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Full Paper

Creation of Ionic Self-assembled Thin Films with Surfactant Benzyldimethyltetradecylammonium (BC14) and Dye Beryllon II with Nanoscopic Order

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This article examines ionic self-assembly (ISA) between a dye and surfactant. ISA is a method used to create supramolecular materials. The material created with the dye known as beryllon II and surfactant benzyldimethyltetradecylammoniumchloride (BC14) is then examined via different experimental methods. For instance, thin film is created to determine if the molecules can be assembled in lamellar stucture. The results show that the material has assembled in a crystalline order. AFM analysis also shows that the material is able to self-assemble on a substrate via a lamellar order and thereby creating a thin film. Results from DSC analysis and the fact that the material was greasy suggests that the material is a liquid or soft crystal with a nematic-like order.

1. Introduction

Regarding ionic self-assembly, previous scientific articles has stated that through utilization of supramolecular chemistry (relatively large molecular building blocks) it has been possible to create complex structures of molecules in assembled order. [1, 2]

According to previous results, these self-assembled molecular materials have been created in solution, solids, and isolated to pure materials.[1,2] The first description of ionic self-assembly that describes layer by layer formation is in the work by Faul and Antonietti[5]. This formation is what is expected when dye and surfactant is mixed in a solution. This gives rich possibilities to investigate further into the world of ionic self-assembly. In the work by Faul[6] it is examined if it is possible to construct nanomaterials with hierarchal combinations. This gives a number of further opportunities for the use of such nanomaterials assembled by ionic self-assembly. Another combination consists of ISA with two oppositely charged dyes[7] this resulted in polymers stacked in a twisted helical formation. All this highlights opportunities of creating materials with ISA across multiple length scales with different functionalities.

The goal of creating such molecular materials is to mimic nature's molecular organizations; thereby creating a link between nature's spontaneously created molecular structures, and human engineering's utilization of micromechanics and lithography.

We have based our experiments off of the authors (instructors and students) of reference 1, who previously succeeded in creating a predictable method of yielding thin film based off of surfactant matrix from alkyldimethylbenzylammonium.[2]

Specifically, we hope to achieve successful creation of two-dimensional thin film nanomaterial through the combination of surfactant BC14 and azo-dye Beryllon II (Bell), shown in figure 1. Note that the molecules are shown in free ionic form.

The theoretical synthesis of surfactant BC14 and dye Beryllon II (with sodium-ion and chloride) resulting in product material is shown in figure 1.

$$\text{Bell}^{4-}(aq) + 4\ \text{BC14}^{+}(aq) + 4\text{Cl}^{-}(aq) \leftrightharpoons \text{Material}_4(s) + 4\text{Na}^{+}(aq) + 4\text{Cl}^{-}(aq)$$

In order to achieve thin film from this synthesis we have chosen to use spin-casting, seen as previous work has yielded organized thin films, through utilization of specific molecular materials.[4,5]

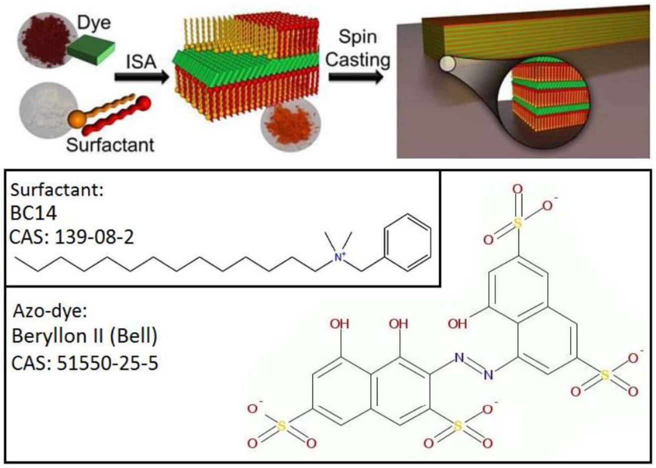


Figure 1[2]**.** The ionic self-assembly process (top) and surfactant BC14 with dye Beryllon II n free ionic form.

2. Experimental section

Before the experiment is set in motion, it is essential to calculate the amount of surfactant and dye required for ionic self-assembly.

The mass (m) of dye Beryllon II that we are going to utilize is equal to a single gram, of which the amount of substance (n) therefore equals the following:

$$n(\text{Beryllon II}) = \frac{1g}{738.52\frac{g}{mol}}$$

To compare this amount of substance with the required amount of surfactant BC14, the amount of dye equals to four times the amount of surfactant, because of the two molecules' difference in charge (four).

Thereby, n(BC14) is:

$$n(BC14) = 4 \cdot \frac{1g}{738.52 \frac{g}{mol}}$$

The required surfactant mass of BC14 was calculated to be equal to 1.9933 gram.

The purity of surfactant BC14 is greater than 99%, meaning that we do not need to consider any scaling. Therefore, we use the same amount, and thus, synthesis begins.

2.1. Procedure

1 g Beryllon II and 1.9933 g BC14 was added separately to two 250 mL Erlenmeyer flasks, where each compound was mixed with 100 mL deionized water.

For two fully dissolved solutions, it was necessary to use a magnetic stirrer with a heating function in the dissolving of surfactant BC14, whereas Beryllon II could be dissolved by hand.

A solution was created by setting the Beryllon II solution in a magnetic stirrer, where BC14 was slowly added with the use of a pipette. The solution was filtered through a funnel into a flask under low pressure, in order to create a suction force.

When filtering process was completed, material could be extracted and collected from the filter by use of a standard glass rod.

Two amounts were then extracted and used for samples in elemental analysis and mass spectroscopy.

Elemental analysis: 10 mg

Mass spectroscopy: A small, unknown amount

For later analysis, the material was prepared for spin casting, where three different concentrations; 1 mg/mL, 5 mg/mL, and 10 mg/mL; yielded three (previously disinfected) spin casting slides.

3. Results and discussion

The surfactant BC14 consists of a 14 carbon long alkyl chain, a quaternary ammonium cation and a phenyl group as shown in figure 1. The surfactant is hydrophilic partly because of the relatively short carbon chain and partly because of the cation. The dye is a β-naphtol derivate with two sulfonate groups. On the other side of the azo-linkage another β-naphtol with two additional sulfonate groups and one hydroxyl-group can be found. Thus, the dye has four negative charges. Because of the dissimilarity in the charges between surfactant and dye the synthesis requires four surfactants and one dye.

3.1. Mass spectrometry

When talking about the synthesis it is very important to make sure, that the product is actually the theoretical pure product expected to be produced. According to accomplishment of said goal, mass spectrometry (MS) and elemental analysis (EA) is highly critical, seeing as it gives an idea of the product material and its purity.

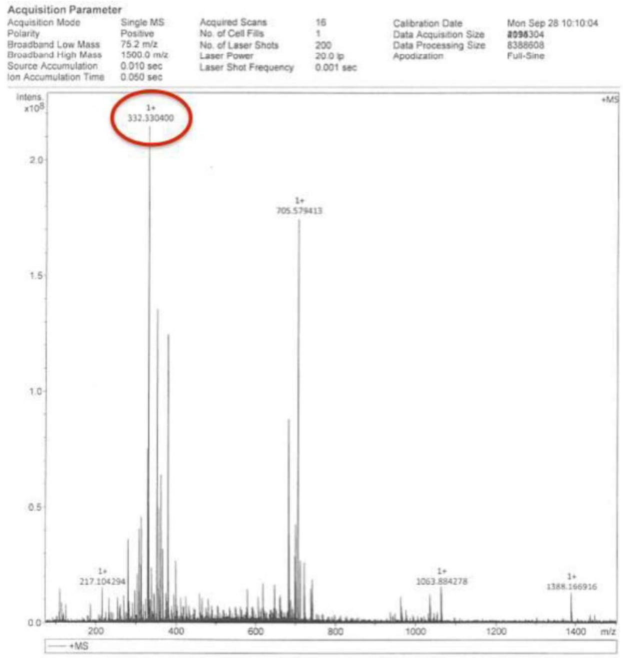
Using MS to identify the mass-to-charges within the molecule, the result portrays a spectrum of the intensity of the detected ions in a function of the mass-to-charge ratio (m/z).

Surfactant BC14's molecular weight is 332.595 g/mol. Because the surfactant has only one charge the result of m/z is 332.595, which is the value expected in MS. The dye has a molecular weight of 649.54 g/mol. Because the dye has four charges, the weight is divided by four, and the result is therefore 161.39, which is the expected result.

As seen on figure 2, portraying masse per positive charge for surfactant, resulted m/z is coherent with theoretical molar weight 332.595, which indicates correct choice of surfactant for synthesis. Mass per negative charge was executed for dye, but results are inconsistent with theoretical molar weight for dye. Two possible explanations for this inconsistency are listed below:

- A proton, sodium and/or surfactant(s) are covering one or more negative charges.
- Given the dye's relatively large size and four negative charges, it will do whatever possible to become more stable. This can be accomplished by creating ionic bonds and/or separating from the negatively charged SO_3^-group, resulting in inconsistent MS results.

New results were calculated, taking into account that the mass has changed, as well as the number of negative charges – however, no correlation between possible theoretical combinations of dye and H^+, Na^+, or surfactant were found. Based on MS results it was concluded that there exists no way to discern the outcome before further experiments.



Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	16	Calibration Date	Mon Sep 28 10:10:04
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	4096304
Broadband Low Mass	75.2 m/z	No. of Laser Shots	200	Data Processing Size	8388608
Broadband High Mass	1500.0 m/z	Laser Power	20.0 lp	Apodization	Full-Sine
Source Accumulation	0.010 sec	Laser Shot Frequency	0.001 sec		
Ion Accumulation Time	0.050 sec				

Figure 2: Mass spectrometry analysis summary. Overview of positive charges in product material. The red circle highlights the result 332.595, thereby indicating that the right surfactant was chosen in the synthesis.

Table 1: Table elemental analysis summary

	Carbon	Hydrogen	Nitrogen
Theoretical values	68.05%	9.08%	4.25%
Results from EA	66.42%	8.75%	3.39%
Theoretical + NaCl	66.09%	8.81%	4.13%

3.2. Elemental analysis

Establishing product purity is possible through use of elemental analysis (EA), seeing as it measures the percentage amount of carbon, hydrogen and nitrogen in a sample of product. Calculating purity in same percentage format is executed based on 100% purity.

As seen in table 1, theoretical data and EA results is incoherent, indicating that product is not 100% pure and that another molecule is present. Because the amount of hydrogen is lower in EA results, the extra molecule is expected to be sodium chloride. Theoretical percentages including a sodium chloride molecule are shown in table 1. Theoretical percentages plus sodium chloride molecule consists with the data from EA. Following elemental analysis, absorption spectroscopy will give a clearer indication regarding whether or not the correct dye molecule was chosen for synthesis.

3.3. Absorption spectroscopy

This method is used to determine if the compound is placed on the substrate in lamellar order. The absorption spectres for the solution and thin films created by spin casting are compared. As it can be seen on figure 3, the different spectres resembles each other. It is then possible to determine the angle at which the material sits on the substrate. The absorbance spectrum also corresponds with the purple colour of the material because the highest absorbance is between wavelengths of 500nm to 600nm, which represent the colours green, yellow and orange. Based on this information, it is determinable that the correct dye was chosen, seen as it does not absorb wavelengths corresponding to purple.

First the corrected spectres for the thin films is plotted to determine three wavelengths with great difference in the spectres. Figure 4 shows that there is not a great difference so the wavelengths: 532nm, 556nm and 588nm are chosen to get three representing values for the angle. These wavelengths are then used to plot three linear regressions ($y = mx + b$) the function's m and b values are then used to calculate the angle at which the compound is set on the substrate. As seen on table 2, the three wavelengths result in three angles (α) with an error margin of around ±3°, which is within the acceptable error margin.

Table 2: A, B, C and α calculated from the corrected spectres.

λ (nm)	A[a]	B[a]	C[b]	α[c]
532	-0.0422	0.0722	0.037314	56.746°
556	-0.04	0.07	0.037013	56.007°
588	-0.046	0.068	0.037072	59.190°

[a] These values are used to calculate a factor k_f for each wavelength, which is necessary to calculate the angle the material is set on the substrate. [b] The C value is determined from the blank absorption spectre of dichloromethane. [c] The angles are calculated through the formula $\alpha = \cos^{-1}(\sqrt{k_f(\lambda)})$

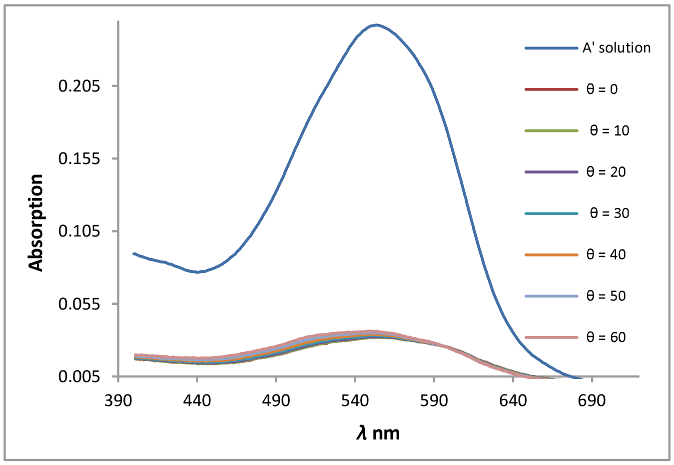


Figure 1: The figure shows that both the solution and thin film absorb at the same wavelengths. This indicates that it is the same material used in both samples. It also confirms that the correct dye was used, seen as the absorption spectra absorbs light other than wavelengths representing purple.

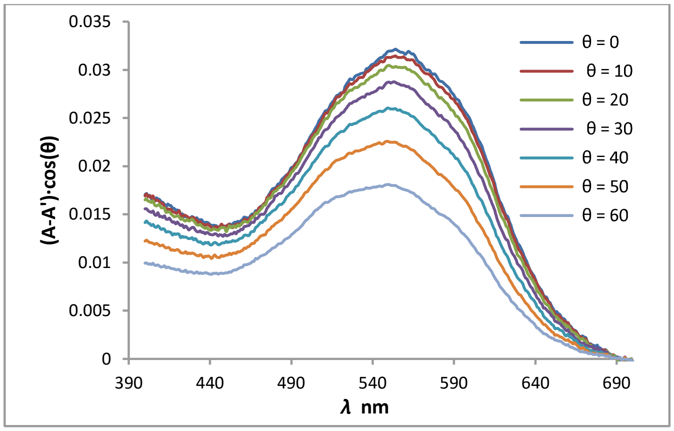


Figure 4: This figure shows the corrected absorption spectres at different angles. Three wavelengths are chosen to determine which angle the material has set on the substrate. In this case, wavelengths are 532nm, 556nm, and 588nm.

3.4. Geometrical molecular structure

In order to further understand ionic self-assembly, it is necessary to know how the molecules are packed. To fully understand how the molecules are packed, it is important to establish their weight and their three-dimensional form. The area of both surfactant and dye was determined using both the bonding lengths and bonding angles between the atoms within the molecule and their Van Der Waals radii, as shown in figure 7 and 8.

To facilitate the determination of the area, the area was determined by drawing the molecules on a squared paper, in the scale 1 Å equivalent to 1 cm., after which the area was determined by counting square centimetres.

Determining volume of the molecules, we account for the various Van Der Waals radii. Different Van Der Waals radii result in different heights depending on the area of the molecule. Volume of a molecule is determined using the molecule's Van Der Waals radii, bonding lengths, and projection of the bonding length, so that the bonding angle is taken into account as well. This method brings a range of uncertainties, but seen as this method was used for each of the molecules, it results in a true size difference.

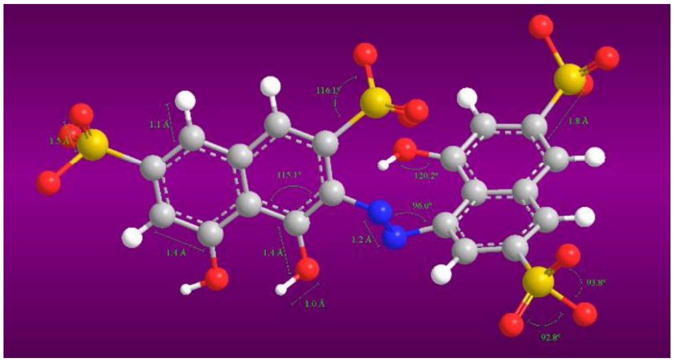


Figure 5: Three-dimensional model of the dye Beryllon II drawn in Chemdraw. The bonding angles and bonding lengths are shown.

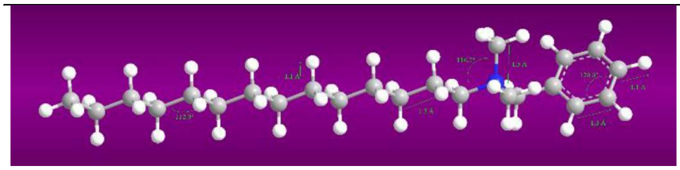


Figure 6: Three-dimensional model of the surfactant BC14 drawn in program ChemDraw. The bonding angles and bonding lengths are shown.

Table 3: The calculated area and volume of both the surfactant and dye.

	Area	Volume
Dye	145.49 Å^3	904.74 Å^3
Surfactant	135.25 Å^3	516.46 Å^3

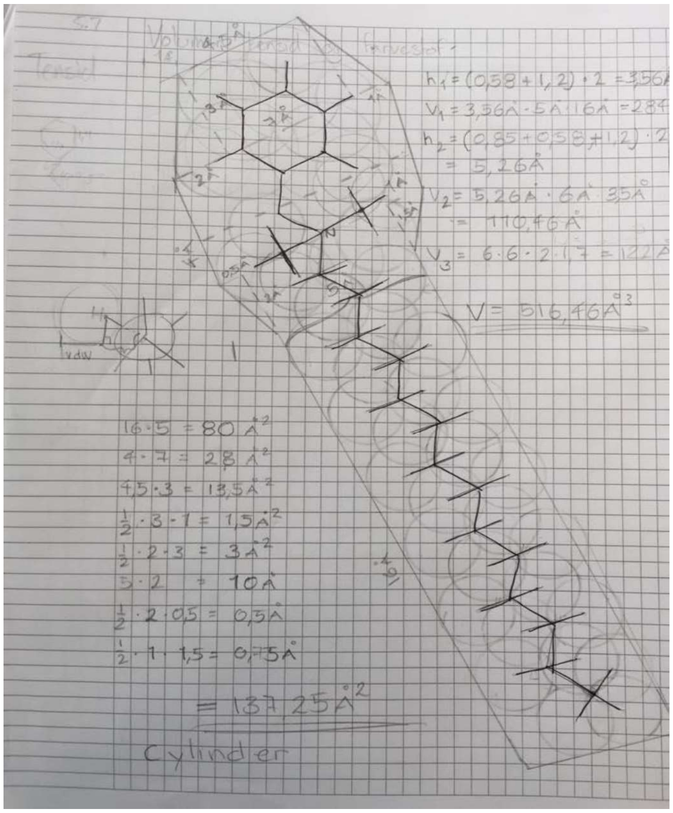


Figure 7: Surfactant BC14's geometrical form. The bonding lengths and angles are drawn and the Van Der Waal radii are shown.

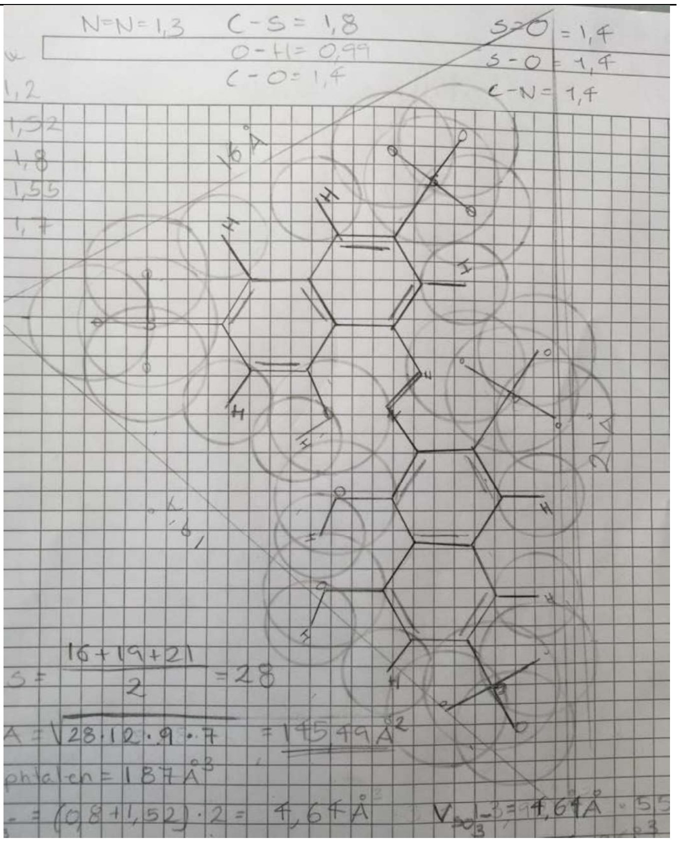


Figure 8: Dye Beryllon II's geometrical form. The bonding lengths and angles are drawn and the Van Der Waal radii are shown.

3.5. X-ray diffraction

To investigate a possible crystalline structure, powder X-ray diffraction (XRD) is used. Figure 9 shows the XRD patterns of our compound. It shows that the dye and surfactant have assembled in a crystalline structure with distances that can be used to suggest a unit cell, see table 4. The d1 length is the lamellar spacing, also seen from AFM. The d2 and d3 lengths may be the width (second axis) and depth (third axis) of the structure. Figure 10 is a suggestion as to how the dye and surfactant may have assembled.

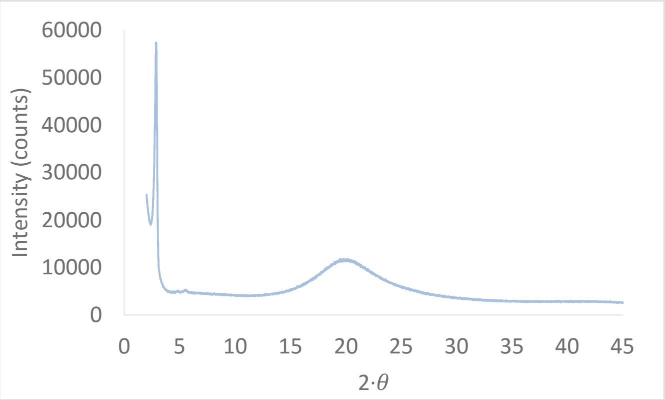


Figure 9: This figure shows the intensity of x-rays that have been diffracted by the crystalline structure at different angles measured in counts. The first peak is shown clearly, the second peak at ~5 $2 \cdot \theta$ is not as distinct. The last peak at ~20 $2 \cdot \theta$ is obvious, but is not as distinct as the first peak. It is possible that the material is not formed completely as crystals.

Table 4: Positions found from XRD results calculated into distances Using Braggs' law..

Compound	XRD [nm]		
Dye +surfactant	d1[a]	d2[b]	d3[c]
Bell + BC14	3.10	1.62	0.44

[a] First diffraction peak corresponding to the longest distance in the material. [b] Other intensity peak. [c] Third intensity peak read on the XRD graph

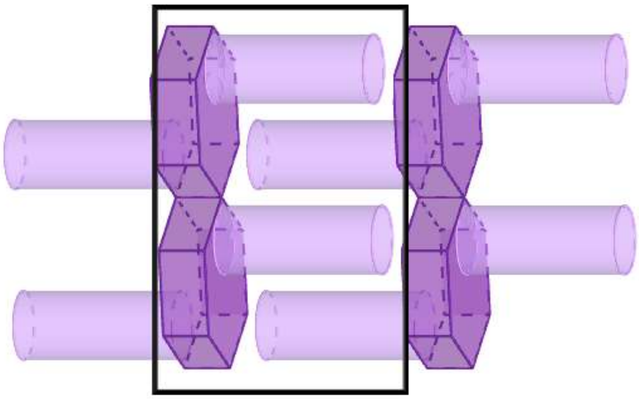


Figure 10: The suggested packing model. The black square indicates the unit cell, with the measurements from the XRD. The vertical length of the cell unit is approximate 16 Å, the horizontal length of the unit cell is approximate 30 Å while the depth of the unit cell is approximate 4 Å. The unit cell consists of one dye Beryllon II molecule (dark) and four surfactant BC14 molecules (light), which bond vertically on each side of the dye.

3.6. Suggested packing model

The results from XRD have suggested a geometrical form of the unit cell, whereas the geometrical forms of the surfactant and dye has given an understanding of how the molecules are packed. In light of the previous analysis, a packing model is suggested.

The distance between repetitions is approximate 30 Å, given from XRD (see table 4), which is the length of one surfactant and the depth of the dye. From that information, it was concluded that the surfactants packs vertically on the dye. In this suggested packing model the surfactants bond on either side of the dye (see figure 10).

By choosing this packing model, the positive and negative charges corresponds. In the suggested packing model both the geometrical form of the unit cell from XRD data and the geometrical form of the surfactant and dye are taken into account.

With a suggested unit cell it is possible to calculate the density of the material, because the volume and mass of a single cell is known. The density is calculated to $1.48 g/cm^3$.

3.7. Self-assembly of the material

Transmission electron microscopy (TEM) has been used to find which kind of structure the material forms when a solution of the nanomaterial is allowed to dry on the cobber grid used for TEM (figure 11). In the TEM images, areas with different thickness and plateaus can be found. These are possibly due to a lamellar structure of the material, causing some areas to contain more layers than others (figure 12). This suggests that the material assembles into a supramolecular structure due to the charge in the surfactant and dye.[1] Plateaus can also be found in other locations, likely due to the formation of a lamellar structure where not enough material is present to form a full layer (figure 13). The material exists with different patterns as can be seen in the images. Possibly due to how the solution has dried, different phases in the material and due to heating by TEM.

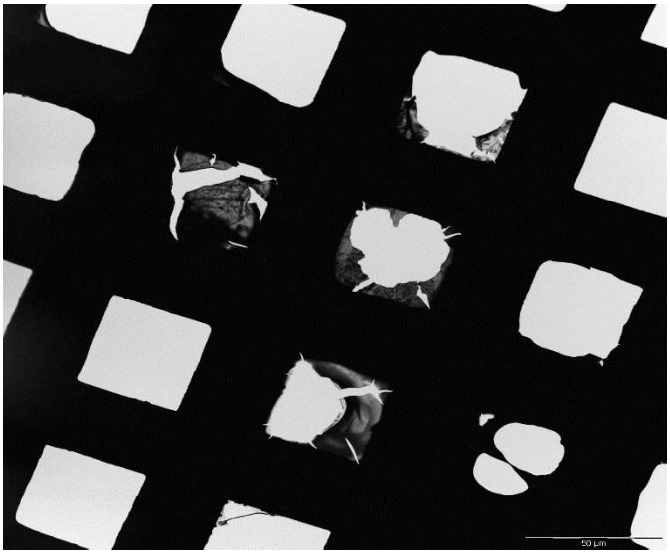


Figure 11: TEM image of films formed by the solution on the TEM grid

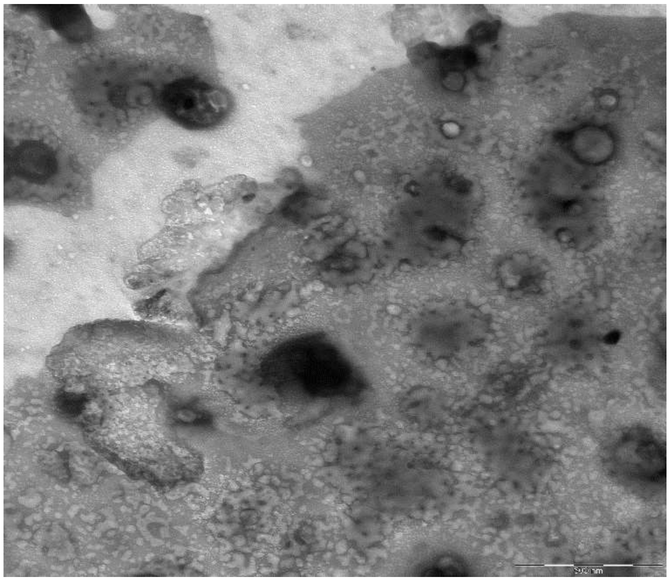


Figure 12: Further zoom on part of the film shown in figure 11. The film in this TEM image has varied thickness and several different patterns.

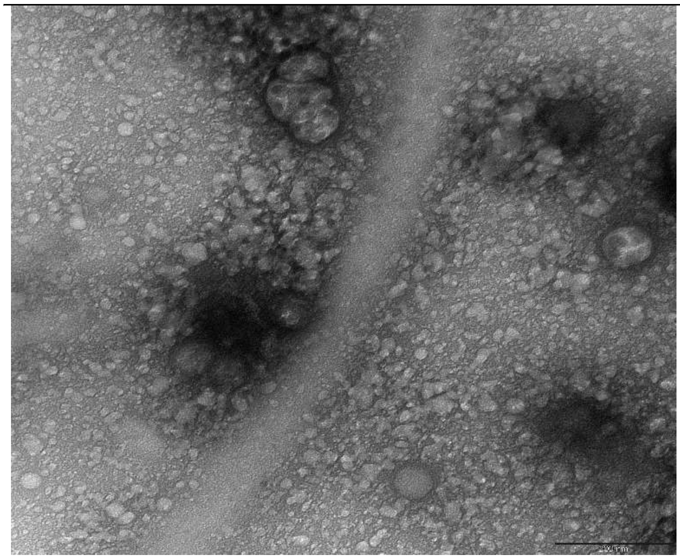


Figure 13: TEM image where another part of the film with plateaus are visible.

Figure 14: An epi bright-field optical microscopy picture of the centre of the film.

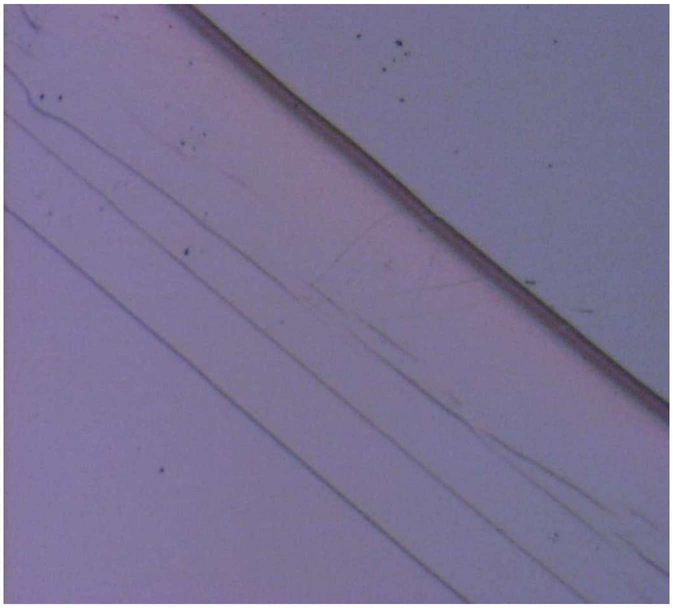


Figure 15: An epi bright-field optical microscopy picture of the edge of the film.

3.8. Structure of the thin film

It is possible to measure and characterize the thin film by using atomic force microscopy (AFM) in collaboration with optical microscopy. Epi bright-field optical microscopy shows that the thin film created from the 10mg/mL solution is flat and homogenous, including a clear and defined edge, seen as all the material seems to have assembled into one continuous film (see figure 14 and 15). This can be due to the spin casting process. The film does contain a few impurities originating from undissolved dye and external factors; dust or water that have condensed on the film (see figure 14).

AFM has been used in tapping mode to see if the structure of the film fits the size of the surfactant-dye complex determined by XRD. By looking at the height trace from AFM, it can be seen that the nanomaterial forms at least one terrace with a height difference of 3.27nm above the next layer's surface (see figure 16 and 17). In the height distribution it can clearly be seen that the layers are at two different heights with an approximate difference of 3nm. A more exact height difference is found by systematically measuring the average height in a 0.1µm x 0.1µm area on both of the layers and comparing them (see table 5). The height difference between the two layers matches the distance determined from XRD and fits the theoretical lamellar packing model of the molecules.

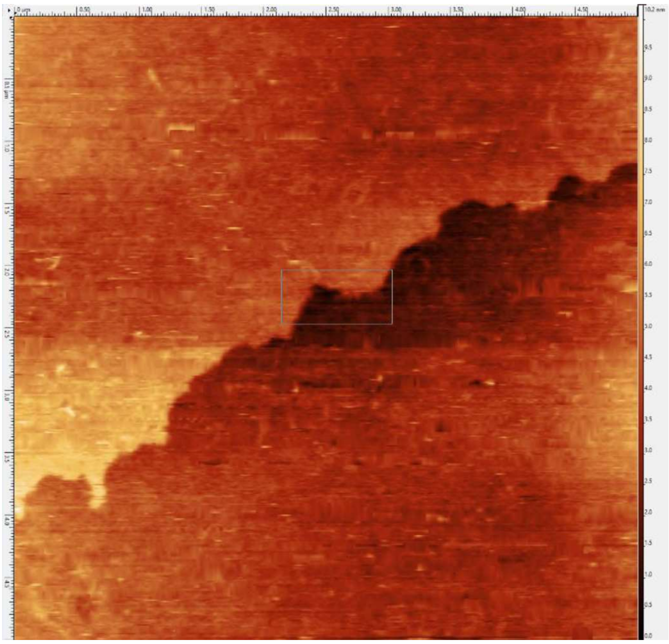


Figure 16: AFM micrograph of a layer edge on the thin film with the square where the height distribution was measured.

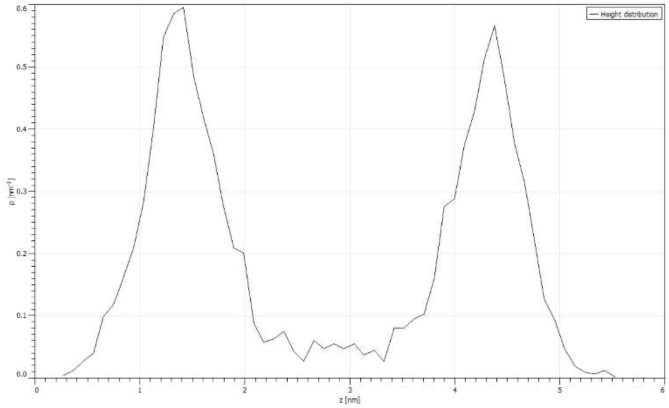


Figure 17: Height distribution over the square marked in figure 16.

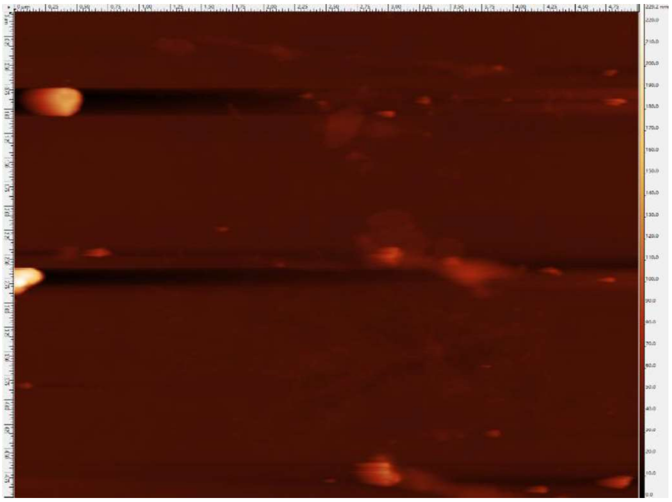


Figure 18: AFM micrograph where dust has contaminated parts of the image. However small plateaus with the same height as the layer height from figure 16 can still be found.

Table 5: Measured AFM layer heights

Layer 1	Layer 2	Layer height
4.72	8.05	3.33
4.04	7.23	3.19
3.39	7.03	3.64
3.42	6.53	3.11
3.16	6.73	3.57
3.09	6.48	3.39
2.68	5.73	3.05
2.51	6.06	3.55
1.55	4.59	3.04
1.25	4.58	3.33
1.10	4.59	3.49
1.44	4.33	2.89
1.35	4.48	3.13
1.24	4.53	3.29
1.07	4.33	3.26
1.19	4.48	3.29
1.20	4.32	3.12
Average layer height		3.27

The surface roughness of the layer has also been measured from the height trace, determined at 0.48 ± 0.19 nm. Note that this value is lower than the roughness of the glass substrate. However the film is soft enough for the AFM tip to drag molecules along the surface and this has affected the measured surface roughness. The markings left by the molecules being dragged along the surface can be removed from the height trace during data processing, but there is no way to differentiate between these and actual surface features.

A second AFM height trace of the sample has been made, but the image appears to be contaminated as there are local height differences of 100-200 nm, which should not be created by spin casting (see figure 18). This is likely due to dust or undissolved dye as determined by optical microscopy. In other areas of the height trace, there are plateaus with a height difference of around 3nm, but they do not form separate layers like in the first image.

3.9. Differential scanning calorimetry analysis:

The Perkin Elmer DSC6 heats up the material to melting temperature and measures the energy input relative to the material's transition state from a solid to liquid. This method makes it possible to discern any of the material's transition states, and more specifically, the energy input required for said transition.

The following graph is a result from plotting the values of energy input (Heat Flow) as a function of temperature in °C.

Note that the test is performed at a starting temperature of 20°C.

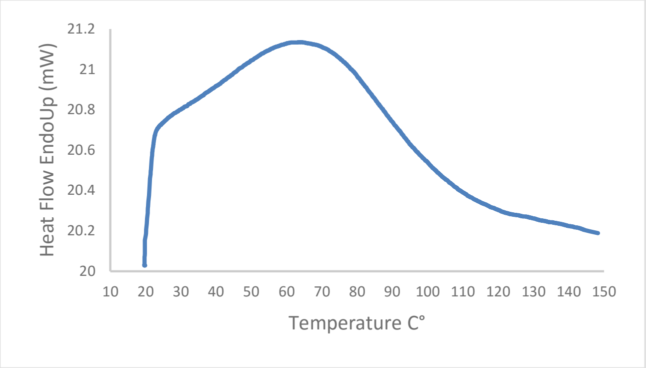


Figure 19: Perkin Elmer DSC6 Analysis graph. Note that no transition state can be found.

As temperature increases, the sample material's energy increases rapidly from the start temperature of 20°C, up until between 21-22°C. From this point forward, a slightly bent curvature is observed, for which the highest temperature is 66 °C. This smooth curvature indicates that a part of the material, sticky and greasy as it is, has only vaporized, leading to shown test results. It is concluded, that DSC analysis does not show any for the material relevant transition states.

Based on AFM and XRD analysis, it is concluded that the material must possess some, if yet varying, degree of crystallized order, given that the material is capable of creating a thin film. DSC data, however, reveals that it is not a fully crystallized order, of which this conclusion can be drawn from the fact that the material has a sticky and greasy texture.

This leads to the belief that the material may be a form of liquid crystal with a nematic order, perhaps with the same capabilities as liquid crystals previously observed.

4. Conclusions

The ionic self-assembling of nanostructures was proven successful. Synthesis between dye Beryllon II and surfactant benzyldimethyltetradecylammonium BC14 resulted to some extent in a material with crystallized order, as XRD and AFM indicate. Due to the fact that DSC test results were inconclusive, and that the product was a bit greasy, it was concluded that the material most likely possesses a nematic crystallized order, also observed in liquid crystals.

The nanomaterial forms a thin film with lamellar order when spin casted on a glass substrate, which the absorption spectra indicate. TEM data applies further support to that a thin film is made by ionic self-assembly. Based on XRD data, AFM data and knowledge regarding the molecules' three-dimensional structure, a packing model was suggested. In the suggested packing model the surfactants pack vertically on each side of the dye.

In summary, utilizing this method, it is possible to synthesize two randomly oriented molecules into a highly ordered compound that possesses crystalline structure.

5. Acknowledgements

We would like to thank Cecilie L. Andersen, Miguel Carro, Marco Santella, Tue Hassenkam and Freja E. Storm for their assistance, both in the laboratory and helping us understand the great amount of data we obtained from the various analyses.
Special thanks go out to Dr. Thomas Just Sørensen, who managed to instruct us, furthermore making this course interesting and highly educational.

6. Notes and references

ADRESS MISSING

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