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Full Paper

Synthesis of a nanomaterial from Trypan Blue and benzyldimethyldodecylamonium

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Benzyldimethyldodecylammonium and Trypan Blue, was mixed in an aqueous solution to form a complex. Then, the solution was centrifuged and rinsed, dried, and collected, before a solution was prepared and spin cast on a glass slide to make a thin film. Mass spectrometry and elemental analyses were conducted to verify the identity of the nanomaterial. A UV/Vis spectroscopy was conducted to deduce the angle of the unit cell in relation to the glass slide. The size of the molecules were theoretically determined from the area of the respective cross sections of the thinnest layer, ranging from 3.2 to 4.2 Å in thickness. A powder XRD analysis was conducted, revealing a unit cell measuring 51x24x4 Å. Hence, a packing model was deduced, suggesting that the molecules were grouped in a 2:8 ratio, corresponding to the charge ratio of 1:4. The thin film was then scrutinized in an optical microscope and an atomic force microscope. The results suggested that the structure of the film was lamellar, and that a thin film with layers directly corresponding to the height of the unit cell was obtained. During transfer electron microscopy (TEM), a thin film was also observed. A DSC analysis showed clear evidence of the surfactant melting at its literature value melting point.

Introduction

Recent developments in nanotechnology has enabled the creation of “self-organized, supramolecular assemblies” to achieve advanced properties in a nanomaterial system, which can be varied with a change in functional building blocks. If executed correctly, a lamellar structure with a high order can be prepared quite simply using normal lab procedures and spin-casting, eliminating the need for a top-down approach, which requires expensive equipment to create a similar structure. Responding to the necessity of creating structures that spontaneously self-assemble, the field of materials nanoarchitechtonics has arisen[1]. According to the work of Faul et. al, a bottom up approach, applying the principle of spontaneous, ionic self-assembly (ISA), synthetic azo-dyes can be mixed with surfactants to form a lamellar structure. Similar lamellar structures have shown great usefulness in industries, such as in solar cells and energy storage[5].

Self-assembly has been present in nature for a long time, and refers to molecules’ ability to self-organize into superstructures of high order. A cell wall, for example, is made almost entirely of a membrane with surfactant-like molecules that, during exposure to water, form membranes with hydrophobic tails inside, and hydrophilic heads on either end[8]. Likewise, ISA exploits the ionic attraction between large ions and the intermolecular forces between polyelectrolytes to create a supramolecular material in a film. Our approach mimics the natural circumstances of self-assembly, using a benzalkonium surfactant (BC12) and a β-napthol azo-dye (TryB) to achieve a lamellar structure, with regularly alternating layers of anioinic surfactants and cationic dyes[9].

Spin-coating the nanomaterial after its production in solution, a supramolecular structure was formed. Upon analysis by AFM, the structure was determined to be lamellar thin film, with a thickness of 60 nm, with the thickness of a single lamella being 5 nm. Hence, the approach used was confirmed to produce a lamellar thin film for the building blocks in question.

Experimental section

Materials

Abbreviations and purity are written I parentheses. Trypan Blue (TryB, 60%) was used as a dye.

The surfactant benzyldimethyldodecylammonium (BC12, <99%) was used as a surfactant.

Deionized water, methanol, dichlormethane (DCM) was used in the preparation of the complex.

Synthesis of TryB/BC12-complex

TryB is a β-naphtol azo-dye consisting of two naphthalene groups, each with two sulfone groups attached. BC12 is a surfactant consisting of a benzyl group attached to a nitrogen with a tail of dodecyl. When synthesizing a TryB/BC12-complex by mixing Trypan Blue (fig. 1) with natrium as a counterion and benzyldimethyldodecylamonium chloride (fig. 2) in water, a centrifuge was used to separate the complex from the water. The samples were centrifuged 3 times and rinsed in between to remove impurities. Methanol was used to quantitatively transfer the pellet to a round bottomed flask, and placed in a rotary evaporator, yielding the desired nanomaterial.

The reaction between TryB and BC12 is given by the following reaction scheme:

$$\text{TryB}_{(aq)} + 4\text{BC12}_{(aq)} \rightarrow \text{TryB/BC12-complex}_{(s)} + 4\text{NaCl}_{(aq)}$$

$$C_{34}H_{24}N_6O_{14}S_4Na_{4(aq)} + 4C_{21}H_{38}ClN_{(aq)} \rightarrow C_{118}H_{176}N_{10}O_{14}S_{4(s)} + 4\text{NaCl}_{(aq)}$$

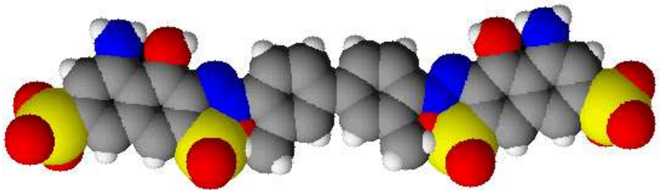


Figure1 Chemical structure of the dye Trypan Blue (TryB) as an ion.

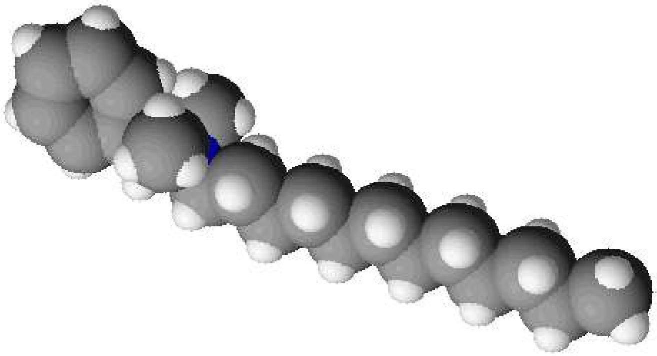


Figure2 Chemical structure of the surfactant benzyldimethyldodecylamonium chloride (BC12) as an ion.

Results and Discussion

Mass spectrometry.

Looking at the positively charged surfactant with a molar mass of 304 g/mol, a similar peak was found in the data received from mass spectrometry. A very clear peak shows 304.3 **(fig. 3)**, which matches the molar mass of the surfactant, and serves as proof that the surfactant is part of the complex. Looking at the dye with four negative charges the molar mass was calculated to be 217.2g/mol per charge. No peak from the data shows a molar mass of 217g/mol **(fig. 4)**.

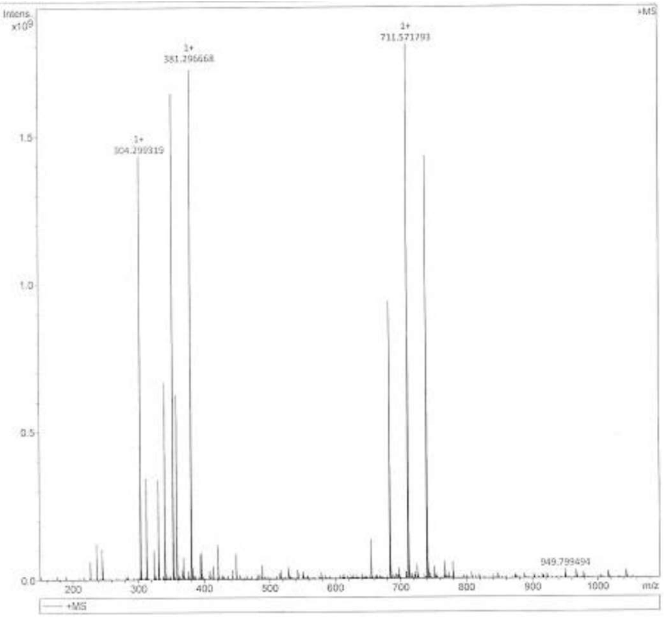


Figure3 Mass spectrometry ESP$^+$ showing a peak at 304.3 matching the molar mass of BC12.

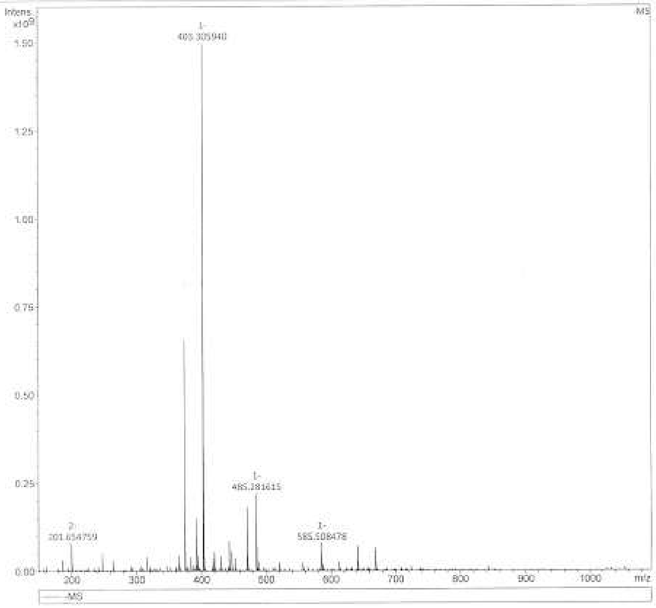


Figure4 Mass spectrometry ESP$^-$ showing no peaks matching the molar mass per charge for TryB.

Elemental analysis (EA).

The purity of the dye/surfactant complex is supported by data from the Elemental analysis. Carbon differed with more than 0.5%, which is the uncertainty of the equipment used to measure. If one molecule H_2O and two NaCl were added, then the found values of both carbon, hydrogen and nitrogen would be within the 0.5% margin from the theoretical values as shown in **table 1** below.

Table 1 Contents of carbon, hydrogen and nitrogen according to elemental analysis.

	Carbon	Hydrogen	Nitrogen
Theoretical	67.9%	8.5%	6.7%
Found	63.6%	8.2%	6.3%
Corrected	63.8%	8.1%	6.3%

UV/vis

When observing the spectres of the film-coated glass slide (fig. 5) and the spectrum of the nanomaterial in solution (fig. 6), it is seen that the spectrums of absorption are displaced by about 30nm from each other, which makes the visible colour of the dissolved sample slightly lighter blue, than the film-sample.

From the processing of the data, on the base of 3 specific points on the graph, it was found that the unit-cells are angled by 68.55° to 69.10° in relation to the glass slide.

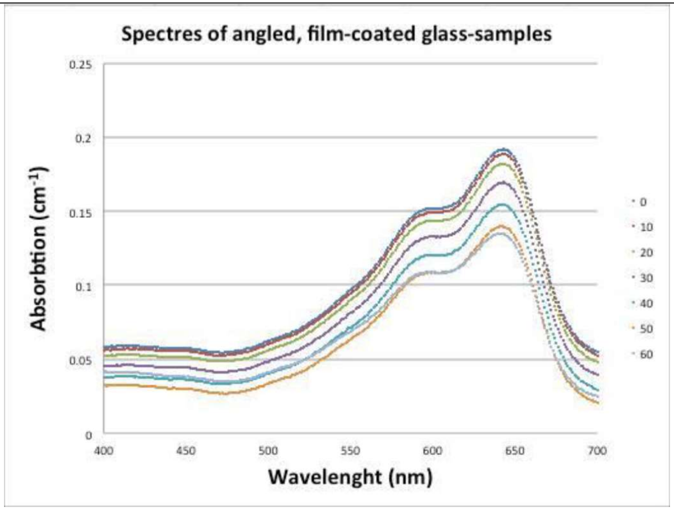


Figure5 A graph showing the absorption spectrum of the film-coated glass sheet at different angles to the light.

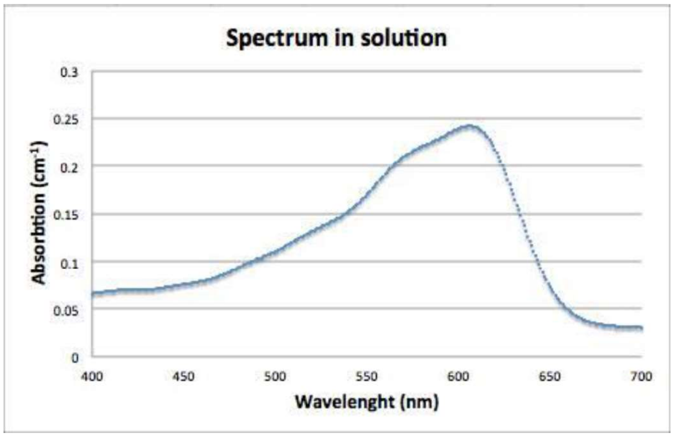


Figure6 A graph showing the absorptions spectrum for the nanomaterial in a solution of 1 part DCM and 1 part methanol.

Dimensions of TryB and BC12

The area, volume and dimensions of TryB and BC12, were found and are listed in **table 2** below. Furthermore, structures of the surfactant and the azo-dye were constructed and are displayed in figures[4, 7] **(fig. 7)** and **(fig. 8)**.

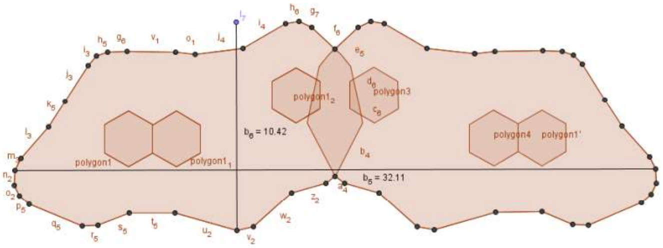


Figure7 Planar structure of TryB, with measures.

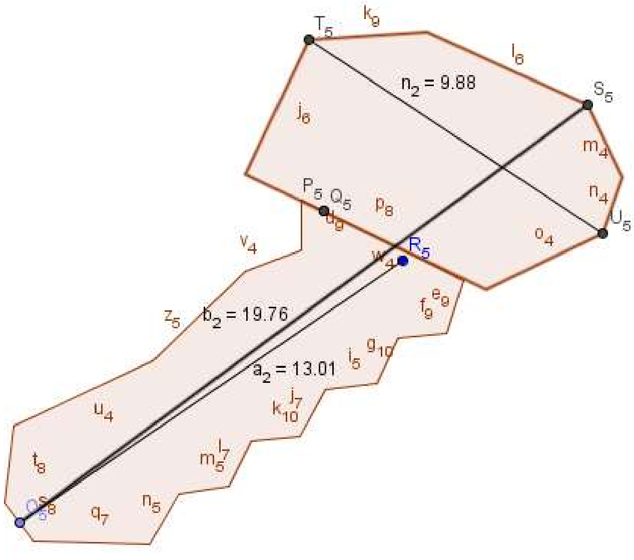


Figure8 Planar structure of BC12, with measures.

Table 2 Measurements of dye and surfactant.

Dye	Volume	Length	Width	Depth	Surfactant	Area Head	Area Tail
TryB	818.38Å	32.11Å	10.42Å	3.4Å	BC12	50Å	53Å

X-Ray Diffraction

A sample was subjected to light of a wavelength 1.5418 Å, and intensity was recorded at 2θ values between 2 and 45 degrees, yielding a spectrum (fig. 9) with photon counts exceeding 57000 at 2θ=2. The peaks for the data obviously lay in a more limited range, so the graph was cropped to decrease the 2θ range to [3, 25] (fig. 10) The peaks were recorded and the corresponding distances were calculated using Bragg's law[3], see **table 3**.

Table 3 Peaks from XRD-graph and corresponding distances.

Peak (2θ°)	Incident photons	d[m]: n=1	d[m]: n=2
3.4734	11341	2.54E-09	5.09E-09
3.6576	13177	2.42E-09	4.83E-09
5.7755	3848	1.53E-09	3.06E-09
7.2899	2316	1.21E-09	2.43E-09
7.515	2220	1.18E-09	2.35E-09
11.1984	2961	7.9E-10	1.58E-09
15.1888	1931	5.83E-10	1.17E-09
17.2556	3203	5.14E-10	1.03E-09
21.7576	5551	4.08E-10	8.17E-10
22.7193	3500	3.91E-10	7.83E-10

From these peaks, the x, y, and z distances of the unit cell were determined to be 50.9Å, 24.2Å and 4.1Å respectively, **table 4**.

Table 4 Dimensions of the unit cell.

Peaks	Å
X	50.9
Y	24.2
Z	4.1

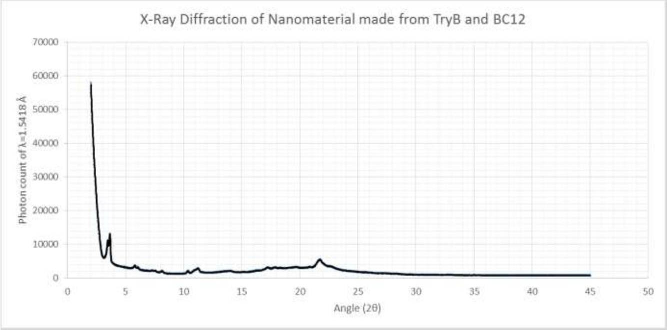


Figure9 XRD Spectrum from 0 to 22.5 degrees

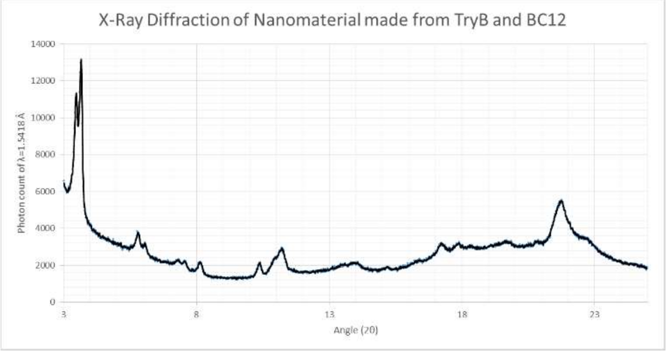


Figure10 XRD Spectrum from 3 to 12.5 degrees

Packing

The unit cell, extracted from the XRD results, was determined to have dimensions as seen in the table below. Hence, the volume will be equal to 5029.6 Å^3. Compared with the volumes of the surfactant and dye, one molecule of the dye would fill 1/6th of the space, while one molecule of the surfactant would fill 1/12th of the space in the unit cell. In order to fill this, and maintain the charge ratio, a model of 2 dye molecules and 8 surfactant molecules per unit cell was determined to be optimal. The molecules would then, with this model, fill 5083. Å^3. With a tight packing model, this closely corresponds to the unit cell.

Hence, a packing model (fig. 11) was drawn, in order to optimally fit the molecules to the cell. However, the dimensions of the theoretical cell will always be greater than that of the actual cell, due to the strong intermolecular forces that take place in a lamellar structure.

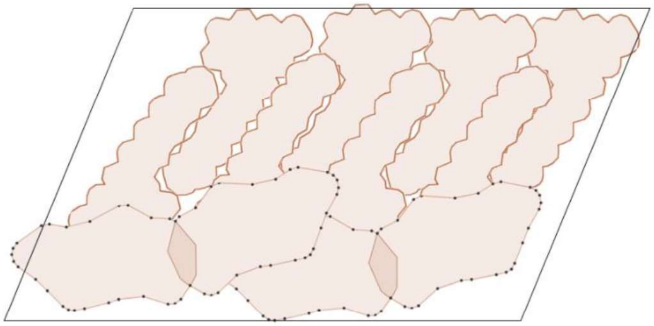


Figure11 A unit cell of the packing model. The rectangle corresponds to the observed dimensions of the XRD (51 Å width, 24 Å height)

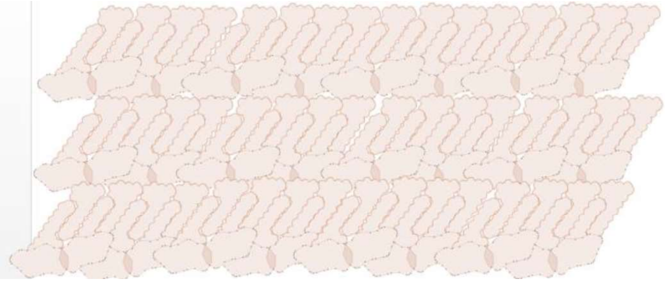


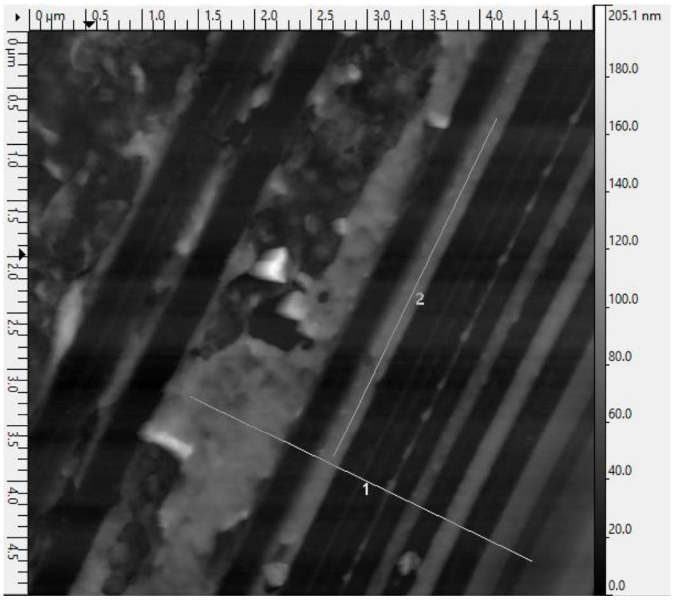
Figure12 Unit cells put together, showing the overall structure of the thin film

Atomic Force Microscopy (AFM)

After spin-casting, the plate cast with 5 mg ml^{-1} solution was subjected to Atomic Force Microscopy. The results were recorded and analysed to find the following results:

First, a picture of scratches in the film, with scratches going all the way through the thin film. A thickness of approximately 50 nm was observed.

Then, an analysis of the surface of the film showed that, while the film had been damaged earlier, some parts were intact, showing a clear lamellar structure[6], with terraces distanced at approx.. 5 nm, hence corresponding to the 50.9 Å observed in the X-Ray Diffraction of the nanomaterial. AFM analysis thus confirms the existence of a lamellar structure.



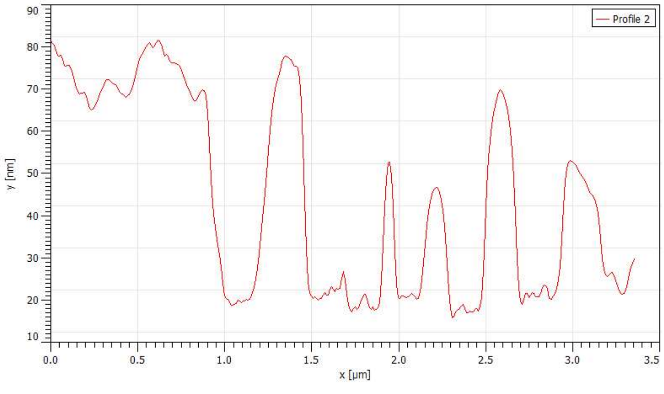
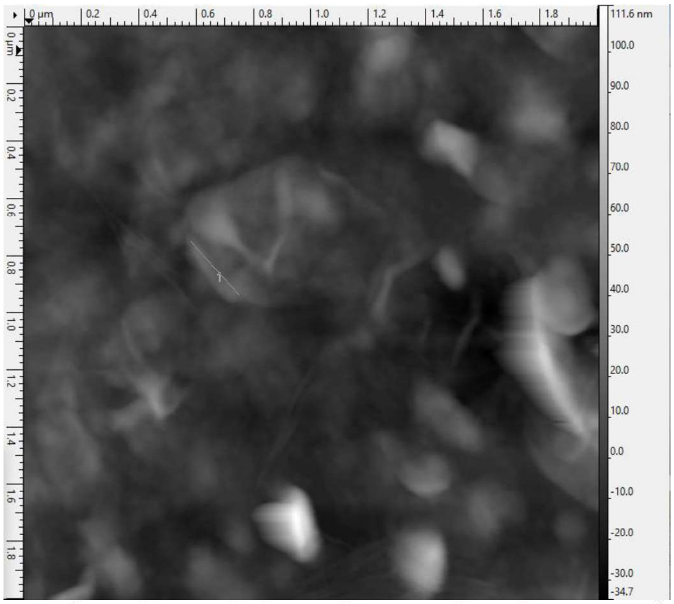


Figure13 AFM 1 AFM mapping with a profile of line 1 on the mapping, demonstrating the thickness of the film at approx. 50 nm



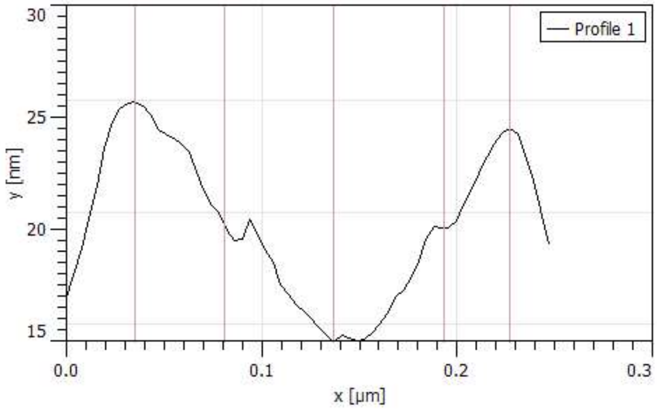


Figure14 AFM 2 – Profile of line 1 on the AFM mapping – clearly showing terraces of approx..5 nm, with small increments at 2.5 nm

The height index of the profile in (fig. 14) – showing the height difference between terraces to be approx. 5 nm can be seen in **table 5**.

Table5 Height differences between terraces in **(fig. 14)**

Points	X [nm]	Y [nm]	Length [nm]	Height [nm]
	35.1	25.77		
	80.9	20.29	45.8	-5.47
	136.8	15.05	55.8	-5.24
	193.3	20.13	56.6	5.08
	227.0	24.57	33.7	4.44

Microscopy

The 5 mg ml^{-1} sample was subjected to optical microscopy, and a banked structure was observed along the edge of the film **(fig. 15)**.
A set of lines in the film was also observed. The lines extended for a remarkable distance, revealing an ordered structure **(fig. 16)**.

Figure15 A picture of the film taken through a microscope at 200 X magnification.

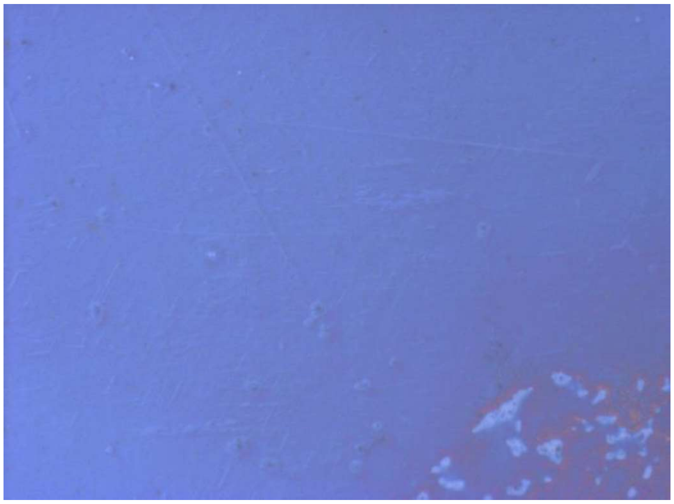


Figure16 A picture of the film taken through a microscope at 200 X magnification.

Differential Scanning Calorimetry (DSC)

A DSC (differential scanning calorimetry) was conducted to observe if any phase transitions occurred. The sample with the Nanomaterial complex produced a graph with two fluctuations **(fig. 17)**. The first was where the surfactant melted **(fig.18)** at 55,9°. The surfactants melting point according to its literature value is 60°[2]. The other fluctuation, which is extremely exothermic, is probably where the complex burned. By finding the area between the fluctuation of the graph and a line connecting the first and last data points for the fluctuation, the change in enthalpy (Δh) was calculated to 17.9[kJ/mol].

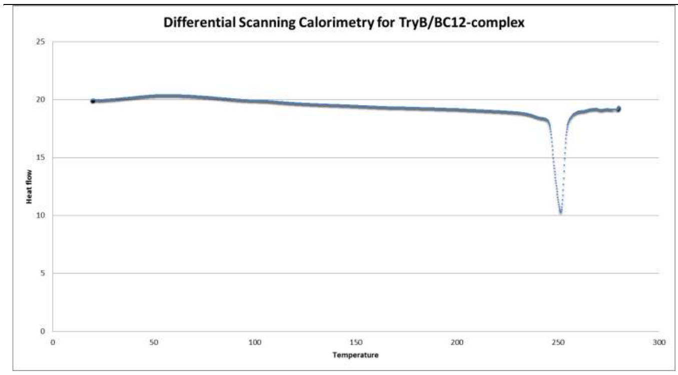


Figure17 A DSC graph showing the phase transitions.

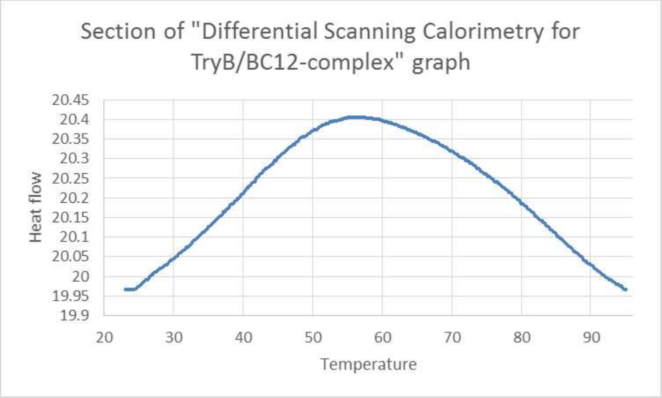


Figure18 DSC graph 2 showing the fluctuation where the surfactant is melting.

Transmission Electron Microscopy (TEM)

Through TEM the existence of what looked like a thin-film, coating the copperplate was confirmed **(fig. 19)**.

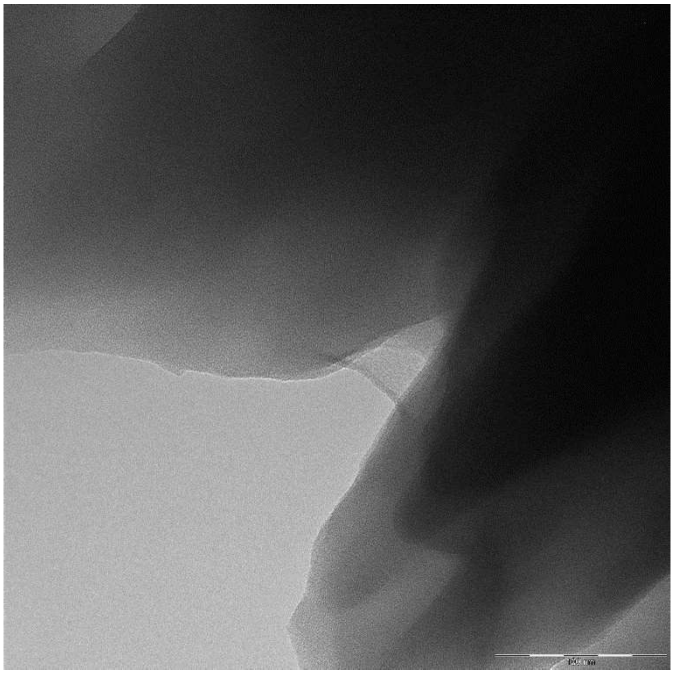


Figure19 A picture of the film taken through an electron microscope, showing the nanomaterial as a thin-film.

Conclusions

In conclusion, out of different types of analyses it is possible to draw the conclusion that a thin film has been created in a lamellar structure with a thickness of approx. 50 Å. The thin film can be described by a unit cell, determined from the XRD spectra. The presence of the surfactant was verified by MS and DSC analysis. EA suggested that though the dye molecule may have broken down during MS, the right ratio of atoms was present. TEM showed the existence of a film in our material. Optic microscopy showed that a lamellar structure existed, while AFM revealed that the thickness of the layers corresponded to the size of the unit cell. UV/Vis spectroscopy revealed that the structure was angled at 68.5-69 degrees, corresponding to the tilt of the unit cell. Hence, it can be concluded that this combination of materials creates a self-assembling lamellar complex.

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Notes and references

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