

EVOLUTION OF SELF-ASSEMBLING TPPS₄ STRUCTURES. FROM NANO TO MACROAGGREGATES

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Meso-tetra (4-sulfonatophenyl) porphyrins (TPPS₄) are hydrophilic molecules, which under acidic conditions exist in zwitterionic forms and tend to self-assemble, forming J-aggregates. The formation occurs when positively charged porphyrin rings and negatively charged SO₃⁻ groups start interacting with each other [1]. Molecules of TPPS₄ are highly promising photosensitizers [2]. However, their tendency to aggregate in acidic environments might interfere with the photoreactivity and suppress their photosensitizing potential [3] and, thus, hindering their applicability for a photodynamic therapy. The aggregation, however, leads to enhancement of nonlinear optical response of TPPS₄ such as second and third harmonic generation. Recently, the nonlinear optical responses of TPPS₄ have been proposed for use as harmonophores, the labels for harmonic generation microscopy, in multimodal imaging applications of TPPS₄ J-aggregates.

In this study, we investigated the evolution of TPPS₄ J-aggregates and correlated their optical and structural properties. After dilution in water, TPPS₄ solution was prepared in 0.1 M of hydrochloric acid (to reach pH = 1). The beginning of J-aggregates formation and their continuous growth into bigger aggregates were followed by means of an atomic force microscopy and a laser scanning confocal fluorescence microscopy. Optical properties of J-aggregates were studied using absorption and fluorescence spectrometers, and applying fluorescence lifetime imaging microscopy.

The results showed that monomers of TPPS₄ porphyrins self-assemble into nanotubes and, given enough time, could form giant aggregates that are easily visible to the naked eye. Such giant aggregates appear as “sea urchin like” structures that can potentially be used in nanotechnology applications, for example as chiral templates for nanomaterials.

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