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Full Paper

Ionic self-assembly forming thin-films from an azo-dye and a surfactant

J. H. M. Andersen, D. Himmelstrup, L. M. Høgel and M. Qasimi

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This paper details a process for creating thin-films using ionic self-assembly with a high degree of ordering. We show through several complementary analyses that we've successfully synthesized our target compound, that we've successfully created an orderly thin-film, and proven our process viable.

Introduction

Look at nearly any green plant and you will see a self-assembled solar panel.[1] This trick from nature has long been sought after but putting together billions of molecules just right has understandably proven to be finicky.[2] To impose order in a world driven towards chaos, nature's favorite tool has got to be self-assembling structures: Everything from DNA replication to protein folding happens through self-assembly given the right conditions.[3,4,5] For example, creating a million identical copies of a DNA strand is as simple as mixing an enzyme with amino acids and applying heat.[6] Nature, through self-assembly, will do the rest. If we could better understand the conditions required for self-assembling structures with high order, we might be able to replicate other useful aspects of Nature such as light-sensitive chlorophyll for making cheaper solar panels.[7,8,9]

In this paper we will explore the process of creating a thin-film using ionic self-assembly. Using two readily available building blocks. The question of whether our process was successful will be answered through analysis of x-ray diffraction, UV absorption, DSC, elementary analysis, mass spectrometry, microscopy images, AFM images, and TEM images.

To summarize the results, our synthesis yielded useful nano material with good purity, verified by elementary analysis. X-Ray diffraction confirmed our postulated crystalline structure, and microscopy images, AFM images, and TEM images confirmed the presence of a layered thin-film.

Results & Discussion

Synthesis

Hydroxynapthol and BC14 salts (table 1) are used as powder. Hydroxynapthol is a flat molecule with a dark blackish color (figure 1, top left and bottom left). BC14 is an elongated module and completely white (figure 1, top right and bottom right).

Since our azo-dye has three negative charges and our surfactant has a single positive charge, we began synthesis by preparing three times as many surfactant molecules as dye molecules. Both the dye and the surfactant readily dissolves in water but the new dye-surfactant compound should have a much lower water solubility. Using this property, we can mix (figure 2, left) our 1% aqueous solution of dye with our 1% aqueous solution of surfactant and any precipitation ought to be the dye-surfactant compound we're looking for. After extensive vacuum filtration (figure 2, right) and drying at 40 °C, we ended up with a blackish powder (figure 3) weighing in at 0.63g (2.32 mmol), which is 25% of the theoretical maximum output. This yield was high enough for all our subsequent experiments.

A 1% and a 5% solution were created by dissolving 100mg of powder in 100ml and 20ml DCM, respectively. These solutions were used to create spin-casted samples by carefully depositing a single drop from each solution on two different slides, rotating at 3000 rpm. The 1% solution did not leave any detectable material on the slide so the rest of this article will only refer to the slide created with the 5% solution.

Table 1: Materials used in synthesis.

class	Molecule name	Chemical formula
Azo-dye	Hydroxynaphtol	$(C_{20}H_{11}N_2Na_3O_{10}S_3)$
Surfactant	Benzyldimethyltetradecylammonium chlorid (BC14)	$(C_{23}H_{42}ClN)$



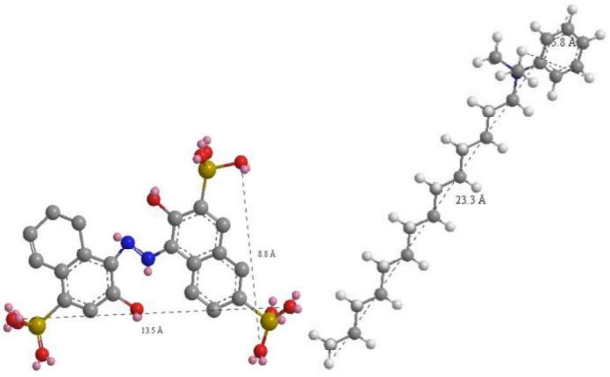


Figure 1. Molecule structure and powder of azo-dye Hydroxynaphtol (left) and surfactant BC14 (right) .



Figure 2: Mixing azo-dye and sulfactant and vacuum filtration of the mixture.

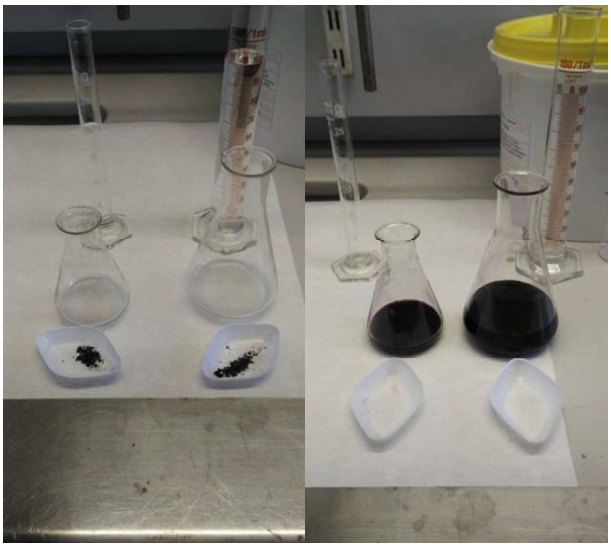


Figure 3: Compound before being dissolved in DCM. A solution with 100 mg to 20 mL (left) and a solution with 100 mg to 100 mL (right).

Mass spectrometry

When determining mass over charge of the ions in our compound, our surfactant stands out clearly at ~332 m/z (figure 4).

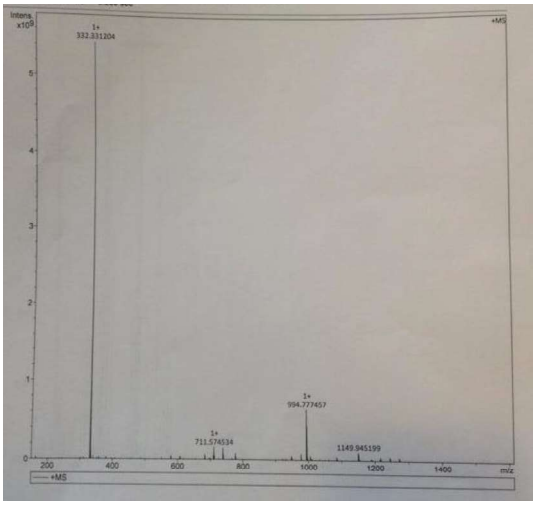


Figure 4: Mass spectrometry results for positively charged ions. The highest peak represents the surfactant.

Elementary Analysis

Given the chemical formula of our compound, $C_{89}H_{137}N_5O_{11}S_3$, we would expect elementary analysis to show 69% carbon, 8.91% hydrogen and 4.52% nitrogen.

Table 2: The theoretical and measured percentages of C, H and N in our compound. The measured percentages correspond to the theoretical when two water molecules is added to every azo-dye surfactant complex.

	Carbon	Hydrogen	Nitrogen	Difference
Expected:	69%	8.91%	4.52%	
Experimental:	67.68%	9.44%	4.17%	1.32pp
With 2(H_2O):	67.43%	8.96%	4.42%	0.48pp

Adjusting for two water molecules per dye-surfactant complex brings our expected values within 0.5 percentage points of our experimental results (shown in table 2). This tells us the product is free of impurities.

Absorption Spectrometry

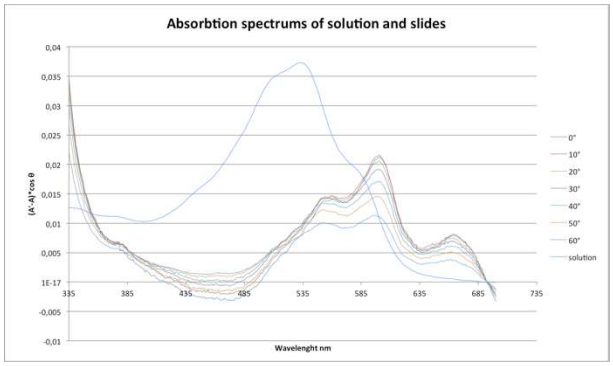


Figure 3: absorptions spectrums showing the different between solution and slide.

Table 3: Calculated dipole angles in material on slide.

Wavelength (nm)	Angle
666	68.81
602	66.27
558	60.80

By shining polarized light through our sample at different angles and measuring the absorbance (figure 5) we can deduce the angles of dipoles. These angles are relative to the normal of our slide and we therefore cannot tell in which direction the dipoles are leaning. Calculating the angle of a dipole at a given wavelength is done with these equations:

$$k = \frac{\frac{(a+b)}{(b-c)}}{2+\frac{(a+b)}{(b-c)}}$$

$$\alpha = \alpha cos\sqrt{k}$$

In the above equations, 'a' is the slope of the linear regression through the absorption measurements of the slides at different angles, 'b' is the intercept point, and 'c' is the absorption of a blank slide.
Calculating the angles at the three peaks (666nm, 602nm and 558nm) hints at two dipoles at 68.81 and 60.80 (table 3).

Structural analysis

We calculated the theoretical dimensions of our azo-dye and surfactant to give a suggestion to how the molecules pack (table 4). Because of the azo-dye having three negative charges (from the three sulfonic groups), and the surfactant having a single positive charge, our compound will make cells in an ion-grid in a ratio of 1:3. That leaves a limited number of options for supramolecular structuring. We know that the heads of the surfactants will 'latch on' to the azo-dye due to the charge being at the nitrogen molecule - while their tails will point away from the dye. It is plausible that the surfactant tails will have lower energy when located along each other because of dispersion forces in the long chains of carbon.

Table 4: Dimensions of the components calculated only from theoretical bond-lengths and vdW-radii.

Theoretically approximations	Hydroxynaphtol Blue	Benzalkonium -14	BZK-14, head	BZK -14, Tail
Side length1	16.5 Å		8.2 Å	4.58 Å
Side length2	11.8 Å		6.1 Å	5.80
Area	194.7 Å^2		50.0 Å^2	19.2 Å^2
Thickness/length	-5.5 Å	25.7 Å	5.7 Å	20.0 Å
Volume	1070.9 Å^3	669.0 Å^3		
Molar mass	620.5 g/mol	368.0 g/mol		

X-Ray Diffraction

By shining x-rays at different angles at our powder sample and measuring the reflections, we are able to gain an insight into the crystalline structure of our dye-surfactant compound. Using Bragg's law which relates the angle of x-rays to grid sizes, we've graphed (figure 6) the unit distances found in our compound as indicated by the peaks.
We see a clear peak around 4-5 angstroms, a peak at ~37 to 45 angstroms, and a small one at 15 angstroms. This information suggests that the unit cells in the crystal has the dimensions equal to the length of the surfactant plus the side length of the azo-dye (around 37.5 Å). Thus, the unit cell is fairly flat: 5x15x37.5 Å^3.

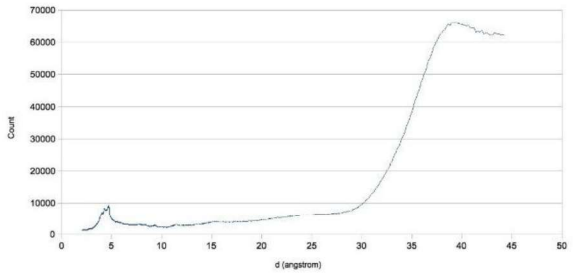


Figure 4: X-ray diffraction graph. We can see that we have 2 very clear peaks, the first peak at about 5 Å and a second peak at 37.5. Å. These lengths correspond nicely with our calculated packing model.

Spatial Packing

When the lengths of the unit cell (adjusted by the XRD-results) are applied to measure the density they yield a number very close to what we thought – considering that it is an organic compound with a density greater than water (as shown below). This supports the idea of the unit cell being a general property to our compound.

$$\frac{1724.5\,g/mol}{\frac{6.022*10^{23}\,n/mol}{5\mathring{A}*15\mathring{A}*37.5\mathring{A}}{10^{24}\mathring{A}^3/cm^3}} = 1.018\,g/cm^3$$

The unit cell of the nano material consists of three surfactants and a dye molecule. The surfactants are attached to the azo-dye from both sides, so that they form layers of alternating azo-dye and surfactant. When packed tightly, the unit cell can be described as a box with a height more than twice that of its width.
Because of the negative charges being placed on opposite sides of the azo-dye it's very likely that the lowest energy level of packing is, when the surfactants lie side to side in alternating direction, to spread out their positive charge (as shown in Figure 7).

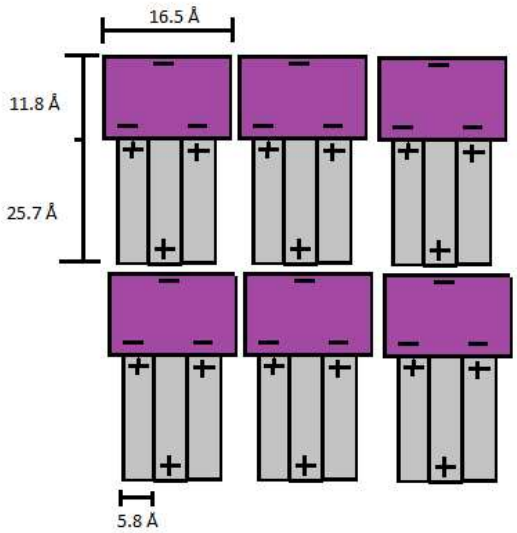


Figure 5: Sketch showing packing structure of our dye (purple) and surfactant (grey).

Microscopy

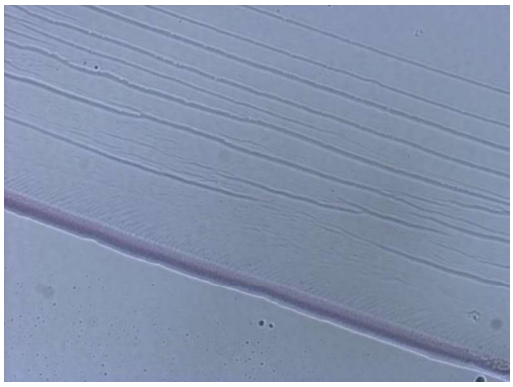


Figure 8: 20x with polarized light on the edge of sample showing clearly visible layers on the spin casted slide with ratio 5:1.

We examined our spin casted slide under 200x magnification and found a clearly visible layered structure at the edge of the sample (figure 8). The center of our slide was also inspected but no layered structure could be seen.

AFM

Through AFM, some of the anticipated and later suggested dimensions were confirmed. A pattern is shown in the graphing of the surface scanning that has a consecutive distance of ~4 nm. This agrees with the length of the unit cell; approximated to be 37.5 Å high. The first picture shows how the compound is arranged in plateaus, repeating similar distances for each step.

The AFM-pictures are taken at the center of our spin-casted slide. It represents a very small area of the presumed thin film - but seeing results that fit with the theoretical proposals shows that our compound has the properties and potential to form a thin film. And maybe under cleaner and more controlled circumstances it would yield a more symmetrical and sharply defined thin film.

The histogram (figure 9) shows the distribution of the different heights in the AFM-picture (figure 10). The evenly spaced distance between the three largest peaks seem to correspond with our unit cell. Figure 11 from the center of the slide show holes that are roughly the height of the unit cell.

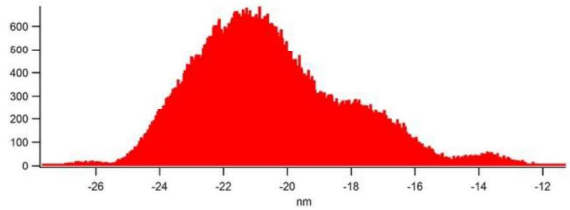


Figure 9. The AFM histogram shows the count distribution of different heights along the x-axis. The three largest independent peaks differ by the largest length of the unit cell.

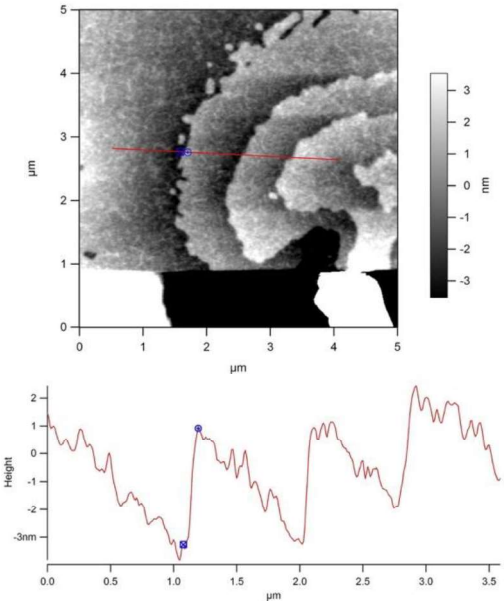


Figure 10: AFM image showing layered structure. The first picture shows plateaus from the center of the spin-casted slide. The second image shows the plateaus heights, which is 4A and is the length of our molecules.

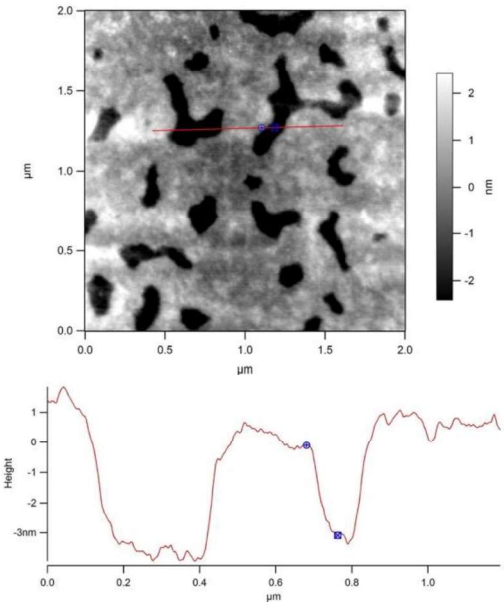


Figure 11: AFM image from the center of the slide. Black areas show vacancies in a plane surface with depth corresponding to the height of a unit cell. The graph is the height sequence highlighted by the red line.

DSC

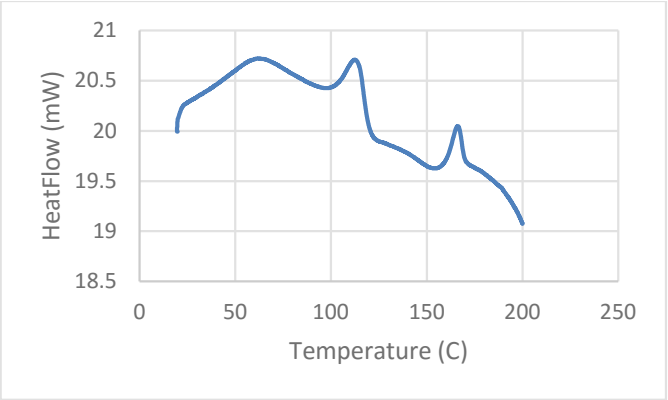


Figure 6: graph over energy required to heat sample, showing three distinct phase shifts.

Table 5: Overview and magnitude of the peaks shown in figure 12.

	Peak start °C	Peak end °C	T peak °C	Area mJ	DH J/g
First Peak	42,70	82,36	60,52	27,71	7,33
Second peak	101	124,17	113,70	39,02	10,32
Third peak	160,17	175,5	165,71	14,98	3,96

By Differential Scanning Calorimetry, (DSC) it is possible to find phase transitions of the nanomaterial. The graph (figure 12) shows the energy that is added to the sample as a function of the temperature. Clearly shown in the graph are three peaks (described in table 5), one curved and two sharp peaks, which indicate phase transitions of the nanomaterial. The three peaks are all endothermic meaning the energy will be absorbed in the sample resulting an increased addition of energy.

TEM

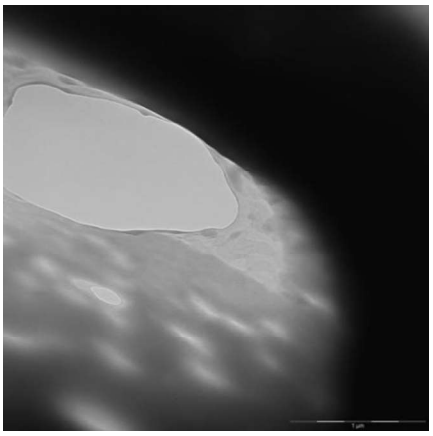


Figure 7: TEM picture of nanomaterial. The material shows the properties of a thin film.

The TEM sample was prepared using the 1% nano material solution. Examining this sample of our dye-surfactant compound using a transmission electron microscope, we see broken film of varying depth. Unfortunately, the material was too disordered for us to observe single layers. The shades in the picture in figure 13 indicate how much material found in the exact spot. The darker the shade the more material.

Conclusions

Based on the results of several experiments and measurements of dye-surfactant compound, our initial assumption of ionic self-assembly in our nano material, is reinforced. The material we got proved, through EA to be the pure synthesized product. Theoretical dimensions of the unit cell was confirmed - both through AFM and XRD. We know from the TEM-results that the hybrid-compound is able to form a thin film, and through AFM that it to a large extend structures itself in layers of high order.

Notes and references

Address: Nano-Science Center, University of Copenhagen, Universitetsparken 5, 2100 København Ø, Denmark.; E-mail: vrs552@alumni.ku.dk

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