Preparation and Optical Properties of Substituted Hydroxyl Porphyrin Nanostructure by UV Light and Green Laser (532 nm) Irradiations

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Abstract—Electronic absorption, florescence excitation and AFM studies of selected homogeneous solutions and thin films of meso-tetrakis (parahydroxyphenyl) porphyrin (THPP) (1), mesotetrakis (2, 3-dihydroxyphenyl) porphyrin 2, 3-OHPP) (2), mesotetrakis (3, 4-dihydroxyphenyl) porphyrin (3, 4-OHPP) (3) as well as Zn(II) derivative of 2, 3-OHPP (4) under UV lamp and green laser irradiation (532 nm) are acquired and analyzed. Our results indicate that in irradiation experiments, the products of the resulting porphyrins strongly depend on the careful choice of the light source. UV lamp irradiation produced J-type aggregated diacid porphyrins from free base porphyrins by simple photochemical technique. The stabilization of the aggregates structure may be achieved through hydrogen bonding between the protonated core and the peripheral hydroxyl groups, mediated by the chloride anions. The results of laser irradiation experiments shown the formation of J-aggregated porphyrin upon green laser (532 nm) irradiation. Green laser irradiation has been caused the hydrogen bonding interactions between neighboring porphyrin molecules through hydroxyl moieties to produce J-aggregated supramolecular porphyrins. The AFM topographic images and Dynamic Light Scattering (DLS) of THPP(1) under green laser irradiation have been indicated nano-structured porphyrin wires about 5 nm high approximately.

KEYWORDS: Green laser, Self assembly, Diacid, Porphyrin, J-aggregates.

I. INTRODUCTION

Organic materials, in particular, with the structure of extensively delocalized π-electrons have received significant attention recently due to their large nonlinear optical susceptibilities, architectural flexibility, and ease of fabrication [1-4]. The remarkable recent progress in nanotechnology is mainly due to the ability to synthesize, investigate, and exploit materials with structural modulation on the nanometer scale. In this respect, Nanostructures display unusual optical and optoelectronic properties, often quite different with respect to single molecules and the bulk material [5]. Porphyrins are attractive compounds because they are relatively easy to synthesize and their photophysical properties can be tuned through careful choice of peripheral substituents and inserted metal ions [6, 7]. Among *meso*-substituted porphyrins, hydroxyphenyl functionalized molecules are particularly appealing for their coordination and hydrogenbonding abilities, which can work together with electrostatics and dispersive forces to organize the chromophores in the aggregates. Indeed, besides the covalent approach [8], self assembly based on weak interactions seems to be a promising alternative since it is synthetically less demanding to obtain organized multi-chromophoric arrays.

Deposition of layers of porphyrins can be achieved through a variety of techniques, such as layer-by-layer electrostatic adsorption [9], self-assembling monolayers on gold or other substrates [10, 11], Langmuir-Blodgett or Langmuir- Schaefer techniques [12], and self-

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organizing supramolecular structures [13]. Well-organized ring like [14] or globular structures [15] have been reported by solvent evaporation, and nanorods have been obtained from self-aggregation of water soluble porphyrins [16].

The main problem faced/ encountered during the application of molecular assemblies and aggregates in the current technology is a difficulty to control the arrangement and orientation of monomers in the aggregates. Among all methods, the deposition of supramolecular assemblies of porphyrins by irradiation with various lights has recently received much attention [17, 18]. This method takes advantage of the possibility of controlling the size and shape of the deposited particles in the nanoscopic range by applying various irradiations. The type of products can be controlled through a carful choice of the light source. In pulsed irradiation experiments, the size and morphology of the resulting porphyrin particles strongly depend on the single pulse duration, the total irradiation time and the delay between pulses [18]. Light induced can form highly organized structures, which are classified according to the orientation of the induced transition dipole of the constituent monomers [19]. The origin of these changes is explained by the formation of an excitonic state through the electronic coupling of tightly packed porphyrin molecules [20, 21].

Hence, the architectures of meso/nano-scaled porphyrin assemblies or particles are expected to be promising candidates for use in photonic devices [22].

To gain new insight to the subject of programmed construction of network solids, and to further extend the behavior spectroscopic and morphologic of derivates porphyrins under laser irradiation, in this work we focused on using different irradiations on hydroxyl derivates of tetraphenyl porphyrin solution in dichloromethane solvent and investigation of products such as monomer diacid porphyrins and self-aggregated porphyrin networks.

II. EXPERIMENTS

All chemicals and solvents were purchased from Merck & Aldrich and used without further purification.

Meso-tetrakis (parahydroxyphenyl) porphyrin (THPP)(**1**), mesotetrakis (2, 3-dihydroxyphenyl) porphyrin (2, 3-OHPP)(**2**), meso-tetrakis (3, 4-dihydroxyphenyl) porphyrin (3, 4-OHPP) (**3**) as well as Zn(II) derivative of 2, 3-OHPP (**4**) were prepared and purified according to literature procedures [23, 24]. Stock solutions were stored in the dark and used within 1 week of preparation. The concentration of solutions was 5μM with the addition of a few drops of methanol (2% v/v) to increase their solubility in all experiments. To obtain samples deposit on surface and to produce samples suitable for AFM analysis, a Novocontrol Technology spin coating system was used. Spin coating was achieved by pouring the solution on a clean substrate to fully cover it. For all samples 20 rpm for 30 second were used. To remove the extra solvent from the layer, the samples were placed in the oven at a temperature of 45°c for 30 minutes after spin coating. For measuring the thickness of the layer, the layer was removed partly to make a step suitable for surface profiling. Surface roughness of the polymer layer and also its thickness were measured using a profile meter (Dektak8000). The power of UV lamp was about 20 W for UV irradiation experiments. A 100 mW Nd:YAG laser (532 nm) was used as a continuous light source for green laser irradiation experiments. The total irradiation time (t.t.) for all samples was 3600(s). All experiments were repeated at least three times to check reproducibility. The experimental set up of laser irradiation has been shown in Fig. 1.The conversion of the porphyrins into the various forms was directly monitored through UV/Vis., and fluorescence spectra. UV/Vis. absorption spectra and emission spectra were recorded on HR4000& USB2000 Ocean Optics spectrophotometer by absorption and emission modes, respectively.

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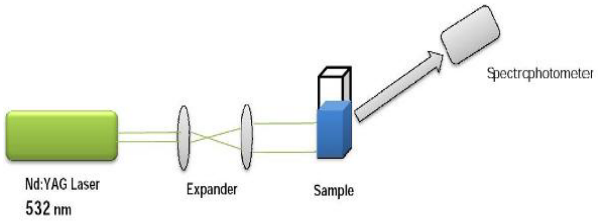

Fig. 1. Experimental set up for green laser irradiation.

Particle size distribution of starch nanoparticles was characterized by using a NANOPHOX Particle Sizer (Sympatec GmbH System-Partikel-Technik) with a He–Ne laser (wavelength 632.8 nm, 10 mW) and a scattering angle of 90° as a light source. Samples for the measurement were prepared by dissolving in dichloromethane and irradiated. Acquisition of the light intensity was adjusted by a valance photodiodes with subsequent correlator. Transfer of measured data was performed via 1.25G bit link to PC. Isolated RS485 interfaced (fiber optic link) by direct control of device functions. The measurements were conducted at 25 ^{o}C.

Atomic force microscopy (AFM) of the samples were obtained using a SPM (Digital Instruments, Nanosurf easyscan 2 AFM) in the contact mode and stylus profilometry (Alpha-step 500). All scans were taken at room temperature in air. Imaging was performed using pyramidally shaped supersharp silicon tips (4 μm thickness, 50 nm width, aspect ratio approximately 1:1, 13 kHz resonance frequency, 0.032 N/m force contact) on silicon nitride cantilevers (typical static load 10 nN, typical dynamic frequency=190kHz). In all AFM scans, there were 512×512 data points across the areas of the scan and contact scans were made. AFM is the preferred measurement technique as the force between the probe and the surface is much smaller than for the stylus profilometer, and the tip has a much smaller radius of curvature. AFM scan head measurements include 14 μm maximum Z-range, 0.21nm drive resolution Z and XY-linearity mean error <1.2 %.

Therefore the AFM results are more representative of the surface topography than those of the profilometer, and also have a greater sensitivity, with the ability to measure height variations with a horizontal resolution.

III. Results and Discussions

Dichloromethane solutions of derivates of meso-tetrakis (hydroxyphenyl) porphyrins display a sharp and intense Soret band accompanied by four weaker Q-bands at longer wavelength in the visible range. Also porphyrin has red fluorescence with two emissions bands. The molecular structures of samples have been shown in Fig. 2.

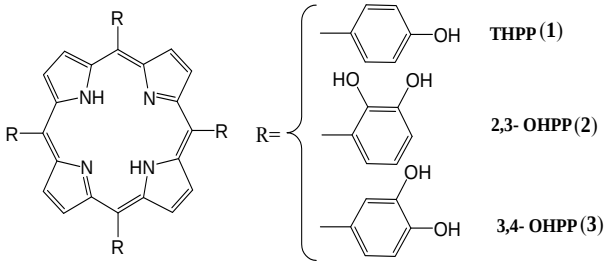

Fig. 2. Molecular structure of the investigated porphyrins.

The experiments were carried out on two type of radiation: (i) UV lamp, (ii) green laser (532 nm) which is shown in Fig. 3.

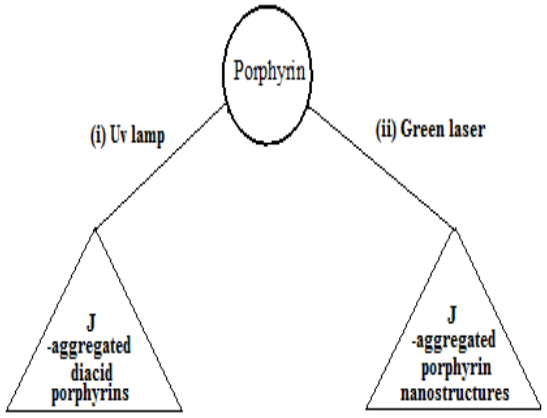

Fig. 3. The processor of syntheses and obtained products

Figure 4 shows the changes of UV/Vis. spectra of sample (**1**) after irradiation with UV light in dichloromethane. As shown in Fig. 4, the sharp soret band of the irradiated solution of compound (**1**) is completely disappeared and a new soret band is found at longer wavelength (red shift) accompanied by intense Q-bands in 705 nm.

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Changes in the absorption spectra of THPP(1) on formation of H_2THPP^{2+} (Fig. 4) specially a single Q band, indicate that symmetry of the system is higher than D_{2h} [25].

The symmetry of H_2THPP^{2+} in crystalline form is inferred as S_4 due to tilting of pyrrole rings from the mean plane of the nitrogen due to Van der Waals repulsion of the inner hydrogen atoms of the porphyrin ring [26] and indicates a similar symmetry in solution.

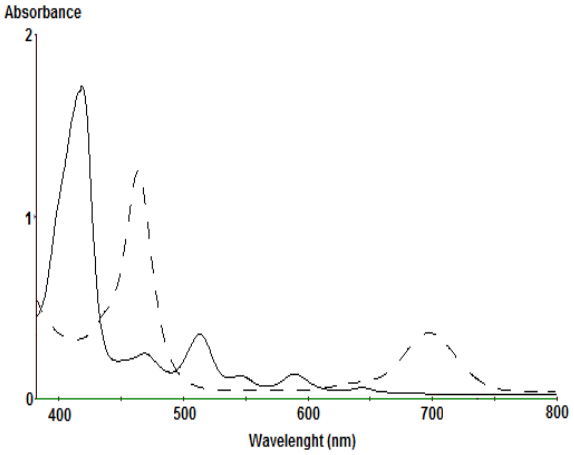

Fig. 4. UV/Vis. spectral changes of dichloromethane solution of THPP(**1**) before UV lamp irradiation (solid line) and after irradiation (dashed line). Total irradiation time, 3600 s.

Generally, in the case of *meso*-aryl substituted porphyrins, the two protonation steps are almost indistinguishable, yielding the corresponding porphyrin dication (Fig. 5), while the monoprotonated species has not been usually detected [27].

In general, the addition of two protons red-shifts the Soret band by nearly 30 nm and the Q (0,0) band by nearly 16 nm with enhanced intensity compared to THPP(**1**) [26, 28]. In fact, photodecomposition of the chlorinated solvent can occur during the irradiation with the UV light, leading to the production of hydrochloric acid and, thus, to the formation of the porphyrin acid derivatives. These evidences have been mentioned in several literatures to verify of the formation of H_2THPP^{2+} [29, 30].

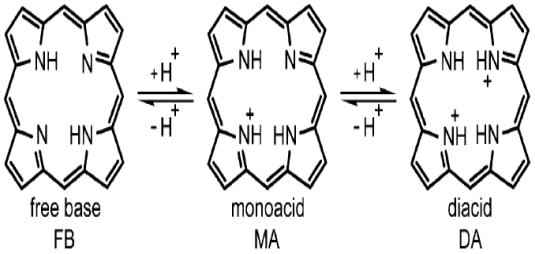

Fig. 5. Species involved in the acid-base Equilibria of H_2TPP^a. *a* peripheral substituents and counter anions have been omitted for the sake of simplicity.

When the same experiments are performed on Zn-porphyrin (**4**) solution, the spectrum of the irradiated solution have not shown any changes. This experiment confirms the formation of monomer diacid porphyrin.

In the attempt of proposing a model for the interaction of the porphyrins in the aggregates, a J-type arrangement of the monomers can be proposed on the basis of the red shift (+40 nm) of the aggregate extinction bands with respect to the monomeric diacid intermediate.

In addition, the increase of the intensity of florescent spectra without no stock (Fig. 6) during irradiation can be ascribed to form J-aggregation phenomena in diacid monomer porphyrins.

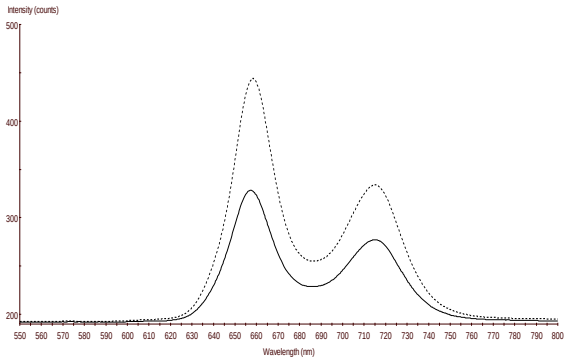

Fig. 6. Emission spectra changes of dichloromethane solution of (**1**) before UV lamp irradiation (solid line) and after irradiation (dashed line). Total irradiation time, 3600 s.

Based on literatures, two types of molecular aggregates involving dipolar coupling are considered with unique electronic and spectroscopic properties: J- and H-type aggregates [31]. When chromophores such as porphyrins are parallel aligned, two new

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excitonic bands are generated according to a simple exciton theory: one with higher energies and the other with lower than the monomer energy level [31]. In J aggregates, transitions only to the low energy states of the exciton band are allowed. As a consequence, J aggregates exhibit a red-shifted absorption band with respect to the monomer band, and are characterized by almost no Stokes-shifted fluorescence that has a high quantum yield. In H aggregates, on the other hand, transitions only to the higher level are allowed, yielding a blue shift of the absorption peak. Another consequence of the dipolar coupling in the H aggregate is quenching of fluorescence caused by a rapid internal conversion to the lower energy level and a subsequent forbidden transition to the ground state. Therefore, a shift of the Soret band to longer wavelengths should be attributed to the self-association of porphyrins into J-type aggregates.

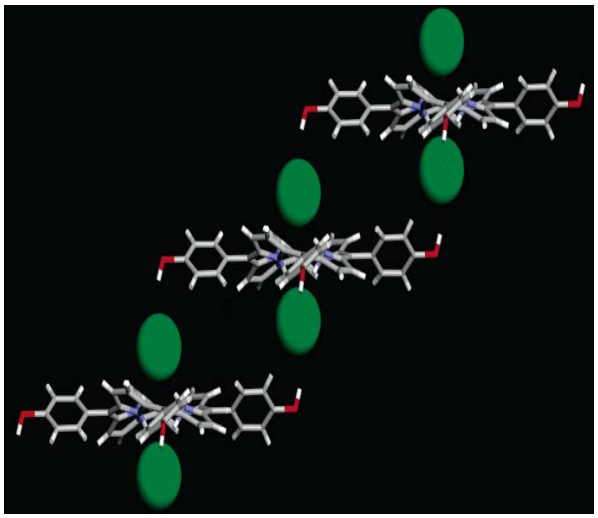

Fig. 7. Side view of the proposed model for the J-aggregation of $\{H_2THPP(Cl)_2\}$ through the intermediacy of chloride anions (green spherical), shown as green spheres (charges omitted for clarity) [34].

In fact, the stabilization of the aggregates structure may be achieved through a network of electrostatic interactions and hydrogen bonding between the protonated core and the peripheral hydroxyl groups, mediated by the chloride anions [32, 33] (Fig. 7).

Figure 7 suggests a model that may account for this explanations, describing the interaction between tetraprotonated $\{H_2THPP(Cl)_2\}_{agg}$ molecules and the relative chloride anions [34].

On one hand, the formation of extended hydrogen bonding networks has been observed in the solid-state structures of free base porphyrins bearing hydroxyphenyl *meso*substituents [35-38]. On the other hand, the proposed model is further supported by a recent analysis performed via DFT and TDDFT calculations on the diacid derivatives of tetraphenylporphyrin ($\{H_2TPP(X)_2\}$, X) F, Cl, Br, I) [28, 29]. This study shows that a strong interaction is present between the halides and the protonated N-H groups of this diacid and that, besides electrostatics, covalent interactions are a relevant component in the total energy of this hydrogen bond.

For these reasons the nature of the solvent should also play a very important role to obtain spramolecular self-assembly porphyrins. In this manuscript, we obtained J-type aggregated diacid porphyrins from THPP by simple photochemical technique with UV lamp.

Finally, in order to determine the role of irradiation on self-assembly behavior of porphyrins, a series of irradiation experiments have been carried out over the mentioned porphyrin solutions by green laser (532 nm) in order to excite Q band region and cut off the UV component of the UV lamp and avoiding the formation of haloacids by photodecomposition of the halogenated solvent.

UV–vis absorption spectra of irradiated sample THPP(**1**) solution by green laser are shown in Fig. 8. As shown in Fig. 8, the Soret band and Q bands exhibit a bathochromic shift compared to those of the porphyrin solution. The spectra of the irradiated solution display extremely no isosbestic points can be detected in the spectral changes occurring upon irradiation.

Therefore, a shift of the Soret band to longer wavelength (about 10 nm) should be attributed to the self-aggregation of porphyrins into J-type aggregates. Here we observed the

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formation of diacid porphyrin from porphyrin derivates by simple photochemical UV irradiation in dichloromethane solution.

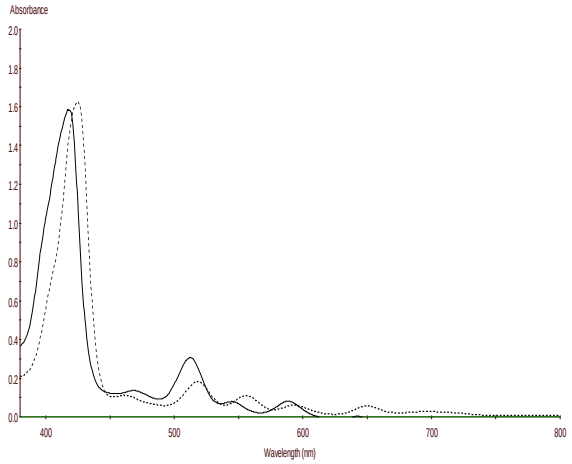

Fig. 8. UV/Vis. spectral changes of dichloromethane solution of porphyrin before green laser irradiation (532 nm) (solid line) and after irradiation (dashed line). Total irradiation time, 3600 s.

The same as later section, to confirm whether the porphyrin moieties are self-aggregated or not, fluorescence measurements were carried out. Fig. 9 is shown a typical fluorescence spectrum of (**1**) that the emission of the final solution is increased without any stock.

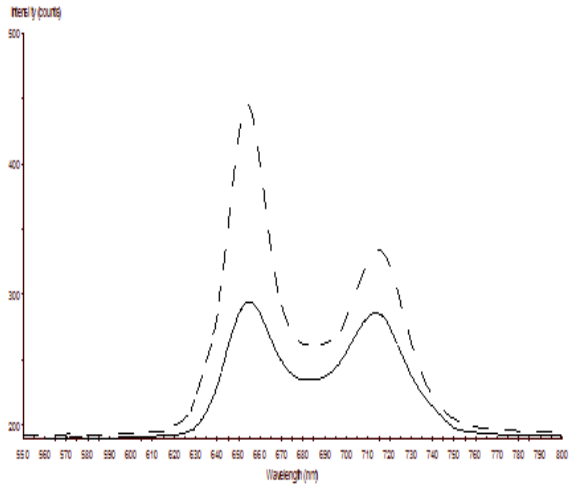

Fig. 9. Eimission spectra changes of dichloromethane solution of porphyrin before green laser irradiation (solid line) and after irradiation (dashed line). Total irradiation time, 3600 s.

It is important to note little changes in the fluorescent spectrum of starting solution due to change in the concentration were not considered. The comparison of mentioned evidences with the results reported in the literature for the aggregation processes involving the porphyrin isomers [18] suggests the formation of J-aggregated porphyrin upon green laser irradiation.

In order to determine the shape and size of the porphyrin nanoparticles, AFM and DLS observations of porphyrins were carried out. Fig. 10 shows typical DLS diagram of compound **1** in a CH_2Cl_2 solution after green laser irradiation. A regular size distribution of 3-5 nm was observed for sample **1** in dichloromethane solution. From DLS measurement, the surface mean dimeter (SMD) and volume mean diameter (VMD) of sample **1** estimated as 1.46 and 6.58 nm, respectively (supporting information).

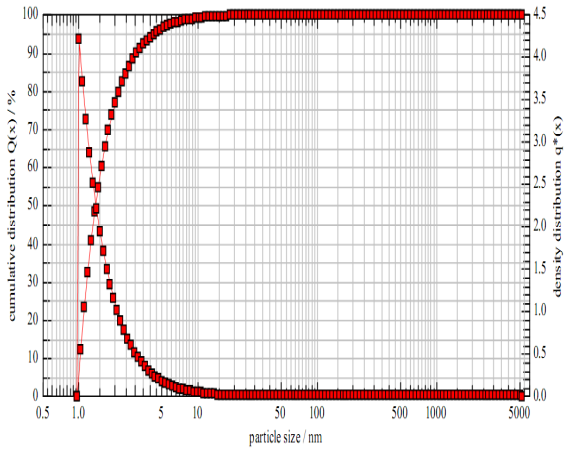

Fig. 10. Particle size distribution of compound **1** in a CH_2Cl_2 solution after green laser irradiation.

These results are in good agreement with AFM images (Fig. 11), which indicate that nanoparticles was formed in solution by irradiation. These nanoparticles structure is preserved in solution stored under dark at room temperature for at least 30 days.

AFM studies have been carried out on sample THPP(**1**) deposited on glass by green laser irradiating of the same solution for total irradiation times (3600s), (Fig. 10).

The AFM topographic image of Fig. 10a indicates the size of observed porphyrin wires was 300- 400 nm wide and approximately 5 nm high.

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The AFM image of the 3-D image porphyrin nanoproduct with Z-axis is shown in Fig. 10b. The line fit of irradiated porphyrin is calculated 8.95 nm from the 3-D AFM image. Fig. 10c shows the image profile of particle size with mean fit 9.81 nm. As shown in Fig. 10a, the molecules closely packed linearity and the lines are parallel to each other. From this image, one can observed the most molecules packed in a regular rows pattern with a period of dispersed molecules. The distance between two lines in the same period is about 200 nm. A few molecules are not packed in this pattern.

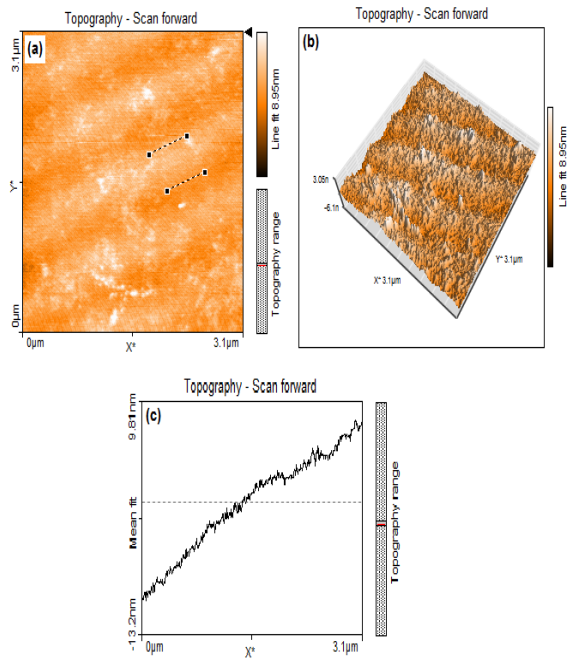

Fig. 11. (a) The topography AFM images of the deposits obtained (4) with green laser in CH_2Cl_2 solvent of porphyrin (4), (3.1µm×3.1µm). (b) 3-D AFM image of (a). (c) related size distributions of (a).

Generally, two types of topology pattern have been observed for supra molecular self-assembly porphyrins: Closed topologies and open topologies [39]. Open topology is formed the long porphyrin wires which is composed of many porphyrin dots, wherein the ends have recognition motifs that are not used in structural organization. The long wires had linear structures and were aligned the parallel row. With regard above explanations, the open topology has been proposed for our deposited porphyrins.

Figure 12 suggests a model that may account for this observation, describing the hydrogen bonding interactions between neighboring porphyrin molecules through hydroxyl moieties to produce J-aggregated supramolecular porphyrins. However, it should be mentioned that it is just an idealistic imagination and in real world generally systems tend to from the twisted H-and J –or oblique aggregates (generally combined forms) [31, 40].

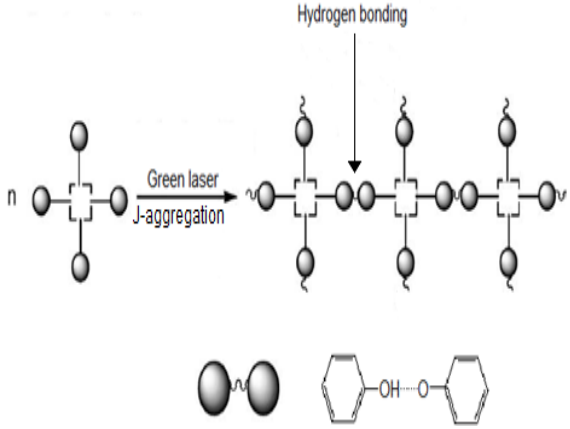

Fig. 12. Representation of J-aggragated porphyrin of THPP(**1**) by green laser.

Also, the same our obtained porphyrin wires, M. Kawao *et al.* have been reported porphyrin molecule wires by oxidative coupling reaction [41].

All deposited porphyrins on substrate have been monitored by absorption and emission spectra again and no changes in spectrum pattern between deposited porphyrins and irradiated porphyrin solutions have been confirmed except decrease in intensity in deposited porphyrins.

Furthermore, we think that J-aggregated supramolecular porphyrins are obtained from the H-bonding between hydroxyl groups with neighboring porphyrins [18, 28-30, 32-36, 39]. So, the structures which form upon irradiation stabilized by contributions of hydrogen-bonding and the reduction of the repulsion among neighboring porphyrin monomers allow aggregates formation.

The difference spectroscopic features observed in the presence of the various irradiation points

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to a certain degree of selectivity of the system. These self assembled structures can be used in sensors, molecular sieves and photonics devices [39].

IV. CONCLUSION

This work demonstrate a number of useful guidelines in the applications and effects of two type irradiations on substituted hydroxyl porphyrin-based supramolecular architectures. The experimental results of this investigation illustrate the relevant parameters underlying the present method, which easily allows depositing a variety of porphyrin derivatives by irradiating their solutions in dichloromethane with a Green (532 nm) laser and UV lamp as irradiation sources. We demonstrate clearly J-aggregate in porphyrins through the changes of UV/Vis. and florescence spectra under UV light and green laser irradiations. In this way, hydrogen bonding interactions have key role to obtain J-aggregated supramolecular porphyrins. We used AFM to observe deposited porphyrin structures under green laser irradiation on glass substrate. The AFM images clearly showed dispersion and morphology of the products that indicated the size of observed porphyrin wires was 300- 400 nm wide and approximately 5 nm high. Further work on irradiated porphyrins and their applications in nonlinear optical properties are in progress in our laboratory, and we believe that these experiments provides a useful way to improve nonlinear optical properties of porphyrin compounds and obtain a new organic and inorganic light emission diodes (OLEDs) under controlled aggregation with more efficiency than non-suprumolecular dyes, and it could be promising for constructing artificial photochemical systems.

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