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## COMMUNICATION

# Nanohybrids from Nanotubular J-Aggregates and Transparent Silica Nanoshells

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**Organic-inorganic nanohybrids have been synthesized by *in-situ* coating supramolecular nanotubular J-aggregates with helically wound silica ribbons, reflecting the J-aggregates' superstructure. The J-aggregates retain their morphology and optical properties in the nanohybrids, and display improved stability against elevated temperatures, chemical ambient and photo-bleaching.**

Tubular J-aggregates formed by amphiphilic cyanine dyes have attracted significant attention<sup>1,2</sup> since they can serve as model systems for artificial nanostructures to mimic chlorosomal light-harvesting (LH) complexes of green sulfur and non-sulfur bacteria, which are known to exhibit the highest LH efficiencies.<sup>3</sup> Similar to the natural LH centers, the tubular J-aggregates are comprised of dyes and display double-walled tubular structures with well-defined molecular orientations.<sup>4,5</sup> Owing to the highly ordered molecular stacking, these structures exhibit the typical optical properties of J-aggregates, such as strong and narrow absorption bands with a large red-shift relative to the monomer, a nearly resonant narrowband fluorescence emission, and the strong exciton delocalization and migration.<sup>6,7</sup> However, the application of these J-aggregates has posed a long-standing challenge due to their poor stability against elevated temperature, high ionic strengths, photo exposure, and mechanical stress. Therefore, a method that can increase the stability of the J-aggregates in solution is desirable.

Silication of functional organic building blocks is a known tool to build organic-inorganic hybrid systems and has attracted much interest, because of the optical transparency of silica in combination with biocompatibility, structural robustness, improved environmental stability, and feasibility of chemical modification.<sup>8,9</sup> Therefore, promising attempts were made to combine J-aggregates with silica, using silica sphere encapsulated J-aggregates or silica/J-aggregate films<sup>10</sup>. Mann *et al.* have reported template-directed synthesis of silica-coated

porphyrin J-aggregate nanotapes exhibiting retention of the optical properties.<sup>11</sup> Within the silica host matrix, the optical properties of J-aggregates could be modulated by tuning the coupling to localized plasmons.<sup>12</sup> In this work, we report the controlled synthesis of organic-inorganic nanohybrids by coating the surface of tubular J-aggregates with a silica shell *via* a sol-gel method, where the thickness of the silica shells was facily adjusted by varying the reaction conditions. Under certain conditions the as-synthesized silica shell exhibits helical superstructural features that may be attributed to the transcription from the internal helical superstructure<sup>13</sup> of the tubular J-aggregates. The silica-coating not only retains the morphology and optical properties of J-aggregates, but also provides an enhanced stability of the self-assembled system. Herein, we have achieved the strengthened stability of the J-aggregates against high temperatures, divalent metal ions, and photo exposures in the organic-inorganic nanohybrids.

The cyanine dye 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-diocylbenzimidacarbocyanine (C8S3) is known to self-assemble into nanotubular J-aggregates in a water/methanol solution (100/13, v/v).<sup>1,14</sup> The resulting J-aggregates are double-walled nanotubes with an outer diameter of  $13 \pm 1$  nm, an inner diameter of  $6.5 \pm 1$  nm, and lengths up to tens of micrometers (Fig. S1). The UV-vis spectra show a large red-shift upon the formation of the J-aggregate. Using these supramolecular nanotubes as supporting scaffolds, optical transparent helical silica nanoshells were prepared through the sol-gel process with 3-aminopropyltriethoxysilane (APTES), and tetraethoxysilane (TEOS) as silica precursors.

Cryogenic transmission electron microscopy (cryo-TEM) was employed to visualize the silica-coated J-aggregates *in-situ*. As shown in Fig. 1a, thread-like structures were obtained, which are deemed as silica nanoshell coated J-aggregate hybrids. Cross-sectional line profiles were taken across the nanohybrids as presented in Fig. 1b. An overlay of line scans

taken from different hybrid nanotubes resolves the average diameter of the nanohybrids to be  $21 \pm 1.5$  nm, as measured by the full width at half maximum (FWHM). The line scans show similar diameters manifesting the uniformity of the hybrid nanotubes. Compared to the diameter of the bare J-aggregate of  $13 \pm 1$  nm, the mean diameter of silica coated J-aggregates has increased by  $7 \sim 8$  nm. This increase is assigned to a silica shell with a mean thickness of 3.5 to 4 nm. The growth of the silica shell on the outer surface of tubular J-aggregates is illustrated further by Fig. 1c. An end section of the nanohybrid is shown in a magnified view. The remaining of the original tubular J-aggregate and a protruding part of a silica nanowire filling inside of the tube can be seen as they both protrude from the silica shell. The diameters of the J-aggregate tube are similar as observed for the bare J-aggregates (13 nm outer diameter and 6.5 nm inner diameter).<sup>2</sup> Obviously, the sol-gel process does not cause significant changes to the size and morphology of the J-aggregate nanotubes as is further supported by optical spectroscopy. In Fig. 1d, a top view of the open end of an upstanding nanohybrid is captured accidentally. The center of the tube is filled with a high contrast material that may be identified as a silica wire, whose diameter is close to that of silver wires previously synthesized inside J-aggregates through photoinitiation.<sup>15</sup>

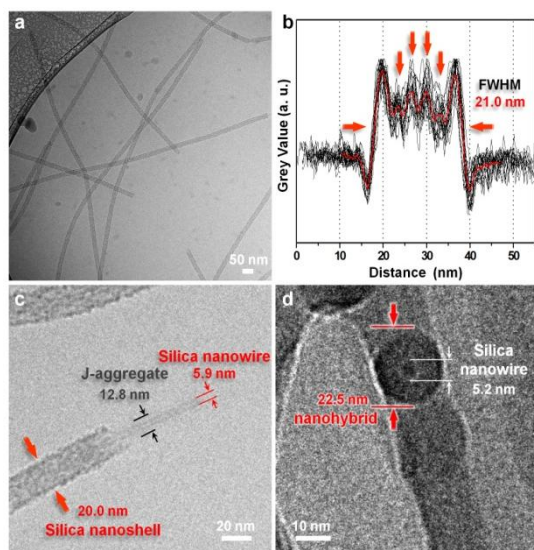


Fig. 1 Cryo-TEM images and analysis of silica helical nanoshell coated J-aggregates. (a) An overview of nanohybrids. (b) Overlaid line scans across different individual nanohybrids reflecting the highly structural homogeneity. The red curve is the average curve which displayed the average diameter was  $21 \pm 1.5$  nm. The four peaks in the red curve proved the repeated periods of the helical silica nanoshells. (c) An end section of the nanohybrid denoting the remaining of the original tubular J-aggregate and the silica inside of the nanohybrid. (d) An upstanding nanohybrid indicating the inner tube was filled by silica.

As verified in Fig. S2, the nanohybrids with a high product yield can extend in length up to tens of micrometers. Negligible amounts of non-templated silica were noted. It is important to note that no obvious bundling effect of the J-aggregate is

observed after the silication with APTES/TEOS and most of the nanohybrids are isolated. Additionally, the deposition of the silica nanoshells increased the stiffness of the nanotubes, as is concluded from the typical increase of bending radius. High resolution-TEM (HR-TEM, Fig. S3) and energy dispersive X-ray spectroscopy (EDXS, Fig. S4) measurements support that the nanohybrids are comprised of J-aggregates (origin of S-signal) and silica (origin of Si-signal).

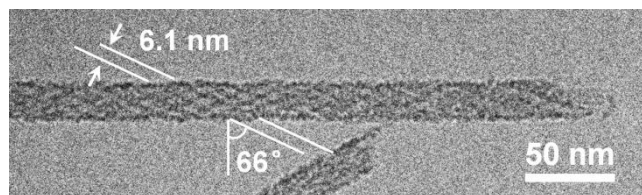


Fig. 2 Magnified view of a cryo-TEM image of single silica nanoshell coated J-aggregate. The width and the helix angle of the silica ribbons are indicated.

In magnified cryo-TEM images (Fig. 2 and S5), typical silica/J-aggregate nanohybrids revealed well-ordered net-like patterns which are indicative of repetitive patterns expected from the projection images of helical structures. A close inspection reveals the width of the ribbons that constitute the helix is  $6.1 \pm 0.3$  nm with a helix angle of  $66 \pm 2^\circ$ . The helical handedness, however, cannot be identified from the projection images obtained by cryo-TEM. These helical structures are reproducible in experiments, although we have noticed the helical pattern cannot be observed in all of the silica nanotubes. A sketch of a proposed 3D model of the nanohybrids using the parameters extracted from Fig. 2 is shown in the ESI (Fig. S6). It is important to note that the width of these ribbons as well as the pitch differ from the values proposed for the pure J-aggregates<sup>13</sup>, which means the silica super structure is not a direct one-to-one transcript of the aggregate structure. The formation of the silica nanoshell is initiated and driven by electrostatic forces that require charge matching between silica precursor and template (Fig. S7).<sup>16,17</sup> The surface of the tubular J-aggregates is assumed to be negatively charged due to the sulfonate groups of the C8S3 anions. The cationic species, such as  $[\text{Si}(\text{OH})_3(\text{NH}_3)]^+$  hydrolyzed from APTES, are attracted by the negative surface potential, forming an ultrathin silica layer. Further condensation of hydrolysis products of TEOS, e. g.  $[\text{Si}(\text{OH})_4]$ , leads to the formation of ribbons of the silica nanoshell, specifically at the J-aggregate surface that was previously covered by APTES. It is supposed that the silica nanoshell can inherit and amplify small corrugations of the J-aggregate surface. Therefore, the helical winding of the ribbons is proposed to be induced by the helical superstructure of the tubular aggregates.<sup>13</sup> A control experiment without the addition of APTES was conducted, in which spherical particles instead of silica ribbons were observed (Fig. S8a), indicating the essential role of APTES in the formation of silica nanoshells.

The optical properties of the silica coated J-aggregates were investigated by UV-vis and fluorescence measurements (Fig. 3a), which show that encapsulation of the J-aggregates by silica does not lead to significant changes of the spectrum and hence

reorganization of the J-aggregate structure. The very minor differences may be either due to the different polarizability<sup>18</sup> of the close environment of the dyes, or due to very slight structural change. Since in cryo-TEM images all J-aggregates are covered by silica, the spectra truly represent the spectra of silica covered J-aggregates. Fig. 3b illustrates fluorescence spectra showing that the emission of silica nanoshell-coated J-aggregate remains unchanged besides some difference in intensity. Using rhodamine B as a standard, the fluorescence quantum yield ( $\Phi_f$ ) of silica nanoshell-coated J-aggregate ( $\Phi_f = 8\%$ ) was determined to be approximately 1.3 times that of bare J-aggregates ( $\Phi_f = 6\%$ ) (Fig. S9).

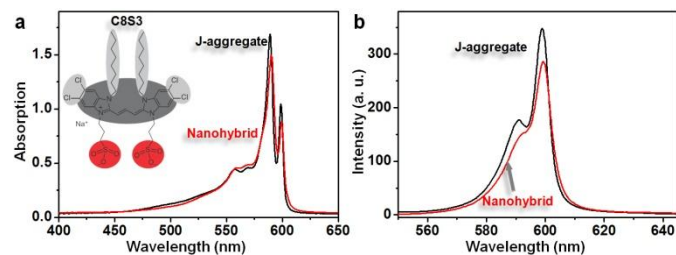


Fig. 3 Optical properties of nanohybrids and J-aggregates of the dye C8S3. (a) Absorption spectra; (b) PL spectra of as-prepared nanohybrid and J-aggregate ( $\lambda_{\text{ex}} = 500 \text{ nm}$ )

The thickness of the silica nanoshell can be facilely adjusted by varying the concentration of the silica precursors. The mean thickness of the silica nanoshell on the J-aggregate was found to increase almost linearly with TEOS in the concentration range of 3.6 mM to 14.3 mM with an increase of 0.5 nm/mM (Fig. S10, S11). It is therefore proposed that this method is a straightforward, effective, and adaptive way to synthesize silica nanoshell coated J-aggregate with defined shell thickness.

The enhanced thermal, chemical and optical stability of J-aggregates was demonstrated after coating with silica shells. As shown in Fig S12, bare J-aggregates started to dissociate at 45 °C, as observed by a decrease of J-band absorbance and an increase of monomer absorbance peak. For silica coated J-aggregates the dissociation started at 65 °C, indicating an increased thermal stability. Metal ions such as  $\text{Zn}^{2+}$  were found to decrease the absorption peak of J-aggregates (Fig S13a) due to the strong interactions between divalent ions and C8S3 which causes damages to J-aggregates. It is interesting that silica-coated J-aggregates were stable at  $\text{Zn}^{2+}$  concentrations of 6.72 mM while the absorption peak of J-aggregate was reduced by ~80% with 3.36 mM  $\text{Zn}^{2+}$  (ESI, Fig. S13). To study the photostability, the nanohybrid and J-aggregate were irradiated with 500 nm light and the fluorescence intensities at 600 nm were recorded vs. time. As shown in Fig. S14, after 60 min the fluorescence emission of the nanohybrids was bleached to approx. 60%, while, under same conditions, the fluorescence of uncovered J-aggregates was bleached to almost 10% of the original intensity. Since photobleaching of cyanine dyes is known to be caused by a chemical reaction with singlet oxygen or hydroxyl radicals<sup>19</sup>, we conclude that the silica nanoshell is dense enough to significantly reduce the penetration of such

radicals. However, exact quantification of photobleaching turned out to be difficult due to the qualitative change in spectra during the bleaching process and is therefore beyond this communication.

## Conclusions

An *in-situ* synthesis of silica nanoshells on nanotubular J-aggregates was developed based on the electrostatic attraction between silica precursors and the J-aggregates. The resulting nanohybrids exhibit a helical superstructure, induced by the supramolecular helical structure of the J-aggregates. The nanometer sized silica shell provides higher mechanical stiffness, an improved stability against elevated temperatures, chemical ambient, and photobleaching. All these factors make this hybrid nanomaterial very promising for advanced optical spectroscopy studies, and also for the hierarchical build-up of robust and complex functional systems for light harvesting experiments.

## Notes and references

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Electronic Supplementary Information (ESI) available: materials and methods, TEM and HRTEM images of nanohybrids, EDXS analysis, measurement of fluorescence quantum yields, and photo bleaching experiments are presented. See DOI: 10.1039/c000000x/

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