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Full Paper

Production of Thin Films with ionic self-assembled supramolecular order using the Dye Congo Red and the Surfactant Benzyldimethyldodecylammoniumchloride (BC12)

Anders A Rosenberg, Christoffer R Hilbert, Daniel C Andersen and Sarah M Matrawy

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The chemical process known as ionic self-assembly (ISA) creates highly ordered supramolecular structures through ionic interactions. In this paper we have taken this principle and applied it to the creation of a compound made from the dye Congo Red and the surfactant benzyldimethyldodecylammoniumchloride (BC12). The product, and its structural properties, has been analysed through a variety of methods to further our understanding of different factors effects on the ISA process. Clear signs have been found that point to a supramolecular structure in our material.

Introduction

Previous scientific articles have demonstrated that by using the ionic forces between molecules, it is possible to create ordered supramolecular structures through the process ionic self-assembly.[1] This article examines the chemical and structural properties of the self-assembled nanomaterial created by mixing the dye Congo Red and the surfactant benzyldimethyldodecylammoniumchlorid. This article is part of a greater project to examine the different resulting structures, created by different dyes and surfactants.[2] The goal of this grand project is to research and map out the different factors that affect the ISA process. By more intimately understanding the different factors that affect ISA, we can more easily design a reliable method of creating structured materials. During this project, several different types of analysis, including elemental analysis, transmission electron microscopy (TEM), spin casting, X-ray diffraction (XRD), ultraviolet and visual spectrometry (UV / VIS), atomic force microscopy (AFM) and differential scanning calorimetry (DSC) were used to examine the chemical and structural properties of our nanomaterial. We have spin casted the nanomaterial to examine the structural properties in thin films, through a variety of different methods of analysis. We will in this article describe and discuss in detail the synthesis and the results and data for each analysis.

Experimental Section

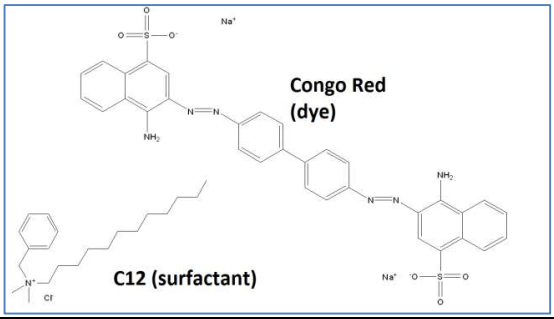
Materials. The dye Congo Red and the surfactant BC12 were used (Figure 1). To prepare the aqueous solutions, and all other uses of water, deionized water was used.

Synthesis and Characterization. The reactants were mixed in a 2:1 mole relationship, of surfactant:dye. 2% solutions of the reactants were created using deionized water. 1 gram of dye was used, and the appropriate amount of surfactant was then calculated as:

$$\frac{1g}{696.66\frac{g}{mol}} * 2 * 339.98\frac{g}{mol} = 0.976g\ surfactant$$

The surfactant was then slowly added to the dye solution in 0.5 mL aliquots while stirring. The resulting compound was after 3 hours, vacuum-filtrated through a normal filter. The resulting powder was then dried. To analyze our material in future tests, some of the compound was dissolved in solutions of 50/50 dichloromethane/methanol. The dichloromethane and methanol used for this were of purity percentages above 99%. Elemental analysis (C, H, N) and mass spectrometry were performed to determine the purity and make-up of our compound. The phase transitions of the compound were studied by differential scanning calorimetry (DSC). The compound was heated from 20 Celsius to 230 Celsius at a rate of 10 K*min^{-1}. Optical microscopy and transmission electron microscopy (TEM) were used to study the structural nature of our compound. X-ray diffraction (XRD) was used to examine the thin film structure. Atomic force microscopy (AFM) was applied to examine the topographical surface of our thin film compound. The software Gwydion was used to analyze the data from the AFM. UV-VIS spectroscopy was used to examine the thin film structure.

Figure 1. The dye (Congo Red) and the surfactant (BC12) used to create our nanomaterial.



$$D(aq) + 2\,S(aq) + 2Na^{+}(aq) + 2Cl^{-}(aq) \rightarrow DS_2(s) + 2Na^{+}(aq) + 2Cl^{-}(aq)$$

Figure 2. The reaction between our dye (D) and surfactant (S) in water, gives us our nanomaterial (DS_2) and some Na and Cl as waste products.

	C	H	N
Theoretical %	68.59	7.93	8.65
Experimental %	69.01	7.89	8.66
Deviation	1.54	0.05	2.64
Deviation with water	0.42	0.04	0.01

Table 1. The elementary analysis results. The table shows the deviations of the experimental results from the theoretical value, without and with 2 added H_2O molecules.

Discussion

Synthesis

A nanomaterial has been synthesized using ISA by mixing the dye known as Congo Red, and the surfactant benzyldimethyldodecylammonium chlorid, both shown in Figure 1. This article has its focus on the dye Congo Red, and seeing what kind of effect a surfactant with a carbon-chain of twelve, as opposed to 14 or 16, has on the structural properties. The two compounds were first dissolved in water, to split the ionic bonds of Na and Cl in the dye and surfactant respectively. The dye and surfactant solutions were then mixed in the proportion given in the reaction formula (1:2) as seen in figure 2. By mixing the two solutions, the positively charged ammonium ions in the surfactant
should create ionic bonds with the negatively charged sulfonate ions in the dye, leaving behind our nanomaterial as the product, as

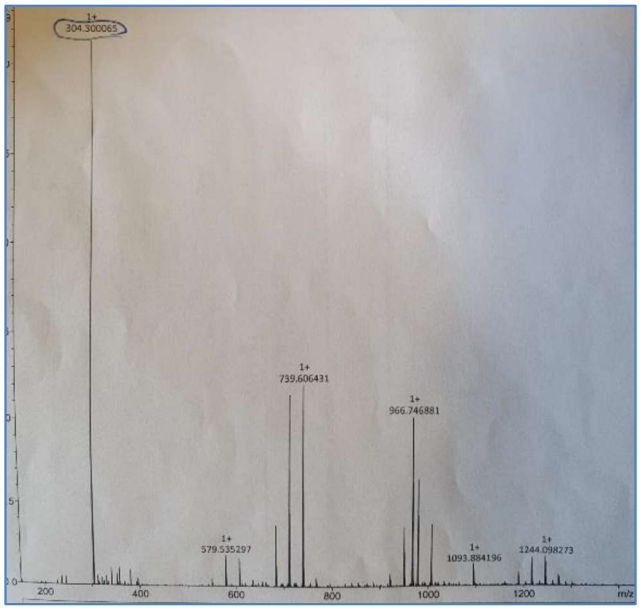


Figure 3. The positive mass spectrometry spectrum for our nanomaterial, showing a tall marked peak at 304, which is also the molar mass of our surfactant.

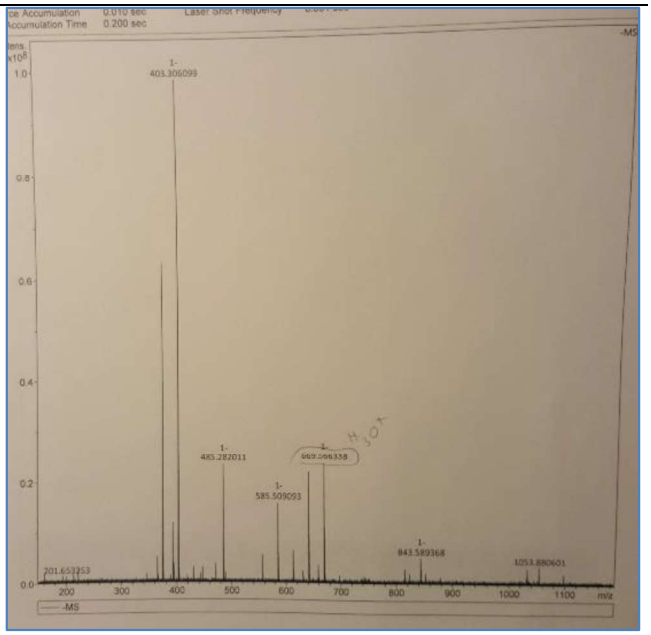


Figure 4. The negative mass spectrometry for our nanomaterial, showing the marked peak at 669, which is also the molar mass of our dye molecule + a hydronium ion.

well as aqueous sodium chloride. Our percent yield was calculated to be 148.4%, implying that there is large amounts of either impurities or leftover water. This corresponds with the fact that even after drying, the product still seemed moist. To confirm that the nanomaterial our theory suggests was created, and to determine the purity, the product was analysed through elemental analysis and mass spectrometry. Elementary analysis is a method that can experimentally determine the relative mass-percentages of different atoms in the molecule, which can then be compared to the theoretical mass percentages as shown in Table 1. Initially the deviations seemed much too high, but by adding two water molecules to the equation, the deviations fell to acceptable values. This implies that there was leftover water in our product, which was hence picked up in the elementary analysis. Mass spectrometry was used as another tool to determine purity. The molar mass of our surfactant ion is 304.54 g/mol. This ion only has one positive charge and a clear peak at 304.3 can be seen because of it, as shown in Figure 3, marked with a blue circle. Our dye ion has a molar mass of 650 g/mol, but has two negative ions, so a peak at 325 g/mol should be seen on Figure 4. The peak at this value is extremely small, but the peak at the value 669 is seen clearly, as seen in Figure 4, marked with a circle. It is assumed this value is the combined molar masses of our dye and a hydronium ion (650.7+19). In conclusion, the surfactant can clearly be identified in the analysis, while the dye isn't as clearly represented. There is clearly some leftover water left in our product, clearly shown in the elementary analysis. As such, our final product includes water, but the nanomaterial can clearly be identified.

Structure

Molecular Models

To understand how our nanomaterial is packed, it is crucial to know the geometric shapes and sizes of the individual molecules. In order to find the shapes, the molecules were drawn out on paper

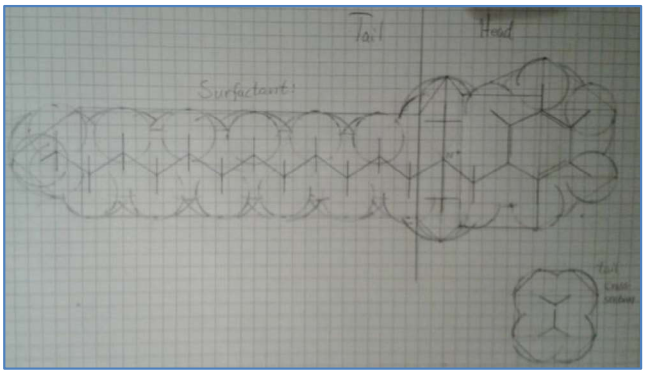


Figure 5. The molecular model for our surfactant BC12. Along with a model of the carbon-chain cross-section in the bottom right.

in 2D to visualize the approximate shapes of the molecules. The results are shown in Figures 5 and 6. In Figure 6, the estimated geometric shape was chosen to be a parallelogram, but due to uncertainty in the drawing and chem draw not allowing us to measure the angel, the shape of a rectangle was chosen. In Figure 6, two oxygen atoms were ignored due to the functional groups being the only part of the molecule to have a 3D shape in or out of the paper. For the surfactant, see Figure 5, the approximate shape is a rectangle, but due to the larger sizes of the benzene and amine

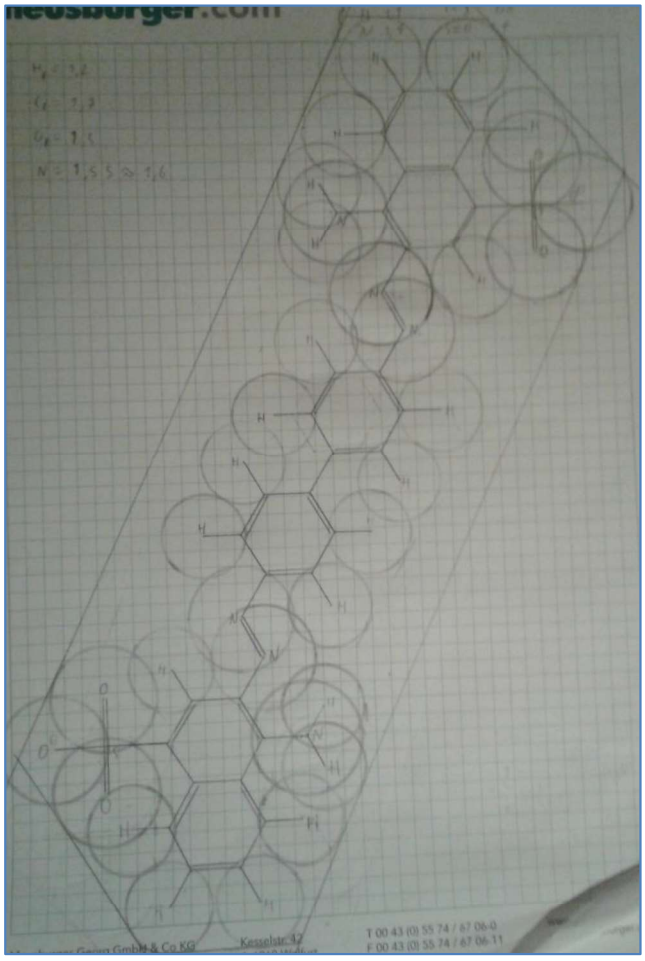


Figure 6. The molecular model for our dye Congo Red.

	Dye	Surfactant Head	Surfactant Tail
Length	27.87Å	8.8Å	15.1Å
Width	6.67Å	6.7Å	4.6Å
Depth	4.3Å	5.57Å	4.2Å
Area	185.89Å^2	58.96Å^2	19.32Å^2
Volume	632.04Å^3	328.41Å^3	291.73Å^3

Table 2. The estimated dimensions, area and volume of our dye and surfactant.

head, the shape was separated into a rectangle and an ellipse. To avoid as many miscalculations as possible, when measuring the size and dimensions, a program called "chem-draw 3D" was used, more specifically version 15.0 of the program. The program allowed measurements across the molecule without any hand calculations, the program gave the results in table 2.

X-ray Powder Diffraction

X-ray diffraction was used to examine the structure of the created nanomaterial. The examined product was first pulverized into fine powder using a mortar and pestle and then analysed. By charting the data in a plot of intensity against 2θ, we get the powder XRD pattern for our nanomaterial, as shown in Figure 7. To find the relevant dimensions of our product molecule, the 2θ values are converted to distances, d, in accordance with the modulated Bragg's Law:

$$d = \frac{n \times \lambda}{2 \times \sin(\theta)}$$

Where n is 1, λ is the fixed wavelength of the apparatus and θ is our angle. By doing this for all the data points, and plotting it once again, the distances at which the intensity peaks can be found. These three distances are shown in Table 3, along with their approximate uncertainties.

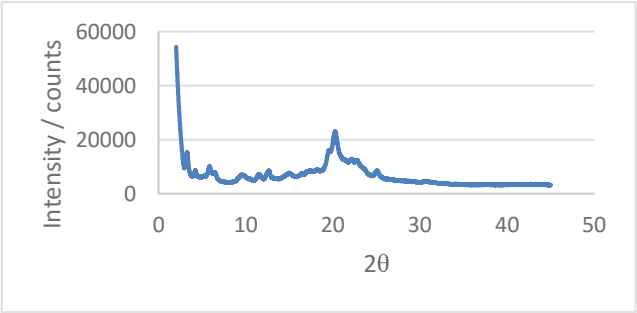


Figure 7. The Powder XRD pattern for our nanomaterial. A graph of the intensity against 2 times the angle.

	Distances [Å]	Uncertainty [&]
d^x	27.09	5.44
d^y	20.97	2.37
d^z	4.37	0.52

Table 3. The distances, d, found at the 3 peaks of the XRD data, along with their respective estimated uncertainties.

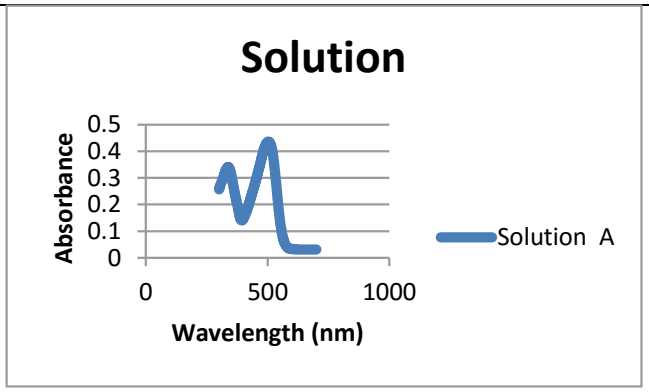


Figure 8. The absorbance of our nanomaterial in a 50% DCM, 50% Ethanol solution

With these 3 distances, a model for how the unit cell of our supramolecular structure is formed, can be produced. The three distances roughly correspond to the expected values, with the exception of d^y. Given the clear similarity between the distances found through molecular models, as shown in the "Molecular Models", chapter and the distances found via. XRD, it is clear that the unit cell of our structure only consists of a single molecule. These three distances multiplied also give us a volume of 2485 Å^3. The theoretical volume of our molecule was earlier estimated to be 2078 Å^3. This gives us a percent deviation of 16.38. However, there is a large margin of error in the theoretical estimates of volume of molecules, given that it is close to impossible to fully predict the way a large molecule structures itself three-dimensionally. Assuming the molecular volume is 2482 Å^3, the density of our nanomaterial can be determined. The molar mass of our material can be found by adding the unit weights of the individual atoms and adds up to $1295.8\ g/mol$

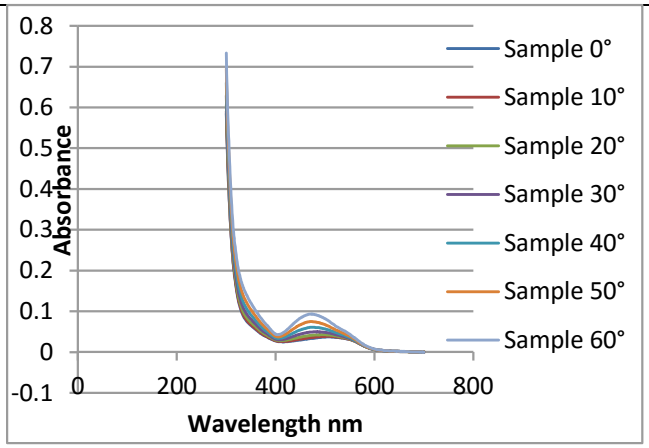
$$2482Å^3 * (6.022 * 10^{23}) \frac{1}{mol} * 10^{-24} = 1494.9 \frac{cm^3}{mol}$$

$$\left(\frac{1295.8 \frac{g}{mol}}{1494.9 \frac{cm^3}{mol}} \right)^{-1} = 0.87 \frac{g}{cm^3}$$

The volume of one molecule is known, so the avogrado constant is first multiplied to get the volume of one mole, and then convert that to cm^3. Then the molar mass is divided with the volume per mole to get the density.

Ultraviolet-visible Spectroscopy

UV-Vis was run on our solution to determine the absorbance of our nanomaterial at wavelengths going from 300nm to 700 nm. It can be seen that the absorbance of wavelengths in the proximity of 350 nm (UVA) and 500 nm (green) is very high; the absorbance of violet light at 400 nm is lower while the absorbance of red light, at 600-700 nm, is almost zero with the absorbance most likely being background absorbance from the cuvette. With our nanomaterial being a red azo-dye, this would be expected. Looking at our thin films, a lower absorbance can be seen all across the spectrum, which should be expected, seeing as it is a very thin sample that was shot by the light. The points of high absorbance, while almost the same as in the solution, differentiates itself by having its peak absorbance at 300 nm. This indicates that the thin film's absorbance of UV light is a lot



higher than our solution. Light was

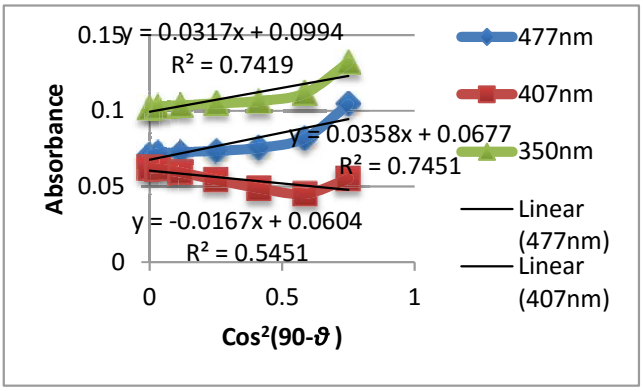


Figure 9. The different absorbance observed by looking at our thin-film at different angles.

Figure 10. The absorbance observed at the different wavelengths and angles of our thin-film, used to determine our angle.

then shot through our film at 6 different angles, by doing this the angle at which our azo-dye builds itself up can be determined, by looking at the absorbance of the different angles. Plotting all the angles at 3 different wavelengths (477, 407 and 350) with $cos^2(90 - \theta)$ on the x-axis, linear regression was performed on the plots. Using the a and b values in our linear functions and our background spectrum as a c value, the constant $K_f = \frac{\frac{a+b}{b-c}}{2+\left(\frac{a+b}{b-c}\right)}$ was found, which was used to determine our angle: $\alpha = \arccos(K_f)$. It was found that at the 3 different wavelengths the angle differed by a maximum of 6 degrees, with an average value of 79,48°. With this information it was concluded that the azo-dye is angled at approximately 80° in our nanomaterial.

Packaging

A suggestion for the packaging of our unit cell is shown in Figure 11. This model was created using the correct molecular heights and widths, and minimizes the amount of free space within the unit cell. The black box surrounding the unit cells are the unit cell dimensions, as found in the XRD chapter.

Images of the Compound

Optical Microscopy

A very uniform surface was seen on the microfilm, shown in figure 12, except for some lines assumingly are due to scratches in the underlying glass, from when the glass was cleaned with acetone

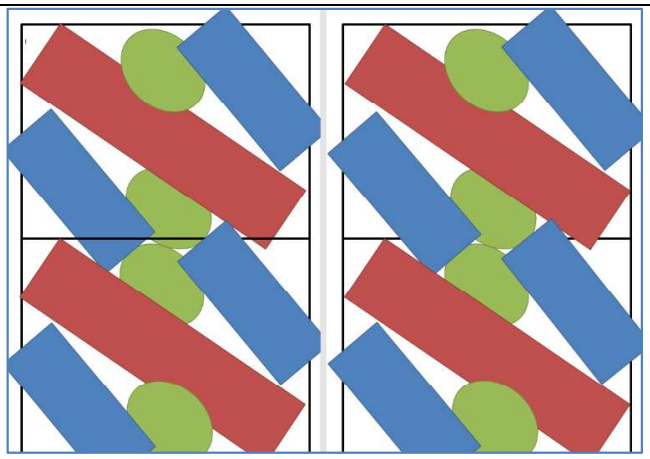
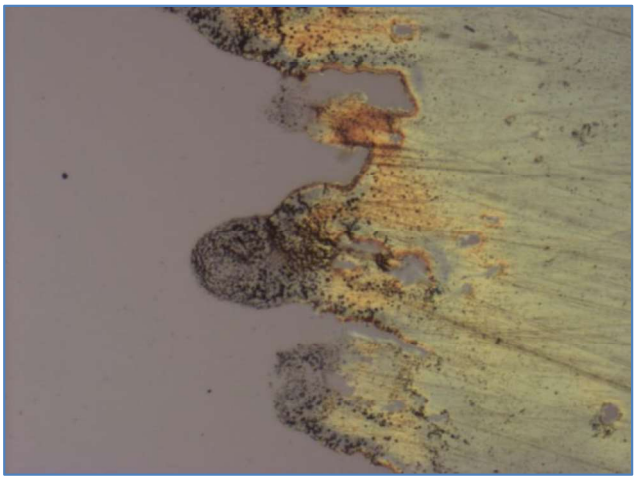


Figure 11. Suggested packaging model. The red box represents the dye part of the molecule, the green represents the surfactant head, and



the blue the surfactant chain.

Figure 12. Shows the edge of the sample, and the concentrated undissolved material therein. 10x EpiBF

and methanol, and used some paper towels to dry the glass. On the edges of the microfilm, as seen in Figure 12, sharp edges and black spots can be seen. The sharp edges indicate, that there is a microfilm as opposed to a random collection of matter. The black spots could be dust or other contaminations that have landed in the solution, or collection of undissolved nanomaterial, both heavy enough to be spin-cast to the edge of the microfilm.

Transmission Electron Microscopy (TEM)

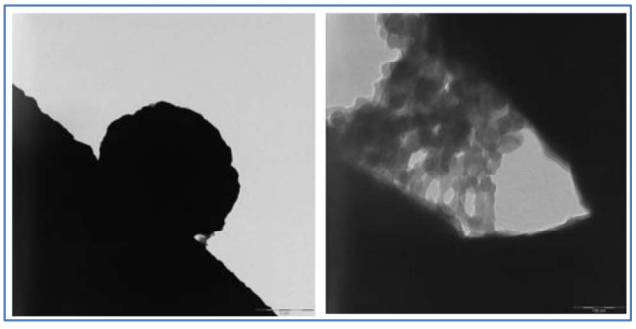
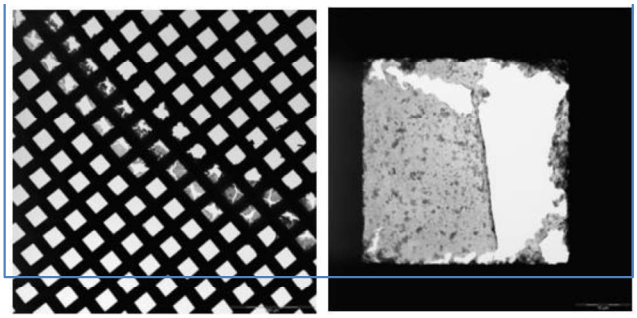


Figure 13. TEM micrograph of nanomaterial test 1

Figure 14. TEM micrograph of nanomaterial test 2



To better examine the structural properties of our dye, a transmission electron microscope (TEM) was used. TEM has the advantage of operating at a lower wavelength than normal optical microscopy, since it uses electrons instead of electromagnetic radiation. This allows it to study things of a much smaller order. Two tests were performed. In the low concentration test, a little lump could be seen, as shown in Figure 13. There was no easy way to analyze this test. The second test, as shown in Figure 14, shows a specific structure of clean folded edges. Upon shooting electrons through our material, the test displayed motion as a result

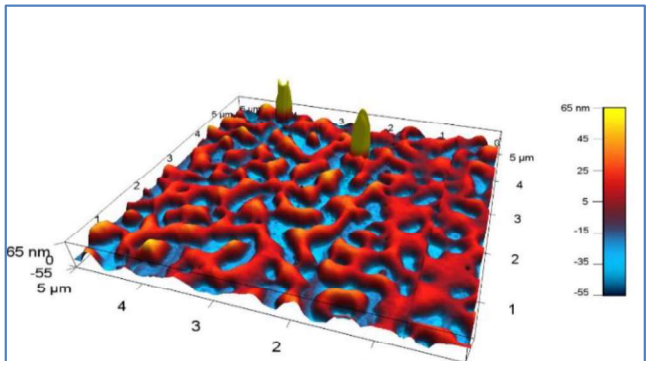


Figure 15. 3D render of our AFM data. Shows a mountain-like/valley structure.

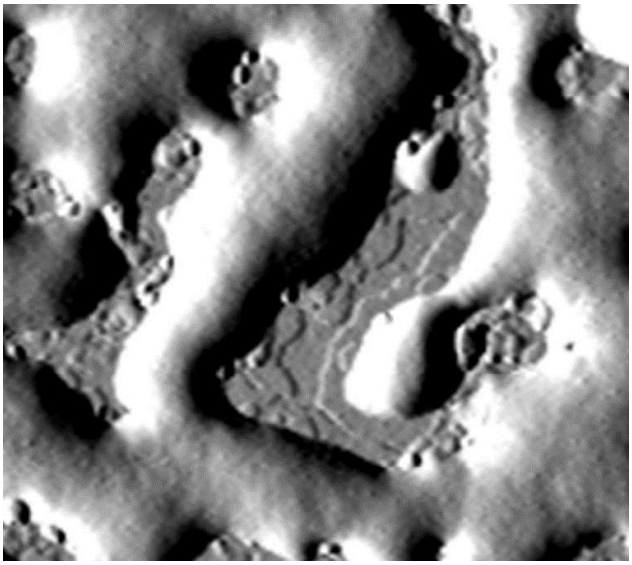


Figure 16. A zoom where the structural layers are clearly visible.

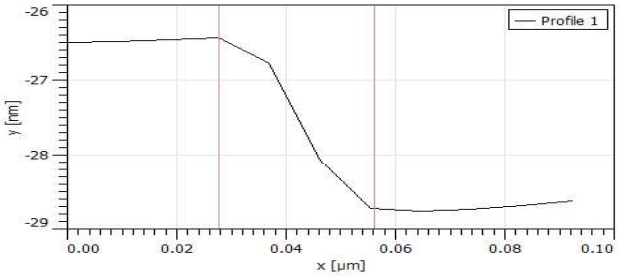


Figure 17. The graph showing the difference in height of the two layers.

of the heat. In Figure 14, the image scaling can be seen in the lower right corner, and is shown to be $10\mu m$, which is 100.000 Å. From interpreting Figure 14, it can be concluded that the nanomaterial has formed a clear ordered structure.

Atomic Force Microscopy (AFM)

AFM was used to directly examine the surface of our material on a thin film. As shown in Figure 15, the surface looks like a mix of hills and valleys and no large micro films can be seen, which was expected based on the microscopy pictures (see Figure 14). On Figure 16 small indentations on the bottom of the valley can be seen, which could be an example of our materials special lamellar structure. Measuring the height of the layer through a graphing tool (see Figure 17), it was found to be 2.28nm or 22.8Å tall, which is similar to our unit cell height of 20.97Å. This height, 22.8Å is our assumed layer height.

Differential Scanning Calorimetry (DSC)

DCS means ”differential scanning calorimetry”, and is used to analyze transition states by heating a sample at a specific rate, while measuring the temperature change in the sample. There are 3 peaks in our data, so 3 possible transition states, as shown in Figure 18. After calculating the transition energy (the area under the peaks) in each transition state, the following data has been collected in Table 4. Comparing Table 4 with results from previous articles[1], has shown that the melting point for a similar nanomaterial, with the same dye and a longer surfactant (BC16),

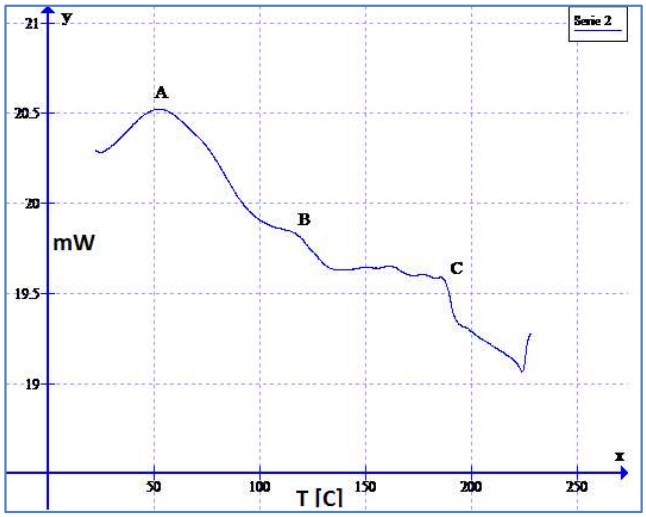


Figure 18. The DSC data plotted as temperature (Celsius) against heat flow (mW).

Peak	Degrees	Area from average.	ΔH
A	54,2C	164,827mJ	42,92J/g
B	117C	8,929mJ	2,33J/g
C	187C	5,448mJ	1,42J/g

Table 4. The data from the DSC analysis, shown in a table.

has a melting point around 228-235 degrees Celsius. The only difference between BC12 and BC16, is 4 carbon atoms at the end of the carbon chain. Compared with the highest measured result, peak C, it gives a temperature difference of 41-48 degrees Celsius, caused by a total of 8 carbon atoms. Such a large jump in melting point is highly unlikely, and other previous results from the same collection of melting points, show that a difference in BC1X chains for identical dyes, gives a melting point difference of either 3 or 12 degrees Celsius in both higher and lower melting points, per two carbons per chain removed for most dyes. So our melting point and corresponding transition state must be somewhere to the right on Fig 18, beyond our measurements, possibly the top of the unfinished peak at the end of the graph around 225+ degrees Celsius, close to the previous result.

Conclusions

The structural properties of the nano-material, created by combining Congo Red and BC12. Most of our analysis’s point towards a specific structure. Our results, on the whole, point towards a macroscopic structure created by ISA. The XRD and UV-VIS data, points towards a unit cell within a larger ordered structure, which was sketched in Figure 11. Pictures from TEM also hint at a supramolecular structure. The only result that throws doubt on this structure is the AFM results, which show an overall structure of valleys that looks a bit off. But at the same time, the AFM also showed small lamellar structures on the bottom of the valleys which points toward, at the very least, localized ISA-structures.

Acknowledgements

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Notes and References

Address: Nano-Science Center, University of Copenhagen, Universitetsparken 5, 2100 København Ø, Denmark.; E-mail: mhj720@alumni.ku.dk

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