

Hierarchical Structure of TPPS₄ J-Aggregates on Substrate Revealed by Atomic Force Microscopy

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The spatial structure of the J-aggregates of *meso*-tetra(4-sulfonatophenyl)porphine (TPPS₄) formed in acidic aqueous solutions and coated on silicon substrates was analyzed by means of atomic force microscopy (AFM). The AFM experiments indicate the presence of the striplike J-aggregate structures on the surface. The size of the individual stripes ranged from $4.5 \times 40 \times 200$ to $4.5 \times 40 \times 1000$ nm³ (height \times width \times length). The length of the striplike structures varied, whereas stripe width and thickness remained unchanged. The stripes stacked into larger domains, “fibers”, containing typically 2–20 stripes aligned parallel with a longitudinal shift with respect to each other. The size of individual stripes remained the same when interacting side-by-side in fibers. At lower magnification it is clearly seen that fibers form a network-like structure. The J-aggregates assemble into large (up to several millimeters) bushlike structures. It takes several weeks to form such structures in acidic aqueous solutions. On the basis of our experimental findings, it is also suggested that the stripes consist of rings that form nanotube-like TPPS₄ J-aggregates, which are flattened as a result of attractive interactions with the substrate.

Introduction

The structural characteristics of molecular aggregates recently have attracted much scientific interest because of the special properties and possible technological applications of mesoscopic materials. Aggregation of porphyrins, for example, occurs spontaneously from monomers dispersed in a medium and can lead to controlled structures if the selective and directional noncovalent interactions are carefully controlled. Such aggregates could be considered as model structures for gaining insight into the roles of optically induced transient phenomena in photosynthesis. The realization of bio-organic devices with advanced functions requires molecular building blocks that are processable, meaning that it should be possible to deposit them, for example, onto a solid substrate using either wet or dry chemical methods. Molecules can be designed to form assemblies with predictable structures that display analogous properties to the complex molecular assemblies found in the nature. Some nice examples of such supramolecular assemblies are presented in the papers of Yokohama et al.¹ and Weiss.² The next step is to link these molecular assemblies to the outside world through microscopic structures created using standard nano- and microfabrication techniques and to add particular functions to the assembled molecules.

A variety of such self-assembled molecular aggregates adopt a structure that can be classified as being of J-type.³ It is well-known that *meso*-tetra(4-sulfonatophenyl)porphine (TPPS₄), a water-soluble dye of well-defined chemical structure (Figure 1), forms J-aggregates under appropriate conditions.^{4–13} It seems

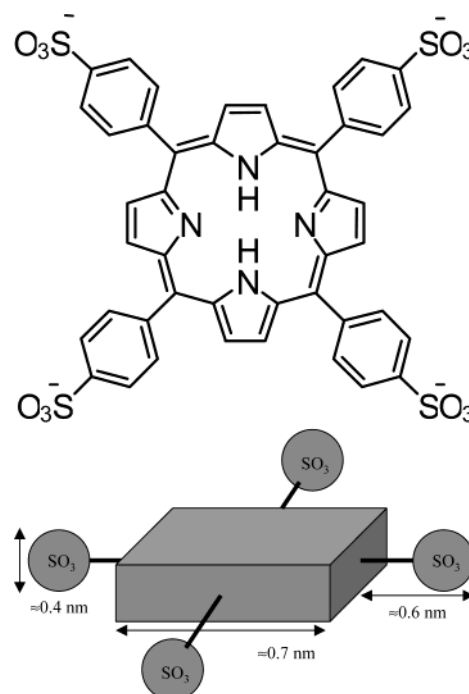


Figure 1. Structure of TPPS₄ at pH7. Data from ref 17.

that the negative charges on the sulfonato groups of monomeric TPPS₄ play a crucial role in the formation of J-aggregates and contribute to the overall stability of the formed structures.^{10–12,14} The structure of the J-aggregates of TPPS₄, has been shown to consist of in-line homoassociated arrays originating from the

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intermolecular association between the positively charged porphyrin ring and the negatively charged sulfonato groups.^{6,8,10,14,17} Such aggregates, presumably, would form one-dimensional structures, for example, zigzag or "spread deck of cards" conformations.¹² Since the first studies on the formation of J-aggregates were reported,^{4,5} a number of investigations have been performed by means of linear and nonlinear electronic spectroscopy.^{6,8–11,13–15,24,29–31} Because of the polarization dependence on absorption, it could be stated that the absorption spectrum of the TPPS₄ aggregate originates from the transient dipole moments that are aligned parallel and perpendicular, respectively, to the aggregate axis (defined as the direction connecting the centers of neighboring molecules composing the aggregate).³⁰ This particular structure of the TPPS₄ aggregate has been discussed earlier.^{8,10,11}

Although much is known about the spectroscopic features and excitonic interactions in molecular aggregates, the mechanisms and conditions of aggregate formation and especially the geometrical structure are subjects of continuing interest.^{16,17,19,21,22,28} Moreover, the adsorption of such aggregated structures on solid surfaces^{1,23,28,32–35} is one of the fundamental processes to be studied for the development of molecular-based nanodevices. Therefore, we have explored the structure and the stability of self-assembled J-aggregates of TPPS₄ deposited on solid substrates using atomic force microscopy.

Materials and Methods

meso-Tetra(4-sulfonatophenyl)porphine tetrasodium salt was obtained from Porphyrin Products (Lugan, UT). The J-aggregate solutions were prepared by dissolving TPPS₄ in acidic aqueous medium (HCl was added to reach pH 1) in the concentration range from 1×10^{-4} to 2×10^{-6} M. J-aggregates of TPPS₄ form immediately in solution, whereas larger clusters require a few days of incubation. For that purpose the solutions were stored at room temperature for 10 days.

Glass and silicon were chosen as supporting substrates. Standard glass cover slides for microscopy were used as substrates without any additional polishing procedure. Hydrophilic silicon substrates were prepared by washing plates, which were cut from standard Si wafers, in a solution of 4.6% HCl and 3.5% H₂O₂ in MilliQ-grade water at 85 °C for 5 min.

J-aggregates were formed by casting a droplet (20–60 μ L) of the porphyrin solution onto the substrate. The droplet was removed after 1 min. The drop covered 0.5–1 cm² on the substrate surface. Then the sample was dried in ambient air. It was necessary to remove the drop in order to avoid formation of NaCl crystals on the surface.

A Nano Scope IIIa (Digital Instruments, Santa Barbara, CA) atomic force microscope (AFM) with built-in Nanoscope IIIa software version 4.23r6 was used to produce high-resolution surface images. The surfaces were scanned in the tapping mode with a point probe silicon tip (type NCH-W) of radius of <15 nm (Nanosensors GmbH&Co.KG, Norderfriedrichskoog, Germany) at an oscillation frequency of 250–350 kHz. Topographic images of $1 \mu\text{m} \times 1 \mu\text{m}$ and $100 \text{ nm} \times 100 \text{ nm}$ were produced at a scan rate of 1 Hz, containing 512×512 data points. The surface roughness parameters were calculated after a third-degree plane fit. No further image processing was performed.

Experimental Results

It is suggested that TPPS₄ molecules do not stack in neutral water solution because the negative charges at the sulfonato groups cause electrostatic repulsion. The changes observed in the absorption spectrum of aqueous solutions of TPPS₄ with

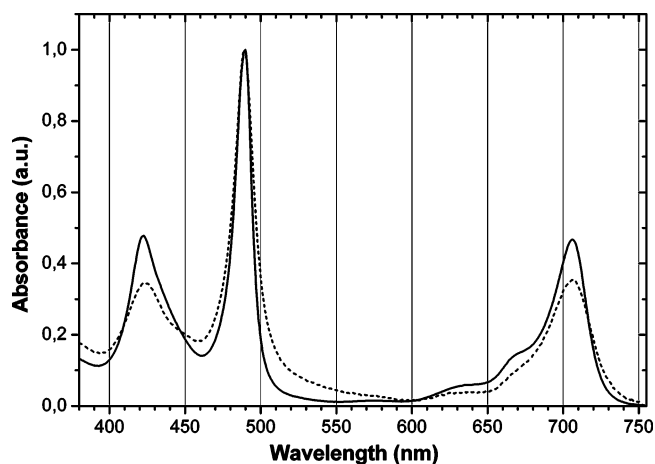


Figure 2. Normalized absorption spectra of TPPS₄ J-aggregates in aqueous acidic solution (concn = 10^{-4} M (light path = 1 mm), pH = 1) (solid line) and in thin layer on glass substrate (dashed line), prepared by the drying of an acidic aqueous solution of TPPS₄ at room temperature.

increasing medium acidity are the result of the formation of diprotonated species, which are the ones forming the J-aggregates. Figure 2 presents the absorption spectra of TPPS₄ in acidic solution and deposited on a glass substrate, respectively. At pH 1 the absorption spectrum of TPPS₄ consists of the Soret band with the maximum at 430 nm and two intense bands at around 490 and 709 nm. The appearance of an absorption band peaking at around 490 nm and increasing absorbance around 709 nm both indicate the formation of J-aggregates.^{8,10,12,13} The obtained spectra indicate also that after drying in ambient air the J-aggregates remained structurally intact on the glass substrate. The slight broadening of the absorption band at 490 nm may appear because of possible distortion of the spatial structure of the aggregate deposited on the glass substrate.

Figure 3 shows typical AFM images of J-aggregates on silicon. Note that no scan-induced damage was observed under present experimental conditions. The lowest TPPS₄ concentration at which the stripelike structures were observed was 5×10^{-6} M. The sizes of the stripes observed on silicon were $4.5 \times 40 \times (200\text{--}1000) \text{ nm}^3$ (height \times width \times length). We have found that the concentration of TPPS₄ in solution influences the average length of the stripelike structures but not the width and the thickness of stripes. Also, the density of stripelike structures on the surface increased with the increase of TPPS₄ concentration, and these structures stacked into larger domains containing a few stripes placed parallel to each other (Figure 4). As shown in Figure 4, the thickness and width of stripes remained almost the same when interacting side-by-side. Stacked stripelike structures of TPPS₄ J-aggregates on the silicon substrate were masked by flocculated structures of TPPS₄ (Figure 4). Another consequence of higher concentration was crossing of the stripes in some areas on the surface (Figure 5). As is seen in Figure 5, the crossing of two stripes affects the geometry of the upper stripe. It seems that strong interaction between the upper stripe and the surface of the substrate deforms its structure. The upper stripe is slightly widened and flattened on the top of the underlying stripe but narrowed on the substrate near the intersection. However, the thickness and width, that is, the cross-sectional profiles of the underlying stripe, remained unchanged, as it was for those lying on the silicon substrate. This shows that the cross-sectional structure is more stable than longitudinal structure. At lower magnifications (Figure 3d) the domains of the stripes exhibit a network-like structure. Separate

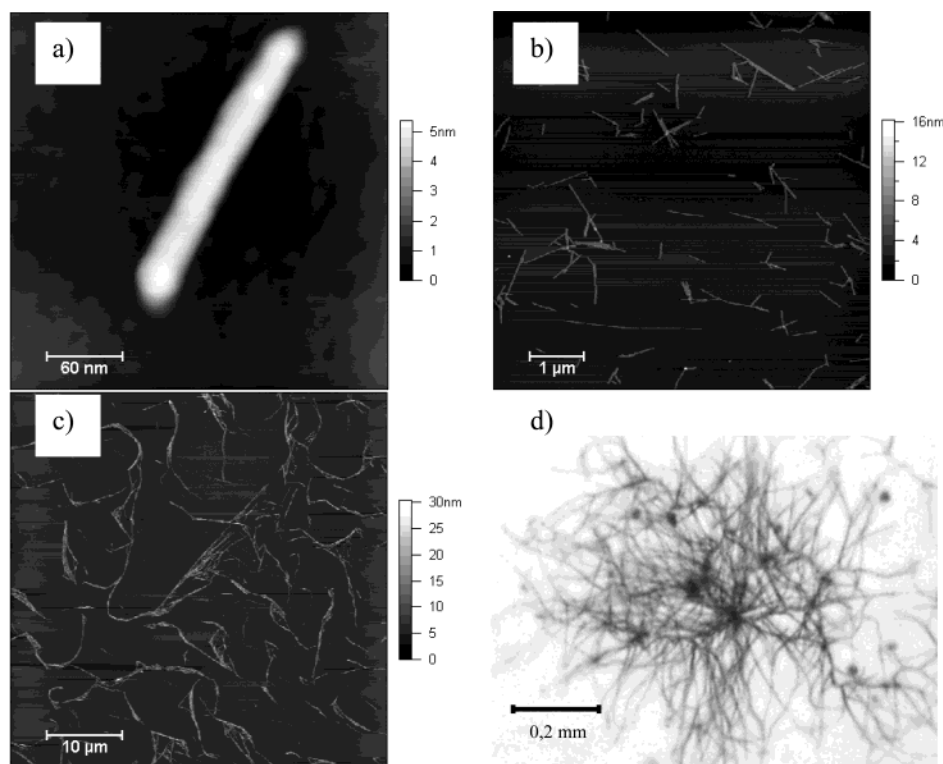


Figure 3. Stripelike structures of TPPS₄ J-aggregates formed in 5×10^{-5} M TPPS₄ solution at pH 1: (a) separate stripelike structure on Si substrate; (b) several stripelike structures on Si substrates; (c) a network-like structure on Si substrate formed by stacking of TPPS₄ mesoaggregates; (d) a large network-like structure of TPPS₄ J-aggregates in aqueous solution (optical microscopy image).

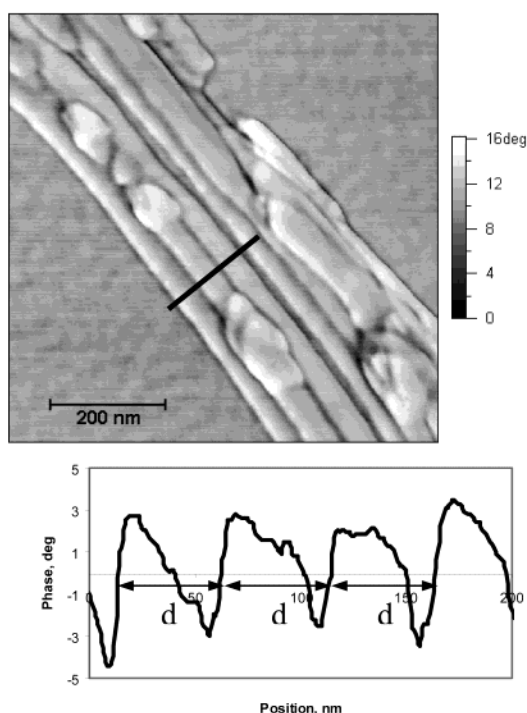


Figure 4. Phase-contrast image of a fiber formed by stacking of TPPS₄ mesoaggregates. Some parts of the fiber are covered by flocculated structures. The profile shows that the width d of the stacked mesoaggregates remained the same ($d \approx 50$ nm).

stripes stack together into long and rather thick (up to 20 single stripes) fibers. Further aggregation of TPPS₄ in acidic aqueous solution resulted in complicated branching of these fibers and the formation of large (up to several millimeters) netlike structures (Figure 3d). However, stirring or shaking of the solution destroys the structures.

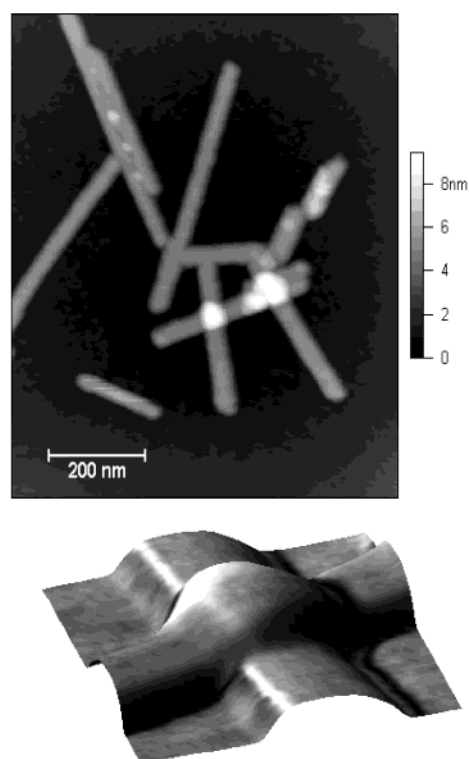


Figure 5. AFM image of two intersecting TPPS₄ mesoaggregates on Si substrate and a three-dimensional view of the intersection (100×100 nm² field of view).

Discussion

The diprotonated form of TPPS₄ has been proposed as being responsible for the formation of J-aggregates, and J-aggregates of different geometrical arrangements have been hypothesized.^{8,10,12,14,17,19,23} The most relevant structure based on

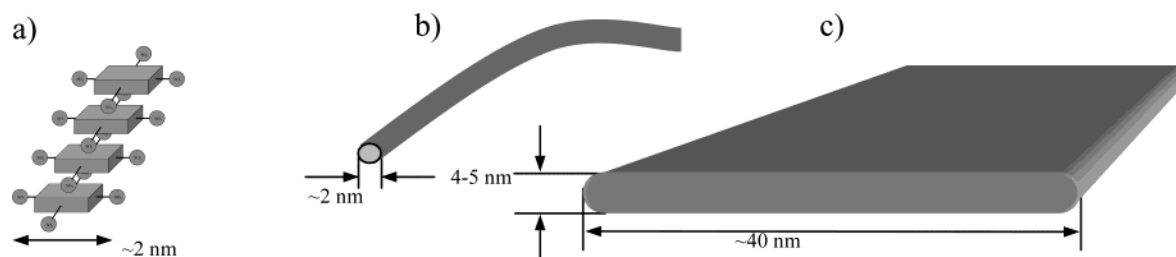


Figure 6. Assuming the spread card deck model (a) the expected image of a TPPS₄ J-aggregate should be a thread (b); the observed structures are much larger, $4.5 \times 40 \times (200\text{--}1000) \text{ nm}^3$ (c).

spectroscopic data and mathematical modeling supports the formation of linear J-aggregates.^{8,10,12,14,17,19,20,22,23,28} The polar groups (in the case of TPPS₄, sulfonic groups) exhibit strong intermolecular interactions with the positive charge of the protonated nitrogens at the center of neighboring porphyrin molecules.

The size of the TPPS₄ molecule is approximately $2 \times 2 \times 0.5 \text{ nm}^3$.¹⁷ Therefore, the expected AFM image of the J-aggregates (assuming the “spread deck of cards” model) would be a thread with a diameter of approximately 2 nm (Figure 6a,b). The number of the interacting monomers would limit the length of such a thread. A combination of results obtained from measurements of flow-induced dichroism, circular dichroism, magnetic circular dichroism, and polarized fluorescence excitation spectra has been utilized to show that TPPS₄ molecules form linear assemblies with an aggregation number of 11, thus consisting of linear oscillators polarized along the longitudinal axis.⁶ On the basis of results obtained from the fluorescence anisotropy decay, the estimated hydrodynamic volume of the J-aggregate was about 22 times larger than that of the monomer, which implied that the J-aggregate is on average composed of approximately 22 monomeric molecules.¹⁰ The size of the J-aggregate, which has been estimated by probing the dynamics of excitation energy relaxation within the J-aggregate by time-resolved fluorescence techniques and applying the theory of exciton singlet–singlet annihilation in restricted domains, was found to be equivalent to an assembly containing at least 20 molecules.²⁴ Assuming that the J-aggregates form linear structures, the expected image of J-aggregates on the substrate could be a thread (Figure 6b). However, topographic AFM images (Figure 3a,b) present long and narrow stripelike structures, which do not match the expected dimensions of the linear J-aggregate. In other words, instead of the expected threads (Figure 6b) we observed stripes with the dimensions of $4.5 \times 40 \times (200\text{--}1000) \text{ nm}^3$ (Figure 3b) as depicted in Figure 6c. Thus, we suggest that TPPS₄ self-organizes into linear treads, in which the porphyrins maintain the arrangement typical for the J-aggregates (such structure is responsible for the observed spectroscopic features). Furthermore, the threads are combined into larger structures (observed by means of AFM). One suggestion might be that TPPS₄ threads (Figure 6b) stack side-by-side to form the observed stripes. If threads were oriented along the stripe, the width and height of the stripe could vary statistically depending upon the number of threads stacked. Thus, increasing of the concentration of TPPS₄ in solution would result in wider and thicker stripes. AFM reveals, however, that the width and height of the stripes is independent of the concentration of the solution. The measured height of the stripes is equal to double the diameter of the threads, which leads to the hypothesis that a single stripe is formed from an “equivalent” bilayer of threads. The constant stripe width leads to the suggestion that threads are oriented perpendicularly to the main axis of the stripe loop and form ring-shaped structural elements

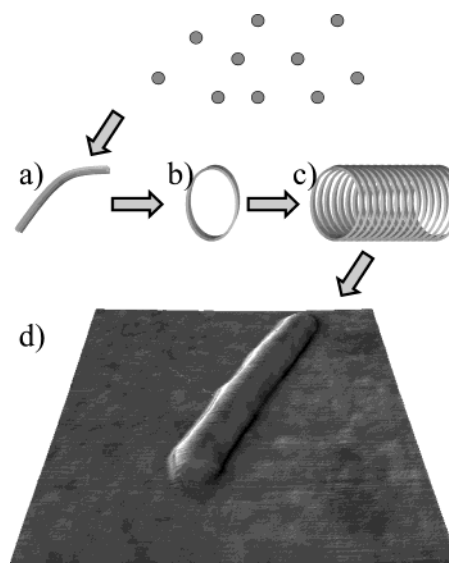


Figure 7. Model of TPPS₄ J-aggregate formation. TPPS₄ molecules aggregate and form linear one-dimensional aggregates (a). These aggregates result in ring-shaped structures of $\sim 20 \text{ nm}$ in diameter (b). Rings stack together and form a nanotube (c), which is flattened on the surface (d) and can be observed directly (by means of AFM).

(aggregate formation takes place in solution, not on the surface, so looped structures should form a cylinder). A slight variation of stripe width when crossing the other stripe (Figure 5) also supports this hypothesis, that is, different aggregate–surface interaction conditions influence the cross-sectional geometry of the stripe. The instability of the longitudinal structure of the stripe in comparison with its cross-sectional stability leads to the conclusion that the stripes on the substrate could be formed by side-by-side interacting rings of the TPPS₄ J-aggregates. A helical structure could also maintain the constant width.

These findings are in favor of a hypothesis, according to which the stripelike structures (Figure 3a,b) might self-assemble from primary one-dimensional ring-shaped linear structures of J-aggregates forming cylinders (nanotubes), which are flattened on the surface (Figure 7). On the basis of the discussed experimental results, we suggest that diprotonated TPPS₄ molecules in aqueous solution form linear aggregates (Figure 7a), which further create one-dimensional rings of approximately 20 nm in diameter (Figure 7b). Further on, such rings stack together and form a nanotube (Figure 7c), which can be seen in the AFM images as a flattened stripelike structure (Figure 7d). The ring should contain 60–70 molecules of TPPS₄ (approximately calculated from the geometrical “spread deck of cards” assumption). We would like to point out that nanotubes on the surface might be flattened because of the interactions with the surface. Note that the measured thickness of the stripe (approximately 4.5 nm) is a result of the flattening of the nanotube until a bilayer of molecules is formed on the substrate.

Such thickness shows that the cylinders should be single walled. Taking into account an average distance of 1 nm of the sulfonic end group from the center of the macrocycle (Figure 1), the ring of 60 molecules of porphyrins should have a radius of 10 nm and can form the flattened cylinder of about 30 nm in width, which (taking into account an additional deformation caused by the interaction with the substrate and tip effects) is in good agreement with the stripe width on the images (Figures 3, 4, and 5).

The size and shape of the J-aggregate structures have been estimated from the angle-dependent light-scattering experiments by Collings et al.²⁵ The authors reported evidence for rodlike aggregates with approximately 10⁴ molecules along the principal axis and 20 molecules across the diameter. These findings are in very good agreement with our observations of the detected stripelike aggregate dimensions on the surface. On the other hand, Micali et al.²⁶ proposed a schematic representation of a fractal model for porphyrin mesoscopic assemblies. Studies of elastic and dynamic light scattering on the J-aggregates show that the clusters are polydispersed with the average size of these aggregates being within the range of 1–1.5 μm . They also suggest the presence of intermediate (100–200 nm) and small (3–6 nm) clusters.²⁶

The investigations reported herein indicate that the TPPS₄ J-aggregates formed clusters, which exhibit self-similar stripelike structures, the length of which depends on the concentration and other experimental conditions. The AFM images show that the originated stripelike clusters are dispersed only in terms of the length of the stripe. The length of the clusters is similar to that estimated previously from dynamic light-scattering experiments.^{25,26}

The mesoscopic structures of the J-aggregates coated on a glass surface were recently examined by means of scanning near-field optical microscopy (SNOM).²⁷ The surface topography and SNOM transmission images also indicated that TPPS₄ aggregates form prolonged structures, which are a few micrometers in length, 0.2–0.5 μm in width, and 5–30 nm in height. The differences in aggregate size and shape might be caused by a lower accuracy of the SNOM technique used and also by the differences in the preparation of the J-aggregates sample. Our present investigations by AFM showed that well-shaped and firm mesoscopic structures of J-aggregates could be masked by flocculated structures formed by TPPS₄ monomers (Figure 4). The spin coating procedure used by Miura and coauthors²⁷ or other similar sample preparation methods may destroy the J-aggregates and increase the monomeric or H-aggregated fraction of TPPS₄, thus complicating the ability to resolve high-quality structural images of the J-aggregates.

Conclusions

For the first time it was shown that TPPS₄ equilibrium aggregates formed in aqueous solutions preserve a stable structure on the substrate and might be used for further optoelectronic applications. The structures of the self-assembled J-aggregates on silicon and glass substrates have been observed directly by means of AFM. AFM images indicate that stripelike ($4.5 \times 40 \times (200\text{--}1000) \text{ nm}^3$) J-aggregates dominated on the surface (Figure 3a,b). The thickness and width of the separate and interacting stripes in domains were independent of the concentration. A model of the porphyrin mesoscopic assemblies has been proposed (Figure 7) on the basis of measured dimensions and the strict stability of the height and width of the stripes visualized on the substrate assuming that the J-aggregates self-assembled into linear one-dimensional struc-

tures (such as “zigzag” and “spread deck of cards” conformations). The J-aggregates, forming small rings of 60–70 monomers, can be considered as the basic structural blocks for the aggregation process yielding the larger cylindrical structures. Separate stripes stack together into long (up to hundreds of micrometers) and rather thin (approximately 20 single stripes) fibers (Figures 3c and 4) forming a bushlike structure, sized up to few millimeters (Figure 3d) in acidic aqueous solution.

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