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Self-Organizing Functional Materials via Ionic Self Assembly: Porphyrins H- and J-Aggregates on Synthetic Chrysotile Nanotubes

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The search for obtaining new nanomaterials through self-assembly is of great interest because of all the features that noncovalent interactions can provide, e.g., reversibility, response to external stimuli, self-healing, etc.[1] Among the secondary interactions exploited in supramolecular chemistry, Ionic Self-Assembly (ISA) takes advantage of Coulombic attraction between oppositely charged building blocks, resulting in a very simple method, of wide applicability, and that allows the formation of very complex materials.[2,3] Recently, this bottom-up approach has also been successfully employed to attain new organic/inorganic nanohybrids.[3,4] In this latter framework, noncarbon nanotubes (NTs) have attracted broad interest as inorganic tectons, showing great potential in fields that span from sensing applications to biotechnology.[5] In particular, synthetic geoinspired chrysotile NTs $Mg_3Si_2O_5(OH)_4$ have been proposed as a nontoxic reference standard to investigate natural asbestos fibers.[6] Here we report on the use of the ISA approach, in either an aqueous or organic phase, for the formation of new nanohybrids consisting of chrysotile NTs as inorganic building blocks and of functional organic molecules such as porphyrin chromophores.

When suspended in water, chrysotile NTs display a positive ζ-potential over a wide range of pH,[7] suitable for the interaction with the anionic tetra(4-sulfonatophenyl)porphyrin (H_2TPPS^{4-}). Therefore, the bulk nanocomposite has been prepared through a mix-and-shake protocol, simply titrating a suspension of chrysotile with a porphyrin solution at pH ~7. UV/vis extinction spectra of optically transparent thin films of the hybrid material reveal a substantial red shift of the porphyrin B-band ($\Delta\lambda = +29$ nm) upon interaction with chrysotile as compared to the parent dye (Figure 1a). In agreement with literature results,[8] such a shift indicates a strong electronic perturbation of the porphyrin ring as a result of the interaction between dyes and the NT surface. If the solution used for preparing the samples is acidic (pH ~2), or the H_2TPPS^{4-}/chrysotile nanocomposite is put into contact with acid vapors, the green color of the material points to the conversion of the porphyrin to its diacid form H_4TPPS^{2-}. Besides, as indicated by the UV/vis spectra of the hybrid thin films, the diprotonated dyes are further organized into J-aggregates[9,10] on the NT surface, displaying extinction profiles similar to those of J-aggregates prepared in the absence of the inorganic matrix (Figure 1b).

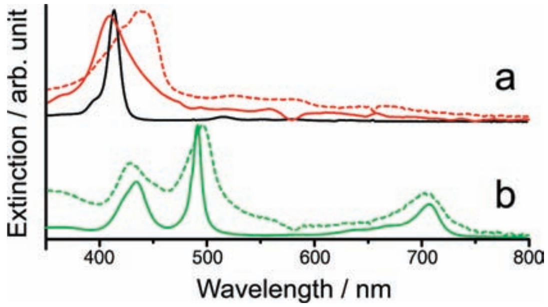
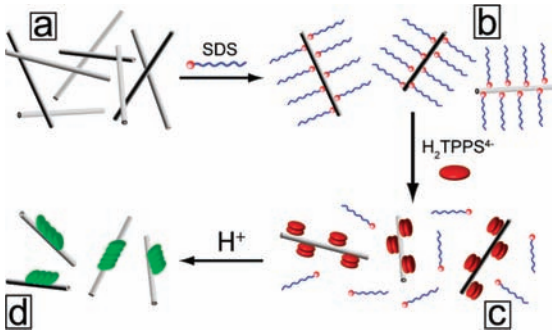


Figure 1. Normalized UV/vis extinction spectra of: (a) H_2TPPS^{4-} as water solution (black line), nujol mull (red solid line), and on chrysotile surface (red dashed line); (b) H_4TPPS^{2-} J-aggregates formed in water (green solid line) and on chrysotile surface (green dashed line).

Scheme 1. Nanohybrids Formation in the CH_2Cl_2/CH_3OH Mixture



Better dispersed inorganic tectons can be obtained through the ISA approach, providing a way for an efficient debundling of the chrysotile NTs. To this purpose, an anionic surfactant (SDS) can easily interact with the positively charged matrix, decorating it with alkyl chains and allowing the formation of a very stable colloidal suspension of the NTs (Scheme 1a,b) in a mixture of CH_2Cl_2 and CH_3OH (9:1 v/v). Light scattering experiments confirm that this colloid consists of well-dispersed, rigid rod-like scatterers. Preliminary results on the deposition of this suspension on surfaces have shown that thin films of chrysotile NTs can be formed very simply and with a very promising degree of alignment. Thus far, the colloid has been drop-cast on highly oriented pyrolytic graphite (HOPG), and atomic force microscopy (AFM) measurements have pointed out that the inorganic tectons are actually arranged along a preferential orientation (Figure 2a). Indeed, the underlying mechanism needs further investigation, first of all to estimate the role of the dispersive interactions between the aliphatic chains attached to the NTs and the apolar HOPG surface, together with that of the shear forces arising during solvent evaporation. As well, the iridescence displayed by the thin film surface under observation

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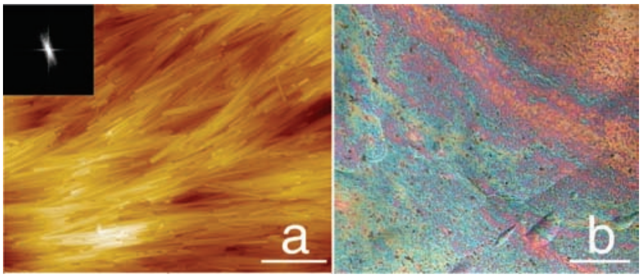

Figure 2. Chrysotile colloid drop-cast on an HOPG surface: (a) AFM topography image, the inset showing the related 2D-FFT graph; bar = 1 μm, z-range = 325 nm; (b) optical microscopy image showing the iridescence exhibited by the surface of the sample; bar = 100 μm.

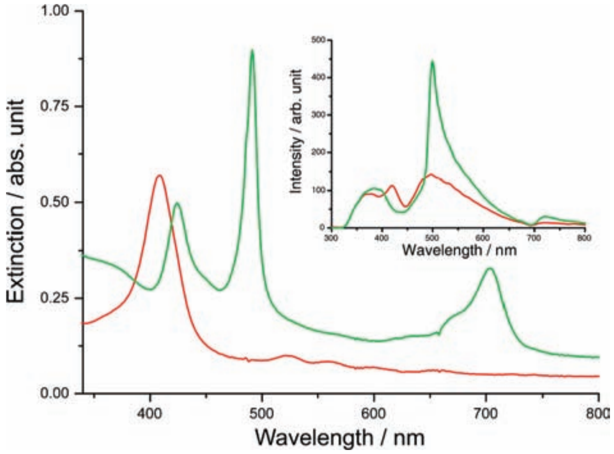

Figure 3. UV/vis extinction spectra of H_2TPPS^{4-} H-aggregates and H_4TPPS^{2-} J-aggregates on chrysotile NTs (red and green lines, respectively) in CH_2Cl_2/CH_3OH suspensions. The inset reports the corresponding RLS spectra.

through an optical microscope (Figure 2b) suggests additional studies on the potential behavior of this self-organized system as a photonic crystal, especially if better control of the degree of alignment at the deposition step will be achieved in the future.

After the inorganic matrix has been efficiently dispersed by functionalization with SDS, H_2TPPS^{4-} can still interact with the NTs, because its higher negative charge is effectively competing with the surfactant molecules and causing their displacement from the chrysotile surface (Scheme 1b,c). The loss of alkyl chains upon addition of the dye (as tetrabutylammonium salt)[11] to the organic phase causes a reduced stability of the suspension, and a fine solid precipitates as the dye loading on the chrysotile surface increases.

Apparently, the strengthening of electrostatic interactions in the low polarity environment given by the CH_2Cl_2/CH_3OH mixture allows an enhanced electronic communication between the chromophores. In fact, as compared to the parent dye, UV/vis extinction spectra of stirred suspensions of this hybrid material present a blue-shifted ($\Delta\lambda = -10$ nm) B-band at 408 nm accompanied by four weaker Q-bands at longer wavelengths (Figure 3, red lines). These features can be attributed to the presence of H_2TPPS^{4-} H-aggregates[10] supported on the NTs. H-type aggregates can be successively converted *in situ* to the J-type simply through the addition of acid vapors to the suspension (Scheme 1c,d), resulting in the diprotonation of the dye molecules and their reorganization right on the surface. This conversion leads to the formation of a nanocomposite having very interesting optical features. Differently from J-aggregates prepared in organic solvents in the absence of the inorganic matrix,[11] the UV/vis extinction profile of a suspension of this bright green solid is very similar to that observed for J-aggregates formed in water (Figure 1b, solid green line). The above-mentioned spectrum shows a very sharp J-band at 491 nm, at whose red edge a very intense signal due to resonant scattering is observed in the corresponding RLS spectrum (Figure 3, green lines), both characteristics pointing to a high degree of organization of the dyes in the J-aggregates. Indeed, more than 25 monomers have to assemble in a J-type arrangement to present relevant RLS signals.[12] Additionally, such a narrow J-band (fwhm = 540 cm^{-1}, after correction for scattering)[13] points to coherence lengths spanning from 3 up to 40 molecular units (see Supporting Information) for linear aggregates.[14] Both factors make these nanohybrids of interest in all those fields where exciton delocalization plays a major role, such as photonics[15] and optoelectronics.[16] Besides, the interaction with the NT surface seems to lead to an increased degree of order in the self-assembling processes involving the chromophore units, with potential relevance in light harvesting applications.[17]

This organizing function of the chrysotile matrix will soon be combined with the preliminary results obtained on its deposition on a surface, to unite the peculiar optical properties of porphyrin J-aggregates to the intrinsic anisotropy of the deposited material.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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