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Supporting Information

A Universal Ultracentrifuge Spectrometer Visualizes CNT–Intercalant–Surfactant Complexes

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Multiwavelength-AUC with band centrifugation:

The setup of the MWL-AUC has been described elsewhere, but has never been applied nor evaluated in the present way.[1;2] For the MWCNT experiments, 15 µL of the sample is put into the reservoir of a vinograd cell. The sample column is filled with 270 µL of a water/deuterated water mixture (50% H_2O and 50% D_2O). The reference column is filled with 285 µL of the H_2O/D_2O mixture. The analytical ultracentrifuge is directly accelerated to 55,000 rpm. Hereby, the capillary between reservoir and sample cell is opened due to the increased pressure to release the sample which is overlaid onto the H_2O/D_2O mixture. During the experiment, 131 scans are taken with radial resolution steps of 50 µm, recording at each point in space and time the full absorption between 250 nm and 850 nm. Each of these scans required 38 seconds so that the total duration of the experiment was 81 minutes. All experiments are performed at 25°C.

Movies of multiwavelength sedimentation

A single snapshot of the experiment produces a 2D plot of $c(r,\lambda)$, i.e. an absorption map of 2048 wavelength values multiplied by about 200 radial steps. The entire experiment comprises typically 100 snapshot and generates thus on the order of 10^7 absorption values, stored in files of a few hundred MBs. That entire wealth of data is represented by the following movies of the complete 3D $c(r,t,\lambda)$ datasets. No further processing was performed, and no data was smoothed or removed.

The following two movies present the full data for the band centrifugation experiment, with three snapshots being shown and evaluated in Figure 1b-d of the main text.

LINK MOVIE HERE

Movie Band1.avi: This movie clearly visualizes the fractionation of fast and slow moving colloids with their distinct absorption profiles. The real duration of this process is 26 minutes, consisting of the first 40 scans, taken with direct acceleration to 55,000 rpm. Two of the snapshots are evaluated as Figure 1b and 1c.

LINK MOVIE HERE

Movie Band2.avi: The movie contains the remaining scans 41 to 131 with faster succession of movie frames. The real duration is 55 minutes.

While it may be difficult to see in the single snapshot in Figure 1d, the movie Band2.avi clearly visualizes that the slowly sedimenting colloids are composed of two discrete fractions: One fraction with an absorption peak at 500 nm does sediment (Range 2b), but another fraction without that absorption component (Range 2a) virtually stands still except for some diffusional broadening.

Sample Preparation and Discussion of the Surfactant-Intercalant Dispersant System

In order to avoid the presence of a large amount of free bulk perylene surfactant convoluting the data of the sedimentation run, 0.1 gL^{-1} HiPco SWCNTs and 0.05 gL^{-1} of PTCDA were immersed in a buffered aqueous solution (borate buffer, pH = 10 purchased from Fischer Scientific) of the surfactant with a concentration of 0.05 gL^{-1}. After sonication (30 min in a bath type sonicator) and mild pre-centrifugation (15 krpm, 30 min) the upper 70 % of the supernatant was decanted and subjected to further analysis.

Samples were initially prepared with varying ratios of **1** and PTCDA in order to gain insights into the dispersion efficiency of the two component dispersant system at pH = 7 and pH = 10 prior to the AUC. The dispersion efficiency is indicated by the optical density at 740 nm (where only nanotube contribute intensity) of the SWCNT-**1**-PTCDA supernatant after mild pre-centrifugation. The dispersion efficiency of **1** has been increased by the addition of PTCDA, as presented by the optical densities. The calculated nanotube concentrations[3] are summarized in table S1.

Table S1: Tabulated optical densities at 740 nm of the SWCNT-**1**-PTCDA supernatant dispersions after centrifugation and the corresponding calculated nanotube concentrations. In all cases, the initial nanotube concentration is 0.1 g/L.

Sample	**pH = 7**		**pH = 10**	
	OD_{740nm} (dilution 1:1)	[SWCNT] / gL^{-1}	OD_{740nm} (dilution 1:1)	[SWCNT] / gL^{-1}
SWCNT-**1**-PTCDA (2:3:0)	0.700	0.039, 39 %	0.957	0.048, 48 %
SWCNT-**1**-PTCDA (2:3:1)	0.984	0.054, 54 %	1.404	0.071, 71 %
SWCNT-**1**-PTCDA (2:3:2)	1.156	0.064, 64 %	1.750	0.088, 88 %

The corresponding optical absorption spectra of SWCNT-**1**-PTCDA are displayed in figure S1. Upon closer inspection of the transitions of the perylene surfactant **1,** subtle differences are observed between the ratio of the 0? 0 (around 550 nm) to the 0? 1 (around 500 nm) transition. This ratio is directly related to the degree of perylene aggregation: While monomeric perylene bisimide derivatives exhibit normal Franck-Condon progression with $A^{0?0}/A^{0?1}$ ~ 1.6, aggregated PBIs have inversed intensity distributions among their vibronic states with $A^{0?0}/A^{0?1} = 0.7$.[4-6]

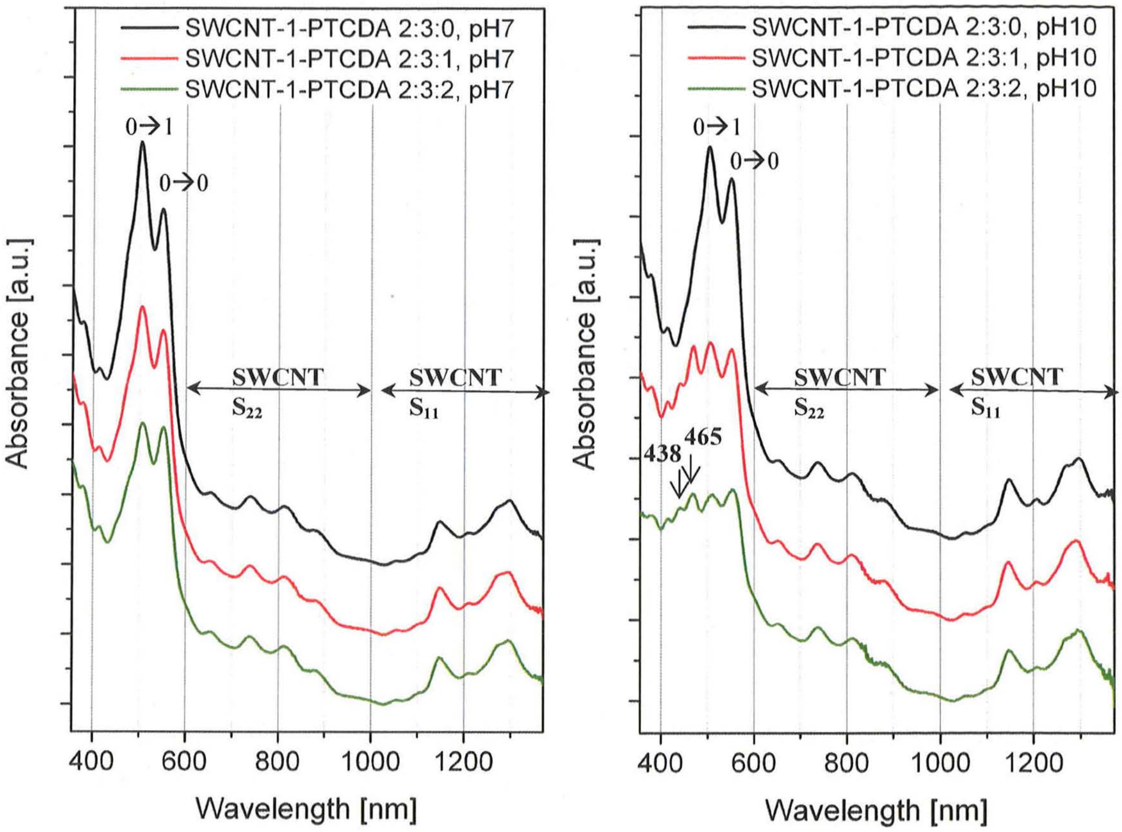

Figure S1: Optical absorption spectra normalized to the minimum of the SWCNT absorbance dispersed in aqueous solutions of **1** with and without the addition of PTCDA ($[SWCNT]_i = 0.1\ gL^{-1}$). In all cases, the supernatant after centrifugation was diluted 1:1 by volume with the buffered aqueous solution of **1**. The spectra are offset for clarity. a) pH = 7, b) pH = 10.

Thus a decrease of the 0? 1 with the respect to the 0? 0 transition as observed in SWCNT-**1** after addition of PTCDA is indicative for the presence of an increased amount of the monomeric perylene surfactant which has been previously associated with the adsorption to the nanotube scaffold.[7] This can be rationalized in terms of an increased surface area of the nanotubes, as more nanotube are efficiently dispersed and exfoliated by the addition of the PTCDA intercalant.

Furthermore, additional two peaks centered at 438 nm and 465 nm appeared in the absorbance spectra of the SWCNT-**1**-PTCDA dispersions at pH = 10 (Fig. 1b). These may be attributed to PTCDA remaining adsorbed on the nanotube surface after sonication and centrifugation. However, this explanation is strongly challenged by the observation that no such species have been detected in the pH = 7 dispersions.

Hydrolysis of PTCDA to PTC

We propose that under the basic conditions employed in the experiment (buffer pH = 10), the anhydride functionalities are hydrolyzed to yield the corresponding perylene tetracarboxylic acid (PTC).[8] To further evaluate this hypothesis, we have immersed the PTCDA in aqueous media at different pH values. As depicted in figure S2, the two main absorption bands centered at 438 nm and 465 nm appear under basic conditions after sonication for 30 min and stirring the sample for three days, while the anhydride functionalities are obviously stable at pH = 7, e.g. no absorption peaks are detected after centrifugation.

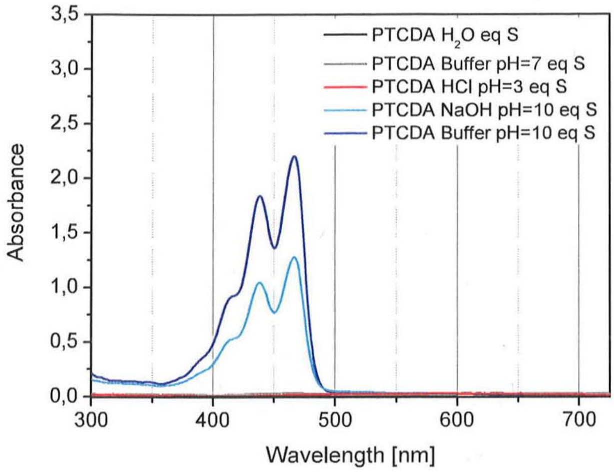

Figure S2: As recorded optical absorption spectra of PTCDA (0.1 gL^{-1}) immersed in aqueous solutions at different pH values. The pH was either adjusted by addition of HCl or NaOH, respectively, or by the use of a buffer solution. In all cases, the supernatant (S) after centrifugation is displayed after 30 min of sonication and 3 d of stirring the mixture (at room temperature) prior to centrifugation, e.g. allowing the system to equilibrate (designated as eq).

Interestingly, in an initial control experiment involving sonication of PTCDA in a buffered aqueous solution of the perylene surfactant in the absence of nanotubes followed by mild sonication and characterization by absorption spectroscopy, no traces of the perylene tetra carboxylic acid have been detected. However, if the sample was left to equilibrate for at least 24 h prior to the centrifugation step, the peaks attributed to the perylene tetracarboxylic acid clearly evolved (Figure S3. This indicates that the presence of nanotubes increases the rate of anhydride hydrolysis, as the PTC is discernable in the supernatant after 30 min of sonication only.

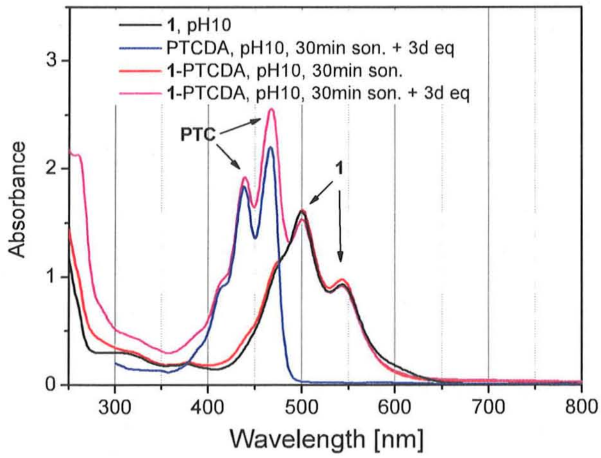

Figure S3: As recorded optical absorption spectra of **1** (0.15 gL^{-1}), PTCDA (0.1 gL^{-1}) and mixtures of both in buffered aqueous solutions at pH = 10. In all cases, the supernatant after centrifugation is displayed. The peaks centered at 438 nm and 465 nm attributed to perylene tetracarboxylic acid only evolve if the sample was given 3 d to equilibrate for the anhydride to be hydrolyzed.

In conclusion we suggest that PTCDA is initially acting as intercalant during the sonication induced exfoliation of the nanotubes. During the sonication process PTCDA comes in contact with the nanotube surface where it is intermittently adsorbed by p-p-stacking interaction. As PTCDA is a rather small molecule compared to the surfactant **1**, it may also slip between the adjacent nanotubes in large bundles therefore increasing the amount of stably dispersed SWCNT material. For the pH = 7 dispersions, the PTCDA intercalant is presumably replaced by the surfactant **1** resulting in re-aggregation with the remaining bulk PTCDA. In the case of the pH = 10 dispersions, the PTCDA is exposed to the basic environment while being adsorbed on the nanotube where it is easily hydrolyzed to yield the perylene tetracarboxylic acid which in turn desorbs and/or is replaced by the surfactant **1** from the nanotube surface. Further experiments to confirm this hypothesis are currently on the way in our laboratory.

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