.

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