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′-dioctylbenzimidacarbo-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 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.

(1) Individual tubular J-aggregates stabilized and stiffened by silica encapsulation
K. Herman, H. Kirmse, A. Eljarrat, C.T. Koch, S. Kirstein, J.P. Rabe
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(2) Adsorption of polyelectrolytes onto the oppositely charged surface of tubular J aggregates of a cyanine dye
O. Al-Khatib, C. Böttcher, H. von Berlepsch, K. Herman, S. Schön, J.P. Rabe, S. Kirstein
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