Self-Assembly of $TPPS_4$ Porphyrin Molecules into Nanorods Investigated by TEM, AFM, STM and UV/VIS Spectroscopy

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ABSTRACT

In this paper we discuss the use of scanning probe microscopy techniques to obtain insight into structural and physicochemical properties of single conjugated (macro)molecules and of their molecular architectures as well as to induce conformational transitions in supramolecular objects with a precision on the molecular scale. The aggregates of the tetrakis (4 -sulfonatophenyl) porphyrin ($TPPS_4$) growth from solution on solid crystalline hydrophilic and hydrophobic substrates were investigated. The spatial structure of $TPPS_4$ deposited on the surface was imaged using Transmission Electron Microscopy (TEM), Scanning Atomic Force Microscopy (AFM). Scanning Tunneling Microscopy (STM) visualized porphyrin rings structure with molecular resolution. The aggregation of $TPPS_4$ was investigated by UV-VIS spectroscopy. The TEM investigation revealed a 3-dimensional rod and wheel like molecular order of the $TPPS_4$ porphyrin assemblies, while a corresponding shorter and mono-disperse oligomer exhibited 2D ribbon-like structure. The $TPPS_4$ porphyrin molecules self-assemble into micrometer-long nanorods and fibers on substrate surface. The investigations revealed a typical thickness of two or four molecular layers and a width of tenths of molecule diameter. We propose here $TPPS_4$ ribbons as polymolecular architectures, which are building blocks of $TPPS_4$ rods and built from the homo-associated porphyrin molecules as revealed by STM. The $TPPS_4$ nanoribbons can find an applications in a molecular-scale electronic and nanooptic devices.

Keywords: porphyrin, self-assembly, nanorods, scanning probe microscopy

1 INTRODUCTION

In the framework of the fabrication of molecular devices based on π-conjugated (macro)molecules, one of the major tasks is an understanding and controlling the physical-chemical properties of the materials over a wide range of length scales. In work in this direction, scanning probe microscopy have played a paramount role, since they allow one to explore organic surfaces on different scale lengths in various ambient [1,2]. Making use of these techniques it has been possible to approach the nanoworld in various ways which go far beyond pure imaging of a surface: manipulating single molecules at room temperature [3] opening new avenues towards the study of the conformational and nanomechanical properties of individual molecules [4], stimulating photochemical reactions with light and following the reaction in real-time at interfaces [5, 6], probing the electronic properties of single molecules by means of scanning tunneling spectroscopy (STS) [7, 8] and inducing with the scanning tunneling microscope (STM) tip the electroluminescence of a conjugated thin film [9] are just a few examples.
In this paper we report on the first study of molecularly resolved images of a $TPPS_4$ porphyrin self-assembly and aggregation at the solid-liquid interface on the growth of this macromolecule into molecularly defined ribbons on the surface.

2 EXPERIMENTAL

2.1 Materials

The tetra sodium salt of tetrakis-5,10,15,20(4-sulfonatophenyl) porphine was obtained from Porphyrin Products (Lugan, UT) and was used without further purification. The J-aggregate solutions were prepared by dissolving $TPPS_4$ in acidic aqueous medium (HCl was added to reach pH 1) at the concentration range ($1\cdot10^{-4}$–$2\cdot10^{-6}$) M. To stabilize the aggregates formation the solution was left at room temperature for aggregation for 10 days, before the thin films preparation. The J-aggregates of $TPPS_4$ formed after solution preparation was confirmed by absorption spectra.

2.2 Preparation of porphyrin films

Highly oriented pyrolytic graphite (HOPG), glass, mica and silicon were chosen as supporting substrates. The thin films of $TPPS_4$ were prepared by drop casting solutions and allowing the solvent to evaporate at room temperature in the dust-free environment, dipping substrate into solution or spin-coating technique at 100 rpm. Then the sample was dried in ambient air. The $TPPS_4$ thin films were generally deposited from $1x10^{-4}$ and $1x10^{-5}$ M solution.

2.3 Scanning probe microscopy

Muscovite mica slices for Atomic Force Microscopy measurements were cut into discs with a punch and die set in order to produce readily cleavable edges. The glass

covers for microscopy were used as glass substrates without any additional washing procedure. The Scanning Tunneling Microscopy (STM) measurements were made on HOPG samples. Molecular resolution was achieved and by varying the tunneling parameters it was possible to visualize the HOPG lattice underneath and therefore to calibrate the piezo in situ. Molecular self-assembly was achieved by applying a drop of solution onto a freshly cleaved mica surface and allowing the solvent to evaporate. High resolution Atomic force microscop (AFM) measurements were made with a home-built AFM interfaced with NT-MDT (NT-MDT, Russia) control electronics and AFM and STM measurements with a Nanoscope III Multi-mode (Veeco Metrology, Sunnyvale, CA).
The dry samples were investigated by SFM in the contact and tapping mode in a range of scan lengths from 5μm to 0.1 μm, and using commercial Si cantilevers NSG11 series (length 100 μm and width 35 μm) with a force constant 11Nm^{-1} and tip curvature 10 nm and resonanse frequency 255kHz (NT-MDT). The Pt/Ir commercial tunneling tips were used for STM measurements. The ribbon widths were measured from images with a resolution of 512_512 pixels and scan lengths 20nm -3 μm, while their heights were determined by the use of the facilities of the SPIP(Image Metrology) and NT_MDT software's. Several tens of images were processed for each polymer length in order to minimize the influence of the choice of sample area and to reduce the statistical error.

2.4 Transmission Electron Microscopy

TEM images were obtained with Hitachi S-4800 electron microscope in STEM mode. Acceleration voltage was 30kV and emission current was 10 μA. Working distance was equal to 8 mm. Droplet of sample solution was placed onto the 200 mesh TEM grid with carbon film coating and was allowed to dry at ambient conditions. After that sample was either directly imaged or additionally stained with RuO_4 vapor. Staining was performed in covered petri dish were specimen containing grids were placed in the center of the dish and droplets of 0.5% aqueous solution of RuO_4 (EMS sciences) were placed around the grid. After 10 minutes grids were removed and used for imaging.

2.5 UV-VIS Spectroscopy

Solution and monolayer spectra for the UV/VIS experiments were obtained on an Ocean Optics Inc. diode array spectrophotometer to confirm the J-aggregates formation. A series of different solution concentrations of $TPPS_4$ were prepared and their absorbance at the Soret band maximum (~432 nm) was used to calculate the solution extinction coefficients using the Beer–Lambert law[10]. To obtain the monolayer absorption spectra each glass cover slip was scanned before and after self-assembly of porphyrin film, and the difference between the two spectra was the porphyrin monolayer absorption spectrum.

3 RESULTS AND DISCUSSIONS

3.1 Porphyrin aggregation in solution

It is suggested that $TPPS_4$ does not stack in neutral water solution since the negative charges at the sulfonato groups cause the electrostatic repulsion between $TPPS_4$ molecules. The changes observed in the absorption spectrum in aqueous solution of $TPPS_4$ with the increase of the medium acidity are the result of the formation of diprotonated species, which are forming the J-aggregates [5]. Fig 1. presents the spectra of $TPPS_4$ aggregates in solution and film deposited on glass substrate.

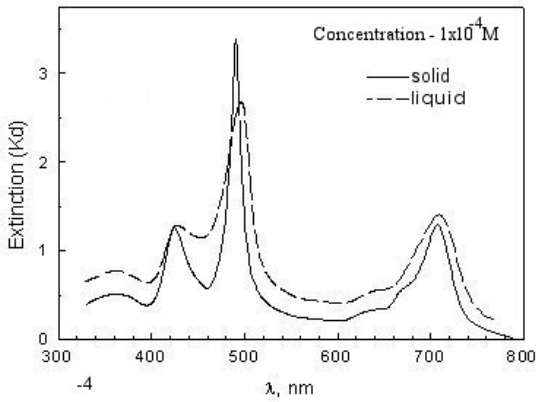

Fig.1. UV-VIS absorption spectra of $TPPS_4$ solution.

The measured UV–VIS spectrum of the acid solutions of $TPPS_4$ has absorption maxima at 423, 490 and 705 nm, which has to be attributed to the formation of J-aggregates (490 nm), which at higher concentrations give H-aggregates (420 nm) [8]. In the dry films, an increased absorption appears in the region about 450 nm. This suggests that the simple dipole exciton coupling model, which explains the absorption spectra of the homoassociate solutions through two independent one-dimensional couplings (H- and J-aggregation), cannot be applied to the condensed phase and the collective 2-D or 3-D exciton model should be applied.

3.2 TEM microscopy of the porphyrin aggregates at the liquid-surface interface

In the evaporation of a drop of the solution, the TPPS film develops from the border to the center of the drop. The film surface in the atmosphere retains water as it is seen from the force-displacement curves of AFM measurements. The water content depends on the water-vapor pressure of the surrounding atmosphere. The $TPPS_4$ phase is textured in the form of elongated fiber-like or a wheel like structures. The detail analysis of TEM images reveled, that the wheel structures are the self-assembly of ring type structures with typical diameter of ~10 nm (Fig.2).

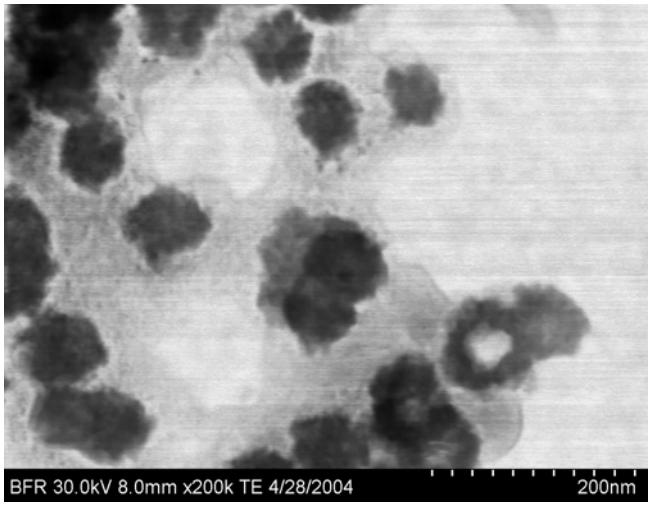

Fig.2. TEM microphotograph of $TPPS_4$ aggregates.

The diameter of the wheel structures vary from about 10 nm up to 250 nm. The central parts of the wheel is composed of phorphyrin dimmers and have a planar structure, in contrast with peripheral area of the wheel composed in 3D structure from TPPS dimmer aggregates. The cross section of strip like structure revealed by TEM have a 8-9 nm in diameter as it was obtained from images using the SPIP (Image Metrology) software and pixels count.

3.3 Atomic Force Microscopy

AFM was used to perform quantitative measurements of molecular arrangements in the wide range of imaging scales (100 nm - 5 μm) and results are presented in Fig.3. The fracture of the film observed by AFM shows that the fiber-like structures are stacked in a ribbons of different structure, depending on the spot location on the $TPPS_4$ drop area Fig.4. The ribbons are built of bricks of parallelogram form with the dimensions ~ (34x 56) nm and conclusion can be made from experiment it consist of the two smaller parts. The bricks consist of nanorods with width of 18-20 nm and height 8-10 nm. The angle between the short axis of building bricks of ribbons and ribbon axis measured by means of SPIP software was in the range of 51-56^o which corresponds with the results on ZnP3 porphyrin aggregation of the work [11]. The cross-section of double-rod ribbon clearly demonstrate the double-rod structure of ribbon. The detail analysis of many images made at different scales demonstrate that the self-assembly of building blocks starts about some kind of backbone structure. These backbone nanorod type structures have a width of 18 nm and the height of 2-2.5 nm. The typical width of nanoribbons is 48-56 nm, but it was found the ribbons with the width around 100 nm. AFM investigations revealed the smallest building blocks with dimensions 12x28x2 nm, the next revealed structure have dimensions 20x56 nm. The measured wheel height was 8 nm and diameter 80 nm.

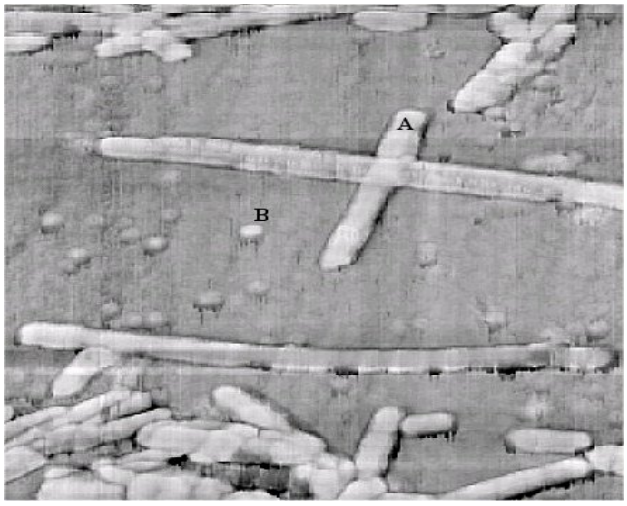

Fig.3. AFM image of $TPPS_4$ self-assembly: A-rod-like, B-wheel-like aggregates. Scan area: (1x1) μm^2.

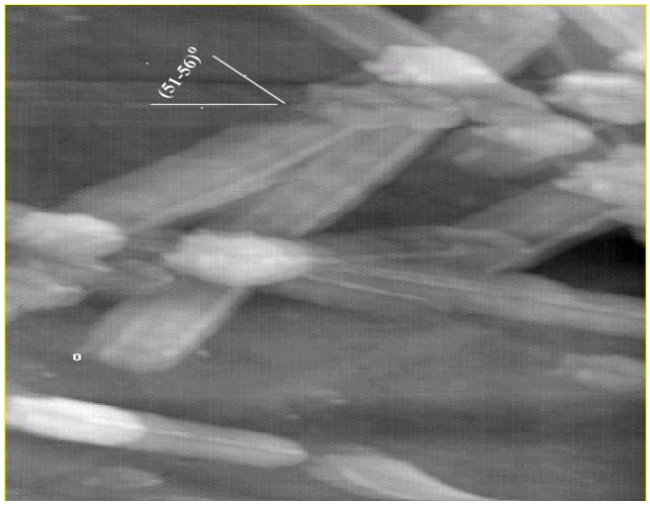

Fig.4. AFM image of ribbon-like $TPPS_4$ aggregates. Scan area: (600x600) nm^2.

3.4 Scanning Tunneling Microscopy

Figure 5 presents the STM image of $TPPS_4$ ribbon-like aggregates on HOPG surface prepared by drop evaporation. Figure 5 is an STM topography scan intended to reveal the gross surface morphology of the aggregated structures. Within the (80x80) nm^2 area it is clear seen a ribbon-like structure, which consist of thin rod-like structures, oriented along the long axis of the ribbon. The thin rod-like structures dimensions have a width ~1.4-1.8 nm measured by the tools of SPIP software, which correspond to the diameter of $TPPS_4$ porphyrin molecule [35]. The image demonstrate the fact that the self-assembly of $TPPS_4$ from the acid aqueous solution during the evaporation into solid-state film is going on the sample surface. The dispersed on the surface aggregates of monomer and dimmer size and the

Fig.5. STM image of $TPPS_4$ assembly process. Scan area (80x80) nm^2. A- rod-like structures.

step-by-step evolving process to the ribbon-like structure it was imaged on the surface.

The higher resolution STM scan have shown the formation of ordered molecular arrays along the ribbon axis. The measured distance was 1.8 nm between the centers of the neighboring linear arrays. It fits very well into the dimensions range obtained by other works on porphyrin homoassociation [4,11].

CONCLUSIONS

We have characterized the self-assembly of a tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) on flat solid substrates. It is a first time demonstration of molecularly resolved images of $TPPS_4$ aggregates formation. At the interface between graphite, glass, Si and an acidic aqueous solution molecularly ordered structures are formed. The different morphologies were observed, as depicted in Fig.2, Fig.4 and Fig.5. The wheel-like and rod type formations were found. The self-organization and grow of long $TPPS_4$ fiber-like structures is based on the aggregation of building blocks (self-assembled nanoribbons) with typical dimensions of (20x40)nm^2, but it is common 80-100 nm width cross-section. The fibers have a double-line structure; can be organized in two layers with flat teramer in cross-section. The building blocks (ribbons) are made of several nanorods packed parallel one to each other. Each rod has a typical width 8-9 nm, which correspond with 5 molecules or 3 dimmers dimension. The height of ribbon varies from the monolayer to several layers. The nanorods in ribbon are connected by monomolecular chains. The wheel like structures found by TEM, AFM and STM as possible building blocks for another type of rods (Fig.2) vary in dimensions from few nanometres to hundred of nanometres. Porphyrin-based materials herein studied showed nanoporous surfaces, and their potential applications are promising.

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