Fabrication processes and molecular organization in organic thin films: theory and simulation meet experiments

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1 Description

The computational study and design of soft, functional organic materials, has made huge progresses in the last twenty years. Single molecule properties can now be calculated reliably and routinely by quantum chemical methods. The application of force-field-based Monte Carlo (MC) and Molecular Dynamics (MD) simulations is not so straightforward, but nonetheless they have progressed to a point where they can predict some basic properties of bulk condensed phases (e.g., the structure and transition temperatures of liquid crystals [1]). However, many technologically relevant applications of functional organic materials do not involve bulk phases but micro- or nano-thick films[2]. Examples range from Organic Solar Cells (OSC) [3,4,5], Organic Field Effect Transistors (OFET) [7,8,9], Organic Light Emitting Diodes (OLED) [10] to Liquid Crystal Displays (LCD) [11,12] and polymeric films for optical applications, non-wetting surfaces,[13] sensors and stimuli-responsive surfaces[14,15].

The computational study and design of these organic thin-films is much more complex than that of bulk phases, for a number of reasons:

a) surfaces and interfaces (also within the organic film) play a key role. A realistic model of molecular organization on a solid substrate may have to include its chemical composition, morphology and roughness.[16] Modelling the delicate balance of intermolecular interactions may be a problem, especially for organic-inorganic interfaces.
b) there is generally a significant change in properties of organic materials (structure, morphology, melting, glass transition, etc.) from the bulk to the nano-scale level relevant for modern applications[17,18];
c) the molecular organization within a film may strongly depend on its history and fabrication technology. Actually, the purpose of some fabrication processes (e.g. shearing[8]) may be to generate and stabilize specific out-of-equilibrium structures with favorable properties (e.g., charge transport[19,20]).

A further source of complication resides in the variety of technologically relevant organic materials that range from low molar mass to polymeric, and moreover are often employed as multi-component mixtures. The preparation processes are also different. For low molar mass molecules, vapor deposition and molecular beam epitaxy are often preferred.[21,22] Thin films of polymers and block copolymers are instead usually produced by wet deposition techniques, including spin-coating, inkjet or roll-to-roll printing.[23,24,25] In all cases, the process parameters and post-deposition treatments (e.g., solvent evaporation and annealing) can have a major effect on the final structure and properties of the films and should be accounted for by simulations.[26,27]

The aim of the workshop is to bring together computational scientists, theorists and experimentalists, to define the state of the art and push forward the boundaries in the field of organic thin films. The theme is broad and ambitious. Speakers and participants will be encouraged to address key questions, including:

- What are the criteria for validating a simulation of an organic thin film, when the film itself may be in some non-equilibrium metastable state and information about its structure incomplete?

- What level of coarse-graining and scale-bridging strategies can make the simulations of organic thin film production processes feasible and closer to experiment?
- How can simulations be made more relevant to the interpretation of experiments? How can experimental information be used to constrain the outcome of the numerical simulations?
- What level of detail in a model is required to reproduce or predict specific properties of the films (e.g., charge transport)?
- What are the best techniques for extending simulations from the study of equilibrium molecular organizations to that of nonequilibrium ones produced by the processing techniques practically used in technology?

Key References

[1] Palermo, M. F., Pizzirusso, A., Muccioli, L., & Zannoni, C. (2013). An atomistic description of the nematic and smectic phases of 4-n-octyl-4' cyanobiphenyl (8CB). The Journal of chemical physics, 138(20), 204901.

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2 Program

Wednesday, 17 July 2019		
Time	**Topic**	**Speaker/chair**
12:30	Arrival, registration and lunch	
	Session: small-molecule thin films	Raos
14:15	Organic epitaxy as a tool for controlling crystallinity, orientation, and properties of organic thin films	Sassella
15:00	Crystallisation of Benzothieno-benzothiophene Molecules at Silica Surfaces: Kinetic Effects versus Thermodynamic Equilibrium	Resel
15:45	Break	
16:15	Atomistic simulations of organic crystal growth from vapor	Muccioli
17:00	Predicting molecular self-assembly at surfaces: a statistical thermodynamics and modeling approach.	Conti

Thursday, 18 July 2019		
Time	**Topic**	**Speaker/chair**
	Session: polymers	Doi
09:00	Phase Diagrammes of Complex Materials: From the Katana, Swiss Chocolates to Organic Semiconducting Devices	Stingelin
09:45	Microstructure-charge transport relationship in polymer field-effect transistors	Caironi
10:30	Break	
11:00	Modelling and determining polymer crystal structures: two interdependent approaches to a single endeavor	Meille
11:45	Molecular simulation of polymers far from equilibrium	Rutledge
12:45	Lunch	
	Session: devices and sensors	Caironi
14:15	Smectic polymer networks: controlled molecular packing leading to new functionalities	Broer
15:00	Photo-responsive, glassy, thin, liquid crystalline films	Warner
15:45	Break	
16:15	Single-molecule sensing of biomarkers	Torsi
17:00	Neuromorphic organic electronics biosensors	Biscarini
19:00	Social dinner	

Friday, 19 July 2019		
Time	**Topic**	**Speaker/chair**
	Session: organic electronics	Milano
09:00	Role of atomistic simulations of complex morphology in multiscale electronic structure and transport modeling	Baumeier
09:45	Searching for the best molecular semiconductors	Troisi
10:30	Break	
11:00	How microstructure defines function in organic electronics. Insights from modelling	Manoj
11:45	Molecular Stacking Induced by Intermolecular Interactions: Atomistic View of the Molecular Organizations in Organic Thin Films	De Nicola
12:45	Lunch	
	Session: structure formation	Zannoni
14:15	Self-assembly of liquid-crystalline semiconductors in double-shot inkjet printing of organic thin-film transistors	Yoneya
15:00	An efficient computational model for phase coexistence	Sevink
15:45	Break	
16:15	Structure Formation in Soft Matter Solvent Evaporation	Doi
17:00	Round table and closing comments	

Saturday, 20 July 2019	
09:30	Visit to the headquartes of LAMPRE SpA in Usmate

Notes:

- All lectures will take place in room B.01 (ground floor).
- All speakers’ slots (45') include time for discussion (10').
- Stands for the exposition of posters will be available next to the lunch area (1st floor) throughout the duration of the conference.
- The abstracts of the poster presentations begin on page 29 of this document.

3 Abstracts of oral communications

Organic epitaxy as a tool for controlling crystallinity, orientation, and properties of organic thin films

Adele Sassella

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In the research field of functional organic materials interesting for technological applications[1], the possibility of growing thin films with controlled properties is a main goal. Indeed, the architecture of all devices requires integration of different materials in the form of thin films, which have to display the intrinsic physical properties of the corresponding bulk materials, free from growth-dependent defects, impurities, or structural characteristics related to non-equilibrium states. Among the different techniques for thin film growth, organic molecular beam epitaxy (OMBE)[2] offers the possibility to reach not only a high control on material purity, on film thickness and morphology, on surface and interface quality, but also on film crystallinity and orientation, thanks to organic epitaxy (OE)[3].

Here, after reviewing the concept itself of OE and its evolution, some examples are given where different organic molecules may form epitaxial interfaces on properly selected organic crystalline substrates. In some cases, crystalline thin films displaying the crystal structure and properties of the bulk single crystal are grown, while in other cases nanostructures with precise crystal structure and orientation are obtained and deeply characterized.

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Crystallisation of Benzothieno-benzothiophene Molecules at Silica Surfaces: Kinetic Effects versus Thermodynamic Equilibrium

Roland Resel

Institute of Solid State Physics, Graz University of Technology, Graz, Austria

The family of benzothieno-benzthiophene based molecules have gained a lot of scientific interest due to their outstanding performance in organic thin film transistors. Within this talk the thin film formation of selected benzothieno-benzthiophene molecules is studied from sub-monolayer coverages up to device relevant film thicknesses of 100 nm. Atomic force microscopy studies and X-ray diffraction investigations are used to characterise the thin film morphology and the crystallographic properties. Several outstanding properties are observed which are related to the formation of new polymorphs within thin films [1-3]. It will be introduced how the crystal structure is solved from a thin film by a combination of grazing incidence x-ray diffraction and molecular dynamics simulations. Such substrate induced phases are kinetically formed and can be transferred to the thermodynamically stable phase. Close to the melting temperature of the crystalline state we observe a pronounced dewetting of the substrate surface which is followed by the formation of single closed monolayers in the liquid crystalline state. [4] As a function of temperature a discrete number of monolayers appears, the reversibility of this observation reveals thermodynamic stable states. [5] Asymmetric molecules show besides ordered (crystalline and liquid crystalline) states also highly disordered states which are kinetically trapped and cannot be transferred into the thermodynamically stable phase.

[1] A. O. F. Jones, et al., Substrate-induced and thin-film phases: polymorphism of organic materials on surfaces, Advanced Functional Materials 26, 2233-2255 (2016).

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Atomistic simulations of organic crystal growth from vapor

Luca Muccioli

Università di Bologna, Italy

Understanding and controlling the growth of organic films by deposition from the vapor phase is fundamental in several materials science applications, and in particular in organic electronics and pharmaceutical industries. This presentation will describe how the process can be studied by means of a computational approach inspired by the experimental vapor deposition process [1,2], with particular focus on the growth of pentacene nanocrystals on silica [3].

Simulations indicate that the formation of crystalline islands develops in two separate nucleation and growth steps: the first is characterized by partially diffusing aggregates of a few flat-lying parallel molecules. In the second step, occurring at a critical size that is layer- and substrate- dependent, a lying-to-standing transition occurs, accompanied by the onset of crystalline order involving hundreds of molecules. After that, the growth proceeds via attachment of incoming molecules at terrace edges as in standard nucleation and growth models.

The overall agreement, obtained between calculated and experimental physical properties for pentacene, suggests that the proposed methodology could be successfully applied to other organic materials, also in a predictive perspective.

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Predicting molecular self-assembly at surfaces: a statistical thermodynamics and modeling approach

Simone Conti

Harvard University, USA

Molecular self-assembly at surfaces is a prominent example of self-organization of matter with outstanding technological applications. The ability to predict the structure of the self-assembled monolayer (SAM) formed at equilibrium is of great fundamental and technological importance. In this talk I present a self-consistent theory for a first-principle interpretation of 2D self-assembly based on modeling and statistical thermodynamics [1,2,3]. The developed framework provides access to the thermodynamic stability of the SAM and to its concentration dependence. This allows to study competitive equilibria at surfaces and to rationalize the 2D polymorphism evidenced by scanning probe techniques. The theory predicts the existence of a critical concentration of monomers, which is used to set an absolute scale for the 2D self-assembly propensity. Last, technological applications are discussed, showing the potentials of the developed framework [4,5,6].

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[3] S. Conti and M. Cecchini "Modeling the adsorption equilibrium of small-molecules gases on graphene: effect of the volume to surface ratio." Physical Chemistry Chemical Physics, 2018, 20, pp. 9770–9779.

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Phase Diagrammes of Complex Materials: From the Katana, Swiss Chocolates to Organic Semiconducting Devices

Natalie Stingelin

Department of Materials and Centre for Plastic Electronics, Imperial College London, UK
School of Materials Science and Engineering, Georgia Tech, USA

The physical organisation, from the molecular to the macro-scale, of essentially all macromolecular materials can profoundly affect the properties and features of the resulting architectures. I will discuss how rules that explain the mechanical properties of the Katana and distinguishes good from lesser tasty chocolates, can be applied to organic semiconductors to manipulate their properties and, hence, and their consequent performance when used as active layers in organic optoelectronic devices, including organic thin-film field-effect transistors, organic light-emitting diodes or organic photovoltaic cells. Here, we present a survey on the principles of structure development from the liquid phase of this interesting and broad class of materials with focus on how to manipulate their phase transformations and solid-state order to tailor and manipulate the final ‘morphology’ towards technological and practical applications. We will discuss blending, nucleation and use of processing aids to control the microstructure targeted for field-effect transistor applications, organic photovoltaic cells and beyond.

Microstructure-charge transport relationship in polymer field-effect transistors

Mario Caironi

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In this contribution I will report on our recent findings regarding the relationship between electron and hole transport and film microstructure in uniaxially aligned polymer field-effect transistors through the combined use of microstructural, electrical, and electro-optical investigations. We first analyze the specific impact of inter- and intra-molecular interactions on the transport properties within the ordered fraction of a model copolymer film, with the aim of revealing intrinsic factors selectively favoring holes or electrons mobility. Then, we investigate strategies to overcome thermal activated transport. We evidence that molecular alignment and tailored thermal treatments are key factors to achieve a single-crystal like, voltage independent mobility, with vanishing activation energy close to room temperature. Overall, specific molecular interactions within crystallites and interconnectivity of the ordered regions control the degree of ambipolarity and thermal barriers to transport.

Modelling and determining polymer crystal structures: two interdependent approaches to a single endeavor

Stefano V. Meille

Politecnico di Milano, Italy

From its origins polymer crystallography has been extensively interrelated with molecular and crystal modelling of polymers. The relationship is not unidirectional, as the two fields have benefitted from the respective developments: detailed molecular models have been, because of the limited quality of polymer diffraction data, a prerequisite to solve polymer crystal structures and, as the quality and the reliability of modelling is increasing, so does its role in polymer crystallography. On the other hand experimental crystal structures, lattices and symmetries, not to speak of crystal morphologies and their evolutions represent essential constraints or testing grounds for our modelling ability. They are features hardly predictable from molecular data, while structure based rationalization of properties and of structural developments under specific conditions is becoming increasingly viable. The relative difficulty to solve polymer crystal structures from diffraction data, along with the apparent accessibility of modelling approaches, has made the latter increasingly popular, whereas the detailed determination of polymer crystal structures is relatively less attractive, and its necessity underestimated.

Polymer crystal structures, contrary to low molecular mass crystal structures, remain difficult to solve and refine. The role of the small size and of the inherent anisotropy of polymer crystals, the possibility extensive disorder, the stability of mesophases, often dependent on molecular masses, are key aspects of such specificity along with the conformational properties of polymer chains. In other words, for modelling approaches to be effective, we often need to identify and implement essential *a priori* model features, or constraints considering experimental data in a process relating to the fact that polymers in the semicrystalline state attain equilibrium only at localized scales.

Selected recent examples in the fields of conjugated polymers but also of more traditional polyolefins will be reported and discussed, especially with reference to the significance of so called “limited ordered” models and to the treatment of disorder in crystallographic and in modelling perspectives.

Molecular simulation of polymers far from equilibrium

Gregory Rutledge

Massachusetts Institute of Technology (MIT), USA

As engineering materials, solid polymers in bulk and thin films are remarkable for the variation of properties they can exhibit. This diversity is due as much to changes in the processing and history of the material as to changes in chemical composition or molecular architecture. The variability is made possible by the broad range of relaxation times typical of macromolecular materials, and the existence in particular of some very long relaxation times. For this reason, the engineering application of molecular simulations to the study of polymers in the real world often requires that the simulation be cognizant of process history or the existence of trapped, local equilibrium states. When such conditions arise, the constraints are introduced to enforce the perturbation of the system from its thermodynamic equilibrium, lowest free energy state. The semicrystalline state of polymers is one such well-known case, wherein the chains are trapped in a heterogeneous local equilibrium comprised of both crystalline and amorphous domains. This seminar will discuss methods by which such a constrained, local equilibrium state can be studied at the molecular scale. It will then illustrate how constraints can be introduced to study flow-induced orientation in polymers, even on time scales relevant to the lab. Finally, the idea of constrained equilibrium is used to construct molecular simulations that directly reproduce experimental data.

Smectic polymer networks: controlled molecular packing leading to new functionalities

Dirk Broer

Eindhoven University of Technology, The Netherlands

Liquid crystal elastomers and networks are known for a variety of application in optics and photo-mechanics. In most cases these materials have a nematic molecular order which enables to adjust gradients in the director and the scalar order parameter. Less studied are polymer networks with a smectic molecular order. The lecture will demonstrate new properties originating from smectic elastomers and networks, both for optical, photo-mechanical and membrane applications. Existing applications not only benefit from a higher degree of molecular order but also new functions can be developed that cannot be realized with the traditional nematic materials.

Smectic liquid crystals are known to form easily homeotropic films stabilised by the surface energy at the interface to air, which can be exploited to control the macroscopic alignment. During the fabrication of the networks from smectic reactive mesons loss of order is often observed. By better decoupling of the aromatic rods from the growing polymer main chains, the order can be maintained. The lecture will discuss the molecular aspects to enhance smectic order in the polymeric systems and to utilise this for high-contrast dichroic guest host systems. Membrane technology benefits from controlled molecular pores directed by the smectic network. This will be discussed for the two examples: the formation of selective absorbing nanopores and light-stimulated emission of liquids at the interface with air.

Photo-responsive, glassy, thin, liquid crystalline films

Mark Warner

University of Cambridge, United Kingdom

Liquid crystalline glasses can change shape by 10-20% following changes in temperature or illumination. Shape change, that is, elongation along a particular direction rather than simply change of volume, can be imaginatively arranged induce intrinsic curvature in initially flat spaces, leading to new mechanics and strong actuation [1] paradigms. I will give, with demonstrations, examples of the geometry.

Three major challenges:

1. Thin sheets need patterning at the micro-level to be curvature responsive. How to pattern, and what patterns?

2. Deformation and recovery mechanisms for photo-glasses are not really understood in the way statistical mechanics informs the huge photo-response of nematic elastomers. Can one develop a microscopic picture? It is known that free volume and dynamics play a vital role for glasses [2].

3. Light interacts non-linearly with the population of photo-responsive molecules in order that a bias leading to mechanics arises. The penetration of light is non-Beer and there is a dynamics associated with bleaching waves into films where thickness plays a crucial role.

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Single-molecule sensing of biomarkers

Luisa Torsi

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Digitization is a major driver in biomarkers assay and can enable precision medicine to enter into the everyday clinical practice. Among the single-molecule detection methods proposed so far, only few are, however, exploitable for clinical assays.

The selective sensing platforms assessed in this lecture encompass low-background-noise fluorescent microscopies, plasmonic and electrical nano-transducers, all inherently unfit to sense a single-molecule in a bulk milieu. Recently commercialized label-based technologies relying on micro-beads that can find and detect few biomarkers in the bulk of real biofluids, have paved the way to a revolution in early-diagnostic. Lately, label-free, mass-manufacturable, bioelectronic capacity-coupled large electrolyte-gated transistors have been proven capable to detect a biomarker at the physical-limit in real bovine-serum.[1-6]

This lecture aims at discussing the material-science and devices-operational aspects underpinning the sensing-principles of the assessed technologies critically prioritizing them according to scrutinized figures-of-merit such as limit-of-detection, need for a labelling-step and feasibility to assay biofluids.

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Neuromorphic organic electronics biosensors

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Organic electronics devices are emerging as ultra-sensitive and specific biosensors. Electrolyte gated organic field effect transistors (EGOFET) and organic electrochemical transistors (OECT) are the most used architectures. According to the current understanding two different doping mechanisms intervene in these devices: EGOFET operate in accumulation due to electrostatic doping of ions at the electrical double layer at the interface between the organic semiconductor and the electrolyte; OECT operate in depletion by electrochemical doping upon gate-modulated cation exchange. I will discuss here a unified view of ion-gating mechanism in the two architectures by means of a common mechanism that is based on ion-pi conjugated molecule interaction, a strong non-covalent interaction that is widely studied in protein chemistry and ion batteries, but still largely ignored in organic bioelectronics. The shift of HOMO-LUMO levels in the pi-materials indicate that that the ions can modulate the hopping rate of the charge carriers, and specifically for p-type materials, cations will slow down producing a lower conductivity, while anions will accelerate it, thus increasing the current. This scenario also hints to the fact that the "bulk" of an organic semiconductor thin film is involved in the modulation of the charge transport in EGOFET, similarly to the mechanism invoked in OECT.

These concepts have inspired us to design a new sensor for dopamine (DA), which can be ultra-sensitive and specific at the same time. The sensing device is operated in frequency as a “synapse-like transistor”, either in a two terminal or a three-terminal device. The characteristic time scale of the synapstor is used as the signal correlate to the concentration. DA levels in the brain of healthy people are in the nanomolar range of concentration and decrease to 100-picomolar range in patients with Parkinson’s disease (PD). The selectivity of the sensor was also tested in operational conditions nearer to the *in vivo* ones in co-presence of physiological concentration of ascorbic acid and uric acid. We also assessed the sensor against the whole series of DA catabolites, showing the capability of the sensor to discriminate sub-molecular changes of the chemical structure, or non-covalent interactions. Once properly engineered, the proposed sensor could be coupled with actuating devices, leading to the implementation of implantable architectures for the Central Nervous System, that may perform loco-regional delivery of L-Dopa in response to [DA] lowering in animal models, and later in patients, affected by Parkinson’s disease.

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Role of atomistic simulations of complex morphology in multiscale electronic structure and transport modeling

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Functionality of molecular devices, such as organic solar cells or light emitting diodes, is determined by the dynamics of electronic excitations and conversion processes within multilayered structures. Typically processed from solution, the material morphology in the functional layers and at their interfaces is characterized by a substantial amount of structural disorder, which is further amplified by thermal disorder at room temperature operating conditions.

This situation constitutes an enormous challenge for an ab-initio modeling of dynamical electronic processes in such materials, since the complex morphological details can typically only be accessed by classical atomistic methods. In my presentation, I will specifically discuss the role classical atomistic Molecular Dynamics simulations play in our multiscale approach [1,2], which combines electron transfer theories, excited state electronic structure methods in QM/MM setups, and rate-based dynamics. Within this framework, I will discuss strategies to transfer classical geometries to the quantum level calculations without loss of relevant features and without introducing artifacts due to, e.g., mismatch of equilibrium properties.

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Searching for the best molecular semiconductors

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We present several approaches to screen a large database of molecular materials in search for known compounds with selected optimal properties. In the first part, after reviewing our recent work on the prediction of charge mobility in molecular crystals [1] we discuss approximated methods to enable the rapid computational screening of many thousands of materials [2,3]. We then present the results of such screening and try to identify the maximum achievable charge mobility within this class of compounds. In the second part, we tackle the search of optimal materials for singlet fission [4]. After a new calibration of the computational procedure we show that hundreds of good candidates can be easily identified among known compound.

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How microstructure defines function in organic electronics. Insights from modelling

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The optoelectronic properties of conjugated organic materials are notoriously sensitive to the supramolecular arrangement of their constituent molecules. Because intermolecular interactions in molecular materials are driven by relatively weak van der Waals forces, various supramolecular organizations are possible in the solid state, which translates into multiple polymorphs in crystalline samples. The situation is even more complex in polycrystalline thin films where local microstructure may vary substantially, while impacting significantly fundamental processes such as (photoinduced) charge transfer. Here, we will present some recent modeling studies aiming at deriving structure-property relationships between local packing of electroactive conjugated molecules and function, in the context of charge (photo)generation, charge transport and singlet exciton fission. We will in particular discuss the electronic structure of doped and mixed molecular crystals based on pentacene. Such theoretical studies provide the needed framework for the interpretation of experimental investigations using light, namely ultraviolet photoelectron and (transient) optical spectroscopy, as a probe for local intermolecular interactions.

Molecular Stacking Induced by Intermolecular Interactions: Atomistic View of the Molecular Organizations in Organic Thin Films

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Experimental evidence demonstrated that intermolecular interactions and the subsequent horizontal molecular orientation in OLED devices play a significant role to improve both, optical and electron carrier properties. [1-3] A fine control on the orientation of B2PyMPM, B3PyMPM, and B4PyMPM molecules in organic thin film, from vacuum deposition, has been reported by Yokoyama *et al.*[4], which experimentally measured how much the horizontal molecular orientation, anisotropy and thickness of organic thin films have an effect on electron mobility, and hence, on performances of OLEDs.

It is evident how the understanding and controlling the intermolecular interactions can make it possible to build complicated higher-order structures and improve OLEDs, organic photovoltaic cells (OPVCs) and organic field-effect transistors (OFETs) performances.

We present a computational study to investigate and understand, at atomic detail, how the intermolecular interactions can modify the molecular orientation in thin film/vacuum interface. In particular, based on OPLS-AA force field,[5-6] we optimize torsional profiles and parameters by using *Ab initio* calculations. Then, we studied molecular orientation and staking distances between molecules in thin films composed of B2PyMPM, B3PyMPM, and B4PyMPM molecules.

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Self-assembly of liquid-crystalline semiconductors in double-shot inkjet printing of organic thin-film transistors

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Fabrication of single-crystal organic semiconductor (OSC) thin-films by means of printing technologies is still a challenge and use of material's self-assembly properties is one strategy for that. Recently, technology called double-shot inkjet printing (DS-IJP) proved to capable of growing single crystalline OSC thin-films for organic field effect transistors [1]. Here we report on molecular dynamics simulations of film growth dynamics at the air-liquid interface in the DS-IJP process [2]. The difference in dynamics between two different OSC materials, 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene, that has a smectic liquid crystal phase and 6,13-bis(triisopropylsilyl-ethynyl)pentacene that does not, was studied. For the former OSC material, we obtained spontaneous formation of aligned lyotropic liquid-crystal-like layers at the air-liquid interface, whereas the latter showed no layer formation. Because only the former OSC material produces single crystal films through the real DS-IJP process, our results imply that the ability to spontaneously form aligned layers at the air-liquid interface is the key OSC material property for obtaining single crystal films due to the aligned layers serve as a good precursor for that.

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An efficient computational model for phase coexistence

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Hybrid approaches that combine the detailed molecular representation of molecular dynamics (MD), either in terms of all atoms (AAMD) or in terms of small clusters of heavy atoms (CGMD), for key constituents with a much coarser continuum representation for constituents of which the internal structure is of lesser importance, *e.g.* in the case of solvent, or that describe ‘expensive’ intermolecular interactions at the continuum level after projection, are gaining interest in the computational community owing to the significant increase in system sizes and/or trajectories length that they promise. Compared to methods that exclusively consider continuum variables, such as self-consistent field theory (SCFT) and dynamic density functional theory (DDFT), these hybrids have the advantage of introducing molecular resolution while circumventing the compute-intensive calculations of two-body interactions that are known to limit the dimension of systems that are suited for AA-/CGMD.

Among the methods that employ a projection scheme is hybrid MD-SCF,[1] which combines MD-based forces for the intramolecular interactions with forces for intermolecular interactions that are derived from the (mean-field) chemical potentials for the non-ideal part of the free energy in SCF/DDFT. While such partial coarsening speeds up calculations by several factors compared to standard CGMD, drawbacks are not only the expected loss of resolution at close distances but also a loss of momentum transfer, as proper transfer can only be incorporated by sacrificing a considerable part of the readily gained efficiency. Recently, however, we showed that we can use a Multi-Particle Collision Dynamics (MPCD) description of the kinetics to introduce momentum transfer and conservation at very modest costs, thereby restoring the long-ranged interactions that are known to significantly accelerate structure formation, coarsening and dynamics.[2]

In this presentation, I will start by reviewing some of the lessons learned about the phase behaviour of thin block copolymer films based on field-theoretic DDFT calculations in different settings. Consequently, I will illustrate the potential and drawbacks of the new hybrid MD-SCF/MPCD method and show how it can be adapted to describe the phase behaviour and dynamics of a gas/liquid coexistence, e.g. the situation that exists when thin films are annealed, in a very natural way.

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Structure Formation in Soft Matter Solvent Evaporation

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When a thin film of polymer solutions or colloidal suspensions is dried up on a substrate, it leaves a dried film on the substrate. This process is commonly seen in many micro fabrication processes used in modern technology such as coating and printing. Though commonly used, the process is complex since various things are taking place simultaneously: flow and diffusion of solvent, skin and cavity formation, gelation and other phase transitions. In this talk, I will describe our recent study on the modeling of these phenomena focusing on the structure of colloidal solution formed after the evaporation of solvent.

4 Abstracts of poster communications

Exploring the magnetic coupling of Co and Ni tetra phenyl porphyrins on oxygen-passivated Fe(001)

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Spinterfaces, *i.e.* interfaces between a ferromagnet and an organic semiconductor, are a topic of great interest since they can effectively combine the spin-polarized character of ferromagnets with the great responsivity to external stimuli of molecules, which makes them very appealing for spintronic applications [1]. Co- and Ni-Tetra Phenyl Porphyrins (TPP) are ideal candidates for building spinterfaces because of their flat morphology and the fact that their ion core can possess its own magnetic moment, which might lead to an enhancement of the spin-dependent properties of the system. However, ferromagnetic materials typically strongly interact with organic molecules, making it difficult to obtain well-ordered structures.

This contribution focuses on the growth and the magnetic character of a single layer of Co- and Ni-TPP on the oxygen-passivated Fe(001) surface, investigated by means of Spin Resolved photoemission (SR-PES), inverse photoemission (SR-IPES) and Low Energy Electron Diffraction (LEED). The LEED results highlight that the passivation of the metal surface promotes an ordered self-assembly of the molecules, following Ref. [2], while SR-PES is able to reveal a different magnetic behaviour of the two molecules, distinguishing between the role of the ion core and the peripheral groups.

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Modeling Organic Blends with the Martini Coarse-Grain Force Field.

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Blends of organic semiconducting materials are paramount in several subfields of organic electronics – organic photovoltaics or organic thermoelectrics to name a few. The self-assembly process which takes place during the solution-processing step employed to fabricate these devices leads to kinetically trapped morphologies consisting of intimately intermixed materials. The morphology of the blend is as important for the device functioning as the electronic properties of the single components. The absence of robust molecular structure-morphology-performance relationships hinders further developments in this field.

Here, we showcase how coarse-grain (CG) molecular dynamics employing transferable models based on the Martini [1] CG force field can be used to model soft matter blends relevant for organic electronics [2-4]. CG molecular dynamics simulations are used to generate morphologies taking into account the processing conditions, such as spin-coating and thermal annealing [2,3]. These CG simulations can also be used to probe the miscibility of a certain molecule in molecular environments of different polarity [4]. Martini models possess the key advantage of being transferable, thus allowing for a broad range of applications without the need to reparametrize the force field each time. This is important in order to speed up the computational time scale related to the development of models. Moreover, Martini models retain a sizable degree of chemical specificity and can be directly back-mapped to atomistic resolution. This is also paramount to connect morphological arrangements in the blends to molecular features and electronic properties.

With the recent development of Martini 3.0 [5], the Martini framework has been refined and expanded after more than 10 years of applications and lessons learned thereof. The new parametrization, along with the modularity of the Martini force field, is expected to boost the application of the Martini 3.0 CG force field in soft materials science.

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Modeling and simulation of transport and growth of organic molecules on inorganic surfaces.

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Our work focuses on the modeling and simulation of transport, nucleation and growth of organic molecules on inorganic surfaces. In particular, we have studied the effects of chemical tuning of the organic para-sexiphenyl (p-6P) molecule on its diffusion and binding to a zinc oxide surface by all-atom molecular dynamics (MD) simulations.[1] Furthermore, we are interested in studying the influence of molecular length, starting from a single phenyl ring to a six-ringed p-6P molecule, on diffusion and binding on the surface of amorphous silica. Our work then extends to investigating the influence of polarity on the growth of organic molecular thin films on amorphous silica. For this, we use a computational approach inspired by the experimental deposition process to study how sensitive the thin film growth behavior is on the chemical tuning of the organic molecules. As the atomistic simulations employed in our work can reveal some of the interesting microscopic features of the molecular surface kinetics and binding, they can be used to rationalize and guide thin film growth to obtain desired structures and properties and can complement interesting experimental findings.

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Assessment of liquid crystalline morphologies of Ph-BTBT-C10: phase transitions and carrier mobility estimates via atomistic models.

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The organic semiconductor Ph-BTBT-C10 has recently been shown to have very high charge mobilities in FETs, thanks to the possibility of producing highly ordered polycrystalline films by annealing solution-processed thin films with a microstructure reminiscent of the originating smectic E phase into a herringbone bilayer structure [1]. We have studied the thermal behavior of bulk Ph-BTBT-C10 by atomistic molecular dynamics (MD) simulations, either by subjecting the experimental crystal structure to a stepwise heating ramp or by subjecting an equilibrated isotropic melt structure to a stepwise cooling ramp. A remarkable agreement with experiment is obtained for the smectic-isotropic phase transition, both in terms of transition temperature and associated transition enthalpy, with no appreciable hysteresis in either direction [1,2]. A crystal-smectic phase transition was only observed in the heating sequence, at a temperature in good agreement with experiments [1,2]. However, hexagonal and tetragonal order parameters are more consistent with a smectic A than a with smectic E phase.

Hopping dynamics in the absence of an explicit electric field, and in the presence of both energetic and positional disorder, returned lower-bound limits for charge carrier diffusivity as a function of temperature across phases. Carrier mobility estimates in the range of 1 cm^2/Vs were obtained for the crystalline state, and of the order of 10^{-2} cm^2/Vs for smectic and isotropic phases. In particular, charge transport orthogonally to smectic layers appears to be quite relevant. This latter consideration, together with the rather high molecular diffusivities extracted from MD simulations, suggests the dynamical formation and annihilation of three-dimensional conduction pathways in the liquid-cristalline phase.

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Controlling the morphology of polymer-nanoparticle mixtures with tunable nanoparticle interaction potentials

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Polymer nanocomposites (PNC) are composed of polymer melts with nanoparticles (NPs) dispersed within the matrix and are used in a broad range of applications, from solar cells and chemical sensors to automotive tyres, due to their enhanced properties [1]. In order to design and produce PNC with specific characteristics, it is important to understand the complex interplay between composition, structure and properties, with particular focus on how NPs and polymers interact with each other and which are the factors that mainly affect their miscibility.

Following the approach of Meng *at al.* [2], in this work we employed Molecular Dynamics simulations and the well known “bead and spring” model [3] to explore various situations of miscibility between polymer chains and nanoparticles by means of tunable interactions. The polymer-NP and NP-NP interactions are represented by potentials derived from the Hamaker approximation [4]. The monomer-NPs interaction can be controlled simply by changing the value of the corresponding Hamaker constant, that we used as an adjustable parameter. In order to tune the interaction between nanoparticles, which is of equal importance to determine the miscibility of the system, we developed a “mix” potential. The latter is a weighted linear combination of a purely repulsive and an attractive interaction which allows us to explore in a continuous manner all the intermediate situations, that are not accessible with standard potentials.

Our results show that for weak monomer-NPs interactions, the potential acting between nanoparticles determines the aggregation state of system; moreover, the transition between aggregated and dispersed system is strongly affected by the “mix” potential. The NP-NP interaction also determines the size, number and geometry of the nanoparticles clusters.

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Growth of Extended DNTT Fibers on Metal Substrates by Suppression of Step-Induced Nucleation

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Due to their anisotropic optoelectronic properties, crystalline organic fibers constitute an interesting class of nanoscale materials with great potential for integration into future optoelectronic devices based on organic-inorganic hybrid systems. While chemical synthesis allows for flexible tailoring of electronic molecular properties, structural control of hybrid structures is hampered by the incompatibility of traditional structuring methods such as, e.g. lithography, with these molecular materials [1]. Therefore, other approaches must be used. Here we examine the formation of crystalline fibers of dinaphthothienothiophene (DNTT), a recently synthesized chemically robust organic semiconductor with high charge carrier mobility, upon film growth on noble metal substrates. Based on a comparison of the film growth on a regularly stepped, vicinal surface, we show by combined STM and LEED measurements that substrate steps affect the azimuthal molecular orientation in the seed layer [2]. In particular, they induce a fiber orientation which competes with that of fibers formed on flat terraces and thereby strongly limits the fiber dimensions. We demonstrate a strategy to suppress this parasitical step-induced fiber nucleation by first exposing Ag(111) surfaces to oxygen , or even briefly to ambient condition, which causes a selective saturation of the active step sites, while subsequent deposition of DNTT yields strongly enlarged fibers that are epitaxially aligned on the (111) surface.

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The Software Package GIDVis and its Application to Rotating Grazing Incidence X-Ray Diffraction Data

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Grazing incidence X-ray diffraction (GIXD) is an experimental method frequently applied to characterize a wide variety of thin films and surfaces. Depending on the texture of the sample's crystallites, special care is required during the experimental measurements and successive data evaluation. For example, samples with large individual crystallites on a surface resulting in poor statistics or epitaxially grown samples with defined in-plane alignment of the crystallites require both a full sample rotation around the surface normal during data collection. This is necessary to obtain all information for phase, texture and epitaxy analysis. Moreover, this experimental approach opens new possibilities for advanced characterisation methods which in simple static experiments are inaccessible, e.g. the determination of the in-plane mosaicity. GIDVis is a software package developed in MATLAB for visualization and analysis of GIXD data in general but mostly used for thin films. It is specialized on data obtained during a sample rotation around the surface normal, i.e. a rotating GIXD experiment. Due to the geometrical independent character of the underlying algorithms implemented, most features can be used independently from the input data type. GIDVis allows the user to perform detector calibration, data stitching, intensity corrections, standard data evaluation (e.g. cuts and integrations along specific reciprocal space directions), crystal phase analysis, etc. Further, these features are not limited to a single experimental setup, data from mostly all diffraction setups can be processed. To fully take advantage of the measured data in the case of sample rotation, pole figures can be calculated from the experimental data for any q value covered. As an example, GIDVis is used here to investigate the epitaxial alignment of a Metal-Organic Framework (MOF), consisting of copper ions, linked in two dimensions by 1,4-benzenedioic acid (BDC), that has been grown on an oriented Cu(OH)2 nanobelt substrate, illustrating the importance of the sample rotation. GIDVis is available online free of charge (http://www.if.tugraz.at/amd/GIDVis/).

A Quantum-Chemical Study of the building blocks of Benzodithiophene-Based Donor－Acceptor Copolymers Used in Organic Solar Cells

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Conjugated donor－acceptor (D－A) copolymers are promising materials to be used as active components in thin film organic bulk heterojunction solar cells and transistors. [1-3] Appropriate combinations of D－A units enable the tuning of the intrinsic electronic and optical properties of the material. The knowledge of the structure at the atomic level is a key factor to highlight structure-property relationship and to accomplish the fine regulation of these properties. One of the most studied and efficient classes of D-A polymer is based on the poly(benzodithiophene-*alt*-thienopyrroledione) backbone (PBDTTPD), i.e. a sequence of the electron-donating benzodithiophene (BDT) and the electron-accepting thienopyrroledione (TPD) moiety with a variety of alkyl side chains. [4,5] Due to the scarce propensity to crystallization and the low quality of the diffraction patterns of these polymeric materials, the structural analysis must be largely based on molecular modelling techniques. In this contribution we focus on the study of the building blocks of the polymer including conformational analysis of dimers and trimers of the co-units guided by the available experimental data (i.e. X-Ray diffraction and NMR data). Quantum-Chemical calculations (i.e. Density Functional Theory, DFT, and second order Møller–Plesset perturbation theory, MP2) have been performed also including the calculation of NMR tensors and the study of solvent effects (implicit and explicit strategies) in energies and properties of the systems under investigation.

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Molecular Dynamics Supported In Situ X-Ray Scattering on Organic Solar Cell Layers

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Organic solar cells are presently only used for niche applications due to their semi-transparency, flexibility, low weight, and possibilities of custom designs in terms of colours and shapes. However, with their low-cost solution processing and projected energy payback times of only fractions of those of silicon modules, the technology has a great potential to reach commercial viability within few years. However, upscaling the manufacture of organic photovoltaics (OPVs) from laboratory-scale devices to large-scale modules without compromising the device efficiency demands an understanding of the microstructure formation during post-deposition drying of the active layer. By combining the strengths of molecular dynamics (MD) modelling and *in situ* X-ray scattering, we aim to identify the processing parameters that are key to overcome this lab-to-fab challenge and move towards cheap, large-scale, and non-toxic solar cells with record efficiencies.

In situ morphology studies of the active layer in organic solar cells

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Organic photovoltaics (OPVs) continue to be a promising technology for third generation solar cells, but improving both efficiency and life-time is paramount for them to be competitive with their silicon counterparts. Important properties that directly affect the performance of OPVs such as charge carrier mobility and optical absorption are crucially dependent on the morphology of the active layer.

We aim to perform a thorough study of the parameters that affect the micro- and nanostructure formation in the active layer during roll-to-roll (R2R) slot die coating of organic solar cells, namely the interplay between solvents, material composition, temperature, and drying times. The morphology of OPVs is crucial for charge carrier transport and thus for the overall performance of the cell. Understanding and controlling the morphology evolution of the polymer/small molecule (donor/acceptor) active layer after deposition will make it possible to tune the above-mentioned parameters in order to enable cheap, large-scale production of efficient organic solar cells. We aim to investigate these structure-property relationships in solution processed, R2R printed OPVs through a combination of simultaneously *in situ* GISAXS/GIWAXS experiments, and molecular dynamics (MD) simulations of the blend microstructure formation.

The role of crystallization water on oligoaniline properties: theoretical insight

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Due its preparation simplicity, high electrical conductivity and high environmental stability, polyaniline continuously attracts ample scientific attention, both from theoretical and experimental point of view. One of the critical factors for the oligomer chains ordering, which influences noticeably the material macroscopic properties and its potential applications, is the amount of encapsulated water molecules [1, 2]. The aim of the current study is to shed light at the molecular level on the nature of the coupling between the residual water and the oligomers of conducting polyaniline – the emeraldine salt (ES).

Non-covalent complexes of water molecules and HCl-doped ES tetramers in bipolaronic or polaronic form are modelled. Different number of water molecules are considered and placed in various topologies with respect to the oligomer chains. The computational protocol accounting for the non-bonding character of the interaction and of the polarity of the medium has been validated in an earlier study [3]. DFT-D3/PCM calculations are performed in order to highlight the effect of the adsorbed water molecules on the oligomeric chain geometry, charge distribution and energy of frontier molecular orbitals. Computed interaction energies indicate strong water-oligomer coupling when they are coplanar (tangential alignment) due to hydrogen bonding of water with both the -NH- fragments and the chloride counterions. Water molecules mediate tiny charge transfer between the latter, which is influenced by the H_2O position along the chain. Simulated with TD-DFT electron spectra disclose some sensitivity of the longest wavelength absorption on the water molecules configuration in support of experimental findings [4]. The behaviour of the bipolaronic and polaronic systems is analysed and compared.

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Molecular Dynamics Study of the Local Structuring of Diketopyrrolopyrrole-Based Semiconducting Polymers

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Semiconducting polymers have received a great deal of interest for their use in the past few decades. One of distinguishing figures of merit for these materials is their high charge carrier mobility as high as ~10 cm^2 V^{-1} s^{-1} as well as other advantages compared to silicon-based electronics such as being environmentally friendly, low manufacturing cost and flexibility [1]. A higher degree of crystallinity and overall ordering was believed to be an essential factor for better mobility for many years. However, amorphous polymers such as Diketopyrrolopyrrole (DPP) were shown to have as high performance as the crystalline polymers due to the existence of short-range ordered regions of polymer aggregates and segregation [2]. The relationship between local structuring and the macroscopic properties of a semiconducting polymer is not known yet [3]. We study a variety of polymers belonging to the DPP family with the hope of better understanding some of the features of these materials, therefore, their performance using molecular dynamics (MD) simulations.

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6 Notes:

Link to Politecnico's campus in Lecco, with travel information:
http://www.polo-lecco.polimi.it/en/

Link to LAMPRE's web site (workshop sponsor):
http://www.lampre.com/en/

The social dinner will be at the "Azzeccagarbugli" restaurant on the evening of Thusday, July 18th.
The restaurant is in Piazza XX Settembre, in the Lecco city centre:
https://www.azzecca.it/