Chapter 5
Clays as Template for the Synthesis of Highly Ordered C$_{60}$-Aluminosilicate Hybrids

5.1 Motivation

Much of the research effort concerning the nanoscopic properties of clays focuses on mechanical applications such as nano-fillers for polymer reinforcement. To broaden the horizon of what is possible by exploiting the richness of clays in nanoscience, we explore a new bottom-up approach for the production of hybrid materials where clays act as the structure directing interface and reaction media. This new method, based on combing self-assembly (SA) processes with the Langmuir-Schaefer (LS) technique, uses the clay nanosheets as a template for the grafting of C$_{60}$ in a bi-dimensional array, and allows for perfect layer-by-layer growth with control at the molecular level. In contrast to the more common growth of C$_{60}$ arrays through nano-patterning, our approach is performed in atmospheric conditions, can be upscaled to cm$^2$ areas and applied to virtually any hydrophobic substrate. Here we present a detailed study of this approach by means of temperature-dependant X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning tunnelling microscopy (STM).

5.2 Introduction

In recent years, low-dimensional assemblies, where order and organization follow supramolecular principles, have assumed remarkable importance due to their outstanding physical (photophysical, electrical etc) and/or chemical (catalysis, molecular separation etc) and/or biological (drug delivery, biosensing etc) properties. Controlling both the organization of the assemblies and their physical and chemical properties through simple external parameters led to the creation of
new tailored functional materials. Top-down methods based on photolithography were largely developed for integrated circuit (IC) manufacturing and are found to be practical for inorganic materials and metals but less suitable to control the nanostructuring of organic building blocks. An alternative method is the bottom-up approach where, by imitating strategies of biological SA, one can create entirely novel molecular building blocks and form supramolecular architectures, whose final structure is encoded in the shape and properties of the clusters or molecules that are used. In particular, molecular alignment in a two-dimensional assembly can be tuned to modify the physical and chemical properties of the resulting material. Thin films grown by deposition in ultra high vacuum (UHV) are a much-exploited example of this behaviour where the initial monolayer maximizes the van der Waals and Coulomb forces to produce flat adsorption, while the subsequent deposition often makes molecules stand up. However, islanding resulting in both two-dimensional (2D) and 3D arrangements is not easily avoidable in this fabrication method.

Here we take an alternative approach based on one of the most common - though not widely manipulated - materials, namely layered smectite clay, and aim at developing and studying highly ordered 2D assemblies of carbon based nanostructured systems such as fullerenes. Natural or synthetic smectite clays are layered materials consisting of nanometer-size aluminosilicate platelets which present a unique combination of swelling, intercalation and ion exchange properties that make them valuable nanostructures in diverse fields. Their structure consists of an octahedral alumina layer fused between two tetrahedral silica layers. The 1 nm thick layers are negatively charged and neutrality is obtained, for example, by hydrated cations present between adjacent platelets. The intercalation process in these systems is equivalent to ion exchange and, unlike intercalation compounds of graphite, does not involve necessarily charge transfer between the guest and host species. These materials have the natural ability to absorb organic or inorganic guest cationic species (and even neutral molecules) from solutions. It is this cation “storage” that gives unique properties to clay minerals and is the basis for their use as catalysts, templates in organic synthesis or as building blocks for composite materials. The nature of the microenvironment between the aluminosilicate sheets regulates the topology of the intercalated molecules and affects possible supramolecular rearrangements or reactions, such as SA processes that are not easily controlled in the solution phase.

Fullerenes and their compounds exhibit an extremely rich collection of interesting and potentially useful physical properties: they are excellent electron acceptors, can
be transformed into synthetic metals, exhibit superconductivity\textsuperscript{13} at transition temperatures only exceeded by those of the cuprates, support ferromagnetism\textsuperscript{14} (without the presence of $d$ or $f$ electrons) and display remarkable non-linear optical behaviour.\textsuperscript{15} Considerable efforts have been made to develop C$_{60}$-based assemblies and supramolecular nanostructures,\textsuperscript{16,17} however, fullerenes spontaneously aggregate when deposited on solid surfaces where they are not strongly chemisorbed. In spite of this, when fullerene molecules are placed between clay layers, the microenvironment of the interlayer space can avoid aggregation of the C$_{60}$ cages and allow the study of 2D structures of these molecules. Recently\textsuperscript{18,19} we described the insertion and subsequent behaviour of a series of water-soluble fullerene derivatives into the interlayer space of clay where high density and a high degree of ordering were achieved. Fulleropyrrolidine monoadduct and bisadduct derivatives, positively charged and soluble in water, were introduced into the clay galleries through a simple ion exchange. The experiments, complemented by computer simulations, revealed the successful intercalation of fulleropyrrolidine derivatives and demonstrated that the hybrid systems produced possess interesting optical and electronic properties.

Over the past decade a new method combining SA and LB assembly has emerged and enabled the creation of novel clay hybrids grown layer-by-layer\textsuperscript{2,20}. Because of the spatial arrangement of the clay platelets, such an assembly leads to control at the nanoscale and retains order at the macroscale. Although this emerging field of clay nanoscience remains largely unexplored, several studies have demonstrated the successful integration of a variety of guest species within the clay thin film structure either synthesized on the clay surfaces through a cation exchange driven SA process or via the integration of functional molecules\textsuperscript{2,11,21-27}.

In this chapter, we report on the synthesis of highly ordered bi-dimensional arrays of C$_{60}$ sandwiched between clay layers by means of a modified (hybrid) LS method. Our film preparation approach involved a bottom-up layer-by-layer process that included the formation of a hybrid amphiphilic cation–clay mineral Langmuir film hosting C$_{60}$ molecules within its interlayer space. This assembly of the clay stack with its guest molecules is afforded through a succession of charge driven functionalization (or self assembly) exploiting the clay’s templating properties.
5.3 Preparation of hybrid Surfactant Clay Surfactant C$_{60}$ films

5.3.1 Clay

The clay used for the preparation of the hybrid films was a natural sodium-saturated montmorillonite Kunipia F (KUN) provided by Kunimine Industries Co. (Japan) with the structural formula $\text{Ca}_{0.11}\text{Na}_{0.891}(\text{Si}_{7.63}\text{Al}_{0.37})(\text{Al}_{3.053}\text{Mg}_{0.65}\text{Fe}_{0.245}\text{Ti}_{0.015})\text{O}_{20}(\text{OH})_4$ and cation-exchange capacity (CEC) 1.18 meq g$^{-1}$ of clay. The stock dispersion of the clay was prepared by stirring 1 g of clay for 12 hours in 1 liter of Millipore ultrapure water. The dispersion was diluted to a given concentration with pure water before being used as subphase in the LS deposition.

5.3.2 Surfactant

Dimethyl dioctadecylammonium (DODA) bromide (purity 99+ %, Sigma-Aldrich) was used as received. DODA was dissolved in a mixture of HPLC-grade chloroform and methanol (9:1 in volume) to prepare a spreading solution of 0.1 mg ml$^{-1}$. For surface modification, a mixture of ethanol and pure water (8:2 in volume) with 0.5 mg ml$^{-1}$ of DODA was used.

5.3.3 Preparation of the hybrid layers

All films were prepared following the deposition cycle depicted in the scheme of figure 5-1 by means of a Nima Technology thermostated 612D LB trough at a temperature of 21 ± 0.5°C. The pressure sensor employs a Wilhemly plate (small length of chromatography paper) to measure surface pressure (reduction in surface tension). Pure water and clay dispersions in Millipore Q-grade water were used as subphase. A clay concentration in the dispersion of 10 ppm was chosen as the optimal value. Depending on the requirements of the characterization method, samples were deposited either on 150 nm gold film on mica for XPS, AFM and STM, or on SiO$_2$ or glass substrates for XRD. First 200-300 µl of CHCl$_3$-C$_2$H$_5$OH (9:1)-DODA mixture (0.1 mg ml$^{-1}$) were injected at the air water interface. After a waiting time of 20-30 min to allow for hybridization to occur, the hybrid DODA-clay layer at the air water interface was compressed at a rate of 30 cm$^2$min$^{-1}$ until the chosen stabilization pressure of 13 mNm$^{-1}$ was reached. This pressure was
maintained throughout the deposition process. Films were deposited by horizontal lift onto one of the above mentioned substrates, with downward and lifting speeds of 10 and 2 mm min$^{-1}$, respectively. Samples were allowed to touch the water (very gentle dip of max 0.5 mm below the water level) and rinsed directly after dipping in 18 MΩ MilliQ water to eliminate possible weakly attached cations remaining from the hybridization process. To graft C$_{60}$ to the clay surfaces a linker between the two is needed. In this experiment the linker was chosen to be a self-assembled monolayer (SAM) of DODA. As displayed in figure 5-1, the freshly deposited DODA-clay monolayer was lowered in an ethanol-water (9:1) DODA mixture (1 mg/ml) to form a DODA-clay-DODA layer. Again, 18 MΩ MilliQ water cleaning was applied to remove excess material from the sample surface. During the first hybridization, when clay and DODA react through the cation exchange/attachment of the DODA molecules at the clay sheet surface within the LB trough and during the previously mentioned, chemically identical second hybridization, the sodium is substituted by DODA. The X-ray photoemission data discussed below testify to

Figure 5-1. Schematic representation of the deposition cycle for DODA-clay-DODA-C$_{60}$ films. Step 1: deposition of the DODA-clay monolayer onto a substrate. Step 2: creation of a SAM of DODA on the DODA-clay layer. Step 3: grafting of C$_{60}$ onto the DODA-clay-DODA monolayer. Cycle (steps 1-3) can be repeated as many times as needed.
5.3 Preparation of hybrid surfactant clay surfactant C60 films

this cation exchange process. The last step of this deposition procedure (see figure 5-1) was a 2 min lowering of the hybrid layer (DODA-clay-DODA) in a solution of 0.2 mg.ml\(^{-1}\) C\(_{60}\) (Sigma Aldrich sublimed, 99.9% used as received) in toluene (sigma Aldrich 99.5%, used as received), prepared by the mixing and short sonication (~1 min). This final step of the cycle was followed by rinsing with 18 M\(\Omega\) MilliQ water. To avoid contaminating with water any of the other solutions or more importantly, the LB air-water interface, samples were dried under a nitrogen flow after every washing step (step 1-3). We observed that omitting to dry a water droplet remaining on the substrate caused a disruption of the LB stabilization. To go from a single layer to multilayers, one simply repeats the cycle as many times as needed. We produced samples of 1 layer for STM and AFM and of 50 to 100 layers for XPS and XRD analysis.

5.3.4 X-Ray Diffraction (XRD)

XRD patterns were collected using a Philips PANanalytical X’Pert MRD diffractometer with a Cu K\(\alpha\) (\(\lambda=1.5418\) Å) radiation source (40kV, 40mA), a 0.25° divergent slit and a 0.125° antiscattering slit. The reflectivity patterns were recorded in the 2-Theta (2\(\theta\)) range from 0.5 to 10° with a 0.02° step and counting time of 10 s per step for the non-ambient measurements recorded in a temperature range of 25° to 320°.

5.3.5 Atomic force microscopy (AFM)

AFM images of the films were recorded in tapping (non-contact) mode on a Scientec 5100 equipped with Si n-type cantilever with a tip radius <10 nm and a force constant of ~25-75 N/m. Data treatment was performed using WSXM freeware developed by Nanotec.

5.3.6 X-ray Photoelectron Spectroscopy (XPS)

Photoemission spectra were collected with a SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatic Al K\(\alpha\) X-ray source (hv 1486.6 eV) and operating in a base pressure of 3 \(10^{-10}\) mbar. The energy resolution was set to 1.3 eV and the photoelectron take-off angle was 37°. A flood gun providing 0.1 eV kinetic energy electrons in combination with a Mo grid placed above the sample were used to compensate for sample charging. All binding energies were referenced to the Si2p peak of clay at 102.9 eV. Spectral
analysis included a Shirley background subtraction and peak deconvolution using a linear combination of Gaussian and Lorentzian functions with a mixing ratio of 0.9 (90% Gaussian) in a least squares curve fitting program (WinSpec) developed at the LISE, University of Namur, Belgium.

5.3.7 Scanning tunneling microscopy (STM)

STM images of the hybrid DODA-clay-DODA and DODA-clay-DDA-C$_{60}$ layers were recorded at room temperature in the constant current mode using a Molecular Imaging STM with Pt/Ir mechanically cut tips. Further characterization of the DODA-clay-DODA-C$_{60}$ layers was performed using a UHV He-cooled Omicron Multiprobe LT STM working at a base pressure of 5 x 10$^{-11}$ mbar equipped with a Tungsten tip. Data treatment included plane subtraction, smoothing, and adjustment of colour scale and brightness to enhance the contrast.

5.4 Results and discussion

There have been few reports in the literature concerning the layer-by-layer fabrication of hybrid clay material, while other deposition methods allow

Figure 5-2 Left panel: The black curve corresponds to the trough area covered by the hybrid DODA-clay monolayer which can be transferred to a substrate, recorded during the deposition of a 19 layer DODA-clay-DODA-C$_{60}$ film. The grey curve shows the stable surface pressure (here around 9.5 mN m$^{-1}$). Right panel: Photographs of 40 layer DODA-clay-DODA-C$_{60}$ and DODA-clay-DODA films deposited on mylar.
only a poor control of the film growth, our hybrid LS approach is extremely flexible and allows for a control of the growth at the molecular level. The successful transfer of the hybrid layers can be deduced from the plot of the pressure measured at the surface of the subphase in the LB trough versus time. Figure 5-2 displays the time dependence of the total trough area covered by the hybrid monolayer that can be transferred to a substrate. At the beginning of an experiment, the trough barriers are extended and the air-water interface is fully covered by a stable monolayer. As a function of the time, as the substrate is dipped into the subphase, the total trough area reduces due to the transfer of one layer from the air-water interface to the substrate at each dip. This transfer is visible as a sharp step on the curve. If the step height (which gives an area value) is equal to the substrate surface area, the transfer ratio is 1 and the surface is 100% covered by the hybrid layer, each time it is lowered into the subphase. A transfer ratio different from unity indicates an excess (multilayer transfer) or a lack of transfer (incomplete coverage). The curve displayed in figure 5-2 is a typical example of such a curve recorded during the deposition of a 19 layer thick hybrid DODA-clay-DODA-C\textsubscript{60} film. The transfer ratio was close to 1 throughout the deposition, testifying to a successful transfer at each dip. To gain more insight into the integration of C\textsubscript{60} guest within the formed clay template, we compared DODA-clay-DODA with DODA-clay-DODA-C\textsubscript{60} films using temperature dependent XRD measurements. With this technique we can determine the d(00l) basal spacing of the hybrid clay structure. Figure 5-3 displays the XRD patterns of 80 layer thick films of DODA-

![Figure 5-3](image)

Figure 5-3. Room temperature XRD patterns of 80 layer thick DODA-clay-DODA and DODA-clay-DODA-C\textsubscript{60} films deposited on glass and the corresponding sketches of the expected structures (on the right hand side).
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clay-DODA and DODA-clay-DODA-C\textsubscript{60} deposited on glass. A first glance reveals some differences between the patterns. The dotted/top line (C\textsubscript{60} containing sample) is slightly broader and shifted towards low angles compared to the black/bottom curve which corresponds to the pure organoclay DODA-clay-DODA sample. These observations reveal a slight increase in d spacing for the C\textsubscript{60} containing sample and an increased disorder due to the presence of C\textsubscript{60} in the interlayer space. Since the surfactant layers were deposited in steps 1 and 2 (see figure 5-1) in exactly the same conditions (concentration and time) for both samples, the density of deposited surfactant should be identical. We therefore deduce that C\textsubscript{60} is accommodated between the double alkyl chains of the surfactant and not on top of it, therefore not affecting significantly the organoclay structure. To confirm the presence of C\textsubscript{60} in the hybrid structure, we annealed both samples to eliminate the surfactant molecules. The diffraction patterns shown in figure 5-4 left and right panels were recorded during a step by step annealing at the indicated temperatures, starting from room temperature up to 320°C. Using the Bragg formula, from these

Figure 5-4 Temperature dependant XRD patterns of 80 layer thick DODA-clay-DODA (a) and DODA-clay-DODA-C\textsubscript{60} (b) films deposited on glass and the corresponding sketches of the expected structure (on the right hand side).
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Figure 5-5 d(001) value extracted from the X-ray diffraction patterns of DODA-clay-DODA (stripe) and DODA-clay-DODA-C$_{60}$ (dot) films recorded at different temperatures. Final d(001) spacings are ~16.2 and ~13.8 Å for sample with and without C$_{60}$, respectively.

data one can extract the d spacing plotted in Figure 5-5 as a function of the annealing temperature. Starting above 180°C, the melting point of DODA, for both the DODA-clay-DODA and the DODA-clay-DODA-C$_{60}$ film, one can see the d spacing shrinking as a function of temperature. However, the most interesting feature is the difference in final d-spacing of the two samples: ~13.5 Å and ~16.5 Å, respectively, for the layers without and with fullerene. This observation is a first proof of the successful insertion of C$_{60}$ between the clay sheets; because it is the presence of C$_{60}$ (bulk C$_{60}$ decomposes at 900 K$^{33,34}$) that keeps the clay from collapsing to a lower d spacing by creating a pillared clay structure. One can argue that the value of the final d spacing of the pure organoclay is ~1-2 Å too thick; we assign this mismatch to the inevitable presence of cations inside the clay stack, necessary to achieve charge neutrality. The size of coherently diffracting domains can be estimated from the peak width using the Scherrer equation. We found 200 Å for the as-deposited film and 73 Å after annealing. Converted into layer units, these coherence lengths correspond to ~7 layers for the starting material and ~5 layers for the annealed one. One can therefore conclude that a slight increase in disorder is induced by the melting and de-intercalation of the DODA molecules. detailed analysis using background substraction and peak fitting (shown in appendix) lead to the same conclusions except for the observation (only after the background removal) of the same minor second phase/conformation as observed in the pure organoclay system.
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Figure 5-6 X-ray photoemission spectra of the normalized C1s and Si2p core level regions for a 50 layer thick DODA-clay-DODA-C_{60} film deposited on glass, before (+) and after (Δ) annealing (350°C); the top left panel shows an enlargement of the C 1s shake-up region while on the bottom right the structure of the samples is schematically depicted.

XPS is not only a direct method to investigate the chemical composition of the surface but also sensitive to the chemical environment of each element. Figure 5-6 shows a comparison of the C1s photoemission lines of the starting DODA-clay-DODA-C_{60} and of the same film after temperature treatment (main photoemission line and shake up). What one notices first, is the dramatic intensity difference between the as-deposited film and annealed one (both are normalized to Si2p...
5.4 RESULTS AND DISCUSSION

The 3 times higher carbon content of the as-deposited film surface can be explained by the film structure as sketched in the bottom of the figure 5-6: before annealing, the film is expected to be composed of \( C_{60} \) intercalated among the long aliphatic chains of DODA sandwiched between clay platelets as discussed earlier in the XRD section, while after annealing only clay and \( C_{60} \) should be present. Since the probing depth of the XPS is limited to the first few nm, carbon from the long aliphatic chains of DODA dominates the spectrum before annealing, while after annealing, when most of DODA has de-intercalated, the structure has shrunk and \( C_{60} \) prevails in the \( C_{1s} \) spectrum (see scheme figure 5-6). The close-up on the high binding energy region next to the \( C_{1s} \) peak shown in the top right panel of figure 5-6 confirms this picture: before annealing the typical \( C_{60} \) shake-up structure \(^{35}\) is not visible because it is attenuated by DODA, but after the heat treatment it is clearly distinguishable testifying to the presence of \( C_{60} \) within the clay stack.

The \( N_{1s} \) core line is a clear signature for the presence of surfactant molecules. In both the survey spectrum and the detailed scan (available in appendix) we find the \( N_{1s} \) peak for the as-deposited film but not for the annealed film, once more supporting the structural model before and after heat treatment as described in the XRD section. The observed nitrogen signal arises from cyanide bond (CN*-CN+*) of the ammonium head group of the surfactant. The corresponding carbon to nitrogen bonds (C*N –C*N+) are probably responsible for the shoulder that appears in the high binding energy side of the \( C_{1s} \) lines in figure 5-6 at energies of ~286-288 eV.

We sometimes also found spectral evidence for a minute amount of sodium, presumably due to an incomplete cation exchange reaction on the clay at the steps 1 and 2 of the deposition (depicted in the scheme of figure 5-1) where Na\(^+\) are replaced by DODA. Optical photographs of the samples also support the successful insertion of \( C_{60} \) between the clay sheets as shown in figure 5-2: the 40 layer DODA-clay-DODA-\( C_{60} \) film on the left is darker (brownish) than the 40 layer film of DODA-clay-DODA; both were deposited on mylar. This darker colour is due to light absorption by \( C_{60} \).\(^{36}\) Microscopies are extremely useful tools to characterize the layer quality in terms of roughness and homogeneity. The AFM height images and the corresponding phase contrast images of a 1 layer DODA-clay deposited at 11 mNm\(^{-1}\) are shown in figure 5-7a and 7b. Roughness analysis made by calculating the root mean square (RMS) value of the height on a full image (10 \( \mu \)m of lateral size) gave values of around 3.4 nm. Although these results prove the
overall good quality of the deposited hybrid clay films, the low resolution of AFM in non-contact mode made it difficult to demonstrate that C₆₀ were present on the surface. Therefore STM measurements were performed and figure 5-8 displays the STM image of one layer of DODA-clay-DODA-C₆₀ deposited on Au. Also at the higher magnification achievable by STM, the film is still uniform and C₆₀ molecules appear to cover the surface evenly but seem to be located at slightly different heights (more visible in the LT-STM measurements). This result can be interpreted in two ways. In fact, contrary to AFM, STM does not probe the true topographic profile but provides a current map of the scanned area, which in turn reflects the variations in electron density of states (for z constant, a higher density of states increases the probability of tunneling and therefore gives higher current). These variations could therefore indicate that some molecules are more distant from the tip then others but they could also reflect changes in the C₆₀ density of states due to interaction, for example with the surfactant molecules. The experimental data can not exclude either of these interpretations; it is also possible that both effects occur. To the best of our knowledge, STM study of C₆₀ on an organic template (the surfactant self-assembled layer) is still rather unexplored (Li et al.⁴⁷ reported an STM study of C₆₀ within but not on a SAM). Additional evidence for C₆₀-surfactant interaction comes from room temperature STM measurements performed on the same sample in ambient conditions: on the images of figure 5-9 one recognizes the C₆₀ molecules as ball shaped objects with a
Figure 5-8 Low temperature-scanning tunneling microscopy images of one layer of DODA-clay-DODA-C\textsubscript{60} deposited on a gold substrate. Images recorded at 5 K, tunneling conditions $\sim$1 V @ 0.5-0.2 nA.

Figure 5-9 Sequence of ambient STM images of one layer of DODA-clay-DODA-C\textsubscript{60} deposited on a gold substrate. The images were recorded at 300 K, tunneling conditions 1.1 V @ 150 pA.
diameter of \( \sim 6 \) Å; scanning the same area for a (few minutes) induces dynamical processes as one can see by comparing the succession of images in figure 5-9a-k. In fact, some \( \text{C}_{60} \) remain immobile while others move or even disappear from the scanned area. This testifies to the detachment of some \( \text{C}_{60} \) molecules from DODA induced by molecule-tip interaction. One can also observe that \( \text{C}_{60} \) stop moving when they aggregate in chains (examples marked by blue and black rectangle), probably due to stronger bonding with neighbouring \( \text{C}_{60} \) than with the surfactant. It is interesting to observe that aggregation of \( \text{C}_{60} \) appears to be quite low compared to what one would expect \(^{38,39}\) on unfunctionalized surfaces such as graphite.

5.5 Conclusion

In conclusion, we described the controlled layer-by-layer deposition of hybrid films where \( \text{C}_{60} \) is inserted between aluminosilicate layers and surrounded by surfactant molecules. The deposition was performed using an organic-inorganic hybrid Langmuir-Schaefer approach. Characterization of the nanocomposite films by X-ray diffraction, X-ray photoelectron spectroscopy, and scanning probe microscopy proved the presence of \( \text{C}_{60} \) molecules in the clay stack and showed that the two-dimensional layer of \( \text{C}_{60} \) is uniform. The reported fabrication route opens new perspectives for the design and construction of functional organic/clay hybrid materials.

5.6 References

Appendix 5
Complementary X-ray spectroscopy data

A X-ray photoemission spectrum (survey scan) of the sample containing C$_{60}$ is displayed in figure A5-1; one can see the spectroscopic signature of all the expected elements: Silicon, Aluminium and Oxygen that originate from the clay, Carbon from the surfactant and C$_{60}$ (one can even identify the presence of the C$_{60}$ shake up), and nitrogen from the surfactant. Figure A5-2 shows a close-up on the spectral region with the peaks of Si, Al, and Mg testifying to the presence of clay.

Figure A5-1 X-ray photoemission spectra survey scan recorded on an 80 layer thick DODA-CLAY-DODA-C$_{60}$ film.
Figure A5-2 X-ray photoemission spectrum of the low binding energy region recorded on an 80 layer thick DODA-CLAY-DODA-C$_{60}$ film.

The N1s spectra of nitrogen Figure A5-3 were recorded to prove the grafting of the surfactant to clay, as mentioned in the previous chapter, the N1s core level line shows two contributions at binding energies of 399 eV and 403 eV, which we assign to CN* and CN*+, i.e. unprotonated and protonated cyanide bonds, respectively. This cyanide fingerprint disappears after annealing testifying to the de-intercalation of the surfactant.

Figure A5-3 X-ray photoemission spectra of the N1s core level region of an 80 layer thick DODA-CLAY-DODA-C$_{60}$ film–before (left) and after annealing (right).
Figure A5-4: Fitted temperature dependant measurement of DDA-Clay-DDA (top left), DDA-Clay-DDA-C60 (top right) and the corresponding fitted peak positions vs temperature of DDA-Clay-DDA (bottom left), DDA-Clay-DDA-C60 (bottom right).

For the detailed analysis of the XRD diffractogram illustrated above, the fit were perfomed on the line after background substraction. For the peak fitting a linear combination of Lorentzian and Gaussian lineshape with a 25-75% ratio was used. The data of DDA-Clay-DDA-C\textsubscript{60} have been on purpose fitted with multiple peaks.
at and after the transition temperature to evidence the occurrence of a broad range of d values through and after the transition. The plot of the fitted peaks positions vs temperature for the organoclay and organoclay $C_{60}$ film show the presence of the minor phase as observe and describe in chapter 2. It appear as well clearly in the pure organoclay case that 001 and 002 reflection shift simultaneously (to lower d) above the transition temperature. This same process is less obvious in the DDA-Clay-DDA-$C_{60}$ case.