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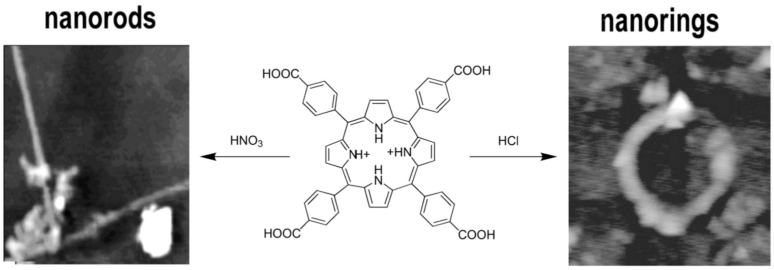

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Counterion Dependent Dye Aggregates: Nanorods and Nanorings of Tetra(*p*-carboxyphenyl)porphyrin

Stephanie C. Doan,[†,§] Saravanarajan Shanmugham,[‡] D. Eric Aston,[‡] and
Jeanne L. McHale*,[||]

Contribution from the Department of Chemistry, P.O. Box 442343, and Department of Chemical Engineering, P.O. Box 441021, University of Idaho, Moscow, Idaho 83844

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Abstract: Atomic force microscopy (AFM) of porphyrin aggregates formed on silica from acidic aqueous solution is used to investigate the basis for the previously reported counterion dependence of the optical spectra of aggregates of H_2TCPP^{2+}, the diacid form of tetra(*p*-carboxyphenyl)porphyrin (TCPP). Resonance light scattering confirms the presence of excitonically coupled porphyrin aggregates in solutions of H_2TCPP^{2+} in both aqueous HCl and HNO_3. Aggregates formed in aqueous HNO_3 solutions show resonance light scattering (RLS) at wavelengths within both the H and J aggregate absorption bands and are imaged on the surface of silica as nanorods about 3 to 4 nm in height. H_2TCPP^{2+} aggregates in aqueous HCl solution exhibit RLS when excited within the blue-shifted Soret band (H band) and produce AFM images on silica of ring-shaped structures ranging from about 200 to 2000 nm in diameter. Fluorescence excitation and emission spectra reveal quenching of the Q-band emission in the aggregates at a pH less than 1 and confirm the existence of a single species, assigned to a dimer, at a pH just above 1. The morphology of the nanostructures as revealed by AFM provides insight into the structural basis for the counterion-dependent optical properties of H_2TCPP^{2+} aggregates.

Introduction

Excitonically coupled aggregates of dye molecules are of interest for their unique optical and electronic properties.[1] In these systems, coupling of strong transition dipoles can lead to dramatic perturbations of the electronic absorption spectrum while preserving the basic structure of the monomer units.[2] Porphyrins in particular are well-known for their tendency to aggregate in aqueous solution, resulting in perturbations to their electronic absorption spectra.[3] In nature, assemblies of porphyrin derivatives are exploited by photosynthetic plants and organisms for their light-harvesting capabilities.[4] Among in vitro systems, the aggregation properties of tetra(*p*-sulfonatophenyl)porphyrin (TSPP) have been widely reported.[5−11] In aqueous solutions of the diacid H_2TSPP^{2-} at low pH and/or high ionic strength, the Soret band is split into a red-shifted and exchange-narrowed J band and a weaker and broader blue-shifted H band. Exciton theory attributes the J and H bands to coupling of the split Soret band transition moments which are respectively parallel and perpendicular to the aggregate chain, and numerous reports of resonance light scattering,[8] resonance Raman spectroscopy,[9,10] and ultrafast spectroscopy[11] have been presented. Recent atomic force microscopy (AFM) experiments have imaged H_2TSPP^{2-} aggregates as rod-shaped structures, or bundles thereof, which are about 4 nm in diameter and greater than 700 nm in length.[12] Another AFM study found similar structures, which were speculated to result from ring-shaped structures stacking to form a flattened tube on a silicon substrate.[13] Using light scattering techniques, Micali et al. concluded that the mesoscopic structure of H_2TSPP^{2-} aggregates exhibits a fractal nature.[14] The primary structure of the aggregate is presumed to be a slipped stack of parallel porphyrin rings which permits favorable Coulombic interactions between the positive charges localized at the porphyrin core and negative charges carried by the peripheral sulfonato groups.

Relatively few reports of aggregates of tetra(*p*-carboxyphenyl)porphyrin (TCPP) have appeared in the literature. Akins

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[†] Department of Chemistry, University of Idaho.

[‡] Department of Chemical Engineering, University of Idaho.

[§] Present address: Department of Chemistry and Biochemistry, Box 951569, University of California, Los Angeles, CA 90095.

[||] Present address: Department of Chemistry, Box 644630, Washington State University, Pullman, WA 99164.

(1) Bohn, P. W. *Annu. Rev. Phys. Chem.* **1993**, *44*, 37−60.
(2) Knapp, E. W. *Chem. Phys.* **1984**, *85*, 73−82.
(3) White, W. I. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. V.
(4) Hu, X.; Schulten, K. *Physics Today* **1997**, *50* (8), 28−34.
(5) Kano, H.; Kobayashi, T. *J. Chem. Phys.* **2001**, *116*, 184−195.
(6) Maiti, N. C.; Ravikanth, M.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem.* **1995**, *99*, 17192−17197.
(7) Maiti, N. C.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem. B* **1998**, *102*, 1528−1538.
(8) Collings, P. J.; Gibbs, E. J.; Starr, T. E.; Vafek, O.; Yee, C.; Pomerance, L. A.; Pasternack, R. F. *J. Phys. Chem. B* **1999**, *103*, 8474−8481.
(9) Guo, C.; Ren, B.; Akins, D. L. *J. Phys. Chem. B* **1998**, *102*, 8751−8756.
(10) Chen, D.-M.; He, T.; Cong, D.-F.; Zhang, Y.-H.; Liu, F.-C. *J. Phys. Chem. A* **2001**, *105*, 3981−3988.
(11) Kano, H.; Saito, T.; Kobayashi, T. *J. Phys. Chem. A* **2002**, *106*, 3445−3453.
(12) Schwab, A. D.; Smith, D. E.; Rich, C. S.; Young, E. R.; Smith, W. F.; de Paula, J. C. *J. Phys. Chem. B* **2003**, *107*, 11339−11345.
(13) Rotomskis, R.; Augulis, R.; Snitka, V.; Valiokas, R.; Liedberg, B. *J. Phys. Chem. B* **2004**, *108*, 2833−2838.
(14) Micali, N.; Mallamace, F.; Romeo, A.; Purrello, R.; Scolaro, L. M. *J. Phys. Chem. B* **2000**, *104*, 5897−5904.

10.1021/ja0430651 CCC: $30.25 © 2005 American Chemical Society

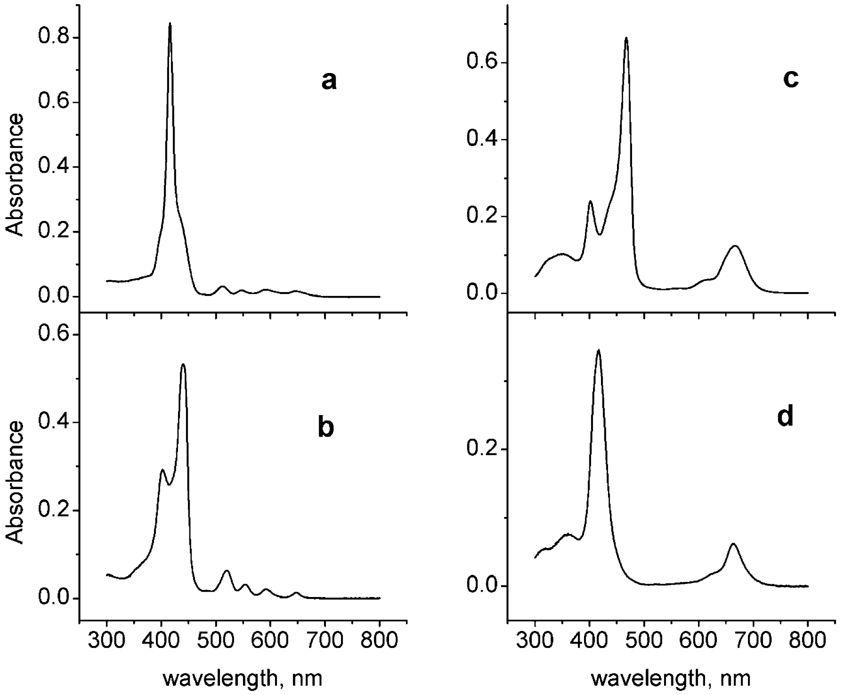

Figure 1. Absorption spectra of 5×10^{-6} M TCPP in (a) ethanol, (b) aqueous HCl at pH 1.2, (c) aqueous HNO_3 at pH 0.8, and (d) aqueous HCl at pH 0.8.

et al. reported signatures of aggregate formation in the resonance Raman spectrum of TCPP dissolved in trifluoroacetic acid, in the form of enhanced low-frequency features.[15] Gong et al. used dynamic light scattering to deduce the existence of nanoparticles in solutions of H_2TCPP^{2+} and other tetraphenyl porphyrin derivatives in a mixed solvent containing poly(ethylene glycol) as a stabilizer.[16] The related uroporphyrins, with eight carboxylic acid substituents, have been reported to form aggregates, or perhaps dimers, driven by π-stacking.[17] We recently reported aggregation of TCPP in acidic aqueous solutions of HCl and HNO_3.[18] At a pH of less than about 5, the expected form of TCPP is the cationic diacid H_2TCPP^{2+}. At a pH just above 1, the Soret band is split and the aggregated species is assigned to a dimer in which the two porphyrin rings are mutually perpendicular.[18] At still lower pH (~0.8−0.9), the optical spectrum is dependent on the counterion and was assigned to excitonically coupled aggregates. Though the optical spectra of the dimer and counterion-dependent aggregated forms of H_2TCPP^{2+} are quite different, resonance Raman spectroscopy revealed similar peak frequencies and thus little perturbation to the ground state electronic structures as compared to the monomer diacid, which is observed in acidic nonaqueous (ethanolic) solution. Unlike its sulfonato analogue, the protonated form of TCPP is kinetically unstable to precipitation in acidic aqueous solution; however, aggregates of H_2TCPP^{2+} can be kept in solution for several hours in the presence of poly(vinyl alcohol). Given that the electronic absorption spectrum of the aggregates is different in aqueous HCl and HNO_3 solutions, it was desired to obtain images of these aggregates deposited on a substrate in order to better understand the microscopic basis for the counterion-dependent spectra.

Figure 1 compares the absorption spectrum of TCPP in ethanol to that of the aggregates formed in aqueous HCl and HNO_3 solutions, at pH values slightly less than one. The electronic absorption spectrum of the diacid in ethanol was found to be the same in solutions containing nitric acid and hydrochloric acid. Also shown in Figure 1 is the absorption spectrum of aqueous TCPP at a pH slightly higher than 1, attributed to a dimer. The optical spectrum of the dimer, which is independent of counterion, and of the aggregates which form in HCl and HNO_3, were explained by considering excitonic coupling of the x and y components of the Soret band transition moments in the postulated structures.[18] A stacking pattern of parallel planes in which the porphyrin centers are superimposed could explain the existence of only the blue-shifted H band in HCl solution, while a slipped chain, similar to that for aggregates of H_2TSPP^{2-}, might account for the observed H and J bands in HNO_3 solution. We speculated that the dimer adopts a perpendicular configuration held together by hydrogen bonding between the protonated pyrroles and the carboxylic acid functions. This speculation was based on the existence of four Q-bands in the absorption spectrum of the putative dimer, suggestive of 2-fold symmetry of the macrocycle core, in contrast to the 4-fold symmetry expected for the diacid monomer. We could not, however, completely rule out the possibility that the features observed at a pH just above 1 resulted from overlapping spectra of different species, such as monomer and aggregate, rather than from a single dimer species.

In the present paper, we report studies of TCPP aggregates using fluorescence spectroscopy and resonance light scattering, to further investigate the possibility of coexisting forms and their state of aggregation at pH values just above and just below one. The fluorescence excitation spectrum of aqueous TCPP above pH 1 is presented as evidence for a single species,

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(15) Akins, D. L.; Zhu, H.-R.; Guo, C. *J. Phys. Chem.* **1996**, *100*, 5420−5425.
(16) Gong, X.; Milic, T.; Xu, C.; Batteas, J. D.; Drain, C. M. *J. Am. Chem. Soc.* **2002**, *124*, 14290−14291.
(17) Shelnutt, J. A.; Dobry, M. M.; Satterlee, J. D. *J. Phys. Chem.* **1984**, *88*, 4980−4987.
(18) Choi, M. Y.; Pollard, J. A.; Webb, M. A.; McHale, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 810−820.

assigned to a dimer. In solutions below pH 1, weak Q-band emission appears to result from residual monomer, and emission excited at wavelengths within the aggregate absorption bands is apparently quenched. Finally, we show AFM images of TCPP aggregates adsorbed on silica from aqueous solutions of HNO_3 and HCl, confirming the existence of distinctly different nanostructures in the presence of nitrate and chloride ions. Structures observed in the AFM images are correlated with the observed differences in the optical spectra.

Experimental Section

Tetra(*p*-carboxyphenyl)porphyrin (TCPP) was purchased from Porphyrin Products, Inc., (Logan, Utah) and used as received. Aqueous solutions of TCPP were initially prepared in 0.01 M NaOH dissolved in deionized water and then acidified using a buffer solution of the desired pH and stabilized by the addition of a saturated (1.4 mg/100 mL) solution of poly(vinyl alcohol) (PVA). PVA with a molecular weight in the range 30 000−70 000 was purchased from Sigma Aldrich. Buffer solutions of pH 0.8 contained either 0.27 M HCl and 0.10 M KCl, for the chloride aggregate, or 0.5 M HNO_3 and 0.25 M KNO_3, for the nitrate aggregate.

Electronic absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer using porphyrin concentrations of 5×10^{-6} M and 1-cm path length quartz cuvettes, using the appropriate aqueous buffer solutions in the reference cell. Resonance light scattering (RLS) and fluorescence excitation and emission spectra were measured for porphyrin concentrations of 8×10^{-7} M using a PTI QM-4/2003 fluorimeter and were corrected for instrument response. RLS spectra were obtained on the same instrument by synchronously scanning the excitation and emission wavelengths. AFM images were obtained using a Nano-R atomic force microscope from Pacific Nanotechnology, Inc., with digital pulsed force mode (WITec, Germany) using Arrow FM cantilevers obtained from Nanoworld. For AFM sample preparation, silica substrates were cleaned with methanol and then soaked for 2 to 6 min in acidic aqueous solutions of 5×10^{-5} M TCPP. To avoid interference from salt crystals and PVA, these solutions were devoid of buffer and stabilizer, permitting only short soaking times. Longer soaking times resulted in AFM images that showed flocculated aggregates and no details of aggregate shape.

Results

Resonance Light Scattering. The existence of an excitonically coupled (delocalized) electronic transition is revealed by strong resonance light scattering (RLS) signals which are slightly red-shifted from the absorption band.[19] We previously reported RLS of TCPP in aqueous HCl and HNO_3 at wavelengths expected for an excitonically coupled Soret band.[18] In the present study, the RLS spectra were re-examined at a wider range of wavelengths with more sensitivity and were corrected for the response function of the fluorimeter. Figure 2 compares the RLS spectra of H_2TCPP^{2+} in HCl and HNO_3 at a pH just below 1 to those at a pH slightly above 1, where the dimer is presumed to exist. While little RLS signal is observed for the latter solutions, the lower pH solutions reveal significant scattering and close correlation between the peaks in the RLS and absorption spectra. The results shown in Figure 2 confirm the existence of excitonically coupled transitions in both HNO_3 and HCl solutions at pH 0.8. The stronger RLS signal associated with the J band in the HNO_3 aggregate appears to correlate with the previously reported exchange narrowing of this band, which suggests that the J-band excited state is delocalized over about four molecules. The H band transitions of the HNO_3 aggregate and the (single) H band transition of the HCl aggregate do not appear to be exchange narrowed, a feature which correlates with weaker RLS intensity associated with these transitions. The RLS spectra shown in Figure 2 are sharper than the previously reported spectra,[18] which may have exhibited nonresonance light scattering from larger aggregates, since slightly more concentrated porphyrin solutions were used in the previous study. The strength of RLS from solutions at a pH higher than 1 was negligible compared to that observed at lower pH. Note that modest RLS intensity is observed in the vicinity of the Q-band (at about 670 nm) in the case of the aggregate in HNO_3. The intensity of the Q-bands in the absorption spectra of H_2TCPP^{2+} aggregates increases relative to the monomer. These aggregation-induced perturbations to the Q-band suggest that simple first-order perturbation theory, which considers only coupling of like transition moments, may be inadequate in this system.

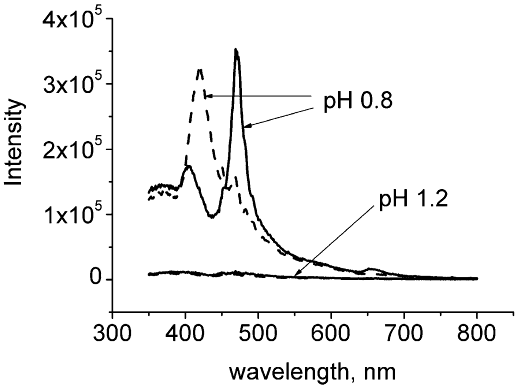

Figure 2. Resonance light scattering spectra of TCPP in aqueous HNO_3 (solid lines) and HCl (dashed lines). The data for the two solutions at pH 1.2 are nearly coincident.

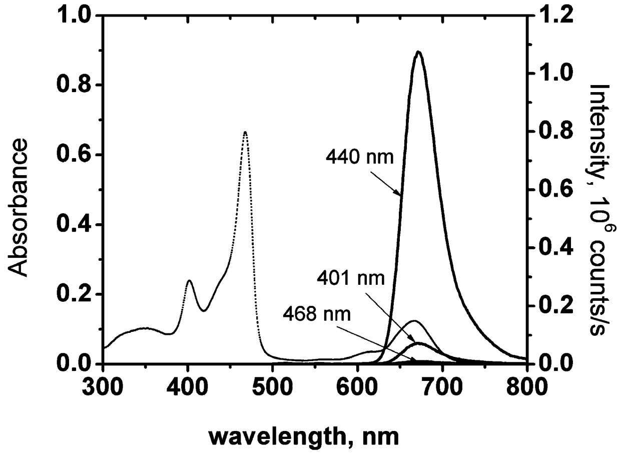

Figure 3. Absorption (dashed line, left-hand scale) and emission (solid lines, right-hand scale) of TCPP in aqueous HNO_3 at pH 0.8. Labels indicate the excitation wavelengths for the emission spectra. The concentration of porphyrin for the absorption spectrum was 5×10^{-6} M, and that for the emission spectra was 8×10^{-7} M.

Fluorescence Spectroscopy. The close proximity of chromophores in dye aggregates can promote nonradiative decay and thus frequently results in fluorescence quenching. Figure 3 shows the absorption spectrum of the aggregate in aqueous HNO_3 at pH 0.8 along with the emission spectra excited at three wavelengths. The strongest emission is obtained when exciting at 440 nm, which is the maximum of the Soret band of the monomer diacid in ethanol. When the emission is excited at

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(19) Kano, K.; Fukuda, K.; Wakami, H.; Nishiyabu, R.; Pasternack, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 7494−7502.

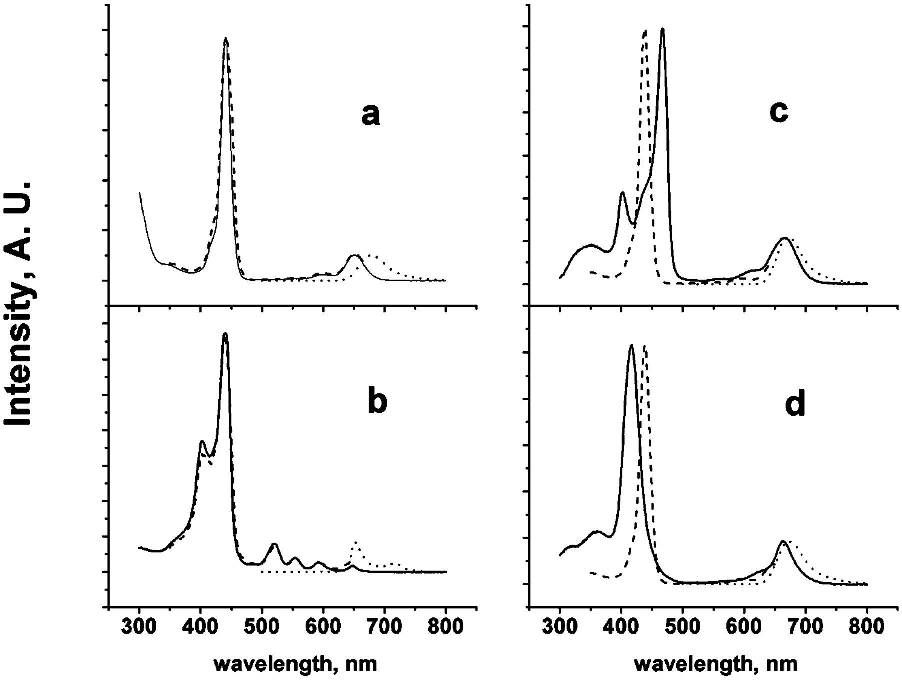

Figure 4. Absorption (solid line), excitation (dashed line), and emission (dotted line) spectra of 8 × 10^{-7} M TCPP. In all cases the excitation spectrum was detected at 670 nm. (a) In ethanol with 0.158 M HNO_3, emission excited at 440 nm; (b) in water at pH 1.2, emission excited at 440 nm; (c) in aqueous HNO_3 at pH 0.8, emission excited at 468 nm; and (d) in aqueous HCl at pH 0.8, emission excited at 417 nm.

401 nm, assigned to the H band of the aggregate, weaker emission is observed, and an even smaller signal is found when exciting at the wavelength of the J band at 468 nm. It is possible that some of the residual fluorescence, especially in the case of H band excitation, results from overlap in the monomer and aggregate absorption bands. Figure 3 suggests that the shoulder in the absorption spectrum at about 440 nm results from residual diacid monomer and that fluorescence is strongly quenched in the aggregate.

Figure 4 compares the absorption, excitation, and emission spectra of H_2TCPP^{2+} monomer in ethanol, the dimer in water at pH 1.2, and the aggregates in HNO_3 and HCl at pH 0.8. In the case of the monomer and aggregate solutions, emission maxima at 670 nm and excitation maxima at 440 nm are observed. For the monomer in ethanol, the excitation spectrum follows the absorption spectrum, whereas the aggregate excitation spectra are quite different from the corresponding absorption spectra. The resemblance of the aggregate excitation spectra to the absorption spectrum of the monomer diacid provides further evidence that the observed fluorescence in these samples results from residual H_2TCPP^{2+} monomer in equilibrium with the aggregate. The putative dimer, on the other hand, has an excitation spectrum which is very similar to its absorption spectrum, suggesting that a single species contributes to the split Soret and Q-bands in the absorption spectrum at pH 1.2. The Soret band splitting has been rationalized by postulating a dimer structure in which the two porphyrin planes are mutually perpendicular.[18] In this picture, excitonic coupling leads to a split Soret band in which one component is coincident with the monomer Soret band and the other is blue-shifted in agreement with experiment. The Q-band is also split into Q_x and Q_y components in the dimer as a result of symmetry-lowering perturbations to the porphyrin core. Consistent with Kasha's rule, the emission of the dimer is attributed to the lower energy component of the Q-band, and the approximately 1500 cm^{-1} splitting of the two peaks in the emission spectrum, assigned to the 0−0 and 0−1 vibronic components, agrees well with the separation of the two longest wavelength Q-bands in the absorption spectrum.

Atomic Force Microscopy. AFM images of H_2TCPP^{2+} nanoparticles deposited on silica from aqueous HNO_3 and HCl are shown in Figures 5 and 6, respectively. Line analysis of a nanorod from aqueous HNO_3, shown in Figure 5, reveals nanorod heights of about 3 to 4 nm. While amorphous structures are observed in both images, nanorod structures of the type shown in Figure 5 were observed in a number of samples formed from nitric acid solutions, while the nanorings apparent in Figure 6 were found only when samples were deposited from aqueous HCl. It was observed that the aggregates in HNO_3 were less kinetically stable than those in HCl. Thus shorter soaking times were used and fewer aggregate structures observed in the case of HNO_3. The image shown in Figure 6, obtained from HCl solution, reveals a large number of rings and partial rings, along with a number of amorphous structures and one apparent stray nanorod. Line analysis of a ring found in an AFM image from HCl solution, shown in Figure 7, reveals a nanoring height of about 4 to 5 nm.

The height of the nanorods shown in Figure 5 are similar to the dimensions reported for H_2TSPP^{2-} aggregates, which form nanorods about 3.8 nm in diameter on mica, graphite, and polystyrene.[12] Greater accuracy in nanorod diameter estimates is not possible due to the physical deformation by the AFM probe as a ubiquitous source of error. The formation of nanorods of H_2TCPP^{2+} in nitric acid is consistent with our previously proposed model[18] in which the porphyrin diacid planes form a chain similar to a spread deck of cards, possibly with the planar nitrate ions intercalated between the porphyrins. The similarity of the optical spectrum of H_2TSPP^{2-} aggregates to that of H_2TCPP^{2+} aggregates in HNO_3 correlates well with the similarity of the corresponding AFM images. The somewhat smaller

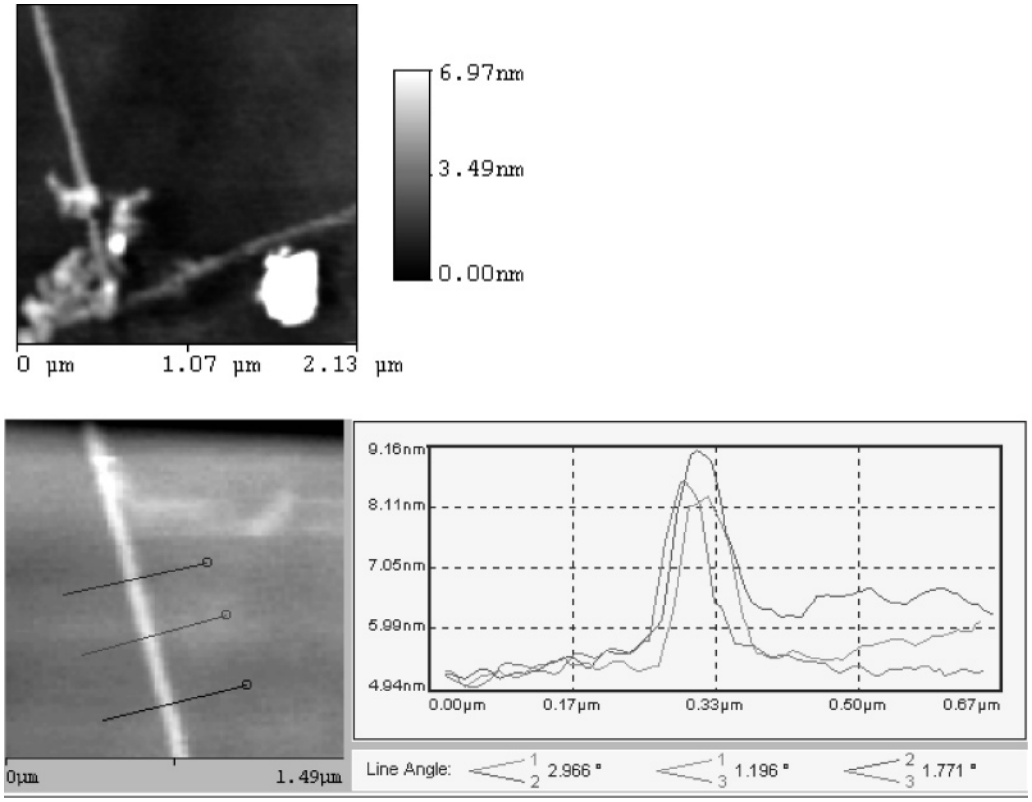

Figure 5. AFM image and line analysis of nanorods of H_2TCPP^{2+} deposited from aqueous HNO_3 on silica.

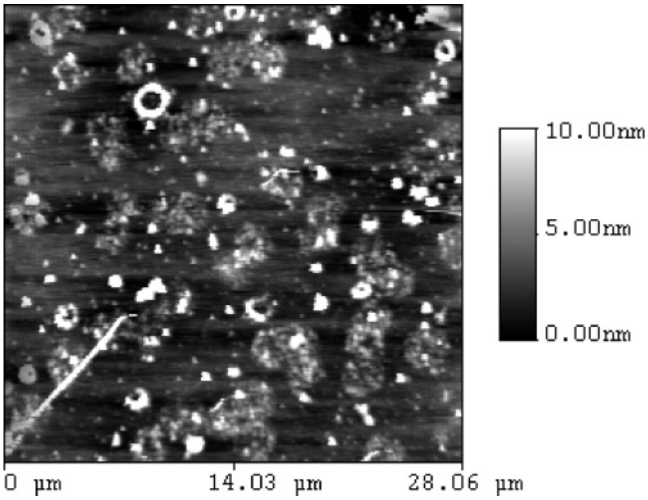

Figure 6. AFM image of H_2TCPP^{2+} deposited from aqueous HCl onto silica showing rings and partial rings of various diameter and height and an apparent lone nanorod.

coherence length in the case of H_2TCPP^{2+} in aqueous HNO_3, compared to the counterion-independent J aggregates of H_2TSPP^{2-}, correlates with less exchange narrowing, smaller red shift of the Soret band, and weaker resonance light scattering in the former. This smaller coherence length and larger interplanar separation, as calculated using simple exciton theory in ref 18, could conceivably result from intercalation of planar nitrate ions between porphyrins in the case of H_2TCPP^{2+}.

Aggregates of H_2TCPP^{2+} deposited from aqueous HCl, on the other hand, reveal ring-shaped structures as shown in Figure 6. The diameters of these nanorings were observed to range from about 200 to 2000 nm. Line analysis of the nanoring shown in Figure 7 reveals a height of about 4 to 5 nm. Line analysis of a variety of rings (not shown) range from about 2−4 nm to as much as ∼15 nm, suggesting a stacked coil of rings. This smallest height of the rings is on the order of the size of a H_2TCPP^{2+} molecule (TCPP itself is about 1.5 nm across[20]), suggesting that a single chain of porphyrins forms the ring, which is more likely to coil into a stack than end with a perfect closed circle.

We can now consider whether the structures observed using AFM are consistent with the optical spectra shown in Figure 1. For an exciton delocalized over N molecules, the excited electronic state is split into a band of states with quantum numbers $k = 1, 2... N$, for which the energies and transition strengths can be calculated from perturbation theory.[2] The transition-dipole coupling energy in the point-dipole approximation in wavenumber units is

$$V_{12} = \frac{\mu_{ge}^{2}}{hcr^{3}}[\hat{u}_1 \cdot \hat{u}_2 - 3(\hat{u}_1 \cdot \hat{r})(\hat{u}_2 \cdot \hat{r})] \tag{1}$$

where μ_{ge} is the transition dipole moment of the monomer (11.7 D for H_2TCPP^{2+}), $\hat{u}_1$ and $\hat{u}_2$ are unit vectors in the direction of the transition moments on nearest-neighbor molecules 1 and 2, r is the distance between them, and $\hat{r}$ is a unit vector pointing from molecule 1 to molecule 2. The Soret band consists of two in-plane polarized components for which the degeneracy is lifted in the aggregate, necessitating consideration of coupling between both components. In the case of a linear chain of molecules, the frequency and transition moments for the transition from the ground state to the k-th exciton state are

$$\nu_k(\text{linear}) = \nu_{\text{mono}} + 2V_{12}\cos\left(\frac{k\pi}{N+1}\right) \tag{2}$$

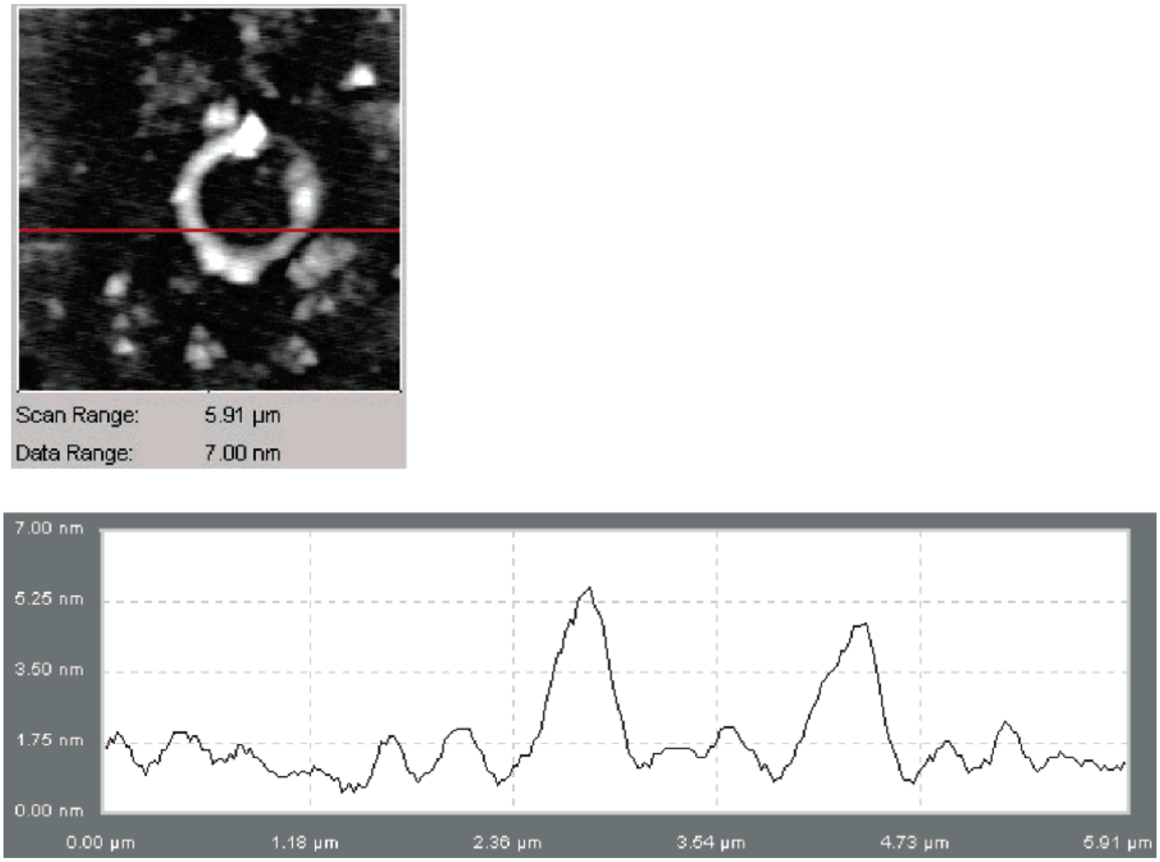

Figure 7. AFM image and line analysis of a nanoring of H_2TCPP^{2+} deposited from aqueous HCl onto silica.

and

$$\mu_{gk}(\text{linear}) = \mu_{ge}\sqrt{\frac{2}{N(N+1)}}\cot\left[\frac{k\pi}{2(N+1)}\right] \text{ for } k = 1,3,5.... \tag{3}$$

where transitions to even-k states are forbidden. Though transitions to all odd-k states are permitted, the bulk of the oscillator strength is carried by the transition to the $k = 1$ state. The application of this theory to the nitrate aggregate of H_2TCPP^{2+}, where $N = 4$, was discussed in ref 18. It was shown that the observed H and J bands are consistent with a slipped chain (spread deck of cards model) in which the distance between neighboring porphyrins is on the order of 0.8 nm and the vector $\hat{r}$ makes an angle of 42° with respect to the x-direction. In this geometry, coupling of the x-components of the transition dipoles leads to negative V_{12} and thus a red-shifted ("J band") transition, while the coupling of the y-components of μ_{ge}, which are perpendicular to the chain, results in positive V_{12} and a blue-shifted "H band." Thus the rod-shaped structures observed in the presence of nitrate ions are consistent with the observed splitting of the Soret band.

For a cyclic aggregate, Knapp[2] has shown that the energies of the exciton states are

$$\nu_k(\text{cyclic}) = \nu_{\text{mono}} + 2V_{12}\cos\left(\frac{2(k-1)\pi}{N}\right) \tag{4}$$

In the case of a cyclic aggregate only the $k = 1$ exciton carries oscillator strength, resulting in an aggregate transition shifted from that of the monomer by $2V_{12}$. Based on the observed blue shift of the Soret band (the H band) and the absence of a J band for the chloride aggregate of H_2TCPP^{2+}, we previously speculated that the porphyrin molecules in HCl solution stack in a column with their planes perpendicular to the aggregate chain.

In this assumed structure both the x and y transition moments are perpendicular to the aggregate chain, leading to a doubly degenerate blue-shifted Soret band in agreement with experiment. Using the observed monomer (440 nm) and chloride aggregate (417 nm) frequencies to estimate V_{12}, eq 1 results in an estimated interplanar separation of about 1 nm, enough space for chloride ions to intercalate between the planes.[18] On the other hand, the formation of a ring of stacked porphyrins requires a finite angle between adjacent porphyrin planes. Taking a 200-nm diameter ring as an example, about 600 molecules would be required to form a nanoring in which the porphyrin planes are aligned radially with a separation of 1 nm, resulting in an angle of only 0.6° between neighboring planes, i.e., a nearly parallel arrangement of neighboring planes. The angle between neighboring planes would be even less in the larger rings; accounting for the absence of a detectable J band in the chloride aggregate of H_2TCPP^{2+}. Thus both the closed rings and apparent spirals shown in Figure 6 are consistent with a stacking structure that results in a single blue-shifted Soret band in agreement with experiment.

Interestingly, quantum chemical calculations have been reported which support the close association of chloride counterions with the macrocycle core of the diacid of tetra-

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(20) Cherian, S.; Wamser, C. C. *J. Phys. Chem. B* **2000**, *104*, 3624−3629.

phenylporphyrin (H_2TPP^{2+}), and the fluorescence yields and lifetimes of H_2TPP^{2+} have been previously observed to depend on counterion.[21] Also, Rosa et al.[22] observed that the Soret band position of H_2TPP^{2+} in CH_2Cl_2 solution depends on counterion in the series F^-, Cl^-, Br^-, and I^-. In that study, in contrast to the present one, the Soret band of the diacid was red-shifted relative to the free base and the effect was not due to aggregation but rather due to close coupling of halide ions with the protonated porphyrin core. One can easily envision how loose association of chloride counterions with the porphyrin core could result in a somewhat random distribution of angles between adjacent planes and thus a range of nanoring diameters. Consequently, there would be a range of exciton splittings, perhaps contributing to the breadth of the H band in HCl solution, despite the evidence of coherence from the resonance light scattering spectrum.

Micrometer scale porphyrin “wheels” have been previously reported,[23−25] but appear to be of a different nature than those reported here. In these reports, the observed diameters of the porphyrin wheels ranged from about 10 nm to several μm, and the heights ranged from about 10 to 200 nm.[24] The wheels were formed from organic solvent and appear to depend on mass transport properties, where aggregates grow at the perimeters of bubbles or holes in the evaporating solution. In fact, it was remarked in ref 23 that wheels were *not* formed from solutions containing porphyrin aggregates. In the present work, some ring structures are observed with heights not much larger than the size of a single porphyrin molecule, and resonance light scattering confirms the existence of aggregates in the solutions from which the rings are deposited. Thus it appears that the nanorings reported here are fundamentally different from the previously reported porphyrin wheels.

Conclusions

In this work, the existence of counterion-dependent aggregates of H_2TCPP^{2+} in aqueous acidic solutions with a pH less than 1 is confirmed by resonance light scattering spectroscopy, which evidences some degree of excitonic coupling for both the H and J band transitions in aqueous HNO_3 and for the single H band transition in aqueous HCl. Fluoresence spectroscopy suggests that Q-band emission is quenched in the aggregates and that the split Soret and Q-bands in the absorption spectrum of the putative dimer at a pH just above 1 indeed derive from a single species.

The nanoparticles obtained from H_2TCPP^{2+} in aqueous HNO_3 solution were observed by AFM to have different structures than those formed from aqueous HCl. In the former case we observe nanorods which are microns in length and about 3−4 nm in height. The similarities in the optical properties of aggregates of H_2TCPP^{2+} in aqueous HNO_3 to those of the well-studied H_2TSPP^{2-} aggregates appear to correlate with the similar structures of these aggregates (nanorods) as revealed by atomic force miscroscopy. Aggregates of H_2TCPP^{2+} from aqueous HCl solution, on the other hand, form nanorings with a range of diameters and minimum heights which suggests that a stack of porphyrin planes can curl around to form a ring or coil with only a very small angle between adjacent planes, consistent with the observation of a single blue-shifted Soret band.

The structures observed in this work are reminiscent of similar aggregates found in nature, such as the rod- and ring-shaped porphyrin aggregates found in photosynthetic organisms. The bacteriochlorophylls present in the chlorosomes of green filamentous bacteria are arranged in rods, and their spectra reveal strong excitonic coupling.[26] It is interesting that the spectral features of these aggregates are preserved when they are extracted into various protein-free in vitro environments.[27] In purple bacteria, excitonically coupled bacteriochlorophyll molecules are arranged in rings.[28,29] Thus the existence of different excitonically coupled aggregates of the same chromophore is not unprecedented for natural porphyrin derivatives.

Interestingly, the AFM images of H_2TSPP^{2-} reported in ref 13 were interpreted to result from flattened tubes. The precursor to the tubes was believed to be a stack of rings about 20 nm in diameter, which flattens on the surface to give a bilayer structure about 4 nm high and 30−40 nm wide. It was speculated that each ring is in turn formed from a J aggregate chain of about 60−70 molecules. The overall observed structure of ref 13 is quite similar to what is seen in this work for the aggregates obtained from aqueous nitric acid solution, but the resolution of the images reported here does not permit us to determine whether the nanorods shown in Figure 5 are actually flattened nanotubes. The occurrence of a stray nanorod among a sea of nanorings, however, as observed in Figure 6, does support the idea that nanorods and nanorings can coexist.

The idea of counterion-dependent aggregates of porphyrins appears to be quite unusual. In contrast to H_2TSPP^{2-} aggregates which require positively charged counterions, i.e., protons, aggregates of H_2TCPP^{2+} require anionic counterions. Perhaps the closest to this report is a recent paper on the formation of J aggregates of a variety of substituted tetraphenylporphyrins (TCPP was not included) at an aqeuous−organic solvent interface, where aggregation was induced by sulfuric acid but *not* by nitric or hydrochloric acid.[30] Negative ions are well-known to perturb the solubilities of polyelectrolytes. We speculate whether the counterion effects reported here are tied to the empirical Hofmeister series, which is a ranking of anions based on their influence on protein solubility.[31] It is believed that the Hofmeister series is tied to effects of anions on water structure[32] or anion polarizability.[33] Interestingly, counterion effects on the formation of rod-shaped and spherical micelles of cationic surfactants have been reported.[34] The so-called structure-making anions enhance the structure of water and

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(21) Avilov, I. V.; Panarin, A. Yu.; Chirvony, V. S. *Chem. Phys. Lett*. **2004**, *389*, 352−358.

(22) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Romeo, A.; Scolaro, L. M. *J. Phys. Chem. A* **2003**, *107*, 11468−11482.

(23) Schenning, A. P. H. J.; Benneker, F. B. G.; Geurts, H. P. M.; Liu, X. Y.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1996**, *118*, 8549−8552.

(24) Hofkens, J.; Latterini, L.; Vanoppen, P.; Faes, H.; Jeuris, K.; De Feyter, S.; Kerimo, J.; Barbara, P. F.; De Schryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *J. Phys. Chem. B* **1997**, *101*, 10588−10598.

(25) Latterini, L.; Blossey, R.; Hofkens, J.; Vanoppen, P.; De Schryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *Langmuir* **1999**, *15*, 3582−3588.

(26) Olson, J. M. *Photochem. Photobiol*. **1998**, *67*, 61−75.

(27) Krasnovsky, A. A.; Bystrova, M. L. *BioSystems* **1980**, *12*, 181−194.

(28) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogde, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517−521.

(29) Trinkunas, G.; Herek, J. L.; Polivka, T.; Sundstrom, V.; Pullerits, T. *Phys. Rev. Lett.* **2001**, *86*, 4167−4170.

(30) Okada, S.; Segawa, H. *J. Am. Chem. Soc*. **2003**, *125*, 2792−2796.

(31) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. *Quart. Rev. Biophys.* **1997**, *30*, 241−277.

(32) Hribar, B.; Aouthall, N. T.; Vlachy, V.; Dill, K. A. *J. Am. Chem. Soc*. **2002**, *124*, 12302−12311.

(33) Bostrom, M.; Williams, D. R. M.; Ninham, B. W. *Curr. Opin. Colloids Interface Sci.* **2004**, *9*, 48−52.

(34) Magid, L. J.; Han, Z.; Warr, G. G.; Cassidy, M. A.; Bulter, P. D.; Hamilton, W. A. *J. Phys. Chem. B* **1997**, *101*, 7919−7927.

reduce the solubility of proteins, while the opposite is true for structure-breaking ions. The chloride ion is considered to be in the middle of the Hofmeister series, which ranges from structure-making (SO_4^-) to structure-breaking (ClO_4^-) anions, and the nitrate ion is considered somewhat more structure-breaking than chloride. The aggregation of H_2TCPP^{2+} appears to be driven by hydrophobic interactions, so it is possible that the counterion effects reported here are tied to their influence on water structure, but firm conclusions along these lines must await further studies of H_2TCPP^{2+} aggregates using additional counterions.

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