

# Template-directed synthesis of silica-coated J-aggregate nanotapes†

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**Self-assembly of porphyrin nanotapes in the presence of alkoxysilane reaction solutions produces hybrid nanofilaments consisting of an optically responsive J-aggregate core encased within an ultrathin shell of amorphous silica.**

Studies on the synthesis and characterization of model systems that mimic photosynthesis or light harvesting processes in general have been extensively reported. Recently, long range electron transport has been demonstrated using cyanine- and porphyrin-based superstructures exposed to visible light.<sup>1</sup> The photovoltaic properties are associated with reversible self-assembly of the chromophores,<sup>2</sup> and originate from the strong coupling of molecular transition dipoles by side-by-side stacking of porphyrins. This leads to an extremely large absorption cross-section and a fast exciton energy transfer over hundreds of molecules.<sup>3</sup> Structural investigations by cryo-transmission electron microscopy (TEM) and atomic force microscopy (AFM) have shown that pseudocyanine dyes self-organize into bundles of long fibres with addition of salt,<sup>4</sup> and that porphyrin monomers spontaneously self-assemble as J-aggregates in the form of nanotubules<sup>5</sup> or helicoidal particles.<sup>6</sup>

Because the use of self-assembled organic chromophores in technological devices is in part constrained by relatively low mechanical, thermal and chemical stabilities, studies involving the intercalation of J-aggregates within robust macroscopic host matrices have been undertaken. For example, silica films containing encapsulated cyanine fibres and exhibiting a high third order non-linear susceptibility,<sup>7</sup> as well as polymer-chromophore aggregates with increased stability<sup>8</sup> and efficient electroluminescence,<sup>9</sup> have been reported. In contrast, few studies have exploited the small-scale and high aspect ratio of chromophore superstructures to prepare discrete nanoscale hybrid materials with optical functionalities. A notable exception is the preparation of conductive polymer rods by coating individual porphyrin J-aggregates and subsequently removing the organic template.<sup>10–12</sup> Here we report the preparation of filamentous hybrid nanostructures using the *in situ* self-assembly of tape-like J-aggregate superstructures as supramolecular templates for controlled silica deposition. Significantly, the nanofilaments, which consisted of a core of self-assembled porphyrin molecules surrounded by an ultrathin shell of amorphous silica, show optical properties

consistent with the retention of stacked arrays of the chromophore within the hybrid nanocomposite.

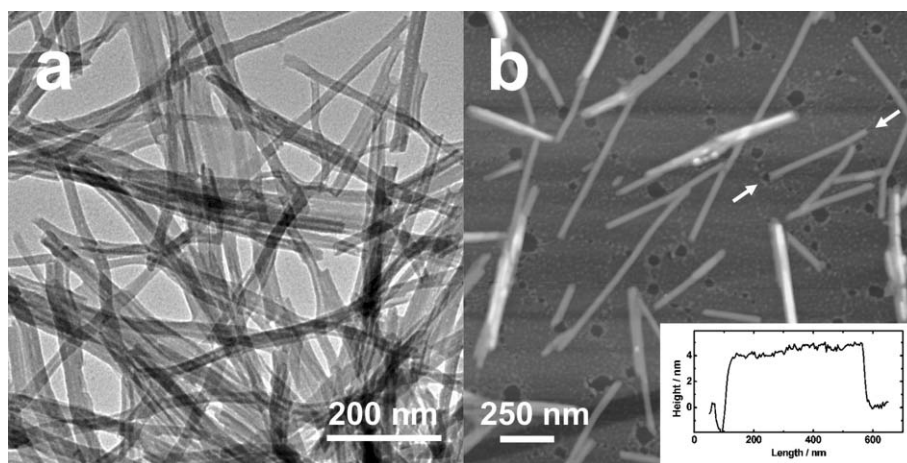
J-aggregates of tetrakis(4-sulfonatophenyl)porphine (TPPS) were prepared by adding 100  $\mu$ L of 1 M hydrochloric acid to 10 mL of 50  $\mu$ M aqueous solution of porphyrin. Acidification to pH values below 4 immediately produced a pink to bright-green colour change due to protonation of  $[\text{H}_2\text{TPPS}]^{4-}$  ions and formation of  $[\text{H}_4\text{TPPS}]^{2-}$  monomers. UV-vis spectra showed a decrease in the intensities of the Soret (413 nm) and Q (515, 552, 580 and 633 nm) bands, and appearance of corresponding bands at 434 nm, and 592 and 644 nm, respectively. Within 20 min, self-aggregation of the  $[\text{H}_4\text{TPPS}]^{2-}$  anions produced a darkening of the green solution, and UV-vis spectra showed an intense red-shifted Soret band at 490 nm along with a broad peak at 707 nm due to formation of J-aggregates in equilibrium with the  $[\text{H}_4\text{TPPS}]^{2-}$  monomer.† Similar characteristic changes—in particular, a marked reduction in the emission intensity on J-aggregate formation—were observed by fluorescence spectroscopy. TEM images of unstained samples of the J-aggregates showed large numbers of needle-like particles (Fig. 1a). In general, the nanofilaments were straight-edged, flexible, uniform in width (15–20 nm), variable in length (0.5–2  $\mu$ m), and depending on the concentrations of monomer and acid used, in the form of discrete particles, networks or co-aligned bundles. AFM measurements of J-aggregates deposited on single crystalline graphite surfaces yielded a uniform filament thickness of 4–5 nm (Fig. 1b), indicating that the TPPS superstructures were assembled in the form of high aspect ratio nanotapes, *ca.* 5  $\times$  20 nm in thickness and width, respectively.

Silica-coated TPPS J-aggregate nanofilaments were prepared by mixing tetraethoxysilane (TEOS), or TEOS-aminopropyltriethoxysilane (APTES) mixtures, with pH neutral porphyrin solutions followed by acidification to produce a dark green suspension that precipitated with time.‡ TEM studies of samples left up to 4 h after adding the alkoxysilane reactants showed the presence of well-defined nanofilaments, 0.5 to 1.0  $\mu$ m in length, with a uniform width typically around 25 nm, depending on the amount and type of alkoxysilane added (Fig. 2a). Negligible levels of non-templated silica were obtained. In general, addition of small amounts (10% v/v) of APTES to the reaction mixture produced nanofilaments that were shorter in length (500 nm), increased in width ( $35 \pm 2$  nm), and surface roughened by silica outgrowths (Fig. 2b). Significantly, energy dispersive X-ray analysis, which showed the presence of silicon and sulfur associated specifically with individual nanofilaments (Fig. 2c), confirmed that the nanostructures comprised J-aggregate superstructures coated in ultrathin coatings of amorphous silica or aminopropyl-functionalized silica. AFM investigations indicated that the surface of the silicified J-aggregate nanotapes prepared

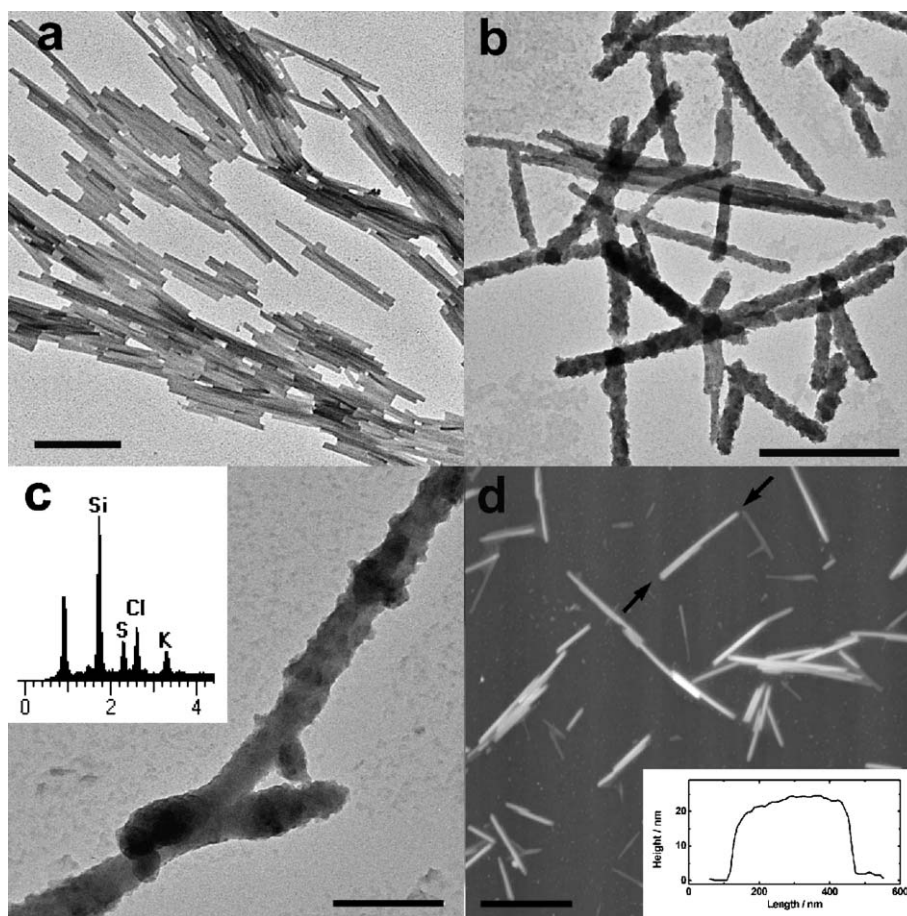
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† Electronic supplementary information (ESI) available: UV-vis spectrum of unmineralized J-aggregate nanofilaments at pH 2; SEM image of calcined nanorods showing intact silica nanofilaments. See <http://www.rsc.org/suppdata/cc/b5/b502436f>



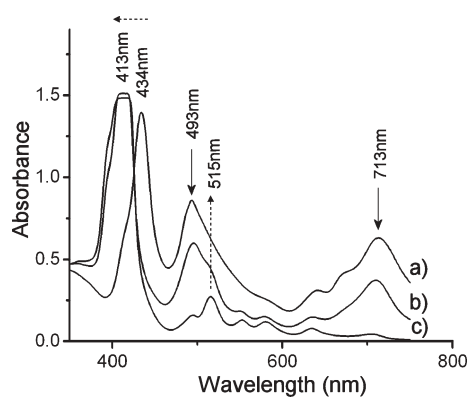
**Fig. 1** (a) TEM and (b) AFM images of TPPS J-aggregate nanotapes. Inset in (b) shows height contour along a single filament (white arrows).



**Fig. 2** TEM images showing silicified J-aggregate nanofilaments prepared using (a) TEOS and (b) 10 vol% APTES-TEOS; (c) TEM image and corresponding EDX analysis (inset, units keV, unlabelled peak is background Cu) of an aged TEOS-derived silicified nanofilament; (d) AFM image of TEOS-derived silica-coated TPPS nanotapes; inset shows height profile along a single filament (black arrows). Scale bars: (a) 500 nm; (b) 500 nm; (c) 200 nm and (d) 1  $\mu$ m.

in the presence of TEOS was smooth, and that the nanostructures had a uniform thickness of *ca.* 25 nm (35 nm for APTES-TEOS mixtures) (Fig. 2d). Calcination of the hybrid nanofilaments at 500  $^{\circ}$ C using a heating rate of 1  $^{\circ}$ C  $\text{min}^{-1}$  produced a white powder that consisted of aggregated bundles of silica nanorods.<sup>†</sup>

The results indicate that self-assembly of protonated TPPS monomers in alcoxysilane reaction mixtures takes place without significant disruption to the J-aggregate superstructure. Moreover, *in situ* formation of the porphyrin-containing nanotapes directs the subsequent deposition of amorphous silica specifically on the surface of the organic template, possibly *via* interfacial interactions



**Fig. 3** UV-vis spectra of silicified J-aggregate nanofilaments: (a) pH 1.8; (b) pH 5.6 and (c) pH 6.

between surface-exposed sulfonate groups of the porphyrin anions and cationic silicic acid species such as  $[\text{Si}(\text{OH})_3(\text{OH}_2)]^+$ . Typically, the silica coatings on the side and top faces of the nanotape template were only 3–5 nm or 10–15 nm in thickness, respectively, indicating that the rate of  $[\text{H}_4\text{TPPS}]^{2-}$  aggregation was substantially faster than hydrolysis/condensation of the alkoxy silane reactants at pH 2. Smooth nanometre-thick films were produced presumably because of the disparity in the initial rates of organic and inorganic assembly; however aging the reaction mixtures for extended periods (e.g. 2 weeks) gave thicker silica coatings with extensively roughened surfaces due to slow but prolonged condensation of soluble silica-precursors present within the reaction mixture. Similarly, shorter nanofilaments of surface-roughened amino-functionalized silica-coated J-aggregates were produced in the early stages of reactions involving APTES because the increased rate of silica deposition associated with this precursor to some extent quenched the *in situ* growth of the organic template.

UV-vis spectra of the hybrid nanofilaments showed a J-aggregate red-shifted Soret band at 493 nm and broad peak at 713 nm, as well as a  $[\text{H}_4\text{TPPS}]^{2-}$  monomer band at 434 nm (Fig. 3a). Thus, no distinct changes in the optical properties were observed for the silica-entrapped J-aggregates, suggesting that encapsulation of the porphyrin nanotapes occurs without significant disruption in supramolecular organization. Interestingly, neutralisation of suspensions of the silicified J-aggregate nanofilaments by sequential addition of 10  $\mu\text{L}$  aliquots of 0.1 M NaOH resulted in spectral changes associated initially with conversion of  $[\text{H}_4\text{TPPS}]^{2-}$  into  $[\text{H}_2\text{TPPS}]^{4-}$  monomers (peaks at 434, and 413 and 515 nm, respectively) (Fig. 3b), followed by disassembly of the porphyrin superstructure at pH 6 (Fig. 3c). Thus the results indicated that the J-aggregates were accessible to hydroxide ions diffusing through the ultrathin silica shell, and sensitive to deprotonation-induced dissociation.

Significantly, TEM images of silicified J-aggregates after pH neutralisation showed retention of the nanofilamentous morphology and corresponding EDX analyses revealed the presence of S, confirming entrapment of the  $[\text{H}_2\text{TPPS}]^{4-}$  monomers within the hybrid nanostructure. Furthermore, acidification of the neutralised samples re-established the J-aggregate assembly within the silicified nanostructure.

In conclusion, supramolecular templating of ultrathin silica layers has been achieved on self-assembled nanotapes comprising stacked arrays of porphyrin anions. The resulting hybrid nanocomposites are in the form of discrete high aspect ratio silica-coated filaments, and show retention of the optical properties associated with the entrapped chromophore superstructure. Future studies will assess the stability of these novel hybrid materials under mechanical and thermal stress, as well as their integration into multi-component systems.

## Notes and references

‡ Typically, 25  $\mu\text{L}$  of TEOS was added to 10 mL of a 50  $\mu\text{M}$  aqueous solution of TPPS followed by acidification to pH 2 with hydrochloric acid under vigorous stirring. Alternatively, 25  $\mu\text{L}$  of a 10% v/v APTES-TEOS mixture was added to the porphyrin solution (50  $\mu\text{M}$ , 10 mL) followed by acidification with 100  $\mu\text{L}$  of 1 M hydrochloric acid, again with vigorous stirring. Samples were studied 2–3 h after addition of the alkoxy silane reactants by UV-vis absorption using quartz cuvettes with a 10 mm light path. Aliquots were taken at various time intervals, typically within 4 h after adding the alkoxy silane reactants, and air-dried onto carbon-coated copper grids for TEM analysis. Samples for AFM were air-dried onto freshly cleaved single crystalline graphite (HOPG) substrates and scanned under ambient conditions in tapping mode using a Veeco-DI Dimension 3000 microscope with a Nanoscope III controller.

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