

Enwrapping of tubular J-aggregates of amphiphilic dyes for stabilization and further functionalization

The fabrication of functional units on mesoscopic length scales (nanometers to micrometers) in an aqueous environment by a self-assembling process is a fascinating but challenging task. It is essentially a biomimetic approach following design rules of living biological matter utilizing electrostatic and hydrophobic forces for the combination of a variety of materials. A peculiar form of such self-assembled structures is represented by tubular J-aggregates built from amphiphilic cyanine dye molecules. Those aggregates have attracted attention because of their similarity with natural light harvesting complexes. In particular, the dye 3,3'-bis(3-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-diocetylbenzimidazo-carbo-cyanine (C8S3) forms micrometer long double walled tubular aggregates with a uniform outer diameter of 13 ± 0.5 nm. These J-aggregates exhibit strong exciton coupling, as seen by a strong shift in the absorption spectrum, and hence exciton delocalization and migration. However, their structural integrity and hence their optical properties are very sensitive to their chemical environment as well as to mechanical deformation, rendering detailed studies on individual tubular J-aggregates difficult.

In a collaboration within the CRC 951 Hybrid Inorganic/Organic Systems for Opto-Electronics, projects A6 (Kirstein, Rabe) and A12 (Koch) we addressed this issue and developed a route for their chemical and mechanical stabilization by in situ synthesis of a silica coating that leaves their absorbance and emission unaltered in solution [1]. By electrostatic adsorption of precursor molecules it was achieved to cover the aggregates with a silica shell of a few nanometer thickness which is able to stabilize the aggregates against changes of pH of solutions down to values where pure aggregates are oxidized, against drying under ambient conditions, and even against the vacuum conditions within an electron microscope. It was possible to measure spatially resolved electron energy loss spectra across a single freely suspended aggregate to analyze the chemical composition and the chemical composition and silica shell thickness. However, their structural integrity and hence their optical properties are very sensitive to their chemical environment as well as to mechanical deformation, rendering detailed studies on individual tubular J-aggregates difficult.

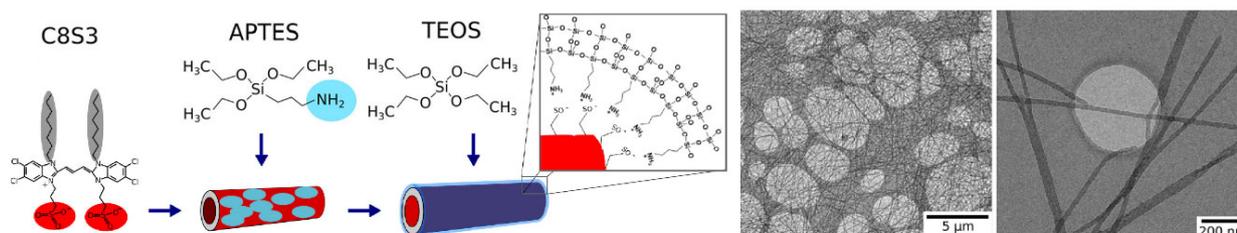


Figure 1: Sketch of chemical structure of the amphiphilic carbocyanine C8S3 and the route to synthesize a closed shell of silica on top of the aggregates of the anionic carbocyanine by successive adsorption of the precursor molecules APTES and TEOS. The TEM images are taken at room temperature and show Room temperature silica coated aggregates deposited on a holey carbon film. The right image is a magnification showing a single aggregate, freely suspended across a hole.

The concept of electrostatic adsorption at the charged surface of the aggregates was also utilized for the adsorption of oppositely charged polyelectrolytes, polycations in this case [2]. It was found that the morphology of the resulting aggregate/polycation complexes sensitively depends on the chemical structure of the polyelectrolyte. But in general, adsorption of a homogeneous layer leads to charge reversal of the surface of the complex, which can be used for further attachment of other chemicals. The adsorption of polyelectrolytes at these amphiphilic tubular structures, stabilized by means of hydrophobic forces, is far from obvious and demonstrates an applicable route to the hierarchical build-up of more complex nanostructures in solution by means of a self-assembling process.

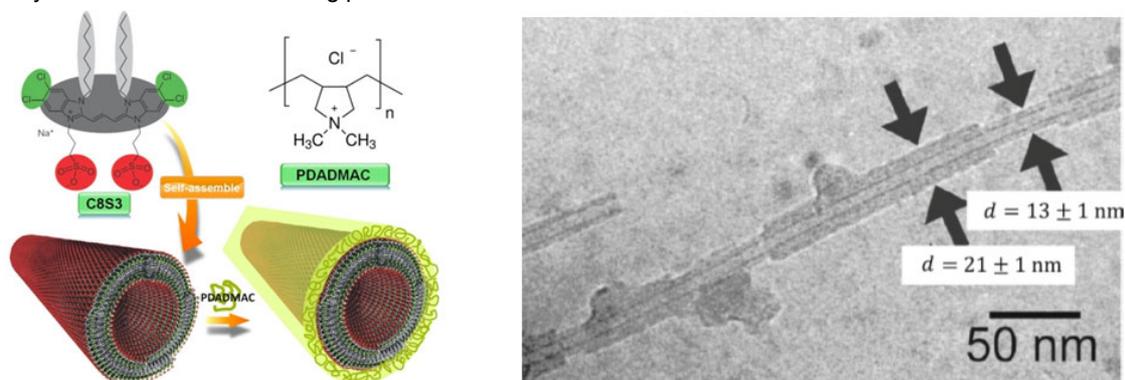


Figure 2 Sketch of the tubular aggregates of C8S3 emphasizing the negative surface charge due to sulfonate end groups of the dye and chemical structure of the polycation PDADMAC. The Cryo-TEM image shows aggregates partially covered with PDADMAC.

(1) Individual tubular J-aggregates stabilized and stiffened by silica encapsulation

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(2) Adsorption of polyelectrolytes onto the oppositely charged surface of tubular J aggregates of a cyanine dye

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