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Self-Assembly of Template-Directed J-Aggregates of Porphyrin

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Organized self-assembly of molecules directed/supported by polymer template are an important class of advanced materials because of their potential applications such as in optoelectronics and solar cells.[1−3] The polymer template gives shape and directionality for the growth of the aggregate.[4,5] Biopolymers such as proteins and polypeptides are chiral and hence chirality can be imposed on the self-assembly of molecular aggregates supported by such templates.[6−8]

Porphyrins are known to form aggregates and they serve as models for artificial solar energy capture as in photosynthesis.[9] The anionic porphyrin, *meso*-tetrakis-(4-sulfonatophenyl) porphyrin dianion (H_4TPPS^{2-}, abbreviated as TPPS) forms highly organized J- and H-aggregates at very low pH, or in the presence of various inorganic and organic cations.[10,11] There is no report of polymer template induced J-aggregation of TPPS to date. We report here that polylysine serves as a template for efficient formation of J-aggregate of porphyrin.

Figure 1 shows the absorption spectrum of the TPPS monomer, which has an intense absorption band at 433 nm (Soret band or B band) and weak absorption bands at 590 and 640 nm (Q-bands). The absorption spectrum of TPPS in the presence of L-lysine showed two additional intense and red-shifted narrow peaks, at 490 and 705 nm, which are the characteristic bands of J-aggregate of TPPS.[11] The absorption spectrum of TPPS in the presence of poly-(DL, D, or L)-lysine shown is similar but the bands are broader (see Figure 1). The concentration needed for the J-aggregate formation is high for lysine (∼100 mM) whereas only micromolar concentration of polylysine (∼1 μM of the polymer or ∼100 μM of lysine residues) was required for efficient and complete J-aggregation of the polymer. Examination of the absorption spectrum of the clear solution after separation of the J-aggregate by ultracentrifugation indicated that TPPS monomer that was left is less than 1%. This demonstrates that polylysine is highly efficient in inducing the J-aggregation. The absorption spectra of the J-aggregates of TPPS obtained with poly-L-lysine, poly-D-lysine, or poly-DL-lysine were similar.

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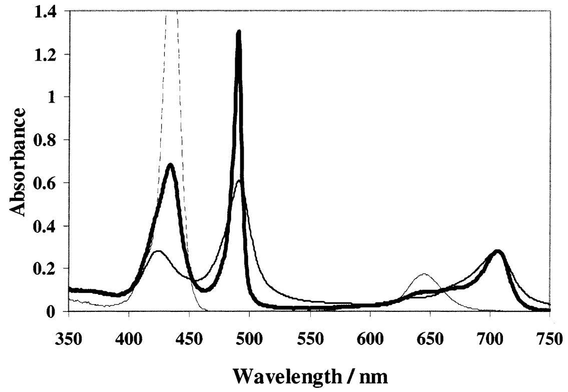

Figure 1. Absorption spectra of the monomer (dashed line) and J-aggregate of TPPS with L-lysine (thick line) and poly-DL-lysine (thin line) in pH 3.0 buffer. Concentration of TPPS is 9 μM in all cases. J-aggregate spectra were obtained using L-lysine (100 mM) and poly-DL-lysine (~5 μM of polymer or 100 μM of lysine residues). Measurements were made at room temperature and samples were made using TPPS (Strem Chemicals, USA), lysine (Loba Chemie, India), and polylysine (Sigma Chemicals, USA).

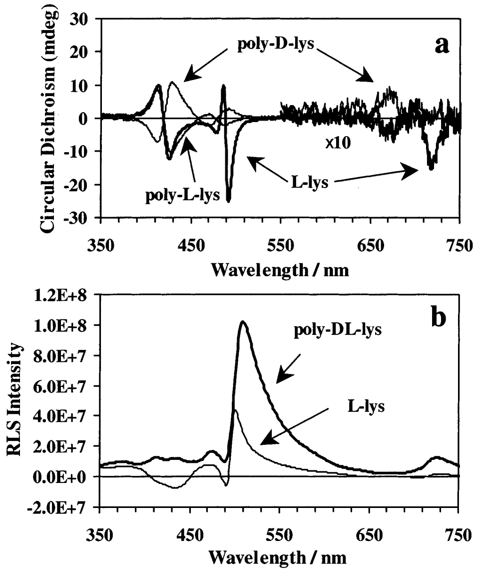

Figure 2. (a) CD spectra of the J-aggregate of TPPS (10 μM) in pH 3.0 buffer. The spectra of J-aggregate with polymer template, poly-D-lysine (60 μM of lysine residues), and poly-L-lysine (60 μM of lysine residues) are shown as thin lines, and that with L-lysine monomer (100 mM) is shown by a thick line. Spectra between 550 and 750 nm are multiplied by 10. (b) RLS spectra of the J-aggregate of TPPS (10 μM) with poly-DL-lysine (thick line) and L-lysine (thin line).

Figure 2a shows the circular dichroism (CD) spectra of J-aggregate of TPPS formed with L-lysine, poly-D-lysine, and poly-L-lysine. The aggregate formed with poly-DL-lysine did not show CD bands. The J-aggregate with L-lysine showed intense circular dichroism bands at 490 and 422 nm, which correspond to the absorption bands of the J-band and the Soret band in the absorption spectrum. The CD band at 490 nm of the J-aggregate of TPPS with L-lysine is as narrow as the 490-nm J-band in the absorption spectrum. The CD band at 490 nm of J-aggregates with poly-L-lysine or poly-D-lysine are relatively broad. The CD band at 720 nm is prominent only for the monomeric L-lysine. These CD spectra show that lysine and polylysine supported J-aggregates are optically active because of induced circular dichroism in the molecular aggregate. It is to be noted that the porphyrin monomer is not an optically active molecule. Induced circular dichroism in ordered molecular aggregate formed by optically inactive molecules is well-known.[12] Induced CD in porphyrin arises from the coupling of transition dipole moments of the TPPS molecules as they orient on the template of optically active lysine residues. The band at 490 nm is intense and narrow in the case of L-lysine J-aggregate and they are weak and broad in the case of polylysine J-aggregates. These differences are consistent with the absorption spectral width and indicate possible differences in the macroscopic chiral structure of the J-aggregates.

Previous studies[10] have confirmed that J-aggregation of TPPS (doubly negative anion) at pH 3 requires organic or inorganic cations. The amino group of lysine is a cation by protonation at pH 3, which promotes J-aggregation. Polylysine is thus a template of a string of cations and thus promotes aggregation with a manifold increase in efficiency compared to lysine. The exact structure and relative positions of porphyrin, lysine, and the backbone are yet to be worked out. The results support that the chirality of the J-aggregate, presumably helical, is induced by the molecular chirality of the amino acid. The polylysine template could itself be helical in the J-aggregate.

Figure 2b shows the resonance light-scattering (RLS)[13] spectra of J-aggregate formed by the polylysine and monomer lysine interaction. The RLS spectrum of the J-aggregate of TPPS with poly-DL-lysine has an intense scattering at 509 nm. RLS of the J-aggregate with L-lysine is less intense than that with poly-DL-lysine. The results indicate the colloidal dimension of the J-aggregate and intense scattering occurs at the main absorption bands of the J-aggregate.

The J-aggregate of TPPS formed with L-lysine, poly-L-lysine, and poly-D-lysine were deposited (by low-speed centrifugation of ~100 rpm for 10 min or by gravity settling onto the substrate which is a slow process taking about 4−5 h) on freshly cleaved mica from the solution and dried at ambient temperature. The surface profile of the deposited film was examined by atomic force microscopy (AFM). Figure 3 shows the AFM image topology of the film of J-aggregate of TPPS with poly-L-lysine. Regular rod-shaped structures were observed in this case. The rodlike structures are rectangular in cross section with a thickness of 42 ± 13 nm, breadth of 240 ± 62 nm, and length of 1.03 ± 0.21 μm. Figure 3b shows the top view of the same film in a small section. The rods are aligned along two directions with an angular separation of 64 ± 1°. Thin films of the J-aggregates of TPPS supported by poly-DL-lysine and poly-D-lysine were also investigated by AFM. These aggregates did not show any regular structures.

These large rodlike structures are due to the macroaggregate of the poly-L-lysine template-directed TPPS J-aggregates. There are 115−230 lysine residues in a single poly-L-lysine polymer and therefore one of the dimensions of the rod may have a maximum length of 60−120 nm if the polymer has an extended structure

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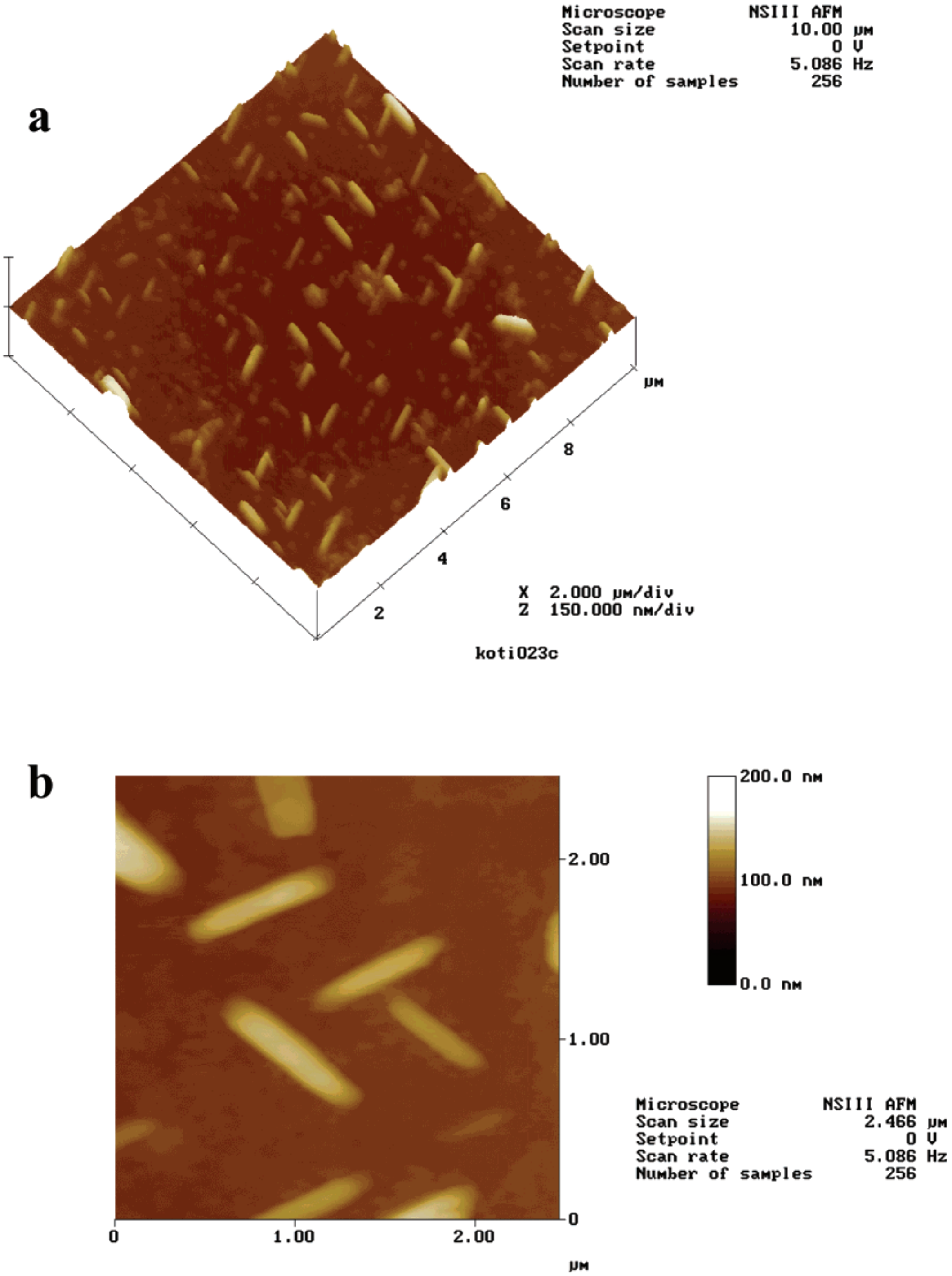

Figure 3. AFM image of the J-aggregate of TPPS formed with poly-L-lysine on mica. (a) 10 × 10 μm$_2$ surface area of the film. (b) Enlarged view of the same film (2.5 × 2.5 μm$_2$).

in that direction. The length of the rod is about 1 μm, which suggests the polymer assembly is stacked in that direction. As mentioned before, the rods are aligned along two specific directions which are separated by an angle of ~64°. This directionality may be coming from the surface of a mica substrate. The exact structural features of mica that are responsible for the formation of oriented rodlike structures of J-aggregate on poly-L-lysine template are not clear.

In conclusion, it is observed that poly-(L, D, or DL)-lysine induces J-aggregation of TPPS more efficiently than monomeric lysine. Only micromolar concentration of polylysine was required for complete conversion of the porphyrin monomer to its J-aggregate. J-aggregates of TPPS are chiral and the chirality is induced by the chirality of optically active lysine in the template. Atomic force microscopy of a thin film of porphyrin J-aggregate with poly-L-lysine template on mica showed rodlike structures with definite direction and size.

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