Molecular Flexibility of Self-Assembled Systems: Effects of Building Block Polarity
Alexandre Dhotel

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Doctoral Dissertation

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Molecular Flexibility of Self-Assembled Systems: Effects of Building Block Polarity

by

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Defended on December 11th, 2013

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Introduction

For a long time, efforts in the field of Materials Science are devoted to the molecular-level analysis and understanding of the relationship between the structure of materials and their overall properties. More recently, an original branch of this research area emerged. This approach aims at gaining control over the inherent structure, composition, morphology and dimensions of materials at the molecular scale in order to precisely tune their properties. Nowadays, this concept is also increasingly employed for the construction of “smart” materials able to change or adapt their structure, and therefore their properties, through the application of an external stimulus or the variation of an environmental parameter. Even though highly challenging, a meticulous control of material structures can sometimes be achieved through traditional lithographic techniques such as photolithography, or more recently, immersion, electron- and ion-beam lithography. Although, these “top-down” techniques have evidenced their ability and efficiency to structure material at the micro- and even nanometer scale over the last four decades, their large financial investment, technical challenges, and potential future limitations have raised the question of their sustainability.

For all of these reasons, the self-assembly of molecules has been considered as one of the most promising alternatives to structure materials at a lower cost than its “top-down” counterparts. Moreover, this “bottom-up” approach offers a true molecular-level control of material structure in three dimensions and is increasingly used to create dynamic or stimuli-responsive advanced materials. However, all of these advancements require a proper understanding of mechanisms conferring structural flexibility, or rigidity, to the final supramolecules.

This study is aimed at gaining insights on the effect of building block composition on these questions. A unique type of rod-shaped building blocks is chosen for its ability to readily form layered materials with long-range molecular ordering. Investigated building blocks are selected according to the number and location of their dipoles, and are defined as follows:

- nonpolar, acene molecules possessing no strong dipolar units
• monofunctional\textsuperscript{1}, alkylsilanes containing one dipole at one extremity

• bifunctional, halogenated alkylsilanes composed of one dipole at each end separated by a nonpolar chain

Self-assembly processes, as well as structural flexibility of final supramolecules, are then carefully investigated. More specifically, the role played by the location and strength of dipoles are examined through five chapters:

• In the first chapter, recent applications of structural flexibility and molecular motions in self-assembled nanostructures are reviewed. Special focus is given to advanced materials exhibiting significant performance changes after an external stimulus is applied. The crucial role played by intermolecular interactions on structural lability and responsiveness is highlighted.

• The second part corresponds to the experimental section where molecular building blocks and characterization methods used throughout this work are described.

• The first experimental stage of this work is described in the third chapter. It is aimed at shedding light on the driving forces governing the assembly of a unique type of nonpolar building blocks. A polyacene-based molecule was selected for its very low polarity. Its structural organization is examined as a function of temperature and time.

• The fourth part of this research is dedicated to the examination of the self-assembly process of mono- and bifunctional building blocks. Organosilane molecules were selected for the construction of highly-ordered nanolayered structures. The effect on molecular organization of an additional polar group located at the chain end of building blocks is investigated.

• The last stage of this work investigates the mobility of molecules composing self-assembled monolayers. Molecular motions triggered by the application of an external electric field are examined for three different types of alkylsilane building blocks under three increasingly constrained nanostructures.

This research work was conducted at the Advanced Mechanics and Materials Engineering International Laboratory (AMME-International) jointly organized between the Laboratoire d’Etude

\textsuperscript{1}The term “functionality” used throughout the dissertation does not refer to its usual definition of a group of reacting elements with specific properties. Functionalities correspond here to dipoles at the extremities of building blocks.
et de Caractérisation des Amorphes et Polymères (LECAP - EA 4528) from the Institute for Materials Research of the University of Rouen and the A-TEAM from the Mechanical & Materials Engineering department of the University of Nebraska-Lincoln. This joint work received the financial supports from the French Department for Higher Education and Research, the EU-US Transatlantic Degree Program in Engineering, and National Science Foundation (1068952).
Chapter 1

Molecular Flexibility of Self-Assembled Nanostructures

Parts of this chapter are extracted from:

*Molecular Motions in Functional Self-Assembled Nanostructures*
A. Dhotel, Z. Chen, L. Delbreilh, B. Youssef, J-M. Saiter and L. Tan
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In this first chapter, recent applications of structural flexibility and molecular motions in self-assembled nanostructures are discussed. Special focus is given to advanced materials exhibiting significant performance changes after an external stimulus is applied, such as light exposure, pH
variation, heat treatment or electromagnetic field. The crucial role played by strong intra- and weak intermolecular interactions on structural lability and responsiveness is highlighted.

### 1.1 Basics of Molecular Self-Assembly

A widely accepted definition for self-assembly is the spontaneous and reversible formation of well-ordered structures from pre-existing discrete components in a disordered state without external guidance\(^1\)–\(^3\) which takes place in order for the system to reach a minimum energy state.\(^4\)–\(^6\) This general definition can be applied to a large number of components whose dimensions can vary from nanoscopic to macroscopic.\(^1\),\(^7\) However, most of research in self-assembly of supramolecules have been confined to the molecular level, thus giving rise to the emergence of an interdisciplinary field at the boundary between Physics and Chemistry, namely molecular self-assembly (MSA). It is worthwhile noting that the criterion “without external guidance” should be treated with caution. Indeed, some sub-branches of MSA use an assisted way of assembling molecules into ordered aggregates. For instance, templated self-assembly, whose self-assembled monolayers (SAMs) are exemplary\(^8\)–\(^11\) and directed self-assembly where components are guided through the application of an external magnetic,\(^12\) electric\(^13\) or flow fields.\(^14\)

MSA is one of the key concepts in supramolecular chemistry. Contrary to molecular chemistry that focuses on the covalent binding of atoms, supramolecular chemistry aims to assemble molecules into larger molecular edifices called supramolecules through noncovalent intermolecular interactions such as van der Waals forces, hydrogen bonding or electrostatic interactions.\(^15\) This feature led supramolecular chemistry to create a whole new branch of chemistry referred to as “chemistry beyond the molecule”.\(^6\),\(^15\) In 1987, the fathers of this discipline, Donald J. Cram, Jean- Marie Lehn and Charles J. Pedersen, obtained the Nobel Prize in Chemistry for “their development and use of molecules with structure-specific interactions of high selectivity”.

This research field was inspired primarily by Nature where many biological nanostructures, such as DNA and Tobacco Mosaic Virus (TMV), form complex structures with remarkable precision through naturally-occurring self-assembly processes. Assembly of such structures is often the result of complex and specific interplay between multiple molecular units or subunits, also called building blocks, making the comprehension of their assembly mechanisms highly challenging. Transferring the knowledge learned from the biological world to synthetic nanostructures is, however, of great interest. Indeed, similar assembly mechanisms can be used to develop sophisticated nanotechnologies or to construct advanced materials able to perform selective operations at the molecular level, thus leading MSA to appeal a broad interest from the scientific community. The large and increasing number of communications on biomimetics and molecular
Molecular self-assembly processes are highly attractive for their ability to construct an almost infinite diversity of structure, shape, dimension, functionality, from a multiplicity of building blocks. Nevertheless, a few fundamental conditions are required for self-assembly to occur:

- The system must be composed of a group of discrete and disordered components that interact with one another in order to form a more ordered final structure. In the case of molecular self-assembly, these components are molecules.
- Assembly conditions or environment must promote the motion and interactions between components. Their mobility in the medium is necessary to bring them closer to each other and form bonds.
- Interactions between building blocks must be reversible to allow molecules to move and adjust their initial position even after aggregation. This specific feature enables the overall system to form a near-perfect crystal structure and reach a minimum free energy state.

The choice of building blocks is one of the crucial points while conceiving self-assembled systems. Efficiency of MSA being strongly dependent on intermolecular interactions, the composition of molecules and their shapes greatly affect the final nanostructure and may even lead to the incapacity of forming ordered aggregates. A careful selection of building blocks not only allow to predict the nature and location of bonds between them, but is also helpful to reach a targeted nanostructure of the final material. Commercially available molecules offer a rich library of possible building blocks, however, development of new functional materials may require a specific molecular design. Molecular chemistry is then often involved in the elaboration of sophisticated elementary units with specific composition, shape and properties. Detailed design of building blocks is particularly suitable to optimize interactions between components and in the development of materials with advanced functionalities.

Because of its processing-ease, low-cost, molecular-level control of structure, morphology, and composition, MSA provides a promising “bottom-up” alternative to traditional “top-down” lithographic techniques for the conception of detailed and sophisticated nanostructures. However, molecular self-assembly processes being exclusively governed by noncovalent intermolecular interactions, all kind of weak physical bonding play a crucial role on the assembly mechanisms as well as on the structural flexibility and responsiveness of the final product. Moreover, in some cases, strong intramolecular bonds can also be highly interesting for the formation of self-assembled materials with flexible or dynamic properties.
1.2 Flexibility of Bonding in Self-Assembled Systems

Understanding the fundamental principles responsible for molecular self-assembly is still highly challenging due to numerous and complex interplays among building blocks. Nevertheless, in order to engineer dynamic or reconfigurable systems, the key role of weak noncovalent bonds involved in self-assembly processes have received continued attentions and is now well-documented.\textsuperscript{17–20} Indeed, such interactions not only rule the assembly process though a balance of attractive and repulsive interactions leading to the formation of the ordered architecture but also control the dynamic behavior and properties of the final supramolecule. In some specific cases, chemical intramolecular bonds can also confer flexibility to self-assembled structures, thus extending the range of potential ways to conceive dynamic materials. In this section, physical and chemical bonds commonly encountered in self-assembled systems are briefly described. A special focus is given to the lability, conformational flexibility and sometimes reversibility of supramolecular architectures.

1.2.1 Weak Interactions

Weak interactions, such as van der Waals forces, hydrogen bonds and π interactions are among the most prevalent low-energy forces encountered in self-assembled systems. Their weakness and reversibility play a crucial role in the self-assembly process of single or multiple types of building blocks. Generation of ordered structures through these interactions requires the building blocks to move and adjust their initial position even after aggregation. This adjustability is necessary for the final system to reach its lowest-energy state and achieve a nearly perfect organized structure. Essentially, weak bonds holding components in self-assembled structures are the reasons for their structural flexibility.\textsuperscript{7}

Among the weak interactions, van der Waals (vdW) forces are the weakest and most ubiquitous interactions at the nanoscale. These forces can be classified into several types depending on the nature of components but are generally caused by the competition between repulsive and attractive interactions between two components with random fluctuations of electric charges. Such fluctuations induce the polarization of the electron shells thus making individual component temporarily polar and causing an opposite polarization in its neighboring body. Oppositely polarized components are then attracted toward each other until, according to the Pauli exclusion principle, they are strongly repulsed due to overlapping of orbitals. Typical energies of such electrostatic interactions vary between \(< 1\) and \(4 \text{kJ.mol}^{-1}\) making their dissociation plausible and easy. Despite their trivial strength, such ever-present forces have a significant influence on the ordering and cohesion of alkyl chains within self-assembled monolayers\textsuperscript{21,22} and multilayered films.\textsuperscript{23–26}
Stronger than van der Waals forces, hydrogen bonding is a special type of dipole-dipole interaction. Even though globally neutral, molecules can have electric dipoles bearing a distribution of partial positive and negative charges. Interactions between these dipoles guide molecules to orient so that attractive interactions are maximized and repulsive interactions minimized. Hydrogen bonds are formed when a hydrogen atom covalently bonded to an electronegative atom (hydrogen donor or electron acceptor) interacts with the lone pair of electrons from another electronegative atom (hydrogen acceptor or electron donor), which comes either from an adjacent molecule or within the former molecule itself. The strength of the hydrogen bond being dependent on both the donor-acceptor distance and their electronegativities, a typical bond energy varies between 4 and 30 $kJ.mol^{-1}$. Even though mildly strong, hydrogen bonds are directional and can greatly affect the physicochemical properties as well as the ordering of building blocks within self-assembled systems and solid crystals. The reversibility and weakness of these bonds is also widely employed for the design and synthesis of self-healing materials and the fabrication of pH-erasable thin films for drug delivery and biosensors. In biological systems, hydrogen bonding also plays a central role in the folding and stabilization of proteins as well as in the specific interactions between DNA strands.

Another weak interaction frequently found in the literature is hydrophobic interaction, also called hydrophobic bonding. Even though this type of interaction causes the apparent repulsion between water and hydrocarbon molecules, it cannot be directly related to the formation of physical bonds. The hydrophobic effect, which is one of the major driving forces for the formation of lipid bilayers and micelles, results from the contributions of both van der Waals forces between hydrocarbon compounds and hydrogen bonding between water molecules. Therefore, the term “hydrophobic effect” should be preferred to “hydrophobic bonding”.

A strong correlation can easily be made between hydrogen and halogen bonding as they both result from the interaction between electron donor and electron acceptor. In a halogen bond, an electrophilic region on a halogen atom (electron acceptor) interacts with a nucleophilic region of a molecule, or molecular fragment (electron donor). While rarely exploited in the past to direct the formation of supramolecular assemblies, halogen bonding is becoming increasingly important in supramolecular chemistry because of its directionality and tunable strength.

Another type of weak interactions commonly observed in self-assembled systems is $\pi$ interaction. This general term refers to the non-covalent interaction involving a $\pi$-electron-rich unit with a cation, an anion, or another $\pi$-system. The latter, namely $\pi-\pi$ interaction or $\pi$ stacking, is defined as an attractive interaction between two stacked aromatic rings. Such interactions are caused by basic electrostatic interactions as described by the widely accepted model established by Hunter and Sanders in 1990. Electrons in $\pi$ bonds of aromatic rings form a quadrupole
moment (i.e., two dipoles aligned so that no net dipole can be distinguished) due to the stronger electronegativity of \( Sp2 \) carbons compared to hydrogen atoms.\(^{47} \) In the case of benzene, this quadrupole creates a partial negative charge on both faces of the \( \pi \) system and a partial positive charge around the aromatic ring (Figure 1.1a). According to this description, a face-centered stacking of \( \pi \) systems on top of each other would be energetically unfavorable and therefore not stable. However, aromatic rings can interact with each other through the edge-to-face (also known as T-shaped or edge-on) geometry or the parallel displaced (also referred to as parallel off-centered) stacking (Figure 1.1b and c) where regions of negative electrostatic potential (faces) can interact with regions of positive electrostatic charges (periphery).\(^{46–50} \) The face-centered stacking geometry suggested by the terms “\( \pi \)-stacking” and “\( \pi-\pi \) interactions” being misleading, the use of these terms is now questioned.\(^{49–51} \) Depending on the chemical nature of units, interactions between \( \pi \)-systems have typical energies between 5 and 40 \( kJ.mol^{-1} \). In self-assembled systems, interactions between \( \pi \)-units are often used in organic electronics\(^{52} \) and to promote and stabilize molecular packing.\(^{23,53,54} \) Their reversibility and flexibility are also commonly employed in host-guest assemblies\(^{48,55} \) and recently, for the specific attachment of carbon nanotubes on surface.\(^{56} \) In biological systems, interactions between aromatic rings are largely involved in protein–ligand complexation\(^{57} \) and stabilization of the double helical structure of DNA.\(^{38,58} \)

Figure 1.1: (a) Electrostatic potential surface of a benzene molecule (Spartan, B3LYP/6-31G\(^*\)) (b) and (c) schematic representations of interaction geometries of a benzene dimer. Reprinted from reference\(^{59} \).

1.2.2 Strong Bonding

Strong bonds, also known as intramolecular forces or chemical bonding, are several orders of magnitude stronger than weak interactions described above. Despite their strength, strong bonding such as ionic, covalent and coordination bonds can play a central role in the formation of
self-assembled materials and also contribute tremendously to the dynamic properties of the final supramolecule.

Ionic bonding, also referred to as electrostatic interactions between two oppositely charged ions, leads to the complete transfer of one or more valence electrons from the negatively charged anion to the positively charged cation in order for them to reach a stable electronic configuration. The strength of interaction between ions is directly related to their charges and can be determined by measuring the lattice energy of the compound. Typical binding energies vary between several hundreds to thousands kilojoules per mole ensuring the cohesion within the ionic structure. Even though remarkably strong in solid state, interactions between ions are not directional and can be readily interrupted or broken in a wet environment, for instance, water dissolution of ionic solids. This versatility makes ionic bonding of great interest for the conception of mechanically robust but chemically reversible supramolecules. These ionic bonds are now widely involved in self-assembly processes leading to the creation of a specific branch in supramolecular chemistry called ionic self-assembly (ISA). Examples of structures made through ISA include ionic self-complementary peptides as well as the assembly of surfactants and lipids in polyelectrolytes.

In contrast to ionic bonds, covalent bonding form between two atoms of similar electronegativities. Such atomic bonds have typical binding energies ranging between 150 and 1100 $\text{kJ.mol}^{-1}$ and arise from the equal sharing of one or more electron pairs between atoms in order to achieve an optimum configuration. Generally, this sharing of electrons is not exactly equal, one or more electrons can belong predominantly to one of the atoms involved in the bond, thus forming a polar covalent bond. Therefore, it might be difficult to distinguish ionic and covalent bonding as ionic bonds may contain covalent characteristics and reciprocally. Due to their strength and directionality, covalent bonds are not classified as one driving force for the formation of self-assembled systems. However, some aspects of these bonds can confer structural flexibility and reversibility. Recent applications of dynamic covalent chemistry (DCC) highlighted the possibility to easily and reversibly fabricate nanostructured complexes through self-assembly strategies. Accurate control of thermodynamic conditions was found to trigger and control the formation of chemical gradients within self-assembled monolayers and reversible formation of micelles. Isomerization is another example of structural flexibility offered by covalent bonds. Photochromic groups, essentially azobenzene derivatives, have been extensively incorporated into building blocks of supramolecular systems thus allowing the formation of photosensitive materials with switchable architectures and properties.

A special type of covalent bonding is coordination bond. Contrary to conventional covalent bonds where pairs of electrons are equally shared between atoms involved in the bond, in
coordination bond all electron pairs are provided by only one of the atoms. Such bonds result from the reaction of a central metal atom or ion reacting with a molecule, atom or ion called ligand. Ligands, also called complexing agents, are Lewis bases able to donate at least one electron pair to a Lewis acid (i.e., central metal atom or ion) through a donor atom. In a coordination complex, the central atom can be bound to one or more ligands thus creating the coordination sphere. Due to the predictable nature and geometries of the metal-ligand coordination sphere, coordination chemistry has been regarded as a powerful tool for the conception of supramolecular complexes. In addition to this predictability, typical energies of coordination bonds (60 - 300 kJ mol$^{-1}$) are weaker than usual covalent bond but stronger than hydrogen or aromatic interactions, which make them ideal candidates for the synthesis of flexible and adaptable supramolecular architectures. Recent examples of adaptive and functional structures made through coordination-driven self-assembly include flexible macrocyclic structures, molecular flasks, sequential self-assembly in metal-organic frameworks (MOFs) and various types of molecular polygons and polyhedra.

Flexibility and adaptability of supramolecular architectures is a predominant need for applications that require conformational changes. As depicted in this section, all physical and chemical bonds involved in the construction of supramolecular edifices have a certain degree of flexibility regardless of their bonding strength. Following sections are focused on how one can take advantages of the intrinsic flexibility of weak and strong bonds to design functional nanostructured materials. Nevertheless, it is worthwhile to note that interactions between building blocks are not the only factors to consider while studying self-assembly of molecules. MSA mechanisms are thermodynamically driven; therefore, other factors such as enthalpy and entropy also affect the formation of the final supramolecules and control their physical properties.

1.3 Flexibility of Functional Self-Assembled Nanostructures

One of the predominant aspects in molecular self-assembly is the flexibility of final nanostructures. Indeed, forces holding molecular units can endue a high dynamic capability to the whole supramolecule, thus the structure is able to readily change its conformation with little energy input. This feature is then often employed to design sophisticated self-assembled structures able to perform specific tasks at the molecular level. In this section, recent applications of structural lability in self-assembled systems are presented. This non-exhaustive list highlights the major benefits offered by this molecular flexibility in pure organic and organic-inorganic hybrid systems.
1.3.1 Organic Nanostructures

A pertinent illustration of the flexibility of organic nanostructures is the controlled folding of planar graphene. This specific assembly governed by van der Waals interactions between carbon atoms of graphene and surrounding water molecules can lead to the fabrication of complex structures such as scrolls, sandwiches, rings and nanosacks.\(^8\) Many other examples of flexible structures can be found in living organisms, such as the double helices of DNA, the secondary structures of protein, and the lipid bilayers in cell membranes. Highly dynamic changes of these systems include the association and dissociation of helices via hydrogen-bonding, folding and unfolding of proteins via amino acid pairing, as well as mass or energy input/output through cell membranes via van der Waals interactions. Inspired by the Nature, people have been able to design and build dynamic nanostructures using synthesized organic molecules. Among them, artificial DNA nanostructures\(^8\) and block copolymer thin films\(^\) are relevant representatives which have gained popularity and fame from early on.

Functional DNA Nanostructures

DNA nanotechnology involves the design and manufacture of artificial structures from nucleic acid. Thanks to the folding of oligonucleotide “staple” strands,\(^9\) nucleic acids can be assembled into arbitrary 3D structure.\(^9\) This programmable assembly is enabled by molecular recognition between complementary strands of DNA, which governs the specific binding of strands with complementary base sequences.

The flexibility of hydrogen bonds within DNA enabled the construction of artificial DNA nanostructures with the ability to reconfigure upon stimulus, making them one type of nanorobots.\(^8\) These artificial structures are constructed as the static structures made from the conventional DNA nanotechnology, but are specifically designed to allow a certain degree of reconfiguration after the initial assembly.\(^9\) Such a reconfiguration is usually triggered by interactions with specific molecules or by modification of their environment.\(^1\) With this responsive behavior, dynamic DNA nanostructures have found applications in a variety of domains such as molecular sensing, intelligent drug delivery and programmable chemical synthesis.\(^1\) Earliest examples of dynamic DNA structures include the use of the twisting motion between the B- and Z-DNA forms to respond when solvent conditions are modified (Figure 1.2).\(^1\) This environment-induced transition is able to change the state of all DNA devices in solution. However, when specific fuel strands are available, multiple devices could perform their motions independently.\(^1\)

DNA is also used to create opening/closing systems which are designed to accurately control
1.3 Flexibility of Functional Self-Assembled Nanostructures

Figure 1.2: Top, molecular model of the molecule constructed entirely from right-handed B-DNA. Each nucleotide is shown as two spheres, a colored one for the backbone and a white one for the base. Three cyclic strands are shown, one in the center drawn as a red strand with a central yellow segment, and two blue strands on the ends that are each triply catenated to the red strand. Fluorescent dyes are drawn schematically as stippled green (fluorescein) and magenta (Cy3) circles attached to the free hairpins near the middle of the molecule. At the center of the connecting helix is a 20-nucleotide region of proto-Z DNA in the B-DNA conformation, shown in yellow. When the B–Z transition takes place, this same yellow portion becomes left-handed Z-DNA (bottom). When the transition occurs, the two DNA double crossover molecules change their relative positions, increasing the separation of the dyes. The switching event induces atomic displacements of 2~6 nm. Reprinted with permission from reference 101. Copyright 1999, Nature Publishing Group.

the release of a functional cargo under specific conditions. For example, Douglas et al. used DNA origami to develop hollow nanocontainers. The barrel structure consists of two domains covalently fastened in the rear, and non-covalently attached in the front by staples modified with DNA aptamer–based locks. When the aptamer detects the binding key, the nanocontainer is opened and the drug inside the barrel is revealed.

Hydrogen bonding is not the only interaction able to confer flexibility to DNA. For instance, stronger covalent bonds between nucleic acids of a same strand can be successively cleaved and rebounded. This feature was used and developed to create DNA walker. DNA walkers are a class of nanomachines that exhibit directional motion along a linear track or on a 2D surface. A large amount of strategies have been investigated already. One of them is to direct the motion along the track using control strands that are manually added in sequence. Another way is to utilize enzymes to cleave the strands and cause the walker to autonomously move forward. A later example has been revealed able to walk on a two-dimensional surface rather than a linear track. It also demonstrated the ability to selectively pick up and move molecular cargo at each step (Figure 1.3), making this technique useful in programmable chemical synthesis. Additionally, the walk speed of a DNA walker can be accelerated by using
Figure 1.3: Overview of the DNAsome system. (a) The system comprises six DNA or DNA-linked molecules. Three substrates (S1–S3) and an initiator (S0) can hybridize on a single-stranded DNA track (T). Each substrate has an amino acid NHS ester at its 5’ end and two ribonucleotides (green dot) in the middle of its DNA sequence. The DNA walker (W) contains a 3’ amine group and an RNA-cleaving DNAzyme (purple line) that can cleave the ribonucleotides in the substrates; (b) DNAsome-mediated multistep synthesis of a triamide product. All steps take place in a single solution under one set of reaction conditions without external intervention. The DNA walker has the ability to pick up and move molecular cargo at each step. Reprinted with permission from reference\textsuperscript{114}. Copyright 2010, Nature Publishing Group.

All of the above stimuli-responsive behaviors involve multiple DNA strands. Nevertheless, modification of solvent pH was also found to trigger the conformational change of a single DNA strand.\textsuperscript{119–121} For example, a four-stranded short structure can unfold into a double-stranded DNA catalysts.\textsuperscript{118}
structure where the length or thickness doubles during the transition. Possibly, such variations of volume and surface roughness could enable future applications in constructing super-hydrophilic/superhydrophobic surfaces or molecular motors for MEMS.

### Stimuli-Responsive Polymer Systems

Molecular recognition between polymer chains is essential for their assembly into well-ordered structures. Polymers are composed of repeating units, called monomers, and can be either totally amorphous or semi-crystalline. In the last couple of decades, the assembly of binary or ternary units to form block copolymers has received a close attention particularly in terms of formation process and final structure.\(^{122-125}\) Such advances allowed block copolymers to be considered as attractive candidates for the fabrication of responsive thin membranes with nearly monodisperse nanopores.\(^{126,127}\) For instance, properties of triblock copolymers (ABA or ABC) can be modulated by mixing functional terminal blocks with stimuli-sensitive middle blocks thus leading to the formation of phase-segregated structures where functional domains are embedded within a stimuli-sensitive matrix.\(^{128-130}\) As an example, Nykanen et al. reported the formation of temperature-responsive membranes made from polystyrene-block-poly(N-isopropylacrylamide)-block-polystyrene (i.e., PS-b-PNIPAM-b-PS).\(^{130}\) This triblock copolymer containing hydrophobic polystyrene (PS) end blocks and a temperature-responsive PNIPAM midblock can undergo a coil-globule transition as a function of temperature (Figure 1.4). Permeability measurements revealed that, when thin films of this copolymer are deposited on top of meso/macroporous polyacrylonitrile (PAN) surfaces, the membrane has a switchable on/off permeability. This switching can be controlled by simple variations of the temperature and permeability was found to increase below the coil-globule transition temperature.

When the molecular recognition process between polymer chains is driven by weak hydrogen bonds, several stimuli, such as pH, temperature and even light, can be used to initiate a structural reconfiguration.\(^{131-134}\) For example, Lee et al. fabricated pH-controlled valves using commercially available track-etched polycarbonate membranes.\(^{135}\) After modification of the membrane pores with PAH/PSS multilayers, pores show the ability to swell and collapse as a function of pH, which makes this system of great interest for pH-triggered separation of small ionic species or to gate the flow of water in microfluidic channels. The similarity in the repeated structures of block copolymers and DNAs has also led to the eventuality of using block copolymers in programmable synthesis where structural flexibility and tunability are essential.

Overall, the versatility, high flexibility and sometimes bio-compatibility of these artificial organic nanostructures make them promising candidates for applications in a wide variety of domains including chemistry, functional biomaterials, sensors and nanodevices.
**1.3.2 Organic-Inorganic Nanolayers**

Another important branch in supramolecular chemistry is the fabrication of organic-inorganic hybrid nanolayered structures through self-assembly strategies. Such molecularly engineered nanomaterials are predominantly used to functionalize surfaces and are particularly appreciated for their versatility. The continuous development of available building blocks and optimization of deposition techniques have significantly advanced their designs for specific applications. Moreover, strong interactions between precursors may confer high chemical, thermal and mechanical robustness. Finally, their processing-ease makes them readily accessible at low cost and without substantial effort. Direct applications of self-assembled organic-inorganic mono- and multilayers extend over a vast range of domains; therefore, this section is intentionally restricted to recent applications employing the structural flexibility of organic-inorganic hybrid nanolayers.

**Functional Coatings**

Organic-inorganic nanolayers are widely used as functional coatings to tailor surface properties without altering the integrity of the underlying substrate. Common examples include protective coatings, electronic thin film devices, sensors, robust textiles and biofunctional membranes,
where self-assembly and layer-by-layer process are the two main strategies for their depositions. For instance, Song et al. produced superhydrophobic surfaces by depositing octadecyltrichlorosilane (OTS) self-assembled monolayers (SAMs) on micro/nano-textured silicon substrates.\textsuperscript{136} The micro/nano-texture of substrates creates superhydrophobic surfaces with water contact angles (WCAs) of 155° after OTS deposition, as compared to 112° for smooth OTS SAMs. More recently, Li et al. reported a convenient and effective method to prepare superhydrophobic surfaces by deposition of fluoroalkylsilane SAMs on CuO surfaces.\textsuperscript{137} As shown in Figure 1.5, tunable water adhesion properties could be achieved by simply controlling topographies of the underlying CuO surfaces through the regulation of the perfluorodecyltiethoxysilane SAM deposition. Highly fluorinated compounds are also used to functionalize polyelectrolyte multilayer films constructed using a layer-by-layer (LbL) deposition technique. For instance, Amigoni et al. prepared LbL films by stacking amino- and epoxy-functionalized silica nanoparticles in which the top layer was made hydrophobic by grafting a highly fluorinated monomolecular layer.\textsuperscript{138} The hydrophobicity of this hierarchical edifice was found to increase with the number of layers, finally forming stable and highly superhydrophobic surfaces.

Due to the very large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), alkylsilane SAMs can be also used in molecular electronic devices as insulating gates. Ever since the pioneering studies in the early 90’s,\textsuperscript{139,140} organic-inorganic mono- and multilayer films gained significant attention for their tunable thicknesses, processing ease and insulating properties leading to their integration in organic transistors.\textsuperscript{141–144} Especially, recently developed self-assembled nanodielectrics (SANDs) were found to exhibit promising properties for a variety of opto-electronic applications, including thin-film transistors (TFTs) (Figure 1.6).\textsuperscript{143–146} This new class of gate dielectrics consisting in the stacking of ordered active molecular assemblies onto solid surfaces allows optimizing device performance by their robust insulating properties. Cohesion and ordering are of paramount importance when self-assembled structures are used in molecular electronic devices. Indeed, poor ordering in molecular packing can often lead to reduced performances.\textsuperscript{147–149} Therefore, strategies are developed to gain a better control of structural organization. Among them, molecular intercalation has been revealed as a simple and efficient pathway, where ordered nanostructure assembled from a binary system can be easily reconfigured by taking advantage of the reversible bonds during self-assembly.\textsuperscript{150}

In this approach, addition of foreign molecules to a solution of already formed supramolecular aggregates is used to trigger a major structural reconfiguration. Essentially, the reversibility of weak physical bonds holding tightly packed molecular aggregates allows foreign molecules to be intercalated within the former supramolecules, thus triggering a reorganization of the whole
structure. Depending on the chemical nature of the building blocks, significant cross-linking stabilizing the final nanostructure may be introduced after this intercalation process. So far, direct applications of the molecular intercalation method have demonstrated remarkably enhanced thermal\textsuperscript{150} and mechanical properties\textsuperscript{151} of films after foreign molecules have been accommodated.
1.3 Flexibility of Functional Self-Assembled Nanostructures

Stimuli-Responsive Nanolayers

Switching properties and dynamic functions are highly attractive for construction of sophisticated devices, sensors and “smart” materials. Predictable molecular packing, low energy bonding and ease of processing make self-assembled structures ideal candidates as dynamic and stimuli-responsive materials. These “smart” materials can be activated through several types of external stimulus, such as light exposure, temperature, pH variations, mechanical forces and electromagnetic fields.

Among them, molecular rotors exhibit promising dynamic features that are designed to perform nanomachine-like tasks at the molecular level. Potential applications of these molecular rotors to power artificial nanomachines have already been demonstrated and are incessantly developed. They are commonly defined as molecules composed of two parts that can rotate relative to each other. Specifically, they contain a stationary part (the stator) with a large
molecular flexibility of self-assembled nanostructures

moment of inertia and a part able to rotate (the rotator) with a smaller moment of inertia. Such molecules can form amphidynamic molecular crystals consisting in a rigid lattice composed of axles and bulky static groups as well as mobile parts performing the rotary motion (Figure 1.7).

Recently, Vogelsberg et al. investigated the effects of reduced dimensionality on rotational dynamics of p-phenylene moieties confined in organic-inorganic hybrid nanolayers. Examination by variable-temperature NMR revealed a sharp motional change of the rotators with temperature. They postulated that the system undergoes a temperature-triggered transition from a relatively rigid to a fluid-like medium, thus providing an additional insight on the responsiveness and tunability of such materials. Carroll et al. also investigated the effect of confinement on rotational dynamics but within a different organic-inorganic system. After depositing an azide-terminated self-assembled monolayer, they covalently attached photo-sensitive molecular rotors to the SAM surface leading to the creation of nanoscale machinery on surface (Figure 1.8). They showed that their molecular rotors are able to undergo photochemical and thermal isomerization even after surface confinement. However, these surface-bound motors have a significantly reduced rate of thermal isomerization due to intermolecular interactions.

The aforementioned isomerization process has been extensively used for the design and construction of different types of stimuli-sensitive supramolecular systems to produce switchable properties. Certainly, azobenzene compounds are the most frequently investigated class of molecules able to undergo photo-isomerization. When irradiated with light tuned to an appropriate wavelength (generally in the UVA region) azobenzene compounds undergo trans-to-cis isomerization. Azobenzene isomerization being reversible the thermodynamically less stable cis isomer can relax back to the trans form either by illumination with visible light or thermally in the dark. As these two isomers can be switched reversibly by light irradiations, azobenzene motifs are ideal candidates for the construction of photo-sensitive molecular switches and functional materials. While the exact isomerization mechanisms of azobenzene compounds are still under discussion, they already found sophisticated applications in a wide variety of domains including biological systems, polymers, electronics, fluidization lithography, textiles, and delivery applications. In supramolecular chemistry, the photoswitchable conformation of azobenzene motifs has been extended to control successive self-assembly and disassembly of building blocks, and to reversibly tune functional properties of resulting supramolecules. SAMs of organometallic and organometalloid compounds are the most frequent examples of self-assembled nanolayers containing azobenzene chromophores. Such SAMs are essentially designed for conceiving switches in molecular electronic devices and surfaces with controllable properties. However, regardless of the applications, one prevalent obstacle has to be overcome. Due to the tight packing of molecules within SAMs, the photoswitching
1.3 Flexibility of Functional Self-Assembled Nanostructures

Figure 1.8: Controlled chemical attachment of light-driven altitudinal molecular motors to a solid substrate provides a monolayer of nanoscale motors. The four stages of the 360° rotary cycle can be addressed with light and heat. Reprinted with permission from reference 157. Copyright 2011, American Chemical Society.

of azobenzene units can be hindered which greatly limits device performances. Several strategies have been pursued to solve this problem. They all aim to laterally space photo-sensitive units from each other to enable a complete and reversible isomerization. Examples of these strategies include co-adsorption of photo-sensitive and inert building blocks,173,174 the use of bulky tripods as anchoring headgroups,175,176 adsorption on porous network,177,178 and addition of lateral group within building blocks to increase the occupied area per molecule.179,180

Among the self-assembly strategies, the layer-by-layer (LbL) deposition method is frequently employed to prepare stimuli-responsive organic-inorganic films. This surface-mediated self-assembly process involves stepwise adsorption of materials of complementary charges. This versatile technique provides a convenient way to control film composition and morphology at the nanoscale and allows the incorporation of an extended variety of functional and responsive components.181–183 Through the selection of specific building blocks, the LbL method has demonstrated its ability to fabricate responsive coatings. Temperature variations, changes in pH, mechanical stimulations, exposure to light and electromagnetic fields are the most widely ex-
Molecular Flexibility of Self-Assembled Nanostructures

explored stimuli in LbL films. Versatility, processing-ease and tunability greatly contributed to the rapid development of an extensive class of stimuli-responsive LbL coatings whose organic-inorganic hybrid architectures are a modest part.

Figure 1.9: Wavelength-selective shape changes in stratified assemblies of polymer-grafted gold nanoparticles and nanoshells. (a–c) Confocal laser scanning microscopy images of light-controlled shape changes in two-strata bNP500-bNS500 cubes upon irradiation using wavelengths at 546 nm (1.1 W/cm²) and 785 nm (2 W/cm²); (d–f) Similar experiments with three-strata bNS300-bNP400-bNS300 cubes. Illumination time was 20 min. Reprinted with permission from reference184. Copyright 2012, American Chemical Society.

To name a few, Schmidt et al. prepared electrostatic-based LbL films incorporating inorganic negatively charged Prussian Blue (PB) nanoparticles and organic positively charged gentamicin sulphate (GS), an antibiotic molecule.185 Electrostatic interactions between these two oppositely charged components ensure the stability and robustness of the layered structure. However, when a sufficient external electrical stimulus is applied, the PB nanoparticles oxidize thus changing their net charge from negative to neutral. Consequently, electrostatic interactions between the PB particles and gentamicin are broken leading the film to dissolve and the gentamicin drug to be released into the solution. Thus, biocompatible organic-inorganic LbL films can be regarded as good candidates for the fabrication of nanocarriers for drug and gene delivery.186 Wang et al. used a chelation-based strategy to tune the release of DNA from a LbL multilayer film.187 This method relies on another type of interactions, coordination bonding, between the two components (i.e., DNA and zirconium ion, Zr⁴⁺). Despite the strength of these bonds, they demonstrated the facile and efficient disassembly of films through their immersion in a solution of sodium citrate. Chelators contained in the solution act as substituents. Their high affinity to Zr⁴⁺ causes the cleavage of coordination bonds between zirconium ions and phosphate groups in the backbone of the DNA chain and the formation of coordination compounds composed of chelators and Zr⁴⁺. DNA molecules are then released from the LbL film as they no longer interact with
zirconium ions. Other examples of stimuli-responsive organic-inorganic LbL multilayer films include temperature, salt and pH-sensitive clay-containing polymer films,\textsuperscript{188} photo-responsive microcapsules for drug release prepared by a combination of LbL assembly and sol-gel methods\textsuperscript{189} and light-controlled swelling of layered polymer/gold nanoparticles composites (Figure 1.9).\textsuperscript{184}

Even though specific, nanolayered organic-inorganic hybrid materials offer a quasi-infinite number of possible combinations between flexible organic compounds and robust inorganic units.Essentially, the main advantage of these hybrid structures relies on the extended range of inter- and intramolecular interactions between components as compared to pristine organic or inorganic materials. Consequently, mixing these two classes of compounds gives access to a large number of possibilities to induce structural flexibility within self-assembled structures, thus enlarging their potential applications.

\section*{1.4 Local Mobility of Self-Assembled Structures}

Most of the research works described in preceding sections employ molecular flexibility to induce advanced, and sometimes reversible, properties to self-assembled materials. These sophisticated functionalities are often triggered by external events, such as light treatments, pH modifications and temperature changes, inducing the motions of large molecular segments or even entire groups of macromolecules. Even though highly effective, the configurational modification of large molecular units is not the unique approach to confer advanced properties to self-assembled structures. Indeed, among others, local conformational fluctuations of the nanostructure can also be suitable for this purpose.

\subsection*{1.4.1 Perspectives}

As depicted previously, the flexibility of building blocks can be employed to construct “smart” materials whose structural units move under definite conditions. However, these materials may require a sophisticated design through the use of active molecules, such as molecular rotors or actuators, and efforts to produce nanostructures allowing large molecular motions. On the contrary, local motions of short molecular segments, such as bond rotations or short-range vibrations, offer the great advantage to occur in a remarkably large range of soft materials, including inherently passive structures. Although its low amplitude may discourage current applications, this submolecular-level mobility could be of interest to conceive nanostructured materials able to perform defined tasks in a very local range. For instance, one representative example of this type of mobility was examined in self-assembled monolayers. Even though apparently passive,
previous works brought precise descriptions of local and cooperative motions of alkyl chains in alkanethiol\textsuperscript{190–193} and alkylsilane\textsuperscript{194,195} SAMs (Figure 1.10).

Such short-range molecular motions can be triggered by either thermal energy or interactions of building block parts, such as dipoles, with external electromagnetic fields. Therefore, accurately controlling the mechanisms governing these motions could be considered as a promising strategy to open up a new range of nanotechnologies with great implications in the conception of molecular motors or sensors.

\subsection*{1.4.2 Characterization Methods}

Investigation of short- and long-range molecular motions in soft materials is a widely investigated research field with increasing interests. However, the nanoscale dimensions of objects found in self-assembled systems seem to slow down the applications of traditional characterization techniques to such materials. Indeed, nanoscopic or even subnanoscopic structures often produce very weak response thus requiring specific apparatus or experimental techniques with extreme resolution.\textsuperscript{194}

Nonetheless, some vibrational spectroscopic methods were revealed as relevant techniques to characterize conformational order in nanosized supramolecular structures. Notably, three sensitive techniques are often employed to track molecular motions in such systems: infrared spectroscopy, dielectric spectroscopy and nuclear magnetic resonance. By using interactions be-
Local Mobility of Self-Assembled Structures

Between electromagnetic radiations and matter, they were revealed as being particularly suitable for the identification of spatial fluctuations of molecular segments, bonds, or even atoms.\textsuperscript{193,196–199} Other effective experimental methods exist for such characterizations. Among them, inelastic neutron scattering is now considered as an emerging but also promising method.\textsuperscript{192,200,201} Recently, Gradzielski reviewed the uses of both elastic and inelastic neutron scattering to examine molecular dynamics in self-assembled systems.\textsuperscript{202} More specifically, the neutron spin echo technique finds increasing applications into this research field.\textsuperscript{203,204} Overall, it is noteworthy that results obtained from such experimental methods not only give information about dynamics and flexibility of molecular systems but also help understanding the intrinsic nanostructure of investigated materials.

The use of molecular motions offers a promising strategy for the elaboration of self-assembled structures with unprecedented dynamic properties. The outstanding flexibility of weak physical and strong chemical bonds is increasingly employed to develop novel “smart” materials able to perform specific tasks at the molecular level through the application of one or several stimuli. Remarkably, this strategy can be applied to an extensive variety of material structures, compositions and dimensions. Moreover, numerous properties such as wettability, magnetism, shape, crystalline structure, mechanical robustness and thermal stability, can be easily tuned without substantial effort. This versatility is thus opening up a wide range of potential applications in multidisciplinary domains including medicine, electronics, sensors, textiles, protective coatings and nanomachinery. Advances in chemistry are however needed to continue the development of such functional materials. By designing new attractive and responsive building blocks that can be self-assembled, molecular chemistry can continuously broaden the number of available functionalities and their efficiency. However, some intrinsic limitations are still to be overcome in order to gain accurate control of structural modifications and increase material performances. It is hoped that gaining comprehension of the highly complex interplays existing between building blocks will encourage the development of novel advanced self-assembled materials with the ultimate goal of constructing systems able to accurately mimic dynamic functions of macroscopic machines or even humans.
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Chapter 2

Experimental Section

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In this section, the molecular building blocks and characterization methods used throughout this work are described. For clarity, preparation processes of samples are intentionally not presented here but can be found in the corresponding following chapters.

2.1 Materials

In this work, five molecular building blocks were studied. All of them have rod-shaped morphologies and intermediate alkyl chain. They are listed below by increasing number of polar extremities or functionalities. Conventionally, the alkylsilane functionality is named headgroup although the second extremity of molecules is called endgroup. It is noteworthy that the headgroup is always polar, even though very weakly, while the endgroup can be totally nonpolar.
2.1.1 Nonpolar Building Blocks

2.1.1.1 2-dodecylanthracene (Ant-12)

2-dodecylanthracene, named Ant-12 thereafter, was obtained as a side product during the synthesis of \((12-(\text{anthracen}-2-\text{yl})\text{dodecyl})\text{diethoxy(methyl) silane}\). The general synthesis procedure is depicted in Figure 2.1. Further details of the synthesis route proposed by Jinyue Jiang can be found in reference\(^1\).

![Figure 2.1: General Ant-12 synthesis procedure.](image)

As depicted in Figure 2.1, Ant-12 is composed of a rigid anthracene headgroup \((-C_{14}H_9)\) to which is attached a flexible alkyl tail \((-C_{12}H_{25})\). Both of these hydrocarbon groups have no net dipoles when isolated. Nevertheless, Ant-12 exhibits a very weak dipole moment caused by the difference in electron density between the \(\pi\)-electron-rich anthracene group and linear alkyl chain. This dipole moment being very weak (see Table. 2.1), the molecule was assumed to be nonpolar in contrast to conventional highly polar building blocks used in self-assembly strategies.

Contrary to conventional MSA approaches which are exclusively based on the use of highly polar molecules and relatively strong intermolecular interactions, the organization process of Ant-12 was examined to aid the understanding of mechanisms governing the assembly of non-polar molecules under thermal treatments (\textit{cf.} Chapter 3).
2.1 Materials

Table 2.1: Characteristic properties of Ant-12

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Molar Mass (g.mol⁻¹)</th>
<th>Length* (nm)</th>
<th>Dipole Moment* (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂₆H₃₄</td>
<td>346.55</td>
<td>2.26</td>
<td>0.59</td>
</tr>
</tbody>
</table>

* determined by the Spartan software (Wavefunction, Inc.), 6-31G*/PM3 Geometry

2.1.2 Monofunctional Building Blocks

2.1.2.1 Octadecyltrichlorosilane (OTS)

Octadecyltrichlorosilane, named OTS thereafter, is a commercially available molecule and was purchased from Acros Organics (OTS, ≥ 95 %). It contains a polar trichlorosilane headgroup (−SiCl₃) to which is attached a nonpolar long alkyl chain (−C₁₈H₃₇) thus creating an amphiphilic morphology (Figure 2.2).

![Figure 2.2: Chemical formula of an OTS molecule.](image)

Due to its long alkyl chain, reactive and polar headgroup, OTS is highly relevant for the rapid formation of nanolayered materials in dilute aqueous medium. Often, OTS is used as a model building block for the construction of self-assembled monolayers (SAMs) for electronic applications as, for instance, in Organic Thin-Film Transistors (OTFTs).

Table 2.2: Characteristic properties of OTS

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Molar Mass (g.mol⁻¹)</th>
<th>Length* (nm)</th>
<th>Dipole Moment* (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₈H₃₇Cl₃Si</td>
<td>387.93</td>
<td>2.58</td>
<td>2.9</td>
</tr>
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</table>

* determined by the Spartan software (Wavefunction, Inc.), 6-31G*/PM3 Geometry

OTS is used in this work for the preparation of SAMs and also to investigate the effect of its long and flexible alkyl tail on molecular mobility within such monolayers (cf. Chapter 5).

2.1.2.2 Hexadecyltrimethoxysilane (HDTMS)

Hexadecyltrimethoxysilane, named HDTMS thereafter, was purchased from Fluka (HDTMS, ≥ 85 %). It contains a trimethoxysilane headgroup (−Si(OCH₃)₃) to which is attached a relatively long alkyl chain (−C₁₆H₃₃) (Figure 2.3).
Experimental Section

Figure 2.3: Chemical formula of an HDTMS molecule.

Its long alkyl chain, less reactive and mildly polar headgroup hinder the hydrophobic effect and slow down the assembly process. Therefore, HDTMS is widely used to study the mechanisms governing the formation of self-assembled nanolayered materials.

Table 2.3: Characteristic properties of HDTMS

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Molar Mass (g.mol⁻¹)</th>
<th>Length* (nm)</th>
<th>Dipole Moment* (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₉H₄₂O₃Si</td>
<td>346.62</td>
<td>2.31</td>
<td>1.35</td>
</tr>
</tbody>
</table>

* determined by the Spartan software (Wavefunction, Inc.), 6-31G*/PM3 Geometry

HDTMS is used as a reference monofunctional molecule with long alkyl chain for the formation of self-assembled nanolayers with a highly ordered bilayered structure (cf. Chapter 4).

2.1.2.3 Dodecyltrimethoxysilane (DTMS)

Dodecyltrimethoxysilane, named DTMS thereafter, was purchased from Alfa Aesar (DTMS, ≥ 95 %). It contains a trimethoxysilane headgroup (−Si(OCH₃)₃) to which is attached a relatively short alkyl chain (−C₁₂H₂₅) (Figure 2.4).

Figure 2.4: Chemical formula of an DTMS molecule.

Despite its amphiphilic structure and low cost, DTMS is rarely employed because of its short alkyl chain and mildly polar headgroup that greatly hinder the hydrophobic effect thus leading to a less organized final nanostructure.

DTMS is used in this study to examine the effect of its short methyl-terminated alkyl tail on molecular mobility within self-assembled monolayers (cf. Chapter 5).
2.2 Characterization Methods

Table 2.4: Characteristic properties of DTMS

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Molar Mass (g mol(^{-1}))</th>
<th>Length* (nm)</th>
<th>Dipole Moment* (D)</th>
</tr>
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<tbody>
<tr>
<td>(C_{15}H_{34}O_3Si)</td>
<td>290.51</td>
<td>1.83</td>
<td>1.31</td>
</tr>
</tbody>
</table>

* determined by the Spartan software (Wavefunction, Inc.), 6-31G*/PM3 Geometry

2.1.3 Bifunctional Building Blocks

2.1.3.1 11-Bromoundecyltrimethoxysilane (BUDTMS)

11-bromoundecyltrimethoxysilane, named BUDTMS thereafter, was purchased from Gelest, Inc (BUDTMS, \(\geq 95\%\)). It contains a trimethoxysilane headgroup (\(-Si(OCH_3)_3\)) to which is attached a relatively short tail (\(-C_{11}H_{22}Br\)) terminated by a bromine atom (Figure 2.5).

![Figure 2.5: Chemical formula of an BUDTMS molecule.](image)

The presence of a bromine atom at the chain extremity makes this molecule a bifunctional building blocks having one polar groups at each of its two extremities. This specific feature is of great interest to study the effect of a second polar extremity on the assembly process as well as on the dynamic properties of the final supramolecular structure.

Table 2.5: Characteristic properties of BUDTMS

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Molar Mass (g mol(^{-1}))</th>
<th>Length* (nm)</th>
<th>Dipole Moment* (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BrC_{14}H_{31}O_3Si)</td>
<td>335.39</td>
<td>1.78</td>
<td>4.14</td>
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</table>

* determined by the Spartan software (Wavefunction, Inc.), 6-31G*/PM3 Geometry

BUDTMS was used to both investigate the effect of a polar endgroup in precursors on the assembly process of nanolayered structures (cf. Chapter 4) as well as on the molecular mobility and dynamic properties of self-assembled monolayers (cf. Chapter 5).

2.2 Characterization Methods

Two types of characterization methods were used throughout this study. First, a set of techniques were employed to characterize the nanostructures of investigated systems. These experimental
methods were used for their accuracy to identify molecular orientation and packing in nanoscaled structures. Other dynamic methods were used to help understanding the fundamental mechanisms governing short- and long-range motions of molecules when external stimulations, such as heat treatment or electric field, are applied. In both cases, molecular modeling was used to corroborate experimental results by confirming the packing pattern of molecules or response of building blocks to external events.

2.2.1 Structural Analysis

2.2.1.1 X-Ray Diffraction (XRD)

The diffraction of X-rays is a very useful non-destructive analytical method to determine the spatial organization of atoms or larger molecules in ordered structures. The basic principle of this technique consist in bombarding a specimen with a X-ray beam and measure the intensity of diffracted rays as a function of the scattered angle (2θ) (Figure 2.6a). Regular arrays of atoms or molecules cause X-rays to scatter into many specific directions after elastic interactions with electronic clouds from the sample, also called scatterer. Although scattered rays originating from disordered parts of the sample tend to cancel one another through destructive interferences, regular arrays of scatterers lead X-rays to interact through constructive interferences in specific directions (Figure 2.6b), thus creating higher intensity recordable diffraction peaks (Figure 2.6c).

Direct relation between angle of the recorded peaks and distance between atomic layers was first presented by William Lawrence Bragg through the following Bragg’s law:

\[ n\lambda = 2dsin\theta \] 

where \( n \) is an integer called the order of diffraction, \( \lambda \) is the wavelength of incident X-ray beam, \( d \) is the spacing between the diffracting planes in the atomic lattice, and \( \theta \) is the angle between the incident ray and the scattering planes.

In this work, two different diffractometers were used at small and wide angles with Bragg-Brentano parafocusing geometry (Figure 2.6a):

- Rigaku D/Max-B Geigerflex diffractometer using a Cu K\( \alpha \) (~1.544 Å) radiation from the Nebraska Center for Materials and Nanoscience (NCMN) at the University of Nebraska - Lincoln
- Bruker-AXS D8 Discover diffractometer using a Co K\( \alpha \) (~1.789 Å) radiation from the Institute for Material Research (IMR) at the University of Rouen
2.2 Characterization Methods

Figure 2.6: Schematic representations of (a) basic principle of XRD measurements with a Bragg-Brentano parafocusing geometry, (b) diffraction of X-rays by atomic plane, and (c) a diffraction pattern showing diffraction peaks as a function of $2\theta$.

All digital data were recorded at an angular resolution of 0.02° and an angular velocity of 0.5°.min$^{-1}$. Self-assembled films were analyzed directly on their silicon or glass substrates. When needed, an in-situ domed hot stage was used as temperature controller to heat and cool samples with a rate of 5 °C.min$^{-1}$. Each scan was recorded ~15 min after reaching the desired temperature.

Temperature-resolved Grazing incidence X-ray diffraction (GIXD) experiments were also conducted on Ant-12 films to obtain higher resolution diffraction patterns. Measurements were performed so that GIXD patterns can be analyzed as conventional powder X-ray diffraction patterns. Experiments were carried out by Zhang Jiang at beamline 8-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), Illinois, with a cooling rate of 5 °C.min$^{-1}$. The film was kept at each temperature for ~15 min before scanning.

Texture measurements were performed on a Bruker-AXS D8 Discover diffractometer using a Co Kα (~1.789 Å) radiation from the Nebraska Center for Materials and Nanoscience (NCMN)
Experimental Section

at the University of Nebraska - Lincoln. This analysis allows determining preferred orientations of structures by measuring the intensity of diffracted X-rays at a fixed 2θ angle while the sample is rotated (Figure 2.7). Intensity of diffracted X-rays is then plotted as a function of sample angular orientation. Texture measurements were carried out by rotating the sample around the direction normal to the substrate (Φ) at a rate of 30° min⁻¹. Further information on the preferred orientations of samples were also obtained by using the general area detector diffraction system (GADDS) at fixed 2θ and Φ angles.

Figure 2.7: Schematic representation of the basic principle of XRD texture measurements.

2.2.1.2 Ellipsometry

Ellipsometry is an optical technique that uses polarized light to determine several properties of thin films, such as thickness (d), refractive index (n) and extinction coefficient (k). Typically, the polarization change of the incident beam is quantified after reflection from the substrate-film interface and interactions with the material being investigated (Figure 2.8a), thus making results highly sensitive to sample structures and composition. The complex reflectance ratio, ρ, of the system is then measured and decomposed in the amplitude component Ψ and phase difference Δ. This technique is commonly employed to accurately characterize thickness of monolayers or more complex multilayered films (Figure 2.8b). Its high resolution allows measuring dimensions ranging from several angstroms to micrometers.

Ellipsometry being a indirect method, extracting material properties from raw experimental data is a very important part of the analysis. This process requires knowledge of sample optical properties and the use of a model describing each layer (d, n, and k) constituting the investigated specimen. Unknown properties are then defined as parameters to fit the model and determined by using an iterative procedure varying Ψ and Δ until convergence. Material properties can then be determined from calculated values of Ψ and Δ.

For this work, a three layers model was used to describe samples of self-assembled monolayer. From top to bottom, the stacking of layers is as follows:
2.2 Characterization Methods

Figure 2.8: (a) Schematic setup of an ellipsometry experiment, (b) illustration of a model describing a monolayer sample on a substrate.

1. air, \( n_0 = 1.0 \)

2. self-assembled monolayer, \( n_1 = 1.45 \)

3. native silicon oxide, \( n_2 = 1.46 \), thickness \( d_2 = 1.8 \) nm (measured on a bare silicon substrate)

4. silicon substrate, \( n_3 = 3.873 \), \( k = -0.016 \)

Measurements were performed by Jianing Sun on a M-2000 spectroscopic ellipsometer from J. A. Woollam Co., Inc. The incident angle of light (\( \lambda = 632.8 \) nm) from normal surface was set at: \( \Phi = 70^\circ \). Each monolayer was measured at least three times on optically clean and homogeneous locations in the center of samples.

2.2.1.3 Wettability Tests

Figure 2.9: Schematic representation of a liquid (water) droplet wetted to a rigid solid surface. The contact angle \( \theta \) is measured between arrows.

Wettability refers to the ability of a liquid deposited on a solid (or liquid) substrate to spread over the surface. It is determined from measurements of the contact angle (\( \theta \)) that corresponds
to the angle between the liquid–vapor and solid–liquid interfaces (Figure 2.9). The value of $\theta$ mainly results from a balance of attractive and repulsive forces between the medium under investigation and the underlying substrate. However, other parameters such as substrate roughness are also of great importance when performing wettability tests.

For this work, wettability tests were used to practically determine the effectiveness of monolayer deposition processes. Static water contact angles (WCAs) were measured with a laboratory made goniometer and then compared to values from the literature. 1 µl drops of milli-Q water were deposited on monolayer surfaces and contact angles were measured using the WinGoutte software. At least 10 measurements were performed on each sample.

2.2.1.4 Scanning Electron Microscopy (SEM)

![Figure 2.10: Schematic representation of SEM basic principle of operation.](image)

A scanning electron microscope is a special type of microscope that uses a finely focused beam of electrons to produce images of a sample placed in a vacuum chamber. The interaction of incident beam electrons and atoms at or near the sample surface leads to the ejection of other electrons, including secondary electrons, back-scattered electrons, characteristic X-rays, and others, coming from the sample area where the primary beam is focused. These signals containing important information about sample surface topography and composition are then collected by specific detectors. For instance, highly detailed images of surface sample can be generated from the intensity variations of secondary electrons recorded on an Everhart-Thornley detector. This microscopy technique is particularly suitable for the observation of objects at the nanoscale with a three-dimensional appearance. A Hitachi S-4700 Field/Emission scanning electron microscope
was used by Ziguang Chen to obtain images of multilayered films after deposition of a ~20 nm-thick chromium coating.

### 2.2.1.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a special kind of scanning probe microscopy that uses a physical probe to scan and form images of a specimen. The probe consisting in a very sharp tip mounted at the end of a cantilever is then brought close to the sample surface so that repulsive and attractive forces between the sample surface and the tip lead to a deflection of the cantilever. This deflection is then quantified by measuring the displacement of a laser beam after reflection on the cantilever top surface by a position sensitive detector made of photodiodes (Figure 2.11). The high resolution of this technique allows measuring sub-nanoscale objects.

![Figure 2.11: Schematic representation of AFM basic principle of operation.](image)

A Dimension 3100 SPM atomic force microscope was used by Ziguang Chen and myself at room temperature to obtain topographic images of mono- and multilayered films. Images were recorded at a maximum resolution of 512 lines under tapping mode. This microscope use a small piezoelectric bimorph mounted in the cantilever holder to generate up and down oscillations of the cantilever.

### 2.2.2 Dynamic Analysis

#### 2.2.2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a technique used to analyze thermal events, such as crystallizations, melttings, or oxidations, occurring in materials as a function of temperature. The basic principle consists in quantifying the difference in amount of heat required to increase
the temperature of a sample and reference. Two main kinds of calorimeter exist, heat-flux and power-compensated DSCs. In the former, the sample material and reference pans are placed in a unique furnace (Figure 2.13a). A variation of temperature is then applied to the whole furnace and heat is transferred to the sample and reference. However, exothermic or endothermic events engendered by the variation of temperature will lead to a temperature difference between the sample material and reference pans. The resulting heat flow $\Phi = \frac{dQ}{dT}$ can then simplified by a thermal equivalent of the Ohm’s law:

$$\Phi = \frac{dQ}{dT} = \frac{\Delta T}{R}$$ \hspace{1cm} (2.2)

or

$$\Phi = \frac{dQ}{dT} = C \frac{dT}{dt}$$ \hspace{1cm} (2.3)

where $\Delta T$ is the temperature difference between the sample and reference, $C$ the heat capacity and $R$ the thermal resistance.

However, actual measurement cells such as in the Q100 DSC from Thermal Analysis Instruments use more complex equations where heat flows are measured as a function of one fixed point, $T_0$, as depicted in the following circuit: \(^3\)

![Figure 2.12: Schematic representation of a circuit equivalent to a DSC cell using the Tzero™ technology](image)

where capital $R$, $T$, $C$ and $\Phi$ indices represent the thermal resistance, temperature, capacitor and heat flow, respectively; and $R$, $S$ and 0 subscripts indicate the reference, sample and 0 locations of measurements. The equivalent equation to this circuit can be expressed as follows: \(^4\)

$$\Delta \Phi = \Phi_S - \Phi_R = -\frac{\Delta T}{R_R} + \Delta T_0 \left( \frac{1}{R_S} - \frac{1}{R_R} \right) \left( C_R - C_S \right) \frac{dT_S}{dt} - C_R \frac{d\Delta T}{dt}$$ \hspace{1cm} (2.4)
where $\Delta T_0 = T_0 - T_S$ and $\Delta T = T_S - T_R$.

On the other hand, in a power-compensated calorimeter, the sample material and reference are placed in separated furnaces (Figure 2.13b). A variation of temperature is then applied to both furnaces and heat is transferred to the sample and reference. The difference in thermal power required to maintain the sample and references pans at the same temperature is then measured. In both methods, the furnace are purged by a constant flow of inert gas ($N_2, He, ...$).

![Figure 2.13: Schematic representation of (a) heat-flux and (b) power-compensated DSC cells.](image)

Both methods were indistinctly used for this study. Heat-flux Q100 and 2920 DSCs from Thermal Analysis Instruments and DSC 204 HP from Netzsch were employed to qualitatively and quantitatively characterize thermal transitions of investigated materials. Q100 and 2920 DSCs were calibrated using indium as reference material, by matching the melting temperature and the associated enthalpy of indium. DSC 204 HP was calibrated using indium and adamantane as reference materials. The ca. -60 °C endothermic solid-solid transition of adamantane and melting of indium were used to calibrate the DSC in temperature and energy. To ensure a good signal-to-noise ratio, mass of samples were always superior to 7 mg. Heating and cooling rates were selected to promote the resolution of investigated thermal events. All experiments were conducted under a nitrogen atmosphere.

### 2.2.2.2 Polarized Light Microscopy (POM) with Hot Stage

Polarized light microscopy (POM) is a simple technique to observe anisotropic structures within materials at the microscale. Typically, this technique is based on the conventional optical microscopy method except that it involves polarized light instead of the common white light. This specific feature allows a detailed perception of ordered microstructures by significantly improving the contrast between zones of different molecular orientations and rendering isotropic regions as a black background. The experimental setup is similar to a conventional optical microscope.
with two additional polarizing filters. A first one between the light source and the sample of interest, named polarizer, and a second one between the sample and the eyepiece or camera, termed analyzer. These filters are used to restrict electric field vectors constituting white light to a single plane (Figure 2.14). All electric field vectors are then vibrating in the same plane and the light is said to be polarized.

In a crossed polarization setup, a second polarizing filters (i.e. the analyzer) oriented perpendicularly to the first polarizer is added thus blocking remaining electric field vectors. Therefore, when no samples are placed on the microscope stage, the light polarized by the polarizer is blocked by the analyzer which results in no visible light in the eyepiece. However, when light coming from the polarizer passes through a birefringent specimen (whose refractive index depends on the polarization and propagation direction of light), such as anisotropic materials, two individual electric field vectors polarized in mutually perpendicular planes are produced. Therefore, electric field vectors composing the resulting light waves that are parallel to the polarization direction of the analyzer are able to pass through this latter filter and be visualized in the eyepiece by the microscopist.

Polarized light microscopy is then highly relevant for the observation of ordered microstructures in anisotropic materials, such as liquid crystals or mechanically stressed polymers. When coupled with a sample temperature controller, crystallization and melting processes of materials can be readily examined and compared with other techniques, such as DSC.

![Figure 2.14: Schematic representation of a light wave passing through crossed polarizers.](image)

Images from polarized light optical microscope were recorded on a Nikon Optiphot-2 with either a Sony DXC 107AP camera or a DS-Fi2 digital camera coupled with the NIS-Elements D software from Nikon Instruments Inc. Observations were performed exclusively on Ant-12 thin films. These films were prepared by melting the powder between two glass slides and cooling the
whole system at 5 °C.min\(^{-1}\). A Mettler FP82HT hot stage connected to a Mettler FP90 central processor was used as temperature controller during observations.

2.2.2.3 Broadband Dielectric Spectroscopy (BDS)

Broadband dielectric spectroscopy is a powerful technique to study both the relaxation dynamics of dipoles and charge migration processes of molecules composing a material. The basic principle of this technique consists in applying an oscillating electric field to a capacitor composed of two electrodes sandwiching a sample of the investigated material forming the dielectric layer. This external field interacts with sample dipoles (permanent and induced) and the apparatus measures the response of the sample in returns. Sample properties such as energy storage, permittivity, resistivity and dissipation are then determined. Such properties give information on molecular motions occurring within the material as a function of frequency. Often, the sample temperature is varied to track relaxation dynamics as a function of frequency and temperature. The dielectric spectroscopy technique is now widely employed to investigate the molecular mobility of an extensive range of polymers,^5,6 liquid crystals,^7 and glass-forming liquids.^8

Between 10\(^{-6}\) and 10\(^7\) Hz, the sample can be regarded as a circuit composed of an ideal capacitor and an ohmic resistor assembled in parallel or serial. The complex impedance \(Z^* (\omega)\) of the circuit is then measured by the spectrometer and subsequently expressed in terms of energy dissipation, or resistance \(R(\omega)\), and energy storage, or capacitance \(C(\omega)\), where \(\omega\) is the angular frequency calculated from the frequency \(f\) through the following equation:

\[
\omega = 2\pi f
\]  
(2.5)

Other properties, such as electrical modulus \(M^* (\omega)\), electrical conductivity \(\sigma^* (\omega)\), resistivity \(\rho^* (\omega)\), and more particularly dielectric permittivity \(\varepsilon^* (\omega)\) are directly derived from the complex electrical impedance \(Z^* (\omega)\).

To measure this complex impedance \(Z^* (\omega)\), a sinusoidal voltage \(U^* (\omega)\) at a fixed frequency is applied to the sample.

\[
U^* (\omega) = U_0 \exp(j(\omega t))
\]  
(2.6)

The current \(I_S (\omega)\) is then measured across the sample.

\[
I_S^* (\omega) = I_0 \exp(j(\omega t + \varphi))
\]  
(2.7)

where \(\varphi\) corresponds to the phase shift between the applied voltage and measured current.
The value of the complex impedance $Z^*(\omega)$ is then obtained by the following ratio:\textsuperscript{9,10}

$$Z^*(\omega) = \frac{U^*(\omega)}{I_5^*(\omega)} \quad (2.8)$$

More particularly, the experimental equipment used in this work calculate impedance from the measurements of two voltages $U_1$ and $U_2$ corresponding to the generated voltage applied to the sample cell and the voltage-converted sample current $I_5(\omega)$, respectively. A schematic representation of an equivalent circuit is shown in Figure 2.15. These voltages are then analyzed with the Fourier transform technique to gain information on their amplitudes and phases.

![Figure 2.15: Schematic representation of a circuit equivalent to the spectrometer analyzer](image)

The complex permittivity is consequently determined from the following equation:

$$\varepsilon^*(\omega) = \frac{1}{j\omega C_0 Z^*(\omega)} \quad (2.9)$$

where $C_0$ is the vacuum capacitance of the sample capacitor.

Permittivity characterizes the ability of charges within a material to displace or reorient in the presence of an external electric field, its experimental determination is then highly valuable to obtain information on the capacity of dipoles within a material to move. The complex permittivity can also be written as:\textsuperscript{11}

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \quad (2.10)$$

where $\varepsilon'(\omega)$ is the real part of the permittivity related to the stored energy within the medium
and $\varepsilon''(\omega)$ is the imaginary part of the permittivity related to the dissipation of energy within the medium.

Due to the very low thickness of our samples, particularly self-assembled monolayers which are a few nanometers thick, interdigitated electrodes (IE) were used for dielectric measurements. These electrodes are made of two interpenetrating comb electrodes made of gold plated copper located on a silica substrate (Figure 2.16a). This interdigitated configuration creates an electric field distribution mainly concentrated within a very thin layer of thickness $d$ at the interface between the substrate and sample material (Figure 2.16b). The height of this layer is estimated at approximately the length of one electrode base cell $d = w + s = 300 \, \mu m$ as shown in Figure 2.16b. This specific electrode structure is highly convenient when analyzing samples with thickness exceeding $d$ as no sample related geometry parameters are required. The capacity measured by the apparatus thus corresponds to:

$$C_m^*(\omega) = C_0(\varepsilon_s^*(\omega) + \varepsilon_{SU}^*(\omega))$$  \hspace{1cm} (2.11)

where $\varepsilon_s^*(\omega)$ is the permittivity of the sample material, and $\varepsilon_{SU}^*(\omega)$ is the permittivity of the electrode substrate. This latter value is necessary to take into account the part of the electric field distributed within the substrate (Figure 2.16b).

However, when studying samples with thickness inferior to $d$, such as SAMs, only a part of the electric field is filled by the sample. Therefore, the investigated system can be separated into two capacitors, one of thickness $d_S$ created by the sample film and another one created by the air with a permittivity of 1 and a thickness $d - d_S$. In this case, the capacity measured by the apparatus corresponds to:

$$C_m^*(\omega) = C_0(\varepsilon_s^*(\omega) \frac{d_s}{d} + \frac{d - d_s}{d} + \varepsilon_{SU}^*(\omega))$$  \hspace{1cm} (2.12)

Dielectric spectroscopy experiments were performed on commercially available high quality interdigitated electrodes ($\tan(\delta) \approx 0.001$) with a comb structure made of gold plated copper and having a sensor diameter of 20 mm (Novocontrol Technologies GmbH). Comb fingers are 150 $\mu m$ wide, 35 $\mu m$ thick and spaced by 150 $\mu m$. Each electrode was calibrated according to sample thickness ($d_S > d$ or $d_S \leq d$) prior to deposition by determining their respective capacity constant ($C_0$) and substrate capacity ($C_{SU}$) through the capacity measurement of a reference material (B-oil mineral oil from Vacuubrand) of known permittivity ($\varepsilon_c = 2.627$). The value of $\varepsilon_c$ was measured by using standard plate electrodes. Further descriptions of interdigitated electrodes and calibration procedures can be found in the Novocontrol Dielectrics Newsletter, Dec. 2006, and interdigitated electrode owner’s manual, respectively.
Complex dielectric permittivity measurements were carried out over a $10^{-1}$ to $10^6$ Hz frequency range on an Alpha-A frequency analyzer from Novocontrol Technologies GmbH. A Quatro Cryosystem (Novocontrol Technologies GmbH) was used to increase the temperature from -160 °C to 170 °C by successive 2.5 °C steps. All models and functions used to fit experimental data and extract properties of investigated materials are described in Chapter 5.

### 2.2.2.4 Molecular Modeling

Molecular modeling is a theoretical and computational method used to mimic and represent the arrangement of one or several molecules of a system. This technique provides information on the static conformation and organization of molecules satisfying a local or global minimum energy state. Simulated structures result from the modeling of molecules, calculations of their charges, and interactions between them. Further time-dependent properties can be achieved through molecular dynamics (MD) simulation.

MD is a computational simulation method that calculates the time-dependent behavior of a molecular system composed of a limited number of bodies. This method developed in the middle of the twentieth century\textsuperscript{12,13} provides detailed information on the physical motions and conformational changes of atoms and molecules interacting for a limited period of time. Typically, the MD simulation method is based on the Newton’s equations of motion. From these equations, trajectories describing the positions, velocities and accelerations of interacting particles can be determined as a function of time. Thus, the arrangement of atoms or molecules within a material under specific conditions and some properties can be determined at any time of the simulation.

A simple example of one common use of MD simulations is depicted in Figure 2.17(a, b)
2.2 Characterization Methods

Figure 2.17: Examples of the use of MD simulations, (a-b) interactions between several pyridine molecules are used to predict the cloud of preferential interaction orientations; (c-d) structure model of water dewetting on surface of a metal-organic framework (MOF) after incorporation of diethylformamide (DEF), water molecules are represented as green balls and DEF as red sticks. Reprinted with permission from reference\textsuperscript{15}. Copyright 2013, John Wiley and Sons.

where interactions between pyridine molecules are simulated. Finally, the preferential interaction orientations can be precisely predicted. Molecular dynamics can also be used to simulate larger and more complex systems as illustrated in Figure 2.17(c, d) where the dewetting of water molecules is depicted after incorporation of a solvent (i.e. diethylformamide, DEF) at the surface of a metal-organic framework (MOF).\textsuperscript{15} MD simulations are applied today to investigate structures, dynamics and thermodynamic properties in many research fields, such as materials science, biological systems and chemical physics.

In this work, molecular modeling was performed by Zhanping Xu, and Hui Li under the supervision of Xiao Cheng Zeng. It was used to corroborate structural organization of molecules determined from experimental results, estimate the average binding energy of these structures, and investigate dynamics of building blocks. Simulations were first performed using the geometry optimization of the Materials Studio software (Accelrys). Then, if needed, MD simulations were further employed. In such a case, MD simulations were performed considering an isothermal-isobaric (NPT) ensemble meaning that the number of moles (N), and values of pressure (P) and temperature (T) are conserved throughout the calculations. The temperature is controlled at 300 K, and external pressure set at 1 atm. The consistent valence force field (CVFF)
was selected to accurately describe interactions among building blocks.
Bibliography


Chapter 3

Assembly of Supramolecular Crystals from Nonpolar Building Blocks

Parts of this chapter are extracted from:

*Thermal Growth of Organic Supramolecular Crystals with Screw Dislocations*
A. Dhotel, L. Delbreilh, B. Youssef, J. Jiang, G. Coquerel, J-M. Saiter and L. Tan
Journal of Thermal Analysis and Calorimetry, 2013, 112, 301-305

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The first experimental part of this work is aimed to shed light on the driving forces governing the assembly of a unique type of nonpolar building blocks. A polyacene-based molecule, Ant-12, was synthesized and its structural organization under thermal treatments was studied. Although conventional self-assembly strategies are often based on the use of highly polar building blocks, this nonpolar molecule revealed its capacity to assemble into large supramolecular crystals without substantial effort.
3.1 Introduction

Supramolecular systems have received increasing interests since the early 90s, especially for their easy configurability, structural reversibility, advanced functionalities and processing flexibility.\textsuperscript{1–6} While amphiphilic molecules are frequently selected for the assembly of monolayers, bilayers, micelles,\textsuperscript{7} and vesicles,\textsuperscript{8,9} flat and rod-shaped polar organic molecules have also demonstrated capabilities in delivering complex structures, such as liquid crystals.\textsuperscript{10–12} Globally, these approaches are all based on the use of highly polar building blocks containing for instance nitrogen, oxygen or fluorine atoms that greatly promote intra- and intermolecular interactions and the overall assembly process. As a consequence of these prerequisites, when a nonpolar molecule with engineering importance is used, lack of polar groups or atoms in its structure might give limited tunability to its solid state structure. To aid our understanding of the driving forces governing the assembly of nonpolar molecules, a polyacene-based molecule was selected for its engineering importance and lack of polar groups in its chemical composition. The solvent-free structural organization of this specific building block was then studied.

Polyacenes, especially anthracene, tetracene, and pentacene, are hydrocarbon compounds that recently found important applications in organic electronic devices such as sensors and organic thin-film transistors.\textsuperscript{13–15} Their alternating double and single bond structures lead to the formation of delocalized electrons promoting charge conduction between neighboring molecules.\textsuperscript{16,17} It has been found that molecular ordering is a prerequisite for efficient electronic devices and complex procedures or conditions need to be maintained before creating a uniform ordered thin film. For instance, solution assembly is the most widely employed means in receiving supramolecules and has also been increasingly used for polyacene crystalline thin films. However, this process involves complex interplay between multiple parameters, such as substrate type, solution concentration, humidity, solvent type, and assembly time, possibly leading to the production of short-range ordered materials, instead of large crystals.\textsuperscript{18–20}

One type of acene-based molecule, Ant-12 (2-dodecylanthracene, $C_{26}H_{34}$), not only revealed the ability to form highly ordered supramolecular thin film through a solvent-free process but also the capacity to undergo several structural reorganizations when simply cooled from the molten state. This remarkable structural flexibility conferred by weak and reversible interactions between building blocks is then revealed as a promising route toward the generation of sophisticated nano- and mesostructures from such nonpolar molecules. More interestingly, differential scanning calorimetry (DSC) and polarized light microscopy (POM) revealed that the high thermal energy of one of these crystallizations enables a continuous reorganization of building blocks leading to the formation of better-defined crystals with central screw dislocations.
3.2 Sample Preparation

Thin films of Ant-12 were prepared by placing parts of the freshly synthesized powder between two glass slides and heating above its melting temperature (~105 °C). The upper glass slide was then slightly pressed to force the melted powder to spread over the surface of the lower slide. For X-ray diffraction experiments, the upper slide was removed and the sample temperature was controlled by a domed hot stage. A cooling rate of 5 °C.min⁻¹ was selected to be in agreement with DSC results. Each scan was recorded 15 min after reaching the desired temperature. POM observations were performed on thin films prepared between two glass slides.

3.3 Investigation of Structural Reorganizations upon Cooling

DSC analysis were conducted to identify the characteristic temperatures and enthalpies of transformations occurring in Ant-12 samples as temperature is progressively decreased from the molten state. Three exothermic events were observed upon cooling from 90 °C at 5 °C.min⁻¹, as shown in Figure 3.1, suggesting multiple structural reorganizations from liquid (L) toward a transient state (TS) and two solid states (S₁ and S₂). Interestingly, while both TS − S₁ and S₁ − S₂ events are characterized by large enthalpy values (13.8 and 19.4 J.g⁻¹, Table. 3.1), possibly indicating two major molecular reorganizations to oriented solid phases S₁ and S₂, the low enthalpy value of the L − TS event (3.6 J.g⁻¹) may suggest a reorientation of Ant-12 molecules from an isotropic liquid to an oriented phase. More specifically, this low enthalpy value could correspond to either a partial crystallization of the isotropic liquid (L) leading to a biphasic state with coexisting liquid and ordered solid phases or a global orientation of molecules similar to liquid crystals.²¹⁻²³ Possibly, this L − TS transition could also originate from a combination of both transition types.

Upon heating, two endothermic events corresponding to the melting of S₂ and S₁ structures are observed at 67.9 and 82.4 °C, respectively. The low enthalpy exothermic peak at ca. 55 °C is likely to correspond to the formation of S₁ crystals. This cold crystallization process may be enabled by a progressively rising thermal energy accompanied by an increasing mobility of molecules caused by the melting of S₂ structures. The melting peak of TS structures is not observed on the DSC curve due to the overlapping S₂ and S₁ broad melting signals. Several heating and cooling processes revealed all these transitions as being totally reversible.

Polarized light microscopy was further conducted to track structural organizations occurring upon cooling from the molten state. As depicted in Figure 3.2, Ant-12 undergoes several major structural reconfiguration. Indeed, the black background at 100 °C (Figure 3.2a) confirms that
3.3 Investigation of Structural Reorganizations upon Cooling

Figure 3.1: DSC curves of Ant-12 showing three exothermic events upon cooling ($L - TS$, $TS - S_1$, $S_1 - S_2$) and two major melting processes upon heating. A rate of $5^\circ C.min^{-1}$ was selected for both heating and cooling.

Table 3.1: DSC peak temperatures and associated enthalpies of Ant-12 exothermic events when cooled from 90 to 0 °C at $5^\circ C.min^{-1}$

<table>
<thead>
<tr>
<th>Exothermic Event</th>
<th>$S_1 - S_2$</th>
<th>$TS - S_1$</th>
<th>$L - TS$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (°C)</td>
<td>31.8</td>
<td>59.5</td>
<td>80.2</td>
</tr>
<tr>
<td>$\Delta H$ (J.g$^{-1}$)</td>
<td>13.8</td>
<td>19.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The Ant-12 film is totally molten at this temperature and forms an isotropic liquid. The formation of large anisotropic domains composed of a stacking of layers is then observed when cooling the sample to 80 °C (Figure 3.2b). According to DSC results, this formation of layers corresponds to the $L - TS$ transition where originally disordered Ant-12 molecules strongly orient to form a biphasic transient state. Further cooling to 60 °C promotes the generation of these strongly anisotropic domains (Figure 3.2c). However, no significant morphology differences can be clearly distinguished which could indicate a nanoscaled or sub-nanoscaled reorganization process of the molecular packing ($TS - S_1$ transition). Additional cooling to 30 °C leads to a surface roughening of anisotropic domains formed at higher temperatures (Figure 3.2d). This roughness change, which according to DSC results can be ascribed to the $S_1 - S_2$ transition, may also indicate a major reconfiguration of the molecular packing within anisotropic domains.

Although polarized light microscopy offers valuable qualitative information on the formation of anisotropic structures within materials, no accurate structural parameters can be extracted from these observations. Temperature resolved grazing incidence X-ray diffraction (GIXD) experiments were then conducted to identify the structural reorganizations occurring in Ant-12.
films upon cooling from the molten state (Figure 3.3). The flat pattern exhibited at 100 °C confirms that Ant-12 forms an isotropic liquid where molecules are totally disordered. Weak intensity peaks at \( q = 0.37 \ \text{Å} \) observed on all GIXD patterns were ascribed to unmelted impurities with ordered structures. After cooling down to 80 °C, a set of diffraction peaks appears thus indicating the formation of ordered molecular aggregates. Two distinct structures could be identified from this pattern, \( q_1 \) and \( q_2 \), with a d-spacing of 4.3 and 2.3 nm, respectively. Considering that Ant-12 molecules have a length of 2.26 nm when the alkyl chain is fully extended, the d-spacing of the \( q_2 \) structure (2.3 nm) indicates a lamellar stacking where each lamella is one molecule-height and therefore possibly composed of fully extended Ant-12 building blocks perpendicular to the substrate surface. However, no further information on the orientation of molecules in such lamellae can be extracted from this set of diffraction peaks. The apparent noise of \( q_2 \) peaks reveals in fact strikingly oriented structures, thus indicating each lamella as
being composed of highly ordered molecules. The second set of diffraction peaks, $q_1$, with a d-spacing of 4.3 nm reveals the presence of bilayered lamellae. In such bilayers, molecules have a head-to-head or tail-tail arrangement which can be slightly tilted from the surface normal. The $L - TS$ transition observed on the DSC curve at ca. 80 °C can then be ascribed to the formation of this dual lamellar structures composed of a stacking of both monolayers and bilayers. Decreasing the temperature down to 60 °C leads to a disappearance of $q_2$ peaks and a broadening of $q_1$ peaks. These two combined phenomena indicate a structural transition ($TS - S_1$) where previously formed monolayers undergo a progressive reorganization to a bilayer packing. Surprisingly, the elevated enthalpy value of this exothermic transition (19.4 J g$^{-1}$) indicates a major structural reorganization whereas GIXD and POM results suggest a nanoscaled modification of the molecular packing. One could then assume that this $TS - S_1$ transition from monolayers to bilayers significantly decreases the energy state of the overall molecular system. Further decrease of the temperature to the onset of the $S_1 - S_2$ transition (35 °C) leads to the appearance of a third set of diffraction peaks ($q_3$) and a slight decrease in the intensities of $q_1$ peaks. Both phenomena being conjugated, one could strongly assume that molecules involved in $q_1$ bilayers are partially reoriented to form $q_3$ structures. The d-spacing of these $q_3$ structures (2.8 nm) being intermediate between the characteristic d-spacing values of bilayers and monolayers, it can be ascribed to interdigitated layers where alkyl chains of opposite directions form interpenetrated comb structures.

Figure 3.3: GIXD patterns of an Ant-12 film recorded during cooling from 100 °C to 80, 60, and 35 °C. Differences in patterns indicate reorganizations of the molecular packing occurring in Ant-12 films when cooled from the molten state. A cooling rate of 5 °C min$^{-1}$ was selected to reflect transitions observed in the DSC curve. Experiments were performed by Zhang Jiang.
Molecular dynamics (MD) simulation was then used to confirm the plausibility, layer thickness, and molecular orientation of $q_1$, $q_2$, and $q_3$ structures. More than twenty different molecular packing modes have been simulated and examined. Only four energetically favorable modes (Figure 3.4) have been retained according to their low average binding energies. Figure 3.4a-b both represent a monolayer packing mode in which the anthracene headgroup of each molecule is next to the alkyl-chain tail of another molecule with opposite direction. While the thickness of the former monolayer packing was estimated at 2.6 nm, a lower thickness of 2.3 nm was found for the tilted-monolayer organization due to the significant tilt of molecules leading to a more dense packing structure. Both of these packing modes can closely correspond to the $q_2$ structure formed during the $L - TS$ transition at 80 °C, therefore, the existence of both modes is plausible. Figure 3.4c depicts the bilayer packing where molecules have a head-to-head or tail-tail arrangement. This specific structure promotes further $\pi-\pi$ interactions between adjacent aromatic rings and van der Waals interactions between alkyl chains which significantly stabilize the overall molecular edifice. Its thickness of 5.1 nm suggests that $q_1$ bilayers are slightly tilted to fit a thickness of 4.3 nm. Finally, Figure 3.4d represents the interdigitated packing mode in which the alkyl chains of Ant-12 molecules with opposite directions are interpenetrated but the anthracene moieties are separated. The layer thickness of this mode (3.2 nm) is close to the d-spacing of $q_3$ structures, thus confirming the interdigitated organization of these structures.

Figure 3.4: Side view of the four most favorable molecular packing modes obtained by MD simulations: (a) monolayer, (b) tilted-monolayer, (c) bilayer, and (d) interdigitated layer packing modes. Color code: white balls represent hydrogen atoms, blue and pink balls represent carbon atoms of molecules in opposite directions. Simulations were performed by Hui Li.

By combining both thermal and structural analysis, the various ordering processes of Ant-12 upon cooling could be accurately elucidated. The highly ordered structures formed by this build-
ing block were found to be tremendously flexible thus enabling the construction of numerous elaborate molecular organizations without considerable effort. Likely, this astonishing flexibility is allowed by the very weak polarity of Ant-12 molecules. Indeed, highly polar building blocks commonly employed in self-assembly strategies often lead to the fabrication of sophisticated but locked molecular edifices through mildly strong intermolecular interactions. On the other hand, the low polarity of Ant-12 conducts molecules to form ordered structures held by weak \( \pi-\pi \)
and van der Waals interactions which can be readily cleaved and then rebounded thus offering flexibility and reversibility to Ant-12 layers.

### 3.4 Isothermal Growth of Supramolecular Crystals with Screw Dislocations

As depicted above, layered structures formed from Ant-12 molecules revealed remarkable flexibility and reconfigurability. In addition, the elevated temperature of the \( L \rightarrow TS \) transition (80.2 °C) as well as its low enthalpy (3.6 \( J.g^{-1} \)) indicate that molecules involved in this transient state may be highly mobile and able to reorganize in order to form better defined crystals of lower energies.\(^{26}\) The isothermal reconfiguration process of this transient state was then examined over time.

#### Reconfiguration Process

In agreement with previous results, Ant-12 building blocks strongly orient to form large layered anisotropic domains after cooling to 80 °C at 5 °C.min\(^{-1}\) (Figure 3.5b). Even though a stacking of layers suggest a high ordering in the direction normal to the substrate (Z-axis), rounded edges of these layers may imply a lack of ordering in the plane parallel to the substrate (X–Y plane). Moreover, the presence of a dark background at some places in Figure 3.5b suggests an incomplete crystallization of the Ant-12 thin film. Brighter spots indicate locations where molecules tend to agglomerate. Presumably, foreign objects such as impurities coming from the substrate could act as scaffolds or nucleation sites that promote the crystal formation to reduce their high surface energies.\(^{26–28}\)

Figure 3.5c-e indicate that Ant-12 molecules progressively reorganize over time to form new anisotropic domains with different morphologies after several tens of minutes at 80 °C. Seemingly, this structural reorganization is made possible by the weakness and reversibility of \( \pi-\pi \)
and van der Waals interactions holding molecules together. Such weak interactions being easily dissociated and formed, parts of the freshly formed LT structure can successively melt and
recrystallize without degrading building blocks and give rise to a large structural reorganization over time.

![Figure 3.5: Polarized light microscopy images of an Ant-12 thin film at (a) 100 °C and during the isothermal transition at 80 °C for (b) 0, (c) 10, (d) 20, (e) 30, and (f) 40 min. The cooling rate is set to 5 °C min⁻¹ and remained zero after reaching the temperature of 80 °C.](image)

Newly formed structures (LT') are strongly anisotropic and exhibit straight edges suggesting a better ordering in the plane parallel to the substrate in addition to the layered stacking, thus implying a good ordering in the three directions. One could guess that the initial cooling rate (i.e., 5 °C min⁻¹) might have been too fast thus forcing molecules to form metastable constraint anisotropic structures (LT). If true, these structures that have a good Z-ordering but a poor X–Y packing will have a rather high internal energy.²⁹ Therefore, to release this excess of energy, molecules inside the firstly formed LT structures can rearrange through a two-step process. First, LT structures melt to release structural strains, then newly free molecules reorganize into better-organized LT' structures exhibiting ordering in the three directions. Finally, the film undergoes a major structural reorganization.

If the recrystallization time is further extended (> 40 min, Figure 3.5f), large helical crystals can be observed at discrete places. Such unusual crystals have a very well-defined hexagonal shape and highly parallel straight edges between neighboring layers in all directions, highly consistent with the formation of screw dislocations. While this type of feature is often considered as defects in metal or inorganic materials, they can also be regarded as a crystal growth promoter for organic materials in specific conditions.³⁰,³¹ In the present case, screw dislocations
guide lamellar layers to form a continuous helical ramp around the dislocation line finally forming a large helical crystal. As in pristine anthracene, the screw dislocation and the hexagonal shape may originate from the (001) basal plane of the crystal. Hypothetically, the formation process of these helical crystals could be as follows: free molecules previously involved in TS structures progressively agglomerate around attractive points such as impurities or defects. Over time, neighboring molecules are physically adsorbed and participate in the growth of the (001) hexagonal basal plane. In contrast to the initial cooling ramp, this isothermal treatment confers very low driving forces to the system that allows the formation of well-ordered layers in the X–Y plane without further packing in the Z-direction. Consequently, molecules start to centralize as a screw dislocation from the basal plane. Finally, the slow growth process and low driving forces lead to the formation of long range and highly ordered hexagonal helical crystals with minimum surface energy.

X-ray diffraction experiments were also conducted to determine the nanostructure of these anisotropic LT’ domains. As shown in Figure 3.6, after tens of minutes at 80 °C, a set of diffraction peaks with a d-spacing of 2.35 nm indicates the layered structures as being predominantly formed by a stacking of monolayers. A minor bump at $2\theta = 3^\circ$, corresponding to a d-spacing of 2.9 nm may indicate the presence of a few interdigitated layers. From these XRD results, one could assume that the bilayers present in LT structures have been mostly reconfigured to monolayers during the formation of LT’ ordered domains. Finally, LT’ structures are essentially composed of a stacking of monolayers.

Figure 3.6: XRD patterns of an Ant-12 thin film. At 100 °C, the sample exhibits a flat pattern corresponding to an isotropic liquid. After tens of minutes at 80 °C, a set of diffraction peaks indicates the predominant presence of monolayers in the film.
3.5 Conclusion

The weak polarity of Ant-12 was revealed as a valuable advantage conferring both reversibility and flexibility to anisotropic structures formed from this acene-based building blocks. Indeed, Ant-12 not only showed its ability to form highly-ordered supramolecular thin film through a solvent-free process but also demonstrated the capacity to undergo several major structural reconfiguration when simply cooled from the molten state. Furthermore, when enough time is given to the system, a spontaneous reorganization of molecules happens at 80 °C. This reorganization leads to the formation of energetically more favorable crystals with better-defined molecular organization in the three directions. The formation of large helical crystals centered on screw dislocations was also observed over time. Seemingly, the appearance of these screw dislocations is required to promote the growth of the new crystals and therefore reduce the free energy of the overall system.

Although mildly strong intermolecular interactions commonly employed in self-assembly strategies confer structural cohesion and robustness, such interactions can also lead to the formation of structurally locked self-assembled edifices. On the contrary, weak and reversible interactions engendered by nonpolar molecules, such as Ant-12, were revealed as a good alternative to confer astonishing structural flexibility leading to the possibility of forming original and highly ordered nano- and mesostructures. The formation of such structures is enabled by the capacity of building blocks to adjust their initial position even after aggregation in order for the system to reach a minimum free energy state. Furthermore, the processing-ease of this finding makes it interesting for the creation of sophisticated supramolecular structures, as well as organic electronic devices often using acene-based nonpolar molecules.
Bibliography


Chapter 4

Effect of Building Block Endgroup Polarity on the Assembly of Organosilane Layered Nanostructures

Parts of this chapter are extracted from:

Self-Assembly of Organic-Inorganic Hybrid Nanolayers: Effect of Endgroup Polarity on Nanostructures
A. Dhotel, Z. Xu, L. Delbreilh, B. Youssef, J-M. Saiter, and L. Tan
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and

Supramolecular Nanolayer Reconfiguration after Molecular Intercalation

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The second stage of this research is dedicated to the examination of the self-assembly process of mono- and bifunctional building blocks. Organosilane molecules were selected for the construction of highly-ordered organic-inorganic hybrid layered nanostructures. More specifically, the effect on nanolayer structures of a second polar group located at the chain end of alkylsilane building blocks was experimentally and numerically investigated.

4.1 Introduction

Molecular self-assembly offers a convenient way to elaborate highly ordered and lightweight organic-inorganic hybrid nanolayers with long-range ordering. Over the past twenty years, many efforts have been devoted to the construction and structural optimization of well-ordered organic-inorganic nanolayers from monofunctional organosilane surfactants.\textsuperscript{1–3} The organization process of such building blocks has been extensively investigated and is known to be governed mainly by the hydrophobic effect arising from a competition of attractive and repulsive interactions between inorganic polar heads, organic nonpolar tails, solvent and water molecules.\textsuperscript{4,5} Such interactions guide the nonpolar chains to aggregate and polar heads to maximize their exposure to the surrounding aqueous medium thus forming structures such as bilayers,\textsuperscript{6} micelles,\textsuperscript{7} or vesicles.\textsuperscript{8,9} Finally, van der Waals forces appear between alkyl chains whereas hydrogen bonds and then stronger covalent bonds are formed between inorganic heads thus conferring thermal and mechanical stability to nanolayers.\textsuperscript{6,10}

This study aims to investigate the effect on nanolayer structures of a second polar group located at the chain end of alkylsilane building blocks. Intermolecular interactions which drive the assembly process being strongly dependent on the chemical composition of precursors, it is expected that the presence of a second polar endgroup will significantly affect, or even disturb, these weak physical interactions and the overall assembly process, thus leading to an alternative structure of nanolayers.

Three different organosilane building blocks were selected for their specific molecular composition. Two monofunctional precursors, hexadecyltrimethoxysilane (HDTMS) and dodecyltrimethoxysilane (DTMS), are composed of a trimethoxysilane headgroup to which is attached a methyl-terminated nonpolar alkyl chain, whereas the third, 11-bromoundecyltrimethoxysilane
(BUDTMS), is a bifunctional molecules that possesses an additional bromine functionality at the extremity of its alkyl chain. All of these precursors were employed independently to construct organic-inorganic hybrid nanolayers whose structures were sequentially characterized and compared after solution assembly and deposition on silicon substrates. The effects of polarity and steric effects of the additional bromine-functionality on nanolayer formation were investigated in terms of structure and energy.

### 4.2 Sample Preparation

500 μm prime grade silicon wafers, P(100) 10-20 ohm-cm and P(100) 1-10 ohm-cm, purchased from University Wafer and Siltronix were used as substrates for the deposition and formation of alkylsilane nanolayers. After being cut into rectangular pieces (1.0 x 2.0 cm²), they were rinsed with water, and sequentially sonicated for 15 min in ethanol and acetone. Their surfaces were then hydroxylated in a piranha solution (70 : 30 v/v, \(H_2O_2 : H_2SO_4\)) for 30 min, copiously rinsed with deionized (DI) water and dried under a stream of gaseous nitrogen before deposition of nanolayers.

Alkylsilane nanolayers were prepared in solution by adding precursors (HDTMS, DTMS or BUDTMS) into a mixture of THF, DI water, and hydrochloric acid according to the following molar ratios:

- \(HDTMS : THF : H_2O : HCl = 0.85 : 100 : 7 : 0.002\)
- \(BUDTMS : THF : H_2O : HCl = 0.95 : 100 : 9 : 0.006\)
- \(DTMS : THF : H_2O : HCl = 0.95 : 100 : 9 : 0.006\)

Ratios among components were varied successively until the best molecular ordering was reached. The elevated amount of solvent, THF, allows molecules to freely move and adjust their initial position to optimize physical interactions between them. Water and hydrochloric acid are used as catalysts to promote hydrolysis and sequential condensation of trimethoxysilane groups of precursors.\(^{11-13}\) Hydrolysis reactions lead to the conversion of methoxysilane groups \(-SiOCH_3\) to silanol \(-SiOH\). This conversion significantly increase the polarity of precursor headgroups encouraging intermolecular interactions, especially through the apparition of hydrogen bonding. Thus, the hydrophobic effect is also greatly promoted. Consequently, neighboring silanol groups may covalently bind through condensation reactions.\(^{11,12}\) Water molecules also play an essential role in the self-assembly process as they promote the solvophobic property of alkyl chains thus leading to a better ordering of molecules within nanolayers.\(^{14,15}\)
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The mixture containing HDTMS was stirred at 400 rpm for 3 h at room temperature while the BUDTMS and DTMS containing solutions were stirred at 400 rpm for 6 h at 5 °C. The shorter chains of BUDTMS and DTMS molecules lowering the hydrophobic effect that drives molecular assembly, specific preparation conditions were selected for these precursors. A lower solution temperature and higher water amount were applied to decrease the solubility of precursors and increase the solvophobic property of alkyl chains, respectively. Higher HCl and water amounts in solutions were also selected to accelerate hydrolysis and condensation reactions that are hampered by the low solution temperature. Finally, molecular ordering was improved by extending the assembly time.

Solutions were dropcasted or spincoated (3000 RPM) onto freshly hydroxylated silicon wafers. Hydroxylation is used to clean organic residues off the substrate and activate its surface through the addition of hydroxyl (-OH) groups. This treatment not only remarkably increases the hydrophilicity of the substrate surface but also enables the covalent binding of headgroup precursors to the surface through condensation reactions. Resulting films were dried inside a covered Petri dish for 24 h at room temperature to allow further condensation of inorganic moieties.

4.3 Structural Characterization of Self-Assembled Films

Molar ratios among components, solvent type, and precursor natures were selected to form multilayer films with a lamellar structure where each lamella (referred to as nanolayers thereafter) is composed of tightly packed molecules oriented along the substrate normal. X-ray diffraction (XRD) was employed for a preliminary identification of film nanostructures. Figure 4.1 shows XRD patterns recorded on thin films of HDTMS (bottom pattern), DTMS (middle pattern) and BUDTMS (top pattern). It can first be noticed that all patterns exhibit sharp peaks indicating strong orientations of building blocks. More specifically, the XRD pattern recorded on the HDTMS films contain only one set of diffraction peaks with a d-spacing of 4.2 nm. Considering a length of 2.3 nm for a HDTMS molecule, this d-spacing value is close to twice the length of a building block suggesting that the film is composed of a lamellar structure where each lamella, or nanolayer, is formed by molecules in a head-to-head arrangement ($C_nH_{2n+2}SiO_x - O_xSiC_nH_{2n+2}$), also known as bilayers. In such bilayers, molecules are tightly-packed and slightly tilted from the surface normal which tend to lower the thickness of the overall nanolayer and better match the experimental d-spacing value. Peaks at higher 2θ values correspond to secondary diffraction peaks of the bilayered structure which indicates that the film is exclusively composed of a stacking of bilayers.

In contrast, the XRD pattern recorded on a BUDTMS film (Figure 4.1, top pattern) contains
two sets of diffraction peaks with different d-spacing values suggesting that the film is composed
of two distinct molecular organizations. Indeed, while the low intensity peak at $2\theta = 3^\circ$, cor-
responding to a d-spacing of 3.4 nm, can be attributed to the presence of bilayers, assuming a
length of 1.8 nm for a BUDTMS molecule, the high intensity peak at $2\theta = 5.9^\circ$, corresponding
to a d-spacing of 1.7 nm, may originate from a second molecular organization.

Figure 4.1: XRD patterns of BUDTMS (top), DTMS (middle) and HDTMS (bottom) nanolayers.

Then, it has been proposed that this hypothetical dual structure of nanolayers arises from
the bifunctional character of precursors. However, the shorter chain of BUDTMS could also
be responsible for a modification of the assembly process leading to the formation of alternative
nanostructures. In order to examine this proposition, nanolayers of DTMS were prepared. DTMS
was chosen for its monofunctional character and short alkyl chain length similar to BUDTMS.
Thus, the effect of chain length can be investigated. The XRD pattern recorded on a DTMS
film is presented in Figure 4.1, middle pattern. This pattern exhibits only one set of diffraction
peaks with a d-spacing of 3.5 nm revealing that the DTMS film is composed of a unique bilayered
structure if a molecule length of 1.8 nm is assumed. Therefore, the chain length has no significant
effects on the assembly process and the hypothetical dual structure of BUDTMS films can be
assuredly attributed to the bifunctional nature of precursors. Indeed, the weak dipole moment
created by the bromine atom at the extremity of the BUDTMS hydrocarbonated chain (Figure
4.2a) is expected to affect, or even disturb, intermolecular interactions driving the assembly
process of building blocks and, therefore, the final molecular organization of nanolayers. Thus,
it can be expected that BUDTMS building blocks will pack into an alternative nanostructure,
possibly different from bilayers.

In fact, a d-spacing of 1.7 nm being very close to the length of a BUDTMS molecule, the
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peak at $2\theta = 5.9^\circ$ in the BUDTMS XRD pattern may correspond to a monolayer-on-monolayer packing where molecules are stacked on top of each other and oriented in the same direction. An interdigitated organization of molecules would also fit a d-spacing of 1.7 nm. In this lamellar packing mode, alkyl chains of adjacent molecules are alternately pointing up and down. Alternatively, this high intensity diffraction peak may also be produced by BUDTMS bilayers in which bromine atoms strongly diffract X-rays.

Atomic force microscopy (AFM) was then employed to help determining the possible causes of BUDTMS nanolayer diffraction peaks. Figure 4.3a shows a topographic image of BUDTMS nanolayers stacked on top of each other. Smooth and homogeneous surface of layers suggest a long-range ordering, however, a significant crack is also observed. Scanning electron microscopy was then used to obtain larger images of film surface. Fig 4.3c shows that numerous cracks are present throughout the film. These cracks are probably formed during the evaporation of solvent after solution deposition. Indeed, in such processes, solvent can also be regarded as a linking agent between nanolayers, consequently, when it evaporates, molecules forming layers may undergo constraints possibly leading to the formation of cracks. Examining the height profile of BUDTMS nanolayers (Figure 4.3b) reveals a layer thickness of ~ 3.7 nm, thus supporting the proposition according to which BUDTMS films are exclusively composed of bilayers. In such a case, the high intensity diffraction peak at $2\theta = 5.9^\circ$ would be produced by bromine atoms of precursors whose elevated number of electrons strongly diffract X-rays.

In order to obtain further insights on the origin of this high intensity diffraction peak, texture measurements were conducted on both BUDTMS and DTMS nanolayers. This technique was selected to determine whether diffraction peaks at $2\theta = 3$ and $5.9^\circ$ (top pattern in Figure 4.1) have similar preferred orientations. Patterns of the diffraction intensity as a function of sample angle are presented in Figure 4.4 for DTMS and BUDTMS. The presence of intensity maximums, also called preferred orientations, on both patterns reveal that all investigated structures are textured. Interestingly, these preferred orientations are similar for diffraction peaks corresponding to a d-
4.3 Structural Characterization of Self-Assembled Films

Figure 4.3: (a) AFM image highlighting the lamellar structure of self-assembled BUDTMS films, (b) height profile recorded along the red line on the AFM image suggesting a bilayered structure, (c) SEM image of a BUDTMS film surface showing large cracks (recorded by Ziguang Chen).

Spacing of ~ 3.5 nm in both DTMS and BUDTMS (Φ ~ 110° and 280°). This similarity suggests that these diffraction peaks originate from analogous nanostructures, such as bilayers. On the contrary, the BUDTMS diffraction peak corresponding to a d-spacing of 1.7 nm exhibits only one maximum, at Φ = 90°, indicating that the diffraction units at the origin of this peak are possibly different from bilayers.

Figure 4.4: Texture measurements of (a) the d = 3.5 nm diffraction peak of DTMS and (b) the d = 1.7 and 3.4 diffraction peaks of BUDTMS.

The intensity variations of these diffraction peaks were further confirmed by performing XRD experiments using a general area detector diffraction system (GADDS) at Φ angles corresponding to preferred orientations. Figure 4.5 shows 1D XRD and 2D GADDS patterns recorded at preferred orientations for the DTMS diffraction peak corresponding to a d-spacing of 3.5 nm and BUDTMS diffraction peaks corresponding to d-spacings of 1.7 and 3.4 nm. The absence of rings and presence of bright spots on GADDS patterns confirm that molecular units diffracting of X-rays are strongly oriented with structural ordering close to single crystals. This trend is further
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Figure 4.5: XRD patterns of (a) the DTMS diffraction peak corresponding to a d-spacing of 3.5 nm, and BUDTMS diffraction peaks corresponding to d-spacings of (b) 3.4 and (c) 1.7 nm. Patterns were recorded at preferred orientations, Φ, and extracted from (inset) 2D GADDS patterns.

confirmed by 1D XRD pattern exhibiting high intensity peaks when recorded along preferred orientations and lower intensity peaks when recorded in other directions.

Overall, experimental structural characterizations of these alkylsilane nanolayers revealed that our experimental protocol is suitable for the formation of strongly oriented HDTMS and DTMS bilayers with long range ordering and tight molecular packing. However, the exact nanostructure of BUDTMS films could not be assuredly addressed. While the presence of bilayers in such films is plausible, the origin of a second set of diffraction peaks, corresponding to a d-spacing of 1.7 nm, could not be clearly identified.
4.4 Molecular Modeling

Molecular modeling simulations were then conducted to determine which molecular packing is the most thermodynamically stable. Three plausible types of molecular packing modes were structurally and energetically investigated: monolayer-on-monolayer, bilayers, and interdigitated layers. The more complex structure of interdigitated nanolayers led to the examination of several interdigitation patterns. The top image in Figure 4.6 shows side views of all examined molecular packing modes along with their corresponding average binding energy (bottom graph). Thickness and average binding energy estimated for each packing mode are also presented in Tab. 4.1. As depicted in Tab. 4.1 and Figure 4.6, the bilayered packing mode exhibits the lowest average binding energy value (-34.9 kcal mol\(^{-1}\)) suggesting this configuration as the most energetically favorable. This results supports the proposition that BUDTMS films are exclusively formed of bilayers and the high intensity diffraction peak corresponding to a d-spacing of 1.7 nm is produced by bromine atoms of precursors. Moreover, the thickness of the simulated bilayer mode (3.22 nm) closely matches the experimentally estimated one (3.4 nm).

Table 4.1: Binding energies and layer thickness of the seven investigated packing modes as determined by molecular simulations

<table>
<thead>
<tr>
<th>Packing Mode</th>
<th>Binding Energy (kcal/mol)</th>
<th>Layer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Monolayer)</td>
<td>-31.8</td>
<td>1.63</td>
</tr>
<tr>
<td>B (Bilayer)</td>
<td>-34.9</td>
<td>3.22</td>
</tr>
<tr>
<td>C (Interdigitated)</td>
<td>-28.2</td>
<td>2.03</td>
</tr>
<tr>
<td>D (Interdigitated)</td>
<td>-26.8</td>
<td>1.98</td>
</tr>
<tr>
<td>E (Interdigitated)</td>
<td>-30.6</td>
<td>1.97</td>
</tr>
<tr>
<td>F (Interdigitated)</td>
<td>-30.4</td>
<td>1.94</td>
</tr>
<tr>
<td>G (Interdigitated)</td>
<td>-29.9</td>
<td>1.91</td>
</tr>
</tbody>
</table>

To further confirm this proposition, the XRD pattern corresponding to the bilayer packing mode of BUDTMS was simulated and is shown below the experimental pattern in Figure 4.7. These patterns are remarkably similar as they both contain two identical sets of diffraction peaks corresponding to d-spacing values of ~ 3.3 and 1.6 nm. Thus, it can be assuredly affirm that our nanolayered films of BUDTMS are composed of a stacking of bilayers.

Finally, both experimental and simulation results suggest that our experimental protocol leads monofunctional HDTMS, DTMS and bifunctional BUDTMS molecules to self-assemble into a bilayered conformation. Likely, the dissimilarity of the BUDTMS XRD pattern compared to
Effect of Building Block Endgroup Polarity on the Assembly of Organosilane Layered Nanostructures

Figure 4.6: (Top) side views of the seven examined molecular packing modes, (a) monolayer-on-monolayer, (b) bilayer, and (c-g) interdigitated layers with different interdigitation patterns. (Bottom) calculated average binding energies of simulated packing modes. Simulations performed by Zhanping Xu.

HDTMS and DTMS patterns is due to the chemical composition of building block endgroups. Indeed, the small amount of electrons within the methyl end of HDTMS and DTMS ($n_{\text{electron}} = 9$) limits these endgroups to diffract X-rays, making them invisible to XRD. In contrast, within a BUDTMS bilayer, bromine atoms ($n_{\text{electron}} = 35$) form a high electron density plane in the middle of each nanolayer as depicted in Figure 4.8. The elevated number of electrons within this plane enables diffraction of X-rays.
4.4 Molecular Modeling

Figure 4.7: (top) Experimental and (bottom) simulated XRD patterns of BUDTMS bilayers.

Figure 4.8: Schematic representation of the path followed by X-rays when diffracted by a BUDTMS bilayer. Silane headgroups (purple circles) are linked to bromine endgroups (red circles) through alkyl chains (black curvy lines).

As a result, BUDTMS bilayers contain two diffraction planes (i.e. the inorganic siloxane network and the plane constituted by the bromine extremities of building blocks) whereas HDTMS and DTMS bilayers contain only one diffraction plane (i.e. the inorganic siloxane network). Therefore, bilayers composed of bifunctional BUDTMS molecules are characterized by two set of diffraction peaks (d-spacing = 3.4 and 1.7 nm), while the bilayered structure formed by monofunctional HDTMS and DTMS are characterized by a unique set of diffraction peaks (d-spacing = 4.2 or 3.5 nm).
4.5 Conclusion

The effect of building block endgroup polarity on the nanolayered structure of self-assembled alkylsilane thin films was investigated by experimental and simulation techniques. Results indicate that the weak dipole moment induced by the bromine atom at the end of BUDTMS alkyl chain has no remarkable effect on the self-assembly process and final nanostructure of films. Indeed, methyl-terminated HDTMS and DTMS and bromine-terminated BUDTMS were found to form a lamellar structure where each lamella is composed of molecules arranged in a bilayered conformation. Although the formation of bilayered nanolayers from monofunctional alkylsilane molecules has been extensively studied earlier, the ability to form such structures from bifunctional precursors is much less known. Therefore, it can be expected that this finding would open up a new range of potential applications of alkylsilane nanolayers by enlarging the number of potential precursor candidates to more complex bifunctional molecules.
Bibliography


Chapter 5

Mobility of Molecules within
Self-Assembled Monolayers

The last part of this work investigates the mobility of molecules composing self-assembled monolayers (SAMs). Motions of molecular segments triggered by the application of an external electric field are examined for three different mono- and bifunctional alkylsilanes.

5.1 Introduction

High molecular ordering, preparation ease, tunable functionality, and low-cost have led self-assembled monolayers (SAMs) to a wide range of applications, such as electronics,\textsuperscript{1-3} lithographic patterning,\textsuperscript{4,5} and modification of surface properties.\textsuperscript{6-11} Nowadays, SAMs and other self-assembled systems are progressively renovated to have dynamic functions with structural lability or the capability to perform sophisticated functions at the molecular level.\textsuperscript{12} Therefore, insights on the flexibility of their molecular units, or building blocks, with and without external stimuli are of primary interest. However, most of the studies on SAMs are focused on their static properties, such as structural ordering, coverage density, and surface properties.

Only a few experimental techniques allow analyzing motions of molecules or molecular groups. Among them, nuclear magnetic resonance (NMR) and scanning tunneling microscopy (STM) are most often employed. However, the use of these techniques to examine fast molec-
ular motions within nanoscopic materials, such as SAMs, is still challenging due to the very weak response signal of samples, or because of the relatively long timescale required for data acquisition.

On the contrary, the high-sensitivity to charge density fluctuations and immediate data acquisition have made broadband dielectric spectroscopy (BDS) an ideal tool to probe fast motions of dipoles within soft materials such as glass-forming systems,\textsuperscript{13,14} polymers,\textsuperscript{15–19} and liquid crystals.\textsuperscript{20,21} Besides, the development of ultra-sensitive detectors has enabled the analysis of micro- and nanoscopic materials like SAMs.

First investigations of molecular motions within alkylsilane SAMs by dielectric spectroscopy have been carried out earlier by other groups.\textsuperscript{22,23} They revealed that motions of molecular segments within monolayers are possible despite their tight and close-packed structure. They analyzed the reorientation of dipoles as a function of temperature, frequency field but also coverage density.

When constituent molecules possess several dipoles, for instance one at each end, the alignment of these molecules in SAMs leads to the formation of two polar planes in the monolayer, one at the monolayer-substrate interface, also named anchoring zone, and another one at the monolayer-air interface, also called canopy. However, to the best of our knowledge, the motions of individual polar planes have never been analyzed independently.

The present work is then dedicated to individually investigating motions of molecular segments forming these two distinct regions of monolayers. Further data analyses will also be performed to gain knowledge about the flexibility of building blocks.

Specifically, three different organosilanes were selected, including octadecyltrichlorosilane (OTS), dodecyltrimethoxysilane (DTMS), and 11-bromoundecyltrimethoxysilane (BUDTMS). While the first two contain only one polar end, the last one possesses an additional polar group at the other end of the alkyl chain. As such, the locations of these dipoles will allow tracking motions of molecular segments within the monolayer anchoring zone and canopy.

Three sample structures were investigated to assuredly ascribe dielectric signals and also track the effect of structural constraints on molecular mobility: pristine molecules, oligomers composed by molecules whose silane functionalities were forced to condense, and finally self-assembled monolayers.

\section*{5.2 Sample Preparation}

Three sample structures are investigated in this work: disordered pristine molecules, oligomers formed by the silane condensation of these molecules, and self-assembled monolayers. While
samples of pristine molecules were deposited onto clean substrates without further preparation, oligomers and SAMs required specific preparation processes as described below.

Oligomers of OTS were prepared by depositing OTS molecules onto clean electrodes and placed in a closed desiccator containing a water-filled beaker for 3 days at room temperature. The high humidity atmosphere created within the desiccator allowed highly-reactive chlorosilane functionalities to hydrolyze and form hydrochloric acid that led to the subsequent condensation of silane headgroups. Films were then heated under nitrogen atmosphere at 390 K for 2 h to confer them an isotropic structure, complete the condensation and remove condensation byproducts such as water and hydrochloric acid. Finally, amorphous film structure was ensured by rapid quenching to 110 K before analysis.

Oligomers of DTMS and BUDTMS were prepared by adding alkylsilane molecules into a mixture of THF, water, and hydrochloric acid according to the following molar ratio:

\[
\text{Precursors : THF : H}_2\text{O : HCl} = 1 : 50 : 20 : 0.5
\]

Low THF, high water and HCl ratios were chosen to ensure efficient hydrolysis and condensation of methoxysilane functionalities as well as to prevent the formation of ordered aggregates. Mixtures were then stirred at 500 RPM for 24 h at room temperature before dropcasting onto clean electrodes. Films were then heated under nitrogen atmosphere at 390 K for 2 h to confer them an isotropic structure, complete the condensation and remove preparation compounds (THF, water, HCl) as well as condensation byproducts such as methanol. Like OTS oligomers, an amorphous structure of DTMS and BUDTMS films was kept by rapid quenching to 110 K before analysis.

Self-assembled monolayers were prepared by modifying the procedure reported by Ito et al.\textsuperscript{24} After dispersing 3 mM of alkylsilanes in chlorobenzene, the solution was dispensed onto UV/ozone treated wafers and electrodes. Samples were then placed in a closed desiccator containing a water-filled beaker for 24 h at room temperature to enable the covalent grafting of molecules to the substrate. Afterwards, samples were thoroughly rinsed with ultrapure water and sonicated in toluene for 15 min. Multilayers and large molecular aggregates were removed by wiping the surface with a toluene-soaked swab. Finally, samples were sonicated in toluene for another 15 min, rinsed with Milli-Q water and dried under a stream of gaseous nitrogen. An additional 1 h annealing process at 330 K under nitrogen atmosphere was found to have no significant effects on monolayer structures.

Before monolayer deposition, wafer and electrode surfaces were cleaned by UV/ozone treatment for 30 min before copious water rinsing and drying under a stream of gaseous nitrogen. The use of UV/ozone treatment was necessary as a piranha etch (70 : 30 v/v, \(H_2O_2 : H_2SO_4\)) could damage the electrode surface. UV/ozone treatments were performed in a homemade chamber as
shown in Figure 5.1. Atomic oxygen, a strong oxidizing agent, is produced by the decomposition of ozone with 254 nm UV rays. It then reacts with organic compounds on the surface converting them into volatile substances and causes the formation of $\text{−OH}$ hydroxyl groups on the substrate surface. The high efficiency of this treatment was evaluated by measuring the water contact angles (WCAs) on a silicon wafer before and after treatment. WCA decreases from $40^\circ \pm 1^\circ$ to $5^\circ \pm 2^\circ$ indicating the formation of hydroxyl groups making the surface highly hydrophilic. Electric contacts of electrodes were protected from hydroxylation by depositing a tape mask.

5.3 Analysis of Experimental Data

In this work, dielectric spectroscopy is used to examine motions of molecules within different structures of alkylsilane materials. Specifically, an alternating electric field is applied to the sample to sense the motions or reorientations of dipoles within the material. These charge density fluctuations are then evaluated by measuring the dielectric responses of the sample, such as complex dielectric permittivity ($\varepsilon^*$) or conductivity ($\sigma^*$).

Here, the imaginary part of the dielectric permittivity ($\varepsilon''$), also called dielectric loss, is measured over wide ranges of temperature (110 to 440 K) and frequency ($10^{-1}$ to $10^6$ Hz). The dielectric loss quantifies the amount of energy of an alternating electric field that is converted into heat by a dielectric material. In other words, $\varepsilon''$ corresponds to the generation of heat resulting from the collision of dipoles caused by the successive variation of the value and direction of the alternating field. Hence, the dielectric loss can be regarded as a measure for the motions of polar groups within a material.

These motions are examined by tracking the evolution of the relaxation time, $\tau$, determined from $\varepsilon''$ vs. temperature and frequency plot, as shown in Figure 5.2a. Relaxation time can be defined as a measure of the time required for a molecular segment to reorient when submitted to an external solicitation. It can be experimentally deduced from experimental data by determining either the frequency value, $f$, at which $\varepsilon''$ reaches its maximum at a fixed temperature, $T$, so that:

![Figure 5.1: Schematic representation of a UV/ozone chamber.](image)
or the temperature value, \( T \), at which \( \varepsilon'' \) reaches its maximum at a fixed frequency, \( f \). In both cases, the peak value of the dielectric loss is tracked as a function of temperature and frequency, as depicted by the red dashed curve in Figure 5.2a.

Often, curves corresponding to the isothermal variation of the dielectric loss are fitted to the conventional model function of Havriliak-Negami (HN). However, as some of our samples exhibit weak dielectric response, this model could not be used. Rather, a temperature-dependent function (eq. 5.2) was fitted to the isochronal variation of the dielectric loss. In this model, Gaussian curves are used to fit each relaxation process. For instance, a signal containing two relaxation processes would be expressed as follows:

\[
\varepsilon''(T) = \sum_{i=1}^{n} a_i \exp \left( -\frac{(T - T_i^{\text{max}})^2}{w_i} \right) + \left( \frac{\sigma_{\infty}}{\varepsilon_0 (2\pi f)^m T^n} \exp \left( -\frac{A}{T - T_0} \right) \right) + \lambda
\]  (5.2)

where \( i \) counts the number of relaxation processes, \( a_i \) and \( T_i^{\text{max}} \) denote the amplitude and maximum position of the Gaussian functions. \( w_i \) corresponds to the width of the peak when its intensity has decreased to 1/e of its maximum value (n.b. e corresponds to the Euler’s number). \( \sigma_{\infty}, A, \) and \( T_0 \) are the parameters describing the conductivity dependence to the VFTH equation (see below, eq. 5.4). \( m, \) and \( n \) are used to describe the linear dependence of the conductivity exponent on the temperature. Finally, \( \lambda \) is an offset. For a better accuracy of fits, an additional broad Gaussian contribution was found to be necessary. This contribution was used as a background signal for fit procedure only. Its substantial width prevented further analysis.

As depicted in Figure 5.2b, eq. 5.2 serves to obtain the temperature, \( T_{\text{max}} \), at which the dielectric loss reaches its peak value at a fixed frequency, \( f \). Three Gaussian contributions were used to fit experimental data (dashed grey curves in Figure 5.2b). One of them, process I, represents the peak of the dielectric loss, process II is used as a background signal and the third one corresponds to the conductivity contribution at high temperature.

The \( T_{\text{max}} \) value estimated at a fixed frequency, \( f \), is then reported into an Arrhenius plot after calculating the relaxation time, \( \tau \), from the frequency, \( f \), through eq. 5.1. Hence, a relaxation map is constructed, so that the evolution of the relaxation time can be observed as a function of temperature (Figure 5.2c).

Relaxation times obeying a linear variation often correspond to local motions of short molecular segments, also called \( \beta \) relaxations. Such relaxations can be fitted by the Arrhenius equation (Eq. 5.3) defined as:

\[
\tau = \frac{1}{2\pi f} (5.1)
\]
5.4 Molecular Mobility of Monomers

Dielectric spectroscopy analyses were first performed on pristine molecules, also called monomers thereafter. Experimental signals are shown in Figure 5.3 and corresponding relaxation maps are

\[ \tau = \tau_0 \exp \left( \frac{E_a}{RT} \right) \]  
\[ (5.3) \]

where \( R \) is the gas constant, \( T \) the temperature, \( \tau_0 \) a pre-exponential factor and \( E_a \) the activation energy corresponding to the amount of energy required to trigger the molecular motion. On the other hand, relaxation times obeying a non-Arrhenius law, as shown in Figure 5.2c, usually correspond to cooperative motions of larger molecular segments, also named \( \alpha \) relaxations. Experimental data are then fitted to the non-linear Vogel-Fulcher-Tammann-Hesse (VFTH) equation (eq. 5.4) defined as follows:

\[ \tau = \tau_0 \exp \left( \frac{DT_0}{T - T_0} \right) \]  
\[ (5.4) \]

where \( T_0 \) is the Vogel temperature, \( D \) and \( \tau_0 \) are constants. A transition temperature can be estimated by extrapolating this fit to the common convention, \( \tau = 100 \text{ s} \) or \( \log(\tau) = 2 \). \(^{32-34}\)

Unless otherwise stated, all spectra obtained from dielectric spectroscopy experiments were analyzed as described above.

5.4 Molecular Mobility of Monomers

Figure 5.2: (a) Dielectric loss (\( \varepsilon'' \)) of OTS monomers as a function of frequency and temperature. (b) Dielectric loss (\( \varepsilon'' \)) data corresponding to the black curve on spectra (a) (f = 29.5 Hz). Dashed grey curves are individual Gaussian functions and conductivity contribution. Red squares correspond to the resulting fit to data. Relaxation times (\( \tau \)) are extracted at the peak maximum (along the red dashed curve on spectra (a)) and then reported on (c) an Arrhenius plot to construct a relaxation map. The red solid curve represents the VFTH fit to experimental points.
presented in Figure 5.4a.

![Diagram of OTS, DTMS, and BUDTMS monomers]

Figure 5.3: Dielectric loss ($\varepsilon''$) of (a) OTS, (b) DTMS, and (c) BUDTMS monomers as a function of frequency and temperature. Dashed curves indicate the $\alpha$ (red) and $\beta$ (blue) relaxations.

All monomers exhibit a high-temperature $\alpha$ motion. Considering the chemical structure of monomers, it can be strongly assumed that these responses originate from the motions of silane headgroups (i.e. trichlorosilane for OTS and trimethoxysilane for BUDTMS and DTMS) as depicted in Figure 5.4b. The non-Arrhenius trend of these motions suggest that intermolecular
5.4 Molecular Mobility of Monomers

Interactions between these polar groups are significant enough to make this process cooperative. The slightly greater relaxation temperatures, $T_\alpha$, of OTS and BUDTMS are likely caused by the chemical composition of their chains. Indeed, the long alkyl chain of OTS molecules ($C_{18}$) and polar bromine-end of BUDTMS monomers increase intermolecular interactions but also imply higher chain molecular weight. Hence, the amount of energy required for the motion of molecular segments might increase leading to higher transition temperatures. Although such temperatures are frequently associated to glass transition temperatures ($T_g$), no glass transitions could be observed on DSC curves shown in Figure 5.5. Endothermic peaks observed on each curve indicate the melting of monomers. It can then be assumed that even though cooperative these motion processes are not energetic enough to cause noticeable heat-capacity steps upon heating.

Figure 5.4: (a) Relaxation map of $\alpha$ cooperative motions and $\beta$ local segmental motions for monomers of OTS (red symbols), BUDTMS (blue symbols), and DTMS (black symbols). Solid curves represent the VFTH fits of experimental points, dashed lines are Arrhenius fits; (b) schematic representations of motions occurring in monomer aggregates.

As shown in Figure 5.3b-c, only DTMS and BUDTMS monomers exhibit $\beta$ motions. Their activation energies are remarkably similar (ca. 35 kJ.mol$^{-1}$) indicating that they originate from the same molecular segments. A closer observation of BUDTMS and DTMS compositions led to the distinction of sub-dipoles within their headgroups. Indeed, methoxy groups in trimethoxysilane (TMS) head constitute flexible dipolar units able to move when stimulated by an electric field. These non-cooperative $\beta$ motions were then ascribed to local motions of methoxy units in TMS headgroups (Figure 5.4b). OTS containing no such sub-dipoles, no $\beta$ motion is observed.

A third motion process ($\gamma$) is observed for BUDTMS. This signal being observed only in BUDTMS monomers, it can be assuredly ascribed to the motions of bromoalkyl dipoles (Figure
Figure 5.5: DSC curves of OTS (red), DTMS (black), and BUDTMS (blue) monomers recorded upon heating at 10 K.min\(^{-1}\). \(T_m\) indicate the maximum temperature of each melting peak.

5.4b). The Arrhenius trend of relaxation times indicates non-cooperative motions. Hence, it can be assumed that monomers are sufficiently dispersed to limit significant electrostatic interactions between bromine ends. The larger activation energy of this \(\gamma\) motion (77 kJ.mol\(^{-1}\)) can then be a consequence of the elevated number of electrons within the bromoalkyl dipoles that requires greater energy to move.

### 5.5 Dynamic Motions of Oligomers

Oligomers prepared from OTS, BUDTMS and DTMS molecules were then analyzed by BDS. When under acidic or aqueous conditions, the trifunctional headgroups of these molecules undergo hydrolysis and subsequent condensation reactions leading to the formation of hyperbranched, linear, or cyclic oligomers.\(^{35–38}\) In such oligomers the main chain is composed of siloxane bonds emanating from the condensation of headgroups to which are attached lateral alkyl chains corresponding to chains of original monomers.

As depicted in Figure 5.6, only BUDTMS and OTS films exhibit both cooperative \(\alpha\) and local \(\beta\) motions, whereas DTMS films present only one local \(\beta\) signal at low temperatures. The ubiquity and similarity of these \(\beta\) relaxations led us to ascribe them to local motions of polysiloxane chains (Figure 5.7b). Contrary to long macromolecules of polymers, the motion of these chains is non-cooperative indicating shorter main chains.\(^ {38,39}\) While \(\beta\) motions of BUDTMS and DTMS have similar activation energies, a barely higher value is noticed for the \(\beta\) process of OTS oligomers. This slight difference can be due to a different polymerization process caused
Figure 5.6: Dielectric loss ($\varepsilon''$) of (a) OTS, (b) DTMS, and (c) BUDTMS oligomers as a function of frequency and temperature. Dashed curves indicate the $\alpha$ (blue) and $\beta$ (red) relaxations.

by the higher hydrolysis and condensation rates of trichlorosilane headgroups of OTS compared to trimethoxysilane.\cite{40} Therefore, higher activation energy may indicate longer siloxane main chains of oligomers prepared from OTS molecules.

An $\alpha$ process can be clearly distinguished at higher temperatures from dielectric loss vs. temperature and frequency 3D plot of condensed OTS film (Figure 5.6). Analogically to side-chain
Figure 5.7: Relaxation map of $\alpha$ cooperative motions and $\beta$ local segmental motions for oligomers of OTS (red symbols), BUDTMS (blue symbols), and DTMS (black symbols). Solid curves and dashed lines are VFTH and Arrhenius fits of experimental points, respectively; (b) schematic representations of motions occurring in oligomer nanodomains.

polymers, this process was attributed to the motions of alkyl side chains of OTS oligomers as shown in Figure 5.7b. It has been reported that polymers with alkyl side chains undergo two distinct glass transitions, one corresponding to the cooperative motion of the polymer backbone and another one arising from nanodomains formed by alkyl side chains.\textsuperscript{41} The latter, named polyethylene(PE)-like glass transition, has been found to be closely related to the average number of alkyl carbon atoms per side chain but only weakly dependent on the polymer backbone composition. Our condensed films can then be compared to such systems where the backbone corresponds to the polysiloxane chain and OTS alkyl chains form independent nanodomains. Thus, the $\alpha$ signal of OTS films likely originates from the side chains within such nanodomains. Furthermore, a transition temperature of 246 K was determined, which is between the glass transition temperatures of bulk amorphous polyethylene (190 K) and amorphous regions of PE constrained by crystalline regions (260 K).\textsuperscript{42,43} Due to their similar molecular structures, DTMS and BUDTMS condensed films should also exhibit comparable chain motions. However, weak sample response and overlapping relaxation processes prevented to unambiguously observe these motions (Figure 5.6).

Nevertheless, oligomers prepared from BUDTMS also exhibit an $\alpha$ motion with a transition temperature ($T_\alpha$) of 211 K. This relaxation was then attributed to the cooperative motions of bromoalkyl groups at the end of side chains (Figure 5.7b). Indeed, considering the phase-separated structure of films, it can be assumed that side chains of BUDTMS oligomers form nanodomains where chain-ends strongly interact, leading bromoalkyl dipoles to move jointly when an electric
field is applied to the film.

5.6 Motions of Molecules within Self-Assembled Monolayers

Quality of self-assembled monolayers was investigated by atomic force microscopy (AFM), ellipsometry and water contact angle (WCA) measurements. AFM images (Figure 5.8) reveal relatively smooth surfaces for OTS and DTMS SAMs, even though several pinholes are apparent. Depths of these holes (measured between blue triangles in Figure 5.8) are remarkably close to estimated monolayer thicknesses (Tab. 5.1). Thus, pinholes were attributed to locations where a few molecules are not grafted to the silicon substrate. Dark straight lines observed on OTS and DTMS images may result from the wiping of sample surfaces performed to remove molecular aggregates formed during monolayer preparation. However, some aggregates are still observed on the BUDTMS monolayer (Figure 5.8c), even after sustained wiping, thus indicating strong affinity between aggregates and the underlying SAM due to interactions between polar ends.

Ellipsometry and water contact angle measurements were performed to further confirm thicknesses and homogeneity of monolayers. Results are presented in Tab. 5.1. Monolayer thicknesses determined by both AFM and ellipsometry are in close agreement with that estimated by theoretical calculations. WCAs measured on monolayers also concord with results reported earlier. Hence, ellipsometry, AFM and WCAs indicate good quality and homogeneous monolayers, even though polar bromine-end of BUDTMS precursors may have slightly disturbed the assembly conditions and led to the formation of small aggregates.

Motions of molecules within these SAMs were then investigated by dielectric spectroscopy. Figure 5.9a-c indicates that only BUDTMS monolayers exhibit one motion signal, whereas no significant signals can be observed for OTS and DTMS monolayers. It was then assumed that motions of silane headgroups cannot be observed under our experimental conditions. Three causes may explain the absence of silane motions: (1) the signal is too weak to be distinguished from experimental noise, (2) this molecular relaxation occur at temperatures out of the temperature range that can be reached by electrodes (i.e. 110 to 440 K), and (3) mobility of headgroups is too constrained by the monolayer structure. Even though, this latter case is highly plausible due to the rigid covalent binding of silane headgroups to the substrate and tight molecular packing, a combination of these causes is also probable.

On the contrary, the flexibility of alkyl chains may offer a certain degree of mobility to molecular segments distant from silane anchoring points, such as the monolayer canopy. Thus, dipolar groups at the extremity of building blocks, like bromoalkyl ends of BUDTMS, are able to move when an external electric field is applied.
Figure 5.8: AFM images of (a) OTS, (b) DTMS, and (c) BUDTMS self-assembled monolayers (recorded by Ziguang Chen). Scan area and height are 2 x 2 μm² and 0-10 nm, respectively. Height profiles are represented along the black dashed lines on AFM images. Blue and green triangles correspond to locations where heights were measured. (Inset) images of a water droplet on each monolayer.

Table 5.1: Thickness, water contact angle and RMS values of OTS, DTMS and BUDTMS monolayers. Ellipsometry measurements were performed by Jianing Sun.

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Monolayer thickness (nm)</th>
<th>Water contact angle (°)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Ellipsometry&lt;sup&gt;b&lt;/sup&gt;</td>
<td>AFM Measured</td>
</tr>
<tr>
<td>OTS</td>
<td>2.43</td>
<td>2.62</td>
<td>2.5</td>
</tr>
<tr>
<td>DTMS</td>
<td>1.68</td>
<td>1.62</td>
<td>1.25</td>
</tr>
<tr>
<td>BUDTMS</td>
<td>1.66</td>
<td>1.52</td>
<td>1.77</td>
</tr>
</tbody>
</table>

<sup>a</sup> thicknesses are calculated considering the length of an all-trans molecule and assuming a tilt angle of 25° from the surface normal.

<sup>b</sup> an error of 0.2 nm is assumed.

Possibly, the relaxation signal of BUDTMS could also originate from motions of molecules within aggregates observed on SAM surface (Figure 5.8). However, molecules forming such aggregates are fairly free to move due to their loose packing, therefore, two distinct signals
should be observed, one corresponding to the motions of alkylsilane headgroups and another one corresponding to bromoalkyl endgroups. As only one signal is observed, it can be assumed that the contribution of these aggregates to the relaxation observed in BUDTMS SAMs is trivial and that its unique cause is the motions of endgroups forming the monolayer canopy.

Figure 5.9: (a) Dielectric loss ($\varepsilon''$) of an (a) OTS, (b) DTMS, and (c) BUDTMS monolayer as a function of frequency and temperature. (d) Dielectric loss ($\varepsilon''$) data corresponding to the black curve on spectra (c) as a function of frequency at a fixed temperature ($T = 310$ K). Dashed grey curves are individual Havriliak-Negami function and conductivity contribution. The black solid line corresponds to the resulting fit to data including both contributions. Inset shows the very weak variation of the dielectric strength $\Delta \varepsilon$ with temperature.

As depicted in Figure 5.10a, this relaxation obeys a non-Arrhenius law indicating that bromine ends move cooperatively. This cooperativity possibly arises from the close-packed structure of SAMs that promotes interactions between adjacent building blocks. This tight molecular pack-
ing and significant intermolecular interactions also raise the energy barrier required to trigger the motions of endgroups, thus leading to a greater transition temperature ($T_\alpha$) of 266 K for the motion of bromoalkyl dipoles.

\[ \Delta H^* = \frac{\Delta H^* - \Delta H_0}{T} \]  

(5.5)

where $\Delta H^*$ is the activation enthalpy, also known as the activation energy $E_a$, derived from experimental data and $\Delta H_0$ corresponds to the theoretical activation energy when $\Delta S^* = 0$ (Eq. 5.6).

\[ \Delta H_0 = RT \left( 1 + \ln \left( \frac{k_B T}{2\pi h f} \right) \right) \]  

(5.6)

where $R$ is the gas constant, $T$ the temperature, $k_B$ the Boltzmann constant, $h$ the Planck constant, and $f$ the frequency. Thus, molecular relaxations with activation entropy $\Delta S^*$ superior to zero, or $\Delta H^*$ superior to $\Delta H_0$, are considered as cooperative. Accordingly, Figure 5.10b confirms the co-

Figure 5.10: (a) Relaxation map for the BUDTMS self-assembled monolayer. The solid curve corresponds to the VFTH fit. Inset illustrates the motions of bromoalkyl dipolar endgroups forming the canopy of a BUDTMS self-assembled monolayer. (b) Activation enthalpy ($\Delta H^*$) (blue diamonds) of the BUDTMS monolayer relaxation as a function of temperature. The solid line corresponds to the calculation of $\Delta H^*$ from the VFTH fit. The values of $\Delta H_0$ are also represented as a function of temperature (red squares). The dotted line between $\Delta H_0$ values is a guide to the eyes.

The cooperativity of this process was further investigated through the concept proposed by Eyring and revised by Starkweather.\textsuperscript{46–48} This approach assimilates the activation entropy ($\Delta S^*$) calculated from Eq. 5.5 to a measure for the cooperativity of molecular motions.
operative nature of bromoalkyl motions in the BUDTMS monolayer as $\Delta S^*$ reaches a maximum value of $0.25 \text{ kJ.mol}^{-1}.\text{K}^{-1}$ at low temperatures. Even though the reorientation of bromoalkyl dipoles could appear local, the activation entropy of this process is remarkably greater than common $\beta$ local processes,$^{49-51}$ and is rather comparable to large molecular motions associated to $\alpha$ processes.$^{52,53}$ Such a large cooperativity suggests that large parcels of the monolayer canopy move collectively. Figure 5.10b also reveals that this cooperativity progressively decreases with temperature indicating that molecular motions are facilitated by the increase in the free volume fraction within the material.$^{54}$

It is worth noting that activation enthalpy and associated entropy values shown in Figure 5.10b are calculated at different frequencies. For this reason, these values tend to decrease with temperature in Figure 5.10b while they are expected to increase as illustrated in Figure 5.11. Overall, the high transition temperature and cooperative nature of this relaxation highlight the significant amount of energy required for this relaxation to occur.

![Figure 5.11: Variation of activation enthalpy and entropy values as a function of temperature and frequency. The color surface corresponds to the variation of the theoretical activation enthalpy $\Delta H_0$ when $\Delta S^* = 0$. Black squares represent the experimental activation enthalpy $\Delta H^*$, and red circles illustrate the contribution of $\Delta H_0$ in $\Delta H^*$. The difference between the experimental activation enthalpy $\Delta H^*$ and theoretical $\Delta H_0$ corresponds to $T \Delta S^*$.](image_url)

Further information concerning the polarizability and cooperativity of this system were achieved by using the autocorrelation function. Time-dependent correlation functions are very useful in dielectric spectroscopy studies to probe the total electrical polarization of the system. In-
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formation about molecular reorientation, such as the distribution of relaxation times, can then be provided as a function of time. In order to use these correlation functions, the $\alpha$ process of BUDTMS SAMs had to be fitted a second time using the frequency-domain Havriliak-Negami (HN) function\(^{25}\) (Eq. 5.7) along with a conductivity contribution (Eq. 5.8) as depicted in Figure 5.9d.

$$\varepsilon^\ast(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (2\pi f \tau i)^\alpha)^\beta} \quad (5.7)$$

where $\varepsilon^\ast(f)$ is the measured complex dielectric permittivity, $\varepsilon_\infty$ the permittivity at the high frequency limit, $f$ the frequency, $\tau$ the characteristic relaxation time, $i$ the imaginary unit, $\Delta\varepsilon$ the dielectric strength, $\alpha$ and $\beta$ are parameters that account for the symmetrical and asymmetrical broadening of the relaxation peak, respectively.

$$\varepsilon''(f) = \frac{\sigma}{\varepsilon_0 (2\pi f)^n} \quad (5.8)$$

where $\sigma$ is the conductivity and $n$ an exponent. Hence, contrary to results shown above, the $\alpha$ process of BUDTMS monolayers was analyzed as a function of frequency at fixed temperatures. Relaxation times directly derived from fits were found to be similar to the ones estimated from temperature-dependent fits.

Havriliak-Negami functions were then converted to the time domain as shown in Figure 5.12. These curves express the time-scale required for molecular units to move, or relax. In the case of the bromoalkyl motion in BUDTMS SAMs, the distribution of relaxation times is remarkably broad as it expands from $10^{-11}$ to $10^5$ s, suggesting a strongly heterogeneous relaxation where some fast molecular units relax well before other slow units. As temperature is increased, distribution of relaxation times narrows indicating that molecular reorientations become faster at high temperatures.

These time-dependent curves were then fitted by the empirical Kohlrausch-Williams-Watts (KWW) stretched exponential function (Eq. 5.9) expressed as follows:

$$\Phi(t) = \exp \left[ -\left( \frac{t}{\tau} \right)^{\beta_{KWW}} \right] \quad (5.9)$$

where $\Phi(t)$ is the time-relaxation function, $t$ the time, $\tau$ the characteristic relaxation time, and $\beta_{KWW}$ a shape parameter varying between 0 and 1 that accounts for the stretching character of the exponential function.

In this expression, $\beta_{KWW}$, sometimes expressed as $(1-n)$, represents the dispersive character of the KWW function. Values of $\beta_{KWW}$ close to 1 thus suggest that a unique relaxation time,
5.7 Conclusions

Motions of molecules within alkylsilane nanostructures were investigated by broadband dielectric spectroscopy as a function of frequency, temperature, and building block structure. Specifically, mono- and bifunctional molecules were selected to probe motions within the anchoring zone and canopy of self-assembled monolayers.

Abundant interactions between silane headgroups of pristine molecules led them to move cooperatively when subjected to an electric field. Interestingly, a totally different molecular
mobility was observed after formation of oligomers. Covalent binding of silane headgroups conducted to a phase-separated structure were side chains forms independent nanodomains. Although molecular segments forming these nanodomains move cooperatively, the polysiloxane chains of oligomers undergo localized motions due to their short length.

The highly-ordered and constrained nanostructure of SAMs was found to greatly affect the motion processes of both polar ends. Indeed, the close-packed structure and rigid covalent attachment of alkylsilane headgroups to the substrate prevented the experimental observation of their motions. Nevertheless, the flexibility of the alkyl groups offers a certain degree of freedom allowing a polar monolayer canopy to move. This motion process is strongly cooperative due to the tight packing of molecules and abundant intermolecular interactions between adjacent endgroups. These structural constraints finally led to a heterogeneous relaxation with a large dispersion of relaxation times.

These findings broaden the understanding of processes governing motions of molecules within self-assembled monolayers and could be greatly appealing to induce dynamic properties to coating materials through the introduction of molecular mobility. Hypothetically, they would also encourage the development of novel stimuli-responsive nanotechnologies by taking advantage of dynamic and reversible molecular motions.
Bibliography


Conclusion and Prospects

This research work was conducted to investigate the flexibility of molecules within a specific type of self-assembled systems. Rod-shaped alkylsilane and alkylacene molecules were selected according to the number and location of their dipoles. Three different groups of building blocks were chosen: regular one with no strong dipole, monofunctional one that contains one dipolar group at one end, and bifunctional one composed of one dipole at each end separated by a non-polar chain. Self-assembly processes of these molecules were then carefully investigated and the influence of building block composition on the structural lability of the resulting supramolecular systems was examined.

The absence of strong dipoles within alkylacene molecules was found to confer structural flexibility to final supramolecules. Molecules forming highly-anisotropic structures are remarkably mobile and thus able to undergo several major structural reconfigurations after a simple variation of the temperature. Interestingly, weak and reversible interactions between molecules also enables a spontaneous reorganization of aggregates leading to the formation of energetically more favorable crystals with better-defined molecular organization. In contrast to mildly strong intermolecular interactions commonly employed in self-assembly strategies, the weak and reversible interactions created between these nonpolar alkylacenes are a valuable advantage to confer reversibility, and flexibility to anisotropic structures.

The influence of molecule endgroup polarity on the layered nanostructure of self-assembled alkylsilane films was also investigated. Structures of supramolecules formed from mono- and bifunctional molecules were successively compared by experimental and simulation techniques. Because of the strong influence of intermolecular interactions on assembly, it was expected that the presence of an additional polar group at the end of molecules would affect the organization of molecules. However, both experimental and simulated results indicate that the bulky polar endgroup of BUDTMS molecules has no remarkable effect on the final bilayered nanostructure of films.

Finally, motions of molecules within self-assembled monolayers was investigated. The highly-ordered and constrained nanostructure of SAMs was found to greatly hinder the motions of con-
stituent molecules. The tight packing of molecules and their rigid covalent attachment to the substrate has prevented alkylsilane headgroup to move. Hence, SAMs composed of monofunctional building blocks are apparently immobile. Nevertheless, motions of dipolar endgroups forming the monolayer canopy could be clearly observed and carefully examined. Further analysis revealed this motion process as being strongly cooperative due to numerous intermolecular interactions and tight molecular packing.

These successive studies analyzed three varieties of building blocks and supramolecular nanostructures, from highly flexible lamellae of Ant-12 to constrained SAMs. They revealed that molecules forming apparently inert or constrained self-assembled systems still possess a certain degree of freedom allowing molecular segments to move when submitted to an external solicitation.

Mobility of molecules within self-assembled materials is of primary interest for the development of novel “smart” materials with unprecedented dynamic properties. Therefore, the versatility and ubiquity of molecular motions emphasized here would possibly extend the application range of self-assembled systems to highly-dynamic materials.

Direct extensions of this research are numerous, including the investigation of more complex or polar molecules, a wider variety of stimuli, and also the use of other characterization methods. All of these prospects would significantly increase our understanding of molecular flexibility within self-assembled systems. However, a direct and promising application would be to incorporate dynamic or stimuli-responsive molecular units within these apparently inert materials. Hence, the inherent structural lability of materials associated to responsive units could lead to the design of highly functional materials.
Abstract.

The self-assembly of molecules is considered as one of the most promising approach to conceive sophisticated and dynamic materials with a molecular-level control of structure, morphology and property. However, recent advancements highlight the need to ameliorate the understanding of molecular flexibility within supramolecules.

Rod-shaped molecules were selected for this study. Composition of molecules were varied according to the number and location of dipoles. Three groups of building blocks were chosen: nonpolar one with no strong dipole, monofunctional one containing one dipole at one end, and bifunctional one composed of one dipole at each end. Self-assembly processes of these molecules were then carefully investigated and compared.

The absence of strong dipoles within molecules was found to confer structural flexibility to the final supramolecules. Within aggregates, molecules are highly mobile and able to undergo several structural reconfigurations. In contrast, more stable supramolecules are prepared when molecules contain one or more polar extremities. Despite this constrained environment, molecular segments can locally move, thus revealing a ubiquitous degree of freedom for molecular motions.

This research work aims at highlighting the flexibility of self-assembled systems, and also bring to light the potential of local molecular motions as an encouraging way to functionalize constrained supramolecules.

Keywords: molecular self-assembly, structural flexibility, self-assembled monolayers, dielectric spectroscopy, molecular dynamics, alkysilane, alkylacene

Résumé.

L’auto-assemblage moléculaire est désormais considéré comme l’une des approches les plus prometteuses pour la conception de matériaux à nanostructures complexes. Cependant, les récents progrès effectués ont aussi amené la nécessité d’améliorer la compréhension des mécanismes régissant la flexibilité des molécules.

Il a ainsi été décidé d’étudier l’effet de la composition des briques moléculaires sur leur processus d’assemblage, et la labilité structurale des systèmes assemblés. De manière à pouvoir comparer rigoureusement les résultats expérimentaux, un seule morphologie de briques moléculaires, en forme de “bâtonnet”, a été choisie et trois groupes distincts de molécules ont été sélectionnés : non-polaires, qui ne possèdent pas de dipôle important, monofonctionelles, lesquelles possèdent une terminaison polaire et une seconde non-polaire, et bifonctionelles, constituées d’un groupe polaire à chaque extrémité séparés par une chaine non-polaire

Ainsi, l’influence des groupements dipolaires sur la labilité de la nanostructure finale du matériau a pu être explorée. Cette étude permet ainsi de mettre en exergue la remarquable diversité des flexibilités structurales qui peuvent être rencontrées dans les systèmes auto-assemblés. De plus, elle dévoile le potentiel des mouvements moléculaires locaux en tant qu’approche encourageante pour fonctionnaliser des structures auto-assemblées supposées inertes ou contraintes.

Mots-clés : auto-assemblage moléculaire, flexibilité structurale, monocouche auto-assemblée, spectroscopie diélectrique, dynamiques moléculaires, alkysilane, alkylacene